Pak. J. Bot., 43(6): 2929-2935, 2011.

RELATIONSHIP OF PLANT AVAILABLE SULPHUR WITH SOIL CHARACTERISTICS, RAINFALL AND YIELD LEVELS OF OILSEED CROPS IN POTHWAR PAKISTAN

RIZWAN KHALID[1], KHALID SAIFULLAH KHAN[1*], ZAHID AKRAM[2], RAHMATULLAH QURESHI[3] AND MUHAMMAD GULFRAZ[4]

[1]*Department of Soil Science and Soil & Water Conservation,* [2]*Department of Plant Breeding & Genetics,* [3]*Department of Botany, and* [4]*Department of Biochemistry, Pir Mehr Ali Shah Arid Agriculture University Rawalpindi, Pakistan*

Abstract

A study was carried out in order to assess the status of plant available S in the 15 rain-fed arable soils of Pothwar, Pakistan and to evaluate its relationships with soil characteristics, rainfall distribution and yield levels of oilseed crops in the region. The contents of plant available S (0.01 M $CaCl_2$ extractable SO_4^{-2}-S) in the soils varied from 5.7 to 21.7 µg g^{-1} soil (mean 11.7 µg g^{-1} soil) and corresponded to 7.0 to 13.8% of the total S in the soils. The adsorbed S contents ranged from 1.9 to 7.8 µg g^{-1} soil (mean 4.8µg g^{-1} soil) forming 2.0 to 7.3% of the total S in the soils. The organic S contents ranged from 68.4 to 140.4 µg g^{-1} soil (mean 97.0 µg g^{-1} soil) accounting for 81.5 to 89.3% of the total S in the soils. The 0.01 M $CaCl_2$ extractable SO_4^{-2}-S was highly significant positive correlated with total S and organic S in the soils. Significant positive relationships also existed between 0.01 M $CaCl_2$ extractable SO_4^{-2}-S and the clay, EC_e, organic C, total N, and extractable P contents in the soils. Significant negative relationships of 0.01 M $CaCl_2$ extractable SO_4^{-2}-S were observed with the $CaCO_3$ and pH_s of the soils. Among the climatic factors, 0.01 M $CaCl_2$ extractable SO_4^{-2}-S showed significant positive correlation with the mean annual temperature, while the significant negative relationships with rainfall from July to August, total annual rainfall and the rainfall from September to June. A strong positive relationship existed between 0.01 M $CaCl_2$ extractable SO_4^{-2}-S contents and the average yield level of oilseed crops ($r = 0.80^{**}$). Among different crops, groundnut yield had highly significant correlation ($r = 0.90^{**}$) with the $CaCl_2$ extractable SO_4^{-2}-S followed by the sunflower ($r = 0.70^{**}$), while the rapeseed/ mustard yield had the lowest ($r = 0.59^{*}$).

Introduction

Sulphur (S) deficiency has been recognized as a constraint to sustainable crop production in many parts of the world including Europe (Eriksen *et al*., 2004; Schonhof *et al*., 2007) and Asia (Saha *et al.,* 2001; Hu *et al*., 2002; Biswas *et al*., 2003). The main causes of S deficiency are: 1) introduction of high yielding crop varieties, 2) application of sulphur free fertilizers, 3) injudicious use of irrigation water and 4) reduction of sulphur dioxide emissions from industries (Scherer, 2001; Eriksen *et al*., 2004). Sulphur is an essential plant nutrient and plays a vital role in the synthesis of amino acids (methionine, cystein and cystine), proteins, chlorophyll and certain vitamins (Zhao *et al*., 1997; Havlin *et al.,* 2004; Tiwari & Gupta, 2006). It is also known to be involved in the metabolism of carbohydrates, proteins and oils, formation of cell wall and flavour imparting compounds (Marschner, 1995). Plants absorb S mainly in the form of inorganic sulphate (SO_4^{-2}) ions through the roots, thus sulphate S must be present in soils in sufficient amount in order to meet crop S requirements (Brady & Weil, 2002). Insufficient availability of sulphur to crop plants not only declines their growth and yield but can also deteriorate nutritional quality of the produce (Hawkesford, 2000; Schonhof *et al*., 2007).

A large proportion of soil S exists in the form of organic compounds which must be mineralized to sulphate S in order to become available to plants (Tabatabai, 1982). In temperate region soils, mineralization of organic S contributes significantly to the S pool available to crops (Haneklaus *et al*., 2002; Hu *et al*., 2002). However, in soils of Pakistan and other tropical/ subtropical areas with low organic matter contents (mostly < 1%) and little or no recycling of crop residues (Khan & Joergensen, 2006), the amount of S mineralized from organic sources may not be appreciable (Ahmad *et al.,* 1994). Soil characteristics particularly the texture, clay minerals, pH, and organic matter may influence the contents of plant available S by controlling the retention and leaching characteristics of highly mobile SO_4^{-2}-S in soils (Haneklaus *et al*., 2002; Biswas *et al*., 2003). Also the climatic factors such as temperature and amount and distribution of rainfall in the area can affect the contents of sulphate S in soils either through the addition of S from atmosphere, controlling the rate of organic S mineralization or facilitating leaching losses of sulphate ions (Brady & Weil, 2002). It is therefore important that the factors controlling bioavailability of S in soils are well understood in order to predict the deficiency of S in different agro-climatic conditions and adopt measures for sustainable land use.

The Pothwar plateau lying in the North Eastern part of the Punjab province of Pakistan constitutes an important area for rain-fed agriculture in the country. Soils of the Pothwar plateau vary greatly in their physico-chemical properties because of their origin from diverse parent materials, different landforms and variable climatic conditions. In general, the Pothwar soils are alkaline, calcareous, low in organic matter and deficient in plant nutrients like N and P (Khan & Joergensen, 2006).). They also suffer from drought stress during most parts of the year, as roughly 70% of the total annual rainfall is received in only two monsoonal months of July and August. At present, information regarding sulphur status of these soils and its relationship with soil physico-chemical properties and crop yields particularly under rain-fed dry farming is generally lacking. Among different crops, sulphur requirements of oilseeds are higher as compared to legumes, cereals and pulses because of the critical role played by the sulphur in synthesis of oil and production of bold grains essential for oil production (Havlin *et al.,* 2004). In view of above facts, the present study was undertaken with the following objectives: 1) to assess the sulphur status of Pothwar soils and to evaluate its relationship with soil characteristics, temperature and rainfall distribution in the region, and 2) to evaluate the impact of sulphur contents in Pothwar soils on the yield of oilseed crops in the area.

[*]Corresponding author: e-mail: khan_ks@yahoo.com

Materials and Methods

Experimental sites and soil sampling: Soils belonging to 15 prominent soil series in the Pothwar tract of the Punjab province of Pakistan were collected in February, 2005 from the relevant agricultural sites. Six of the 15 collected soils i.e., Missa, Basal, Talagang, Rawalpindi, Rawal and Tirnaul belonged to *Inceptisols*, five soils i.e., Balkassar, Chakwal, Therpal, Kahuta and Guliana belonged to *Alfisols*, three soils i.e., Qutbal, Rajar and Qazian belonged to *Entisols*, and one i.e., Satwal belonged to *Vertisols*. The fields selected for sampling were either under rapeseed/ mustard or sunflower crops at the time of sampling. For each soil, three different agricultural fields of approximately 1 ha size but having the same soil type were sampled separately to represent the replicates. Initially, 8 primary samples were taken from upper 15 cm of the field surface using a soil auger, which were then mixed together to obtain a composite sample, transferred into polyethylene bags, and brought to the laboratory. The samples were spread over the polyethylene sheets, air-dried at room temperature (25°C), crushed to pass through a 2 mm sieve and stored in air-tight plastic containers until analysis. These < 2 mm sieved samples were used for the determination of soil texture, pH, electrical conductivity and calcium carbonate. Subsamples of the < 2 mm air dry soils were finely ground to pass a 100 mesh sieve and analysed for organic C, total N, extractable P, $CaCl_2$-extractable SO_4^{-2} and total S. Moisture contents in the air dry soil samples were estimated in order to express the results on oven dry soil basis.

Information about the temperature and rainfall in the study area was obtained from Pakistan Meteorological Department, Islamabad for years 2004 to 2006 and the mean values of the three years data are presented in Table 1. The annual temperature at the experimental sites varied from 21.5 to 30°C (mean 26.5°C). The annual precipitation varied between 400 to 970 mm (mean 680 mm). The precipitation was unevenly distributed over the year at all the experimental sites i.e., approximately 63% of the total annual precipitation was received in the monsoonal months of July and August.

Information on the mean yield levels of three important oilseed crops i. e., rapeseed mustard (*Brassica napus* L.), peanut (*Arachis hypogaea* L.) and sunflower (*Helianthus annuus* L.) in the study area is presented in Table 3. The crop-specific yield levels (seed yield in t ha^{-1}) are based on the data obtained during the three consecutive cropping years from 2004 to 2006 by interviewing farmers of the fields selected for the collection of soil samples. The data reveal considerable variation between the 15 different soil types. Rapeseed/ mustard are mainly grown from October/ November to March/ April in the wetter northern parts (Rajar, Tirnaul, Rawalpindi, Guliana, Missa and Bahatar) of the Pothwar region. Peanut is widely grown from March/ April to August/ September, while the sunflower is grown from February/ March to May/ June.

Table 1. Precipitation total, Precipitation J+A (July + August), Precipitation S-J (September - June), mean annual temperature at the study area and physico-chemical properties of the 15 soil series.

Soil series	Precipitation total (mm)	Precipitation J+A (mm)	Precipitation S-J (mm)	Temperature (°C)	Sand (%)	Silt (%)	Clay (%)	EC_e (dS m^{-1})	pH_s
Balkassar	415	270	145	28.2	40.5	39.0	20.5	0.58	7.6
Chakwal	460	300	160	29.5	31.5	42.0	26.5	0.53	7.7
Talagang	430	275	155	30.0	41.0	36.5	22.5	0.63	7.6
Therpal	400	255	145	28.5	69.0	21.0	10.0	0.40	7.7
Satwal	490	315	175	29.0	52.0	28.0	20.0	0.49	7.8
Basal	685	440	245	28.5	41.5	47.0	11.5	0.38	8.0
Missa	610	385	225	25.5	37.5	54.0	8.5	0.42	8.2
Qutbal	680	435	245	27.5	45.5	41.0	13.5	0.35	7.9
Rajar	665	415	250	25.0	52.0	41.0	7.0	0.36	7.9
Guliana	870	540	330	25.8	39.5	42.5	18.0	0.36	7.9
Kahuta	830	510	320	21.5	47.0	34.5	18.5	0.39	8.1
Qazian	805	495	310	27.5	63.5	24.0	12.5	0.29	7.9
Rawal	945	585	360	24.8	45.0	39.5	15.5	0.34	7.7
Rawalpindi	970	600	370	22.7	43.0	38.0	19.0	0.41	7.9
Tirnaul	955	590	365	23.7	32.0	51.0	17.0	0.33	7.9
Mean	681	427	253	26.5	45.4	38.6	16.0	0.41	7.8
Min	400	255	145	21.5	31.5	21.0	7.0	0.29	7.6
Max	970	600	370	30.0	69.0	54.0	26.5	0.63	8.2
CV (±%)					5.0	6.1	5.9	2.8	1.2

Analysis of physico-chemical properties: Textural analysis was performed according to Anderson & Ingram (1993) using a standard hydrometer after pre-treatment of soil samples with 7% H_2O_2, 10% HCl, and 2% sodium hexametaphosphate. Soil pH and electrical conductivity (dS m^{-1}) were estimated in a saturated soil paste using calibrated *HANNA-212* pH meter and *HANNA HI-8033* conductivity meter, respectively. Calcium carbonate was determined by acid neutralization method as described by Ryan *et al*., (2001). Total organic C was measured after dichromate digestion by a modified *Mebius* procedure according to Nelson & Sommers (1982). Total N (mg g^{-1} soil) was estimated by the *Kjeldahl* method (Bremner & Mulvaney, 1982). The 0.5 M $NaHCO_3$ extractable P was determined colorimetrically (Anderson & Ingram, 1993). Total S was determined by wet oxidation (Tabatabai, 1982). Plant available S was determined in 0.01 M $CaCl_2$ extracts (Williams & Steinbergs, 1959). Adsorbed S was calculated by subtracting available S from S extracted with 0.04M Ca $(H_2PO_4)_2$, and soil organic S was calculated by subtracting 0.04M Ca $(H_2PO_4)_2$ extractable inorganic S from total soil S (Nguyen & Goh, 1992). Sulphur in all the extracts was determined by turbidimetric method using *Cecil-2000* spectrophotometer (Verma *et al*., 1977).

Statistical analysis: The results presented in the tables are arithmetic means and expressed on an oven-dry basis (about 24 h at 105°C). The relationships between different soil properties and climatic variables were analysed by simple correlation or regression analysis using StatView 5.0 (SAS Inst. Inc.).

Results

Mean values of sand, silt, and clay in the 15 soils from the Pothwar region were 45.4, 38.6, and 16.0%, respectively (Table 1). The texture of the soils varied between sandy loam and silty clay. Electrical conductivity varied from 0.29 to 0.63 dS m^{-1} (mean 0.41 dS m^{-1}) and the soil pH from 7.6 to 8.2 (mean 7.8), showing that all the soils were alkaline and none of them was salt affected. The $CaCO_3$ contents ranged between 3.2 to 13.1% (mean 7.1%) indicating that the soils were weak to moderately calcareous (Table 2). The contents of soil organic C ranged from 1.94 to 4.05 mg g^{-1}soil (mean 2.94 mg g^{-1}soil). The total N contents varied between 0.22 to 0.39 mg g^{-1}soil (mean 0.30 mg g^{-1} soil) and the content of 0.5 M $NaHCO_3$ extractable P varied between 3.4 and 7.4 µg g^{-1}soil (mean 4.9 µg g^{-1} soil). The total S contents ranged from 77.9 to 167.1 µg g^{-1}soil (mean 113.6 µg g^{-1} soil) and the organic S contents ranged from 68.4 to 140.4 µg g^{-1} soil (mean 97.0 µg g^{-1} soil) accounting for 81.5 to 89.3% of the total S in the soils. The adsorbed S varied from 1.9 to 7.8 µg g^{-1} soil (mean 4.8 µg g^{-1} soil) forming 2.0 to 7.3% of the total S in the soils. Organic C to total S ratios (C: S) ranged between 20.9: 1 to 32.1: 1 (mean 25.9: 1), while the total N to total S ratios (N: S) ranged from 2.2: 1 to 3.2: 1 (mean 2.6: 1).

Table 2. Contents of organic C, total N, extractable P, calcium carbonate, total S, organic S and sulphate S in the 15 soils.

Soil series	Organic C (mg g^{-1} soil)	Total N (mg g^{-1} soil)	$NaHCO_3$ extractable P (µg g^{-1} soil)	$CaCO_3$ (%)	Total S (µg g^{-1} soil)	Organic S (µg g^{-1} soil)	Adsorbed S (µg g^{-1} soil)	Available S (µg g^{-1} soil)	C: N: S
Balkassar	3.72	0.34	6.1	3.4	145.3	125.2	6.7	13.4	25.6: 2.3: 1
Chakwal	4.05	0.38	7.4	3.6	169.7	140.4	7.8	21.5	23.8: 2.2: 1
Talagang	3.35	0.39	5.1	3.2	146.2	119.1	6.9	20.2	22.9: 2.6: 1
Therpal	2.23	0.23	3.4	7.4	85.7	75.9	3.8	6.0	26.0: 2.7: 1
Satwal	3.86	0.38	5.3	5.2	167.1	139.2	6.2	21.7	23.1: 2.3: 1
Basal	2.12	0.25	4.1	7.5	101.0	87.8	2.5	10.7	20.9: 2.5: 1
Missa	2.43	0.26	4.7	13.1	91.8	82.0	1.9	7.9	26.5: 2.8: 1
Qutbal	2.88	0.28	5.1	5.2	115.3	99.3	3.6	12.4	24.9: 2.4: 1
Rajar	2.23	0.24	4.5	11.3	86.8	76.1	2.7	8.0	25.7: 2.7: 1
Guliana	3.26	0.33	5.1	9.5	113.6	98.2	4.2	11.2	28.7: 2.9: 1
Kahuta	3.05	0.32	5.4	5.2	99.1	85.6	4.0	9.5	30.7: 3.2: 1
Qazian	1.94	0.22	3.9	5.6	77.9	68.4	3.8	5.7	24.9: 2.8: 1
Rawal	2.90	0.27	4.5	8.2	90.4	76.2	6.6	7.6	32.1: 2.9: 1
Rawalpindi	3.20	0.33	5.0	7.3	110.8	93.7	6.4	10.7	28.8: 3.0: 1
Tirnaul	2.95	0.30	4.3	10.7	103.9	88.6	5.9	9.4	28.4: 2.9: 1
Mean	2.94	0.30	4.9	7.1	113.6	97.0	4.8	11.7	25.9: 2.6: 1
Min	1.94	0.22	3.4	3.2	77.9	68.4	1.9	5.7	20.9: 2.2: 1
Max	4.05	0.39	7.4	13.1	167.1	140.4	7.8	21.7	32.1: 3.2: 1
CV (±%)	2.1	3.20	5.4	3.4	11.7	10.6	4.1	2.7	

Table 3. Yield of the three main oilseed crops groundnut (*Arachis hypogaea* L.), rape (*Brassica napus* L.) and sunflower (*Helianthus annuus* L.) along with mean yield level at the 15 sites.

Soil series	Groundnut	Rape	Sunflower	Yield Level*
	(Seed yield t ha^{-1})			
Balkassar	1.35 ± 0.34	1.29 ± 0.37	0.84 ± 0.40	102.5
Chakwal	1.41 ± 0.36	1.45 ± 0.38	0.91 ± 0.37	110.9
Talagang	1.57 ± 0.33	1.41 ± 0.38	0.87 ± 0.37	112.6
Therpal	0.98 ± 0.24	1.09 ± 0.36	0.59 ± 0.32	77.4
Satwal	1.46 ± 0.33	1.53 ± 0.40	0.88 ± 0.40	113.0
Basal	1.35 ± 0.34	1.44 ± 0.36	0.91 ± 0.38	109.1
Missa	1.08 ± 0.39	1.22 ± 0.34	0.70 ± 0.30	87.8
Qutbal	1.28 ± 0.33	1.37 ± 0.34	0.86 ± 0.33	103.4
Rajar	1.09 ± 0.42	1.40 ± 0.32	0.74 ± 0.35	94.1
Guliana	1.24 ± 0.33	1.43 ± 0.40	0.88 ± 0.35	104.6
Kahuta	1.18 ± 0.33	1.50 ± 0.40	0.84 ± 0.35	103.1
Qazian	1.08 ± 0.47	1.05 ± 0.33	0.68 ± 0.24	82.8
Rawal	1.19 ± 0.46	1.33 ± 0.41	0.74 ± 0.34	95.1
Rawalpindi	1.26 ± 0.43	1.50 ± 0.62	0.89 ± 0.42	107.3
Tirnaul	1.21 ± 0.49	1.33 ± 0.45	0.76 ± 0.33	96.4
Mean	1.25	1.36	0.81	100
Min	0.98	1.09	0.59	77.4
Max	1.57	1.53	0.91	113.0

*The yield level was calculated by averaging the 3 crop-specific yield levels calculated by dividing the site-specific mean crop yield by the average crop yield of the 15 sites and expressed as percent.

The amount of 0.01 M $CaCl_2$ extractable SO_4^{-2}-S regarded as the plant available S varied from 5.7 to 21.7 µg g^{-1}soil (mean 11.7 µg g^{-1} soil) and corresponded to 7.0 to 13.8% of the total S in the 15 soils (Table 2). Maximum SO_4^{-2}-S contents (21.7 µg g^{-1}soil) were observed in the Satwal soil, while lowest (5.7 µg g^{-1}soil) in the Qazian soil. Overall, the order of SO_4^{-2}-S contents in the soils was Satwal > Chakwal > Talagang > Balkassar > Qutbal > Guliana > Rawalpindi > Basal > Kahuta > Tirnaul > Rajar > Missa > Rawal > Therpal > Qazian soil. The correlation data (Table 4) showed highly significant positive relationship of 0.01 M $CaCl_2$ extractable SO_4^{-2}-S with total S and organic S contents in the soils. Significant positive relationship of 0.01 M $CaCl_2$ extractable SO_4^{-2}-S was also evident with total N, organic C, clay, EC_e, extractable P and adsorbed S contents in the soils. Significant negative relationships of 0.01 M $CaCl_2$ extractable SO_4^{-2}-S were observed with the $CaCO_3$ and pH_s of the soils. Among the climatic factors, 0.01 M $CaCl_2$ extractable SO_4^{-2}-S showed significant positive correlation with mean annual temperature, while the significant negative relationships existed with rainfall from July to August, total annual rainfall and the rainfall from September to June at the 15 experimental sites.

Table 4. Correlation coefficient of plant available S ($CaCl_2$ extractable SO_4^{-2}) with total S, organic S, soil characteristics, rainfall, temperature and yield levels of oilseed crops at 15 sites in Pothwar.

	r	Reg. Equations	R^2*
Total S	0.97^{**}	y = 0.1732x – 7.9594	0.93
Organic S	0.95^{**}	y = 0.2172x – 9.3510	0.90
Adsorbed S	0.62^{*}	Y = 1.7938x + 2.9967	0.39
Sand	-0.41	y = – 0.2089x + 21.204	0.17
Clay	0.77^{**}	y = 0.7497x – 0.2931	0.60
Ece	0.77^{**}	y = 41.956x – 5.783	0.59
Soil pHs	-0.44	y = –13.709x + 119.39	0.20
Soil organic C	0.82^{**}	y = 6.6451x – 7.8409	0.66
Total N	0.88^{**}	y = 83.149x – 13.329	0.78
Extractable P	0.72^{**}	y = 4.0169x – 8.1704	0.51
$CaCO_3$	-0.60^{*}	y = – 1.0534x + 19.227	0.36
Precipitation total	-0.51	y = – 0.0131x + 20.619	0.26
Precipitation S-J	-0.50	y = –0.0215x + 20.896	0.25
Precipitation J+A	-0.53^{*}	y = –0.0332x + 20.127	0.28
Temperature	0.55^{*}	y = 1.1267x – 18.146	0.30
Crop yield level	0.80^{**}	y = 0.394x – 27.664	0.65
Rapeseed	0.59^{*}	y = 22x – 18.105	0.35
Groundnut	0.90^{**}	y = 29.934x – 25.651	0.81
Sunflower	0.70^{*}	y = 38.257x – 19.108	0.49

r = Simple linear correlation coefficient, R^2 = Multiple regression coefficient
* = Significant at $p = 0.05$ (> 0.52), ** Highly significant at $p = 0.01$ (> 0.64)
Regression $p = 0.013$

The yield level of groundnut crop at the 15 sites ranged from 0.98 to 1.57 t ha^{-1} with the mean yield of 1.25 t ha^{-1} (Table 3). The rapeseed yield level varied from 1.09 to 1.53 t ha^{-1} (mean 1.36 t ha^{-1}), and the sunflower yield level ranged between 0.59 and 0.91 t ha^{-1} (mean 0.81 t ha^{-1}). A strong positive relationship existed between 0.01 M $CaCl_2$ extractable SO_4^{-2}-S contents and the average yield level of oilseed crops ($r = 0.80^{**}$). Among different crops, groundnut yield had highly significant correlation ($r = 0.90^{**}$) with the $CaCl_2$ extractable SO_4^{-2}-S followed by the sunflower ($r = 0.70^{**}$), while the rapeseed/ mustard yield had the lowest ($r = 0.59^{*}$). Significant positive relationships also existed between yield levels of oilseed crops and the $Ca(H_2PO_4)_2$ extractable S, total S and organic S fractions in the soils (values not shown in the Table), however the correlation coefficient values were lower than those observed with $CaCl_2$ extractable S.

Discussion

Inorganic sulphate (SO_4^{-2}-S) present in the solution phase and on exchange complex in soils collectively forms the S pool available to plants (White, 2006). However the amount of adsorbed S is highly pH dependent and becomes negligible in soils above pH 6.5 (Scherer, 2001). Therefore in alkaline soils 0.01 M $CaCl_2$ extractable SO_4^{-2}-S which mainly represents the water-soluble sulphates, is recognized as an indicator of plant available S. In a wide variety of soils from the Indian subcontinent, a level of 10 µg g^{-1} soil $CaCl_2$ extractable SO_4^{-2}-S is considered as a critical limit of S deficiency for most crop species (Tandon, 1991; Srinivasarao *et al.*, 2004). On the basis of this criterion, 7 out of the 15 soils reported in this study were deficient in plant available S, while the 8 soils had S in the satisfactory range. Thus on the whole, the soils in Pothwar region fall under low to satisfactory range with respect to the status of plant available S in these soils.

There were significant positive relationships between plant available S ($CaCl_2$ extractable SO_4^{-2}-S) and the total S, organic S and organic C contents in the soils. Organic S formed the largest fraction of total S in the soils and also had significant positive relationship with total S and organic C contents in the soils. This is in agreement with the findings of Trivedi *et al.*, (2000), Srinivasarao *et al.* (2004), and indicates a strong link between soil organic matter and different S fractions in the rain-fed soils of Pothwar. Sulphur is an integral constituent of soil organic matter (Tabatabai, 1982), and the organic S contributes significantly to S supplying capacity of soils (Haneklaus *et al.,* 2002; Hu *et al.,* 2002), however it must undergo mineralization to sulphate before becoming available to plants. Although the contents of organic matter in the Pothwar soils were quite low owing to little or almost no annual inputs of organic materials into these soils (Khan & Joergensen, 2006) yet a large fraction of total S in the soils existed in organic form. Therefore, slow mineralization of indigenous soil organic S seems to contribute to plant available S in these soils.

The plant available S ($CaCl_2$ extractable SO_4^{-2}-S) also exhibited a significant positive relationship with total N (*r* = 0.88^{**}) contents in the Pothwar soils. Significant positive correlations also existed between organic C, total N, total S and organic S contents in the soil (values not shown). Both the N and S largely exist in soils as a constituent of organic compounds (*e.g.,* sulphur containing amino acids), therefore presence of strong positive relationships between different fractions containing these two elements is quite understandable. This also indicates that the organic fractions containing N and S form relatively consistent proportions of soil organic matter and possess a similar trend of distribution in soils (Acquaye & Beringer, 1989; Havlin *et al.,* 2004).

A significant positive relationship also existed between plant available S ($CaCl_2$ extractable SO_4^{-2}-S) and extractable P (*r* = 0.72^{**}) contents in the Pothwar soils. Plant available fractions of both the P and S exist in soils in the form of anions. The binding strength of orthophosphates ($H_2PO_4^{-1}$, HPO_4^{-2}) for soil colloids is greater than that of the sulphate (SO_4^{-2}). Thus application of phosphorus fertilizers often results in increased occupation of anion adsorption sites on soil colloids by the orthophosphates with the consequent release of sulphate into soil solution (Tiwari & Gupta, 2006). The presence of higher levels of orthophosphates means more release of sulphate into soil solution. Moreover, available forms of both P and S react with $CaCO_3$ under alkaline calcareous soil conditions to get converted into insoluble, non-bioavailable forms (Havlin *et al,* 2004; Tiwari & Gupta, 2006), thus a close positive relationship existed between available forms of both the nutrients.

The plant available S ($CaCl_2$ extractable SO_4^{-2}-S) also showed a significant positive correlation with the clay and a negative correlation with sand contents in the soils. Higher $CaCl_2$ extractable SO_4^{-2}-S contents were found in the soils containing more than 20 percent clay (*e.g.,* Satwal, Chakwal & Talagang soils), while the lowér in soils possessing more than 60 percent sand (*e.g.,* Qazian & Therpal). Although the clay particles particularly the oxides of Fe and Al are known to play a significant role in SO_4^{-2} retention in soils (Espejo-Serrano *et al.,* 1999; Scherer, 2001; Biswas *et al.,* 2003) but mainly under low pH soil condition. Since all the Pothwar soils were alkaline and most of them had relatively low clay contents, therefore, adsorption of SO_4^{-2} in these soils might be negligible. However, the presence of higher clay contents increases water holding capacity of soils and reduces the leaching losses of soluble ions like sulphate. Whereas in coarse textured soils dominated by sand particles, leaching losses of the soluble sulphate ions are high. Thus presence of relatively higher extractable sulphate contents in alkaline soils containing higher clay contents might be related to less leaching losses of soluble sulphate ions under these conditions.

There was a negative correlation of plant available S ($CaCl_2$ extractable SO_4^{-2}-S) with soil pH and $CaCO_3$ contents in the soils. According to Biswas *et al*., (2003), SO_4^{-2} retention capacity of soils decreases with increasing soil pH and becomes almost negligible at pH values above 6.5 (Srinivasarao *et al*., 2004). Thus under high soil pH conditions, SO_4^{-2} retention in soils is minimum which favors its leaching losses. In calcareous soils, SO_4^{-2} may react with $CaCO_3$ to get converted into insoluble forms unavailable to plants (Havlin *et al.*, 2004; Srinivasarao *et al.,* 2004). A significant positive correlation (r^2=0.77^{**}) existed between SO_4^{-2}-S and EC_e of the soils. Since sulphate is highly soluble therefore increase in its concentration in soil solution increases the electrical conductivity of soils. However, being highly soluble, it may leach down to deeper soil layers with downward percolating water in well-drained soils like those of Pothwar. Significant positive relationships of $CaCl_2$ extractable SO_4^{-2}-S with the soil EC were also reported by Tiwari & Sakal (2002) and Gosh & Agrawal (2005) in the Indian soils.

Plant available S ($CaCl_2$ extractable SO_4^{-2}-S) showed a negative correlation with total annual rainfall and the rainfall from September to June in general but more specifically with the rainfall from July to August (monsoon rains) in the study area. The SO_4^{-2} ions in soils are readily repelled by the negatively charged surfaces of the soil colloids to get released into soil solution, where from these are moved down to deeper soil layers by the downward percolating rainwater (Eriksen *et al*., 2002). The process is particularly faster under the conditions of coarse soil texture and low soil organic matter (Scherer, 2001). Thus in Pothwar, the rainfall particularly in the monsoonal months of July and August results in the leaching losses of SO_4^{-2}-S from the soils and exerts a negative effect on plant available S contents in the soils. Summer fallow commonly practised in the area during the summer (monsoon) rains in order to conserve moisture for the subsequent crop might further increase the leaching losses of soluble SO_4^{-2}-S from the soils. Lysimeter studies have shown that leaching is lower in cropped than in fallow soils (Kirchmann *et al*., 1996). Although rainfall might add a significant amount of atmospheric S to soils (Suarez & Jones, 1982; Blair *et al*., 1997) but the amount deposited varies from one place to another, being higher near industrial areas and low in the places away from industry (Wang *et al*., 2005). Thus because of low industrial activities, sulphur addition to soils through rainfall in the Pothwar region is negligible. A significant positive relationship of plant available S (SO_4^{-2}-S) with the mean annual temperature (r = 55^{*}) in the region could be attributed to the fact that increase in temperature increases the rate of mineralization of both the indigenous and added organic materials in the soils and thus contributes to the plant available S.

Oilseeds generally require higher amounts of S in comparison to other crops for their growth, development and oil yield (McGrath & Zhao, 1996; Khan *et al*., 2005). Sulphur is known to play a critical role in the synthesis of oil and production of bold grains essential for oil production in the oilseeds (Brady & Weil, 2002). Thus the mean yield levels of oilseed crops showed a strong positive correlation (r = 0.80^{**}) with plant available S (SO_4^{-2}-S) in the soils. However among the oilseed crops, yield levels of groundnut (r = 0.90^{**}) and sunflower (r = 0.70^{*}) were better correlated to plant available S as compared to the rapeseeds/ mustard (r = 0.59^{*}). The relatively weaker relationship of rapeseeds to plant available S in the Pothwar soils might be attributed to some other factors influencing the yield of rapeseeds in the area. The rapeseeds are traditionally cultivated on less fertile marginal lands in the Pothwar with little or no fertilizer addition due to competition with the wheat as the major winter crop in the area. Also the rapeseeds is sensitive to moisture, and being grown in winter season suffers from moisture stress due to less (20-25% of the annual precipitation) and unpredictable winter rains in the area. On the other hand, groundnut and sunflower being the cash crops are grown on fertile lands under better crop management, and therefore show significantly higher yield levels as compared to the rapeseeds/mustard.

Conclusions

The soils in Pothwar under the rain-fed dry farming are generally low in plant available sulphur. Although the soils receive little or no annual inputs of organic materials, yet a significantly large fraction of total S exists in organic form. Therefore, slow mineralization of indigenous soil organic S seems to contribute to plant available S in these soils. Besides organic matter, clay contents contribute positively to the plant available S most probably by reducing the leaching losses of soluble sulphate ions in the soils. On the other hand, $CaCO_3$ and higher sand contents have a negative effect on the plant available S. Rainfall particularly in the monsoonal months of July and August contribute to sulphate leaching in the summer fallow fields. A significant positive correlation between oilseed crops yield and plant available S indicates the importance of S fertilization for improving oilseeds productivity in the area.

Acknowledgments

Rizwan Khalid thanks Higher Education Commission of Pakistan for providing Ph.D. scholarship and research grant to carryout this study. We thank Pakistan Meteorological Department, Islamabad for providing data on temperature and rainfall distribution in the study area.

References

Acquaye, D.K. and H. Beringer. 1989. Sulfur in Ghanian soils: I. Status and distribution of different forms of sulfur in some typical profiles. *Plant and Soil*, 113: 197-203.

Ahmad, N., M.T. Saleem, M. Rashid and A. Jalil. 1994. Sulfur status and crop response in Pakistan soils. NNFDC Publication No.7/ 94, Planning and Development Division, Islamabad, Pakistan.

Anderson, J.M. and J.S.I. Ingram. 1993. *Tropical Soil Biology and Fertility*. Wallingford, United Kingdom: CABI.

Biswas, H., R.K. Rattan, S.P. Datta and A.K. Singh. 2003. Adsorption and translocation of sulfur in some tropical acid soils. *Journal of Plant Nutrition and Soil Science*, 166: 519-524.

Blair, C.G., G. Anderson, M. Crestani and D. Lewis. 1997. Soil sulfur status, sulfur fertilizer response and rainfall sulfur accessions at trial sites in the national reactive phosphate rock project. *Australian Journal of Experimental Agriculture*, 37: 995-1001.

Brady, N.C. and R.R. Weil. 2002. *The nature and properties of soils*. Singapore: Pearson Education.

Bremner, J.M. and C.S. Mulvaney. 1982. Nitrogen-Total. In *Methods of Soil Analysis*, *eds.* A. L. Page, 595-622. Madison, Wisconsin: ASA & SSSA.

Eriksen, J., J.E. Olesen and M. Askegaard. 2002. Sulphate leaching and sulphur balances of an organic cereal crop rotation on three Danish soils. *European Journal of Agronomy*, 17: 1-9.

Eriksen, J., K. Thorup-Kristensen and M. Askegard. 2004. Plant availablity of catch crop sulfur following spring incorporation. *Journal of Plant Nutrition and Soil Science*, 167: 609-615.

Espejo-Serrano, R., J. Santano Arias and P. Gonzalea-Fernandez. 1999. Soil properties that affect sulfate adsorption by Palexerults in Western and central Spain. *Communications in Soil Science and Plant Analysis*, 30: 1521-1530.

Ghosh, A.K. and H.P. Agrawal. 2005. Distribution and critical limits of sulfur for chickpea cultivation in Inceptisols of Varanasi District of Uttar Pradesh. *Environmental Ecology* 23: 635-639.

Haneklaus, S., E. Bloem and E. Schnug. 2002. Sulfur. In *Encyclopedia of Soil Science- Soil Fertility and Plant Nutrients*. New York, USA: Marcel Dekker.

Havlin, J.L., J.D. Beaton, S.L. Tisdale and W.L. Nelson. 2004. *Soil fertility and fertilizers, An introduction to nutrient management*. Singapore: Pearson Education.

Hawkesford, M.J. 2000. Plant responses to sulphur deficiency and the genetic manipulation of sulphate transporters to improve S-utilization efficiency. *Journal of Experimental Botany*, 51: 131-138.

Hu, Z., Z. Yang, C. Xu, S. Haneklaus, Z. Cao and E. Schnug. 2002. Effect of crop growth on the distribution and mineralization of soil sulfur fractions in the rhizosphere. *Journal of Plant Nutrition and Soil Science*, 165: 249-254.

Khan, K.S. and R.G. Joergensen. 2006. Microbial C, N, and P relationships in moisture stressed soils of Pothwar, Pakistan. *Journal of Plant Nutrition and Soil Science*, 169: 494-500.

Khan, N.A., M. Mobin and Samiullah. 2005. The influence of gibberellic acid and sulfur fertilization rate on growth and S-use efficiency of mustard (*Brassica juncea*). *Plant and Soil*, 270: 269-274.

Kirchmann, H., F. Pichlmayer and M.H. Gerzabek. 1996. Sulfur balance and sulfur-34 abundance in a long-term fertilizer experiment. *Soil Science Society of America Journal*, 60: 174-178.

Marschner, H. 1995. *Mineral nutrition of higher plants*. New York, USA: Academic Press.

McGrath, S.P. and F.J. Zhao. 1996. Sulphur uptake, yield response and the interactions between N and S in winter oilseed rape (*Brassica napus*). *Journal of Agricultural Sciences*, 126: 53-62.

Nelson, D.W. and L.E. Sommers. 1982. Total carbon, organic carbon, and organic matter. In *Methods of Soil Analysis, Part 2, eds.* A. L. Page, 539-577. Madison, Wisconsin: ASA & SSSA.

Nguyen, M.L. and K.M. Goh. 1992. Status and distribution of soil sulphur fractions, total nitrogen and organic carbon in camp and non-camp soils of grazed pastures supplied with long-term superphosphate. *Biology and Fertility of Soils*, 14: 181-190.

Ryan, J., G. Estefan and A. Rashid. 2001. *Soil and plant analysis laboratory manual*. Allepo, Syria: ICARDA.

Saha, J.K., A.B. Singh, A.N. Ganeshamurthy, K. Samaresh and A.K. Biswas. 2001. Sulfur accumulation in Vertisols due to continuous gypsum application for six years and its effect on yield and biochemical constituents of soybean (*Glycine* *max* L. Merrill). *Journal of Plant Nutrition and Soil Science*, 164: 317-320.

Scherer, H.W. 2001. Sulphur in crop production. *European Journal of Agronomy*, 14: 81-111.

Schonhof, I., D. Blankenburg, S. Muller and A. Krumbein. 2007. Sulfur and nitrogen supply influence growth, product appearance, and glucosinolate concentration of broccoli. *Journal of Plant Nutrition and Soil Science*, 170: 65-72.

Srinivasarao, C., A.N. Ganeshamurthy, M. Ali and K.K. Singh. 2004. Sulphur availability and response of mungbean and urdbean to sulphur on different soil types of pulse growing regions of India. *Communications in Soil Science and Plant Analysis*, 35: 1713-1723.

Suarez, E.L. and U.S. Jones. 1982. Atmospheric sulphur as related to acid precipitation and soil fertility. *Soil Science Society of America Journal*, 46: 976-980.

Tabatabai, M.A. 1982. Sulfur. In: *Methods of Soil Analysis. Part 2, eds.* A.L. Page, J.R. Freney and R.H. Miller, 501-538. Madison, Wisconsin: ASA&SSSA.

Tandon, H.L.S. 1991. *Sulphur research and agricultural production in India*. Washington DC, USA: TSI.

Tiwari, K.N. and B.R. Gupta. 2006. Sulphur for sustainable high yield agriculture in Uttar Pradesh. *Indian Journal of Fertilizers*, 1: 37-52.

Tiwari, S. and R. Sakal. 2002. Extractability of soil sulfur in relation to certain soil properties and plant parameters. *Annals of Agricultural Research*, 23: 146-154.

Trivedi, S.K., K.N. Bansal, R.A.S. Tomar and R.S. Verma. 2000. Vertical distribution of forms of sulphur in some profiles of Morena and Bhind districts of Madhya Pradesh. *Journal of Indian Society of Soil Science*, 48: 238-241.

Verma, B.C., K. Swaminathan and K.C. Sud. 1977. An improved turbidimetric procedure for determination of sulphate in plants and soils. *Talanta*, 24: 49-50.

Wang, T.J., H.M. Yang, L.J. Gao, Y. Zhang and C.K. Xu. 2005. Atmospheric sulfur deposition on farmland in East China. *Pedosphere*, 15: 120-128.

White, R.E. 2006. *Principles and practice of soil science: The soil as a natural resource.* United Kingdom: Blackwell.

Williams, C.H. and A. Steinbergs. 1959. Soil sulphur fractions as chemical indices of available sulphur in some Australian soils. *Australian Journal of Agricultural Research*, 10: 340-352.

Zhao, F.J., P.J.A. Whiters, E.J. Evans, J. Monaghan, S.E. Salomon, P.R. Shewry and S.P. McGrath. 1997. Sulphur nutrition: an important factor for the quality of wheat and rapeseed. *Soil Science and Plant Nutrition*, 43: 1137-1140.

(Received for publication 21 May 2009)