ENZYMATIC ACTIVITIES INVOLVED IN S-TRANSFORMATIONS AND THEIR MUTUALISTIC RELATIONSHIPS WITH INORGANIC-S COMPONENTS AND DISTRIBUTIONS IN SALT AFFECTED SOILS

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ABSTRACT

A comprehensive experimental study was conducted at three locations reflecting the semi-arid conditions of Kafr El-Sheikh governorate.

The selected soils are slightly salt-affected and irrigated in non-rational rates for a long-time with different sources of wastewaters, under different drainage conditions. A novel conceptual diagram was constructed to integrate the main labile and stable inorganic-S fractions and the ways by which their amounts are determined and calculated.

The aim of this study was to assess the biochemical activity of some soil enzymes involved in S-transformations and gain informations about the standing stocks and distributions of all inorganic-S fractions in studied soils under different drainage conditions.

Statistical of treatment of the obtained data, could be summarized as follows:

- Grand mean value of biological enzymes activity was 328.4 nanomoles SCN^- released.g^{-1} soil.$hour^{-1}$ for rhodanese, meanwhile, dehydrogenases activity was 9.41 μg TPF produced. g^{-1} soil. $hour^{-1}$.

- Total-S pool recorded 300 mg S. kg^{-1} soil, its standing stock 257.48 kg S. fed^{-1}, which was within the normal range reported in other regions.

- Inorganic-S value was 111.3 mg S. kg^{-1} soil, its standing stock 96.6 kg S. fed^{-1}. Percentage total-S in inorganic-S accounted for 37.7%, which was only a minor fraction compared to the major fraction of organic-S. However, the content of this fraction was higher than reported from temperate and subtropical regions.

- Inorganic sulfate-S content was 106.2 mg S. kg^{-1}, its percentage distribution expressed as % of total-S and of inorganic-S accounted for 36.3% and 95.6, which was the dominate fraction of inorganic-S fraction. This fraction was more pronounced in studied semi-arid soils in comparison with those reported in other regions. Its value had a positive correlation with soil clay content.

- Easily soluble and adsorbed sulfate-S contents were 82.1 and 1.8 mg S. kg soil, their percentage distributions accounted for 77.6% and 1.3% of inorganic sulfate-S. Soluble sulfate-S was the major S form of inorganic sulfate-S and at the same time was greater in comparison with reported in literature. Adsorbed sulfate-S had the opposite trend and negative correlation with soil pH as well as positive with clay content.

- Dissolved sulfate-S fraction contains insoluble sulfate-S plus Co-precipitated/Co-crystallized with $CaCO_3$. Its value was 22.3 mg S-kg^{-1} soil accounted for 21.1% of inorganic sulfate-S, which was positive correlated with $CaCO_3$ content.

- Inorganic non-sulfate-S value was 5.2 mg S. kg^{-1}, accounted for 4.4% of inorganic-S, which was greater than reported in other regions and had a positive correlation with $CaCO_2$ content. Oxygenic highly oxidized-S form and lowly oxidized-S plus reduced-S forms were 4.2 and 0.99 mg S. kg^{-1} soil, accounted for 84.2% and 15.8% of inorganic non-sulfate-S.

- Contents total-S pool and all fractions of inorganic-S as well as their percentage distributions had their maximum values in traditional drained soils in winter seasons. Whereas it reached their minimum values in badly drained soils in summer seasons. These findings in year 1999/2000 were more pronounced than those obtained in year 2000/2001.
- Total-S and inorganic-S, as well as their compounds in salt-affected soils had a positive correlations with: water table depth; $CaCO_3$; clay content; organic-S and total-N. However, their values were negative correlated with ionic strength; bulk density; max. air temp.; soil temp., pH, C/S ratio. Values of biochemical enzymes activities of rhodanese and dehydrogenase had positive correlations mainly with water table depth, pH, organic-C and total-N. Enzymes activities had also positive correlation with inorganic non sulfate-S content and its forms. Whereas, their values were negatively correlated with ionic strength, C/S ratio total sulfate-S and soluble sulfate-S. Maximum biological activity was happened in winter month Feb., whereas its minimum value was in summer month July. These activities had negative correlations with max. air temp. and soil temp. which prevailing in studied area over the experimental period.

Keywords: Rhodanese, dehydrogenase, total-S, inorganic-S, inorganic sulfate-S, inorganic non-sulfate-S, modified Johnson-Nishita apparatus.

INTRODUCTION

Sulfur is an essential element for the plant growth and activity of organisms, its deficiency has been recognized as a constraint to sustainable agricultural production in many regions of the world, especially with escalating costs of S-containing fertilizers (Tisdale *et al.,* 1986 and Haneklaus *et al.*, 2002). Some Egyptian soils suffering from S-shortage, which neither direct-S-fertilization nor balanced S-fertilization are used (El-Kammah and Ali, 1996). Intensification of agriculture with high yielding crop varieties and multiple cropping coupled with use of high-analysis S-free fertilizers has accelerated the depletion of soil S reserves. Sulfur-containing inorganic compounds which are well established species, exist in soils in a number of oxidation states ranging from (+6) in $SO_4^=$–S and its derivates, to (-2) in H_2S and its derivatives. Inorganic-S fractions in most agricultural soils other than aridisols is only minor compared to the organic-S pool (Germida *et al.,* 1992 and Hu *et al.,* 2002) and accounted for less than 25% of total-S. The proportion of organic-S and inorganic-S in soils however, varied widely according to different parameters, several soil properties and environmental conditions. Lowly oxidized-S plus reduced S-compounds such as elemental (S^o), disulfide (HS^-) and sulfide S^{2-} may be abiotic and biotic oxidized (Tabatabai, 1982 and Germida *et al.,* 1992).

Many of the transformation processes of S-compounds (i.e. oxidation and reduction, volatilization, decomposition, mineralization, immobilization and such) are mediated by biological activity (Germida *et al.*, 1992). The following enzymes are involved in the biochemical changes of S-transformations of soil inorganic-S fractions: 1) Rhodanese (EC 2.8.1.1., thiosulfate-cyanide sulfotransferase) is involved in the S-transformation

(cleavage) of the thiosulfate. It catalyzes the formation of thiocyanate and sulfite from thiosulfate and cyanide, 2) Dehydrogenase enzymes catalyzing dehydrogenation processes in soils. In this connection, it is worthy to note that, direct determination of some organic-S and inorganic-S compounds is not possible by the present analytical method. Sulfur X-ray absorption near-edge structure (XANES) spectroscopy will provide advantage over the classical wet methods used here (Morra *et al.,* 1997 and Mansfeldt & Blume, 2002).

Therefore, the main objectives of this comprehensive investigation were to: (1) asses the biochemical activity of some soil enzymes involved in S-transformations in studied soil under different drainage conditions, (2) gain precise full informations about standing stocks and distribution of all inorganic-S fractions and their compounds, and (3) couple seasonal and environmental fluctuations with the biochemical activity and inorganic-S status.

MATERIALS AND METHODS

I. Locations description and soils sampling:

The experiment was conducted at three locations represented a temperate semi-arid conditions at Kafr El-Sheikh region, Kafr El-Sheikh Governorate (Coordinates: latitude $31^{\circ}07`N$, longitude $30^{\circ}57`E$ and elevation 20 m above the sea level). Operationally, this studies elongated 21 months from Dec. 1999 to August 2001. Some seasonal micro-climatological features were obtained from Sedi-Salem Weather Observation Station (4) over this experimental period (Table 1.2). A main criterion for soil sampling before initiation this study, was the selection of sites that representing arable polluted alluvial salt-affected soils with different water table depths under conventional tillage and common agricultural practices. Organic wastes have been supplied in non-rational rates and irrigated for a long-time with different sources of treated and untreated wastewaters under different drainage conditions. Composite surface soil samples (0-30 cm) were taken from different sites and analyzed for their main physical and chemical properties.

Location (1): This site is located at Messier village (S_1) at Kafr El-Sheikh district and has a traditional drained alluvial slightly salt-affected soils with average water table depth 95 cm. The selected soil has been received a heavy loaded sewage sludge applications, and irrigated for a long-time (~25 years) with treated sewage effluents (sometimes for different undefined period of time with untreated sewage effluents). The preliminary obtained data of this location showed that, its particle size distribution was 58.7% clay, 24.7% silt, 10.8% fine and 5.8% coarse sand. Soil organic matter content, $CaCO_3$% and bulk density were 2.97%, 2.26% and 1.28 Mg m^{-3} respectively. Further physicochemical characteristics of these selected soils are given in Table (1.1).

Location (2): This site is located at Kafr Dokhmeas village (S_2) at El-Mahalla El-Kubra district, El-Gharbia Governorate. It has a poorly-drained salt-affected soils and average water table depth 75 cm (Table 1.1).

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This soil has been incorporated for undefined periods with chicken manures and irrigated for a long-time with contaminated agricultural drainage waters from El-Gharbia main drain (Cotchaner drain). Its particle size distribution was 51.4% clay, 30.9% silt, 14.3% fine and 3.4% coarse sand. Soil organic matter, $CaCO_3$ and bulk density were 1.84%, 3.74% and 1.35 Mg m^{-3}, respectively. Additional major properties of these selected soils are summarized in Table (1.1).

Location (3): This area is situated at Kafr El-Sheikh city and has a badly-drained slightly salt-affected soils with average water table depth 60 cm (Table 1.1). This soil (S_3) has not been received sewage sludge or organic manures applications but irrigated for different undefined periods with contaminated waste-drainage waters from Oil and Soap Company. Its particle size distribution soil was 59.8% clay, 28.5% silt, 7.2% fine and 4.5% coarse sand. Soil organic matter, $CaCO_3$ and bulk density were 1.56%, 4.15% and 1.57 Mg m^{-3}, respectively. Another main analytical characteristics of these selected soils used are listed in Table (1.1). Generally, during both consecutive winter seasons (Dec.-Feb.) 1999/2000 and 2000/2001 as well as two successive summer seasons (June-August) 2000 and 2001, representative disturbed and undisturbed soil samples were monthly collected in duplicate from the soil surface (0-30 cm). It was established a permanent sampling plot circular area with a diameter of 6 m (28.28 m^2). Fresh field-moist surface soils samples were collected monthly and homogenized manually, passed through a 2 mm-metal sieve. However, portions of these soils were not homogenized and rapidly sealed in plastic bags and immediately maintained in deep freezer and then thawed just before analysis in order to minimize oxidation of reduced inorganic-S fractions for assaying rhodanese activity and estimation of non sulfate-S fractions. The homogenized soils samples were air-dried, gently crushed with cylindrical wooden roll and again sieved < 2 mm for chemical analysis. A subsamples of this group were finely ground in an agate mortar to pass a 100-mesh sieve, to reduce gypsum and other S-rich minerals, mixed thoroughly and stored in a plastic air tight containers at room temp. for total-N, organic-C, $CaCO_3$% and sulfur fractions analysis. Additionally, undisturbed vertical cylindrical volumes of field moist soil samples were monthly obtained using cylinder core samplers for estimating soils physical properties.

II.   General soils properties: were determined by the following routine work analyses:

Physical characteristics: bulk density (Mgm^{-3}), total porosity (%) and particle size distribution were determined using classical methods Klute (1986) and Carter (1993).

Chemical and organic properties: Soil reaction (pH-value), $CaCO_3$; organic-C (g.kg^{-1} soil); total-N (mg.kg^{-1} soil); total soluble cations and anions meq L^{-1} in saturated soil extracts were classically determined as described by Page *et al.* (1982), Carter (1993) and Rowell (1996). Ionic strength was calculated using the following equation reported by Tan (1993):

Ionic strength = $\dfrac{1}{2}\sum_{i=1}^{i=n}M_i Z_i^2$,

where M_i = conc. of ion (i) in mmoles L^{-1} and Z_i = charge of ion (i).

Table (1.2): Seasonal meterological features at Kafr El-Sheikh region over the experimental period (21 months) during two successive winter and summer seasons 1999/2000 and 2000/2001

Successive seasons from December 1999 to August 2001 (21 months)		Air temperature ºC				Relative humidity %				Soil temperature (ºC)			
										Soil depth sections (cm)			Mean
		Max.	Min.	Average	Dif.	Max.	Min.	Average	Dif.	5	10	20	
Winter Dec., Jan., Feb.	1999/2000	16.14	5.41	10.77	10.73	88.29	40.81	64.55	47.48	12.76	12.98	13.32	12.98
	2000/2001	18.31	5.91	12.11	12.40	92.29	42.08	67.19	50.21	13.97	14.36	15.24	14.52
Mean		17.23	5.66	11.44	11.57	90.29	41.45	65.87	48.85	13.36	13.67	14.28	13.75
Spring Mar., Apr., May	2000	22.00	8.96	15.48	13.04	87.70	30.97	59.34	56.73	-	-	-	-
	2001	25.73	12.66	19.20	13.07	91.56	33.44	62.50	58.12	-	-	-	-
Mean		23.87	10.81	17.34	13.06	89.64	32.21	60.92	57.43				
Summer Jun., Jul., Aug.	2000	29.00	18.28	23.64	10.72	88.50	36.97	62.74	51.53	31.03	30.72	30.06	30.60
	2001	30.99	19.68	25.34	11.31	94.96	42.56	68.76	52.40	32.85	31.96	30.66	31.83
Mean		30.00	18.98	24.49	11.02	91.73	39.77	65.75	51.97	31.95	31.34	30.05	31.28
Autumn Sept., Oct. Nov.	2000	25.42	13.83	19.63	11.59	89.93	39.72	64.83	50.21	-	-	-	-
	2001	26.98	15.21	21.10	11.77	92.17	39.81	65.99	52.36	-	-	-	-
Mean		26.20	14.52	20.37	11.68	91.05	39.77	65.41	51.29				
Annual grand mean	2000	23.14	11.62	12.38	11.52	88.61	37.12	62.87	51.49	21.89	21.85	21.69	21.79
	2001	25.50	13.37	19.44	12.14	92.75	39.47	66.11	53.27	23.41	23.16	22.65	23.10
Overall average		24.32	12.49	15.91	11.83	90.68	38.30	64.49	52.39	22.65	22.51	22.17	22.52

III.   Fractionation and chemical forms of sulfur in soils:
1.   Total sulfur fraction (Total-S fraction): Fraction (1.1)

The most widely accepted procedure for oxidation of total-S to sulfate ($SO_4^=$–S) in soils and soil extracts is the alkaline oxidation with sodium hypobromite (NaOBr), as described by Tabatabai (1982) and Guthrie & Lowe (1984).

This method involved reduction sulfate to hydrogen sulfide by acidic reducing mixture containing hydriodic acid (HI), hypophosphorus acid (H_3PO_2) and formic acid (HCOOH) at ratio 4:2:1 (v/v), using a modified Johnson and Nishita apparatus. The H_2S thus liberated was immediately absorbed in a buffer containing zinc- and sodium acetate and subsequently treated with acidic ρ-amino dimethylaniline hydrochloride and ferric ammonium sulfate solutions for methylene blue color development. The

extinction readings (E-values) of the methylene blue color were spectrophotometrically determined at wavelength of 670 nm. Total-S fraction in µg S. 100 ml^{-1} of the samples analyzed by reference to a calibration graph (stock solution 1000 µg S ml^{-1}).

Standard curve equation obtained as follows:

$$E = 0.010354\ C\,\mu g\ S/100\ ml\ at\ wavelength\ 670\ nm$$

The obtained total-S fraction (Fraction 1.1) was recorded as (mg -S. kg^{-1} soil).

2.   Residual total-S fraction: Fraction (1.2):

This fraction was directly determined in a manner similar to that used for the original total-S, but after extraction of easily and adsorbed inorganic sulfate-S fractions with calcium phosphate monohydrate Ca $(H_2PO_4)_2$ contained 500 ppm-P.

3.   Inorganic sulfur fraction: Fraction (3):

Generally, inorganic sulfur fraction: Fraction (3) was calculated according to the following equation. Fraction 3 = Fraction (3.1) plus Fraction (3.2).

Also, inorganic sulfur fraction (Fraction 3) was indirectly calculated according to the following equation: Fraction (3) = Fraction (1.1) minus Fraction (2). Details informations about the determination and calculation of inorganic-S fraction and its different S-compounds in studied soils are elucidated and illustrated by **El-Kammah (2008)**

3.1.   Inorganic sulfate-S fraction: Fraction (3.1):

The inorganic sulfate-S fraction was quantitatively calculated by summation of its forms, i.e. easily soluble (3.1.1.1.), adsorbed (3.1.1.2.) and insoluble plus co-precipitated co-crystallized with $CaCO_3$ (3.1.2.).

3.1.1. Easily soluble inorganic sulfate-S form: Fraction (3.1.1.1):

This soluble sulfate-S form was directly extracted without delay with weak salt solution containing 0.01 *M* $CaCl_2$ in (1:2) soil weight to extractant volume ratio, after shaken for 30 min (Tabatabai, 1982). The presence of $CaCl_2$ serves to reduce extraction of organic materials and increase flocculation of the soil in the solution. The soluble form thus extracted was spectrophotomertically determined using a methylene blue procedure as described for total-S.

Easily soluble plus adsorbed inorganic sulfate-S forms: Fraction (3.1.2.):

A solution of (500 ppm-P) on the form of calcium phosphate monohydrate $Ca(H_2PO_4)_2.H_2O$ was used at 1:10 soil to solution ratio for extraction these forms together. It is worthy to note that, because of soil aqueous extracts recover reduced inorganic-S compounds as well as sulfate-S, therefore, the associated reduced inorganic non-sulfate-S forms in the extracts [both 10 mM $CaCl_2$ and 0.5 M $Ca(H_2PO_4)_2$] were independently determined as described by Aspiras *et al.* (1972) and allowed for in calculation of the results.

3.1.2. Adsorbed inorganic sulfate-S form: Fraction (3.1.1.2.)

The adsorbed inorganic sulfate-S form was calculated by subtracting the amount of easily soluble sulfate-S from the amounts of easily soluble-plus adsorbed sulfate-S forms.

3.1.3. Insoluble plus co-precipitated/co-crystallized with CaCO$_3$ forms: Fraction (3.1.2.)

These forms were indirectly calculated by difference involving subtraction the amounts of residual total-S fraction after extraction of easily soluble plus adsorbed sulfate-S forms (Fraction 1.2) from amounts of original total-S fraction (Fraction 1.1).

3.2. Inorganic non sulfate-S fraction: Fraction (3.2):

Inorganic non-sulfate-S Fraction (3.2) was determined according to the method described by Tabatabai (1982) and Kowalenko (1993).

This method includes the reduction of all inorganic non sulfate-S fractions by boiling soil samples with zinc-hydrochloric acid and distillation, then subsequent determination of the H$_2$S as methylene blue.

3.2.1. Oxygenic high oxidized forms: Fraction (3.2.1.):

Thiosulfate and tetrathionate forms in soils were independently determined using the methods developed by Nor & Tabatabai (1976). This method involved extraction of these forms with 0.1 M LiCl solution and alkaline cyanolysis of thiosulfate-S in the presence of Cu^{2+}, and alkaline cyanolysis of tetrathionate-S in the absence of Cu^{2+}, determination of thiocyanate anion SCN$^-$ produced as ferric thiocyanate complex F-SCN in acidic medium at wave length 460 nm.

3.2.2. Residual inorganic non-sulfate-S form: Fraction (3.2.2.):

Lowly oxidized-S forms plus reduced forms of inorganic non-sulfate fraction were calculated involving subtraction the amounts of oxygenic highly oxidized forms (Fraction 3.2.1.) from the amounts of inorganic non-sulfate-S (Fraction 3.2.).

Rhodanese activity (EC 2.8.1.1.): was determined by the method developed by Deng & Dick (1990) and Tabatabai (1994). The method based on spectrophotomertic determination of thiocyanate anion (SCN$^-$) produced by soil rhodanese activity when soil sample was incubated with buffered 0.1 M sodium thiosulfate and 0.1 M potassium cyanide solutions at 37°C for one hour.

Thiocyanate anion SCN$^-$ in the filtrate was determined as (Fe-SCN) complex in acidic medium and calculated by reference to a calibration graph using standard curve equation.

$$E = 0.002475 \text{ C nano moles SCN}^{-1}. \ 5 \text{ ml}^{-1}$$

Rhodanese activity was recorded as nano moles SCN$^-$ released. g^{-1} soil. hour^{-1} at pH 7.1 at 37°C.

Dehydrogenase activity was determined using the procedure reported by Tabatabai (1994). This method involves colorimetric determination of 2, 3, 5-triphenyl tetranzolium formazan TPF (C$_{19}$H$_{16}$N$_4$, Mw 300.4). produced by dehydrogenase enzymes activity when soil samples was incubated with 2, 3, 5-triphenyl tetrazolium chloride TTC at 37°C and pH 8.5 for 24 hours. The extinction-readings of the reddish color of TPF in the filtrate

was spectrophotometrically determined at a wavelength 485 nm with methanol as a blank. The produced amount of TPF was calculated by reference to a calibration graph prepared from TPF standard solutions (μg TPF/100 ml). Results were recorded as μg 2, 3, 5-triphenyl tetrazolium formazan (TPF) produced (or H_2 consumed) per gram of soil per one hour using the standard curve formula:

$$E = 0.00033592 \ C_{\mu gTPF/100 \ ml}$$

Statistical analysis:

All tabulated experimental and analytical data were statistically analyzed to clarify the obtained results as stated by Gomez and Gomez (1976)

RESULTS AND DISCUSSION

1.   Total sulfur fraction:

Data of total-S fraction (Fraction 1.1), are given in Table (1.3 and 2) and illustrated in Figs. (1 and 2). Total-S content ranged from 463.3. 237.5 and to 200 mg S.kg^{-1} soil (avg. 300) for S_1, S_2 and to S_3. Its standing stock was 257.5 kg S fed^{-1}, which was within the normal range found in different soils of other regions. Most agricultural soils contain total-S value between 100 and 500 mg S. kg^{-1} soil (Tabatabai, 1982). Similar results were obtained by Neptune *et al.* (1975); and Mansfeldt & Blume (2002).

Statistically, total –S content in winter seasons: (335.5 mg S. kg^{-1} soil, with standing stock 281.2 kg S. fed^{-1}) was greater than those in summer seasons (265 mg S. kg soil, its standing stock 234.9 kg S. fed.$^{-1}$.

Total-S values had negative significant correlations with ionic strength (r = -0.72**), max. air temp. (r = -0.55*) and soil temp. (r = -0.71*) bulk density (r=-0.83**, soil pH (r=-0.75**) and C/S ratio (r = -0.57**). Conversely, total-S had positive highly significant correlations with water table depth (r = 0.93**), organic-C (r = 0.89**), total-N (r = 0.83**) and clay content (r = 0.72**).

2.   Inorganic-sulfur fraction:

Regarding inorganic-S fraction (Fraction 3), data shown in Tables (1.3 and 3) and illustrated in Figs. (1 and 3). Inorganic-S were 169.11, 69.76 and 95.16 mg S. kg^{-1} soil (avg. 111.3) for traditional-drained, poorly drained and badly drained soils, respectively regardless of their bulk densities.

Their corresponding standing stocks taking to soil bulk densities in consideration were 136.5, 59.0 and 94.4 kg S. fed^{-1} (avg. 96.65), respectively.

Percentage distribution of inorganic-S fraction expressed as % of total-S accounted for 37.77%, which is only minor fraction compared with the major fraction of organic-S 62.23%..

These analytical obtained results are in accordance with the data obtained by Neptune *et al.* (1975) and Mansfeldt & Blume (2002) and Hu *et al.* (2002).

Statistical data showed that, this S-fraction and its percentage distribution in winter seasons: (125.8 mg S kg⁻¹ soil, accounted for 37.9% of total-S and its standing stock 106.1 kg S. fed.⁻¹) was higher and significant than those obtained in summer seasons: (96.8 mg S. kg⁻¹ soil, accounted for 37.6% of total-S and its standing stock 87.17 kg S. fed.⁻¹.

In well-drainage soils, most of inorganic-S fractions exist on sulfate-S fraction and the amounts of reduced inorganic-S compounds such as sulfides are generally <1% of total-S (Tabatabai, 1982 and Freney, 1983).

However, it was reviewed in literature that inorganic-S content accounted for less than 25% of the total-S in most agricultural soils in temperate and tropic & subtropic regions.

Thus, results revealed that total inorganic-S content in some Egyptian soils (semi-arid region) is higher than that reported by others.

2.1. Inorganic sulfate-S fraction:

Analytical results pertained to this fraction (Fraction 3.1) are displayed in Figs. (1 and 4). The magnitudes of inorganic sulfate-S fraction were 159.1, 64.5 and 94.8 mg S. kg⁻¹ soil with grand mean average (106.1) for S_1, S_2 and S_3, respectively. Percentage distribution of this fraction, expressed as percentages of the of total-S pool and of inorganic-S fractions accounted for 36.32% and 95.61%. Inorganic sulfates-S value in experimental winter seasons: was 118.6 mg S. kg⁻¹ soil, referred as (36.9% of total-S and 96.9% of inorganic-S fractions). Such values were higher in comparison with the obtained results in summer seasons (93.6 mg S. kg⁻¹ soil, referred as 35.7% and 94.3% of total-S and inorganic-S fractions.

Table (1.3.): Relative distribution of total inorganic-S fractions.

Main Soil-S fractions	Content mg S. kg⁻¹ soil	Percentage distribution values			
		Total S pool	Total inorganicS	Total inorganic sulfateS	Total in organic non-sulfateS
1: Total-S pool (Fraction 1.1)	300.25	100			
Organic-S fraction (El-Kammah, 2008)	188.91	62.2			
2: Inorganic-S fraction (Fraction 3)	111.34	37.7	100.00		
2.1. Inorganic sulfate-S fraction (Fraction 3.1)	106.18	36.3	95.61	100	
2.1.1.: Easily soluble sulfate-S form (Fraction 3.1.1.1)	82.10	27.7	74.05	77.61	
2.1.2.: Adsorbed sulfate-S form (Fraction 3.1.1.2.)	1.80	0.51	1.28	1.347	
2.1.3.: Dissolved sulfate-S form (fraction 3.1.2.)	22.27	8.1	20.27	21.05	
2.2.: Inorganic non-sulfate-S fraction (fraction 3.2.)	5.16	1.4	4.38		100
2.2.1.: Oxygenic highly oxidized-S form (Fraction 3.2.1.)	4.17	-	3.57	-	84.21
2.2.2.: Oxygenic lowly oxidized-S plus reduced-S forms (Fraction 3.2.2.)	0.99	-	0.80	-	15.79

See Fig. (1) and M. & M.

Therefore, it is likely to say that inorganic sulfate-S fraction is the main inorganic-S fraction in the studied soils. Inorganic sulfate-S fraction had a positive significant correlation with clay content (r = 0.85**). Inorganic sulfate-S content in semi-arid Egyptian soils was more higher than that reported for soils of other regions. Brazilian soils (subtropical region) contained from 5% to 23% inorganic sulfate-S fraction, while Iowa soils (temperate region) contained from 2 to 8%, which occurred entirely as sulfate-S (Nepturne *et al.,* 1975 and Tabatabai, 1982 and 1984).

Table (2): Total-S pool and total HI reducible-S contents in studied soils under different drainage conditions.

Successive seasons from December 1999 to August 2001 (21 months)		Total sulfur fraction (Total-S pool) (FRACTION 1.1)						Total hydroiodic acid reducible sulfur fraction (total HI-reducible-S fraction)					
		Messier (S$_1$) Traditional drained		Kafr Dokhmeas (S$_2$) Poorly drained		Kafr El-Sheikh (S$_3$) Badly drained		Messier (S$_1$) Traditional drained		Kafr Dokhmeas (S$_2$) Poorly drained		Kafr El-Sheikh (S$_3$) Badly drained	
		mg S kg^{-1} soil	Standing stock kg S fed^{-1}	mg S kg^{-1} soil	Standing stock kg S fed^{-1}	mg S kg^{-1} soil	Standing stock kg S fed^{-1}	mg S kg^{-1} soil	Standing stock kg S fed^{-1}	mg S kg^{-1} soil	Standing stock kg S fed^{-1}	mg S kg^{-1} soil	Standing stock kg S fed^{-1}
Winter seasons Dec., Jan., Feb.	1999/2000	567	447.2	296	231.0	250	242.1	360.33	284.21	153.01	126.21	154.01	149.13
	2000/2001	474	384.3	244	207.0	182	173.0	269.05	218.15	119.67	95.49	123.48	117.39
Mean		520.50	416.3	270	219.9	216	207.2	314.69	251.68	136.34	111.69	138.74	133.12
Summer seasons Jun., Jul., Aug.	2000	416	321.0	215	191.8	207	211.4	211.64	163.33	92.42	90.85	130.52	133.29
	2001	396	340.0	195	175.1	161	165.7	207.76	178.4	95.48	78.05	95.28	98.08
Mean		406	330.9	205	183.5	184	188.6	209.70	170.85	93.95	84.47	112.90	115.76
Grand mean		463.25	373.6	237.5	203.0	200	198.5	262.20	211.27	115.15	98.94	125.82	124.87

Thus, it is worthy to note that, inorganic sulfates-S is rapidly abiotic incorporated into organic matter as sulfate-esters, sulfonate-S and amino acids-S fractions which regarded as a short term source for S (Ghani *et al.,* 1993); The incorporated of sulfate-S into the ester sulfate pool(as phenolic SO$_4$-ester linkage) occurs in all horizons of the soils (Schindler *et al.*, 1986).

Data reported here are consistent with the importance of organic-S but differed with respect to S-phytoavailablity. Organic-S needs to mineralize because plants absorb S in form of inorganic sulfate-S. However, the incorporation of S into high-molecular weight fractions such as humic acids prevents the rapid S-mineralization (Hu *et al.*, 2002).

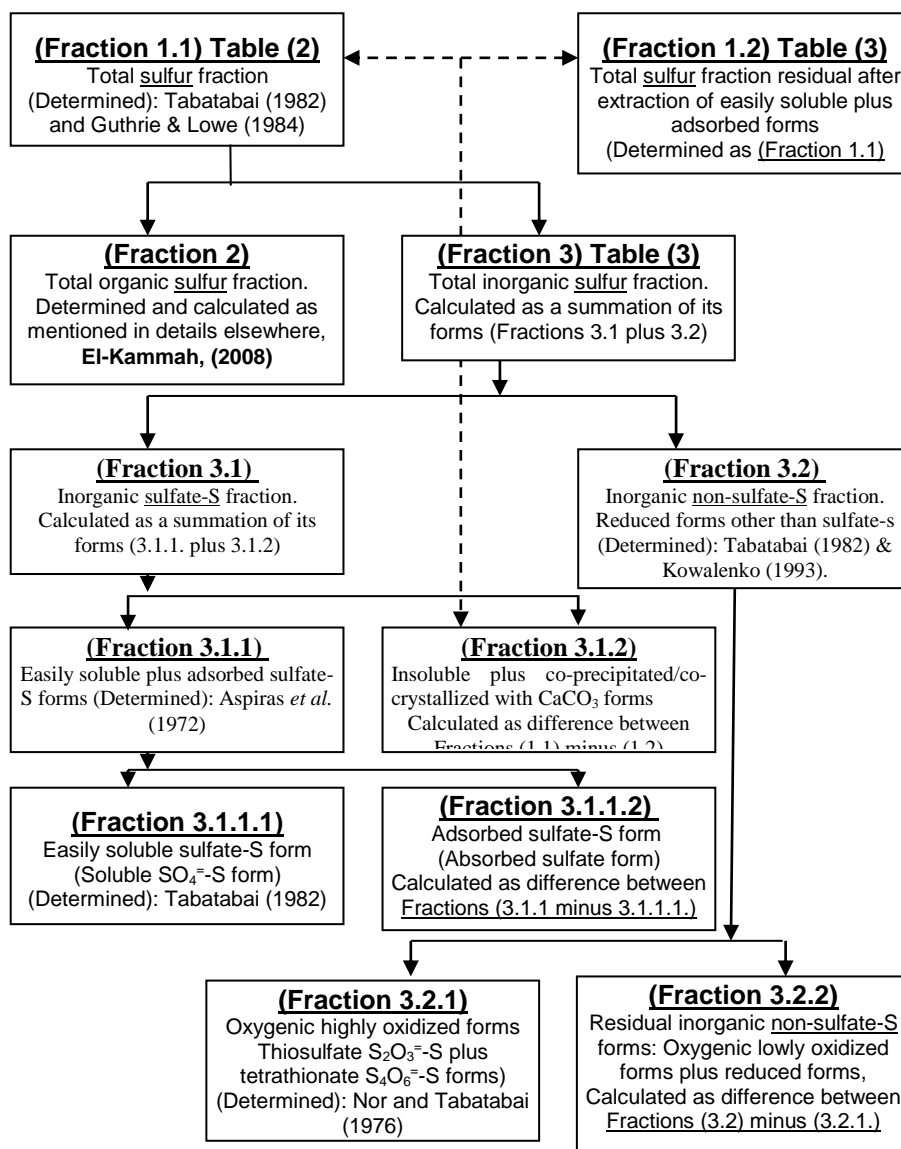### 2.1.1. Easily soluble sulfate-S form:

Analytical obtained data of this form (Fraction 3.1.1.1.) are illustrated in Figs. (1 and 4). Soluble sulfate-S values in studied soils were 124.7, 51.5 and 70.1 mg S. kg^{-1} soil (avg. 82.1) for S$_1$, S$_2$ and S$_3$, respectively. Expressed as percentages of total-S pool, inorganic-S and inorganic sulfate-S fractions accounted for 27.7, 74.0 and 77.6%, respectively (Table 1.3). Soluble sulfate-S fraction and its percentage distribution value. in winter seasons was 92.3 mg S. kg^{-1} soil, referred as (28.4% of total-S; 74.5% of inorganic-S and 78.5% of inorganic sulfate-S fractions).

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Such values were much more higher than those obtained in summer seasons; 71.8 mg S. kg^{-1} soil, referred as follows (27.0%, 73.5% and 76.6%), respectively.

Fractionation of Soil Inorganic Sulfur Components

| **(Fraction 1.1) Table (2)**
Total sulfur fraction
(Determined): Tabatabai (1982)
and Guthrie & Lowe (1984) | **(Fraction 1.2) Table (3)**
Total sulfur fraction residual after
extraction of easily soluble plus
adsorbed forms
(Determined as (Fraction 1.1) |

(Fraction 2)
Total organic sulfur fraction.
Determined and calculated as mentioned in details elsewhere, **El-Kammah, (2008)**

(Fraction 3) Table (3)
Total inorganic sulfur fraction.
Calculated as a summation of its forms (Fractions 3.1 plus 3.2)

(Fraction 3.1)
Inorganic sulfate-S fraction.
Calculated as a summation of its forms (3.1.1. plus 3.1.2)

(Fraction 3.2)
Inorganic non-sulfate-S fraction.
Reduced forms other than sulfate-s (Determined): Tabatabai (1982) & Kowalenko (1993).

(Fraction 3.1.1)
Easily soluble plus adsorbed sulfate-S forms (Determined): Aspiras *et al.* (1972)

(Fraction 3.1.2)
Insoluble plus co-precipitated/co-crystallized with CaCO$_3$ forms
Calculated as difference between Fractions (1.1) minus (1.2)

(Fraction 3.1.1.1)
Easily soluble sulfate-S form
(Soluble SO$_4^=$-S form)
(Determined): Tabatabai (1982)

(Fraction 3.1.1.2)
Adsorbed sulfate-S form
(Absorbed sulfate form)
Calculated as difference between Fractions (3.1.1 minus 3.1.1.1.)

(Fraction 3.2.1)
Oxygenic highly oxidized forms
Thiosulfate S$_2$O$_3^=$-S plus tetrathionate S$_4$O$_6^=$-S forms)
(Determined): Nor and Tabatabai (1976)

(Fraction 3.2.2)
Residual inorganic non-sulfate-S forms: Oxygenic lowly oxidized forms plus reduced forms,
Calculated as difference between Fractions (3.2) minus (3.2.1.)

Fig. (1): A conceptual experimental diagram that integrates the main forms of labile and stable inorganic sulfur fractions in selected soils and the ways by which their amounts are quantitatively determined and calculated
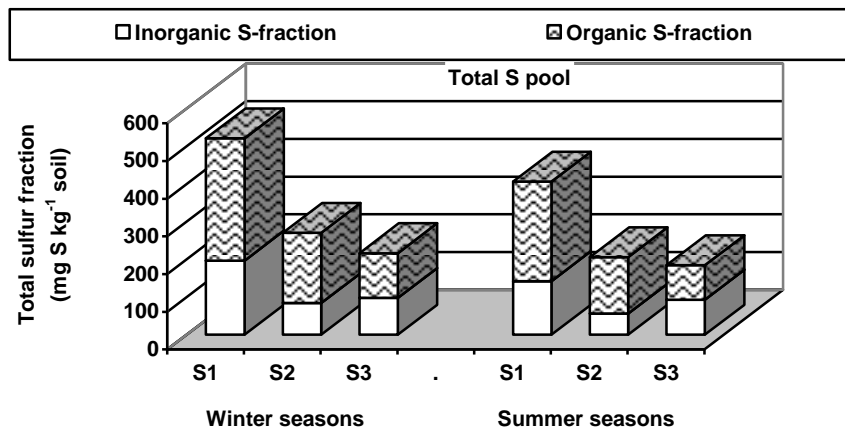
Fig. (2): A schematic diagram shows total-S pool and the distribution of its components in the studied soils.
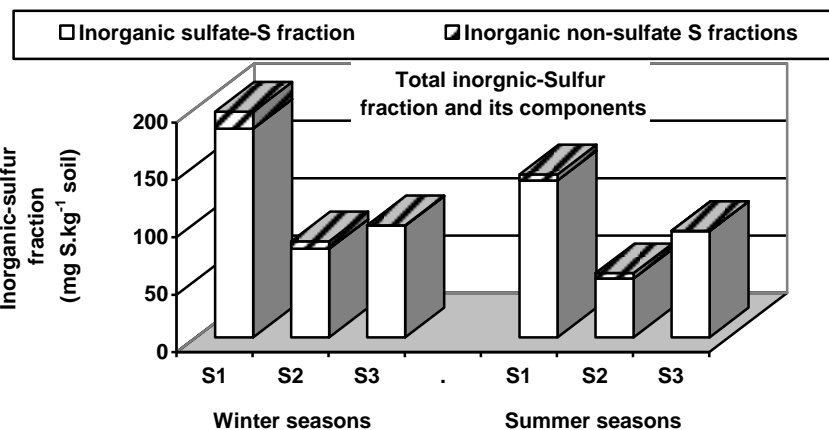

Fig. (3):   A schematic diagram illustrated inorganic-S fraction and the distribution of its components in the studied soils.

Easily soluble sulfate-S was higher than that reported in literature. Germida *et al.* (1992) reported that soluble sulfate-S accounted for less than 5% of total-S in most well-drained temperate soils. However, Tabatabai (1982) reported that higher levels of soluble sulfate-S may accumulate under arid conditions. The higher level of soluble sulfate-S in semi arid region may be due to the effect of seasonal conditions on mineralization of organic-S, the application of fertilizer materials, the sulfate content of rain and irrigation with wastewaters. So, it is very common to observe a considerable seasonal fluctuations in the amounts of soluble sulfate-S. Tabatabai & Laflen (1976) confirmed this elucidation.

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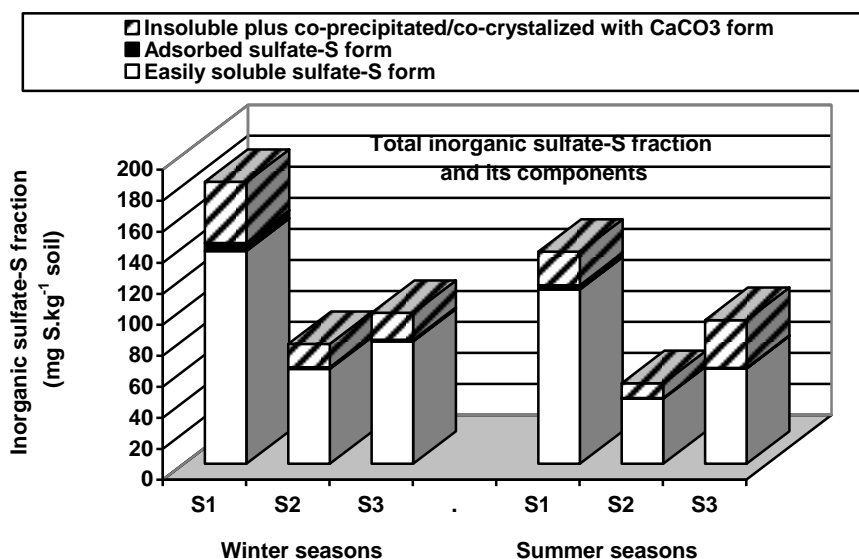
Fig. (4): A schematic presentation of total inorganic sulfate-S fraction and the distribution of its components in the studied soils.

2.1.2. Adsorbed sulfate-S form:

Results of adsorbed sulfate-S values (Fraction 3.1.1.2.) in selected soils are illustrated in Figs. (1 and 4). Examination of the tabulated data appears that, adsorbed sulfate-S values were 3.9, 0.7 and 0.7 mg S. kg^{-1} soil (avg. 1.8) for S_1, S_2 and S_3, respectively (Table 1.3). Distribution of adsorbed-S, expressed as % of total-S, inorganic-S and inorganic sulfate-S fractions accounted for 0.5; 1.2% and 1.3%, respectively. Statistical data revealed that adsorbed sulfate-S value and its percentage distribution in winter seasons: 2.43 g S. kg^{-1} soil, referred as (0.65% of total-S; 1.65% of inorganic-S and 1.65% of inorganic sulfate-S fractions) such values were higher than those obtained in summer seasons; 1.176 mg S. kg^{-1} soil, presented as 0.36, 0.93 and 1.05%, respectively. Magnitude values of adsorbed sulfate-S in year 1999/2000 (1.9 mg S. kg^{-1} soil) was more pronounced than those obtained in year 2000/2001 (1.7 mg S. kg^{-1} soil). So, inorganic adsorbed sulfate-S value was the minor S form of inorganic sulfate-S in studied soils and had negative significant correlation with pH value (r = -0.94**) and positively with clay content (r = 0.88**). Similar results reported by Aulakh and Dev (1976) confirmed this observations. They found that increasing soil pH caused a sharply decrease in sulfate-S adsorption. Also, Kowalenko (1993) stated that soil adsorption capacity for sulfate-S is negligible above pH 6.5 and increase with decreasing pH below this value. Generally, adsorption of inorganic sulfate-S is influenced by soil pH, nature of collidal surfaces, presence of amorphous Fe and Al-oxides, organic ligands and high concentrations of soluble sulfate-S (Tabatabai, 1982; Kowalenko, 1993. On a theoretical basis, the soluble and adsorbed forms of sulfate-S are the primary pools of sulfur in

the soil that are immediately available for plant uptake (Acquaye and Kang, 1986 and Kowalenko, 1993).

2.1.3. Insoluble plus co-precipitated /co-crystallized sulfate-S with CaCO₃ forms:

Analytical results of insoluble plus co-precipitated/ cocrytalized sulfate-S forms (Fraction 3.1.2.) are illustrated in Figs. (1 and 4). Values of these forms were 30.4, 12.3 and 24.0 mg S. kg^{-1} soil (avg. 22.7) for S_1, S_2 and S_3, respectively. Distribution percent of these forms were expressed as % of: total-S; total inorganic-S and total inorganic sulfate-S fractions which accounted for 8.0; 20.2 and 21.0%, respectively. Content of these forms and their percentage distribution in winter seasons was: 23.9 mg S. kg^{-1} soil, referred as: (7.1% of total-S; 18.7% of inorganic-S and 19.8% of inorganic sulfate-S fractions). These values were greater than those obtained in summer seasons: 20.65 mg S. kg^{-1} soil, referred as: 8.9%; 21.7% and 22.2%, respectively. Dissolved sulfate-S compounds were positive significantly correlation with CaCO₃ content (r = 0.79**). Reported data by Roberts & Bettany (1985) and Hu *et al.* (2002) confirmed these obtained results.

2.2. Total inorganic non-sulfate-S fraction:

Analytical data of oxyanions other than sulfate-S (Fraction 3.2) are illustrated in Figs. (1, 4 and 5). Its values were 9.98, 5.25 and 0.27 mg S. kg^{-1} soil (avg. 5.16) for S_1, S_2 and S_3, respectively. Inorganic non-sulfate-S value, expressed as a percent of total-S and inorganic-S accounted for 1.45% and 4.38%. Value in winter seasons: 7.15 mg S. kg^{-1} soil, which referred to (1.77% of total-S and 5.07% of inorganic-S fractions). The value was higher and highly significant than those obtained in summer seasons: 3.18 mg S. kg^{-1} soil, referred to 1.13 % and 3.69%, respectively.
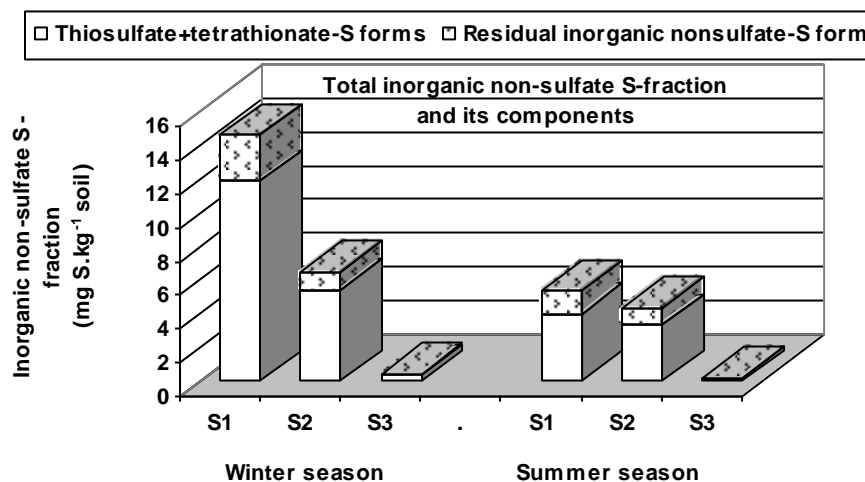

Fig. (5): A schematic presentation of total inorganic non-sulfate-S fraction and its percentage distribution of its components in the studied soil.

Total inorganic non sulfate-S content in studied soils (semi-arid region) was the minor fraction of the total inorganic-S pool comparison with the major inorganic sulfate-S. Nuptune *et al.* (1975) reported that no inorganic non sulfate-S could be detected in Brazilian subtropic soils and Iowa temperate soils. This fraction had a positive significant correlation with $CaCO_3$ content (r = 0.73**) and negative with C/S ratio (r = -0.85**). Similar results reported by (Takar, 1988) who found that, non sulfate-S fraction in alkaline soils was more pronounced than those obtained in acid soils.

2.2.1. Oxygenic highly oxidized-S form:

Data of thiosulfate-S plus tetrathionate-S values (Fraction 3.2.1.) are illustrated in Figs (1 and 5). Contents of these forms were 7.89, 4.37 and 0.26 mg S. kg^{-1} soil (avg. 4.17) for S_1, S_2 and S_3, respectively (Table 1.3).

Its distribution percent expressed, as % inorganic-S and of inorganic non-sulfate-S fractions accounted for 3.575% and 84.21%, respectively (Table 1.3). Content of this form and its distribution percent in winter seasons was 5.87 mg S kg^{-1} soil, referred to (4.20% of inorganic-S and 86.87% of inorganic non-sulfate-S fractions). These values were higher and significant than those obtained in summer seasons: 2.47 mg S. kg^{-1} soil, referred to 2.9% and 81.5%, respectively.

2.2.2. Oxygenic lowly oxidized-S plus reduced-S forms:

Values of these forms (Fraction 3.2.2.) are illustrated in Figs. (1 and 5). Contents were 23.1, 1.0 and 0.02 mg S. kg^{-1} soil (avg. 0.99) for S_1, S_2 and S_3, respectively. Distribution percent of these forms are expressed as % of total-S and inorganic non-sulfate-S. Their accounts were 0.807% and 15.79%. Values and their percentages in winter seasons was 1.278 mg S. kg^{-1} soil, referred to 0.881% and 18.13%, respectively. Such values were significantly greater than those obtained in summer seasons: 0.708 kg S. kg^{-1} soil, referred as (0.733% and 13.45%), respectively. Content of oxygenic highly oxidized-S was the dominant-S component of total inorganic non sulfate-S fraction in studied soils. Meanwhile oxygenic lowly oxidized-S plus reduced-S compounds, which are relatively insoluble, had the lowest values. Data reported in literature revealed that, measurable quantities of thiosulfate and tetrathionate may be found and detected in soils treated with element-S fertilizer or exposed to pollutants from wastewaters irrigation or probably present as intermediates during oxidation or reduction of S-compounds. (Nor and Tabatabai, 1976; Tabatabai, 1982 and 1984; Lawrence **et al.**, 1988 and Kowalenko 1993. Recent research has been shown that the sedimentary organic-S compounds through the abiotic incorporation of reduced inorganic non-sulfate-S compounds are generated mainly by pathways involving the reactions of various S nucleophiles (reduced-S species such as hydrogen sulfide, polysulfides, elemental S^o) with functionalized organic molecules under a reducing environment (Morra *et al.,* 1997 and Mansfeldt & Blume, 2002). The reduction of sulfate-S which generates S-nucleophiles is mediated by microorganisms, but subsequent incorporation of the reduced S species into sedimentary organic matter is abiotic process (Mansfeldt & Blume 2002). In addition, the depositional conditions favorable for abiotic S incorporation could depend on the compeitition between S binding to organic matter,

versus iron (Morra *et al.,* 1997). Therefore, Parameters such as organic matter, iron and clay contents are important for C/S ratios. In general, grand mean values of all different inorganic-S fractions and their percentage distributions in studied soils in year 1999/2000 were markedly pronounced and high significant in comparison with their obtained data in year 2000/2001.

2.   Enzymes involved inorganic-S mineralization:

1.   Rhodanese enzyme activity (EC 2.8.1.1.):

Rhodanese activity in studied soils are illustrated in Figs. (6 and 7). Statistical results indicated that grand mean values of winter and summer seasons were 539.5, 260 and 185.5 nano moles SCN^- released. g^{-1} soil. $hour^{-1}$ (avg. 328.3) for S_1, S_2 and S_3, respectively. Also, obtained data revealed that, an average conditions, of the soils, grand mean activity in winter seasons (476) was high significant and greater than those obtained in summer seasons (180.7) Monthly distributions of this enzyme activity in the course of the experimental winter seasons were 348, 553 and 527 on winter months Dec. Jan. and Feb., respectively. On the other hand the values within summer seasons were 255.7, 170.3 and 116.1 on summer months June, July and August, respectively. With respect to annual fluctuations, rhodanese activity in experimental year 1999/2000 (385.6) was highly significant and greater than those obtained in year 2000/2001: (271.2). In literature, rhodanese activities ranged from 120 to 875 and from 38 to 130 nmole SCN^- produced per gram per hour in Iowa and Saskatchewan soils, respectively (Lawrence *et al.*, 1988; Deng and Dick, 1990 and Germida *et al.*, 1992).
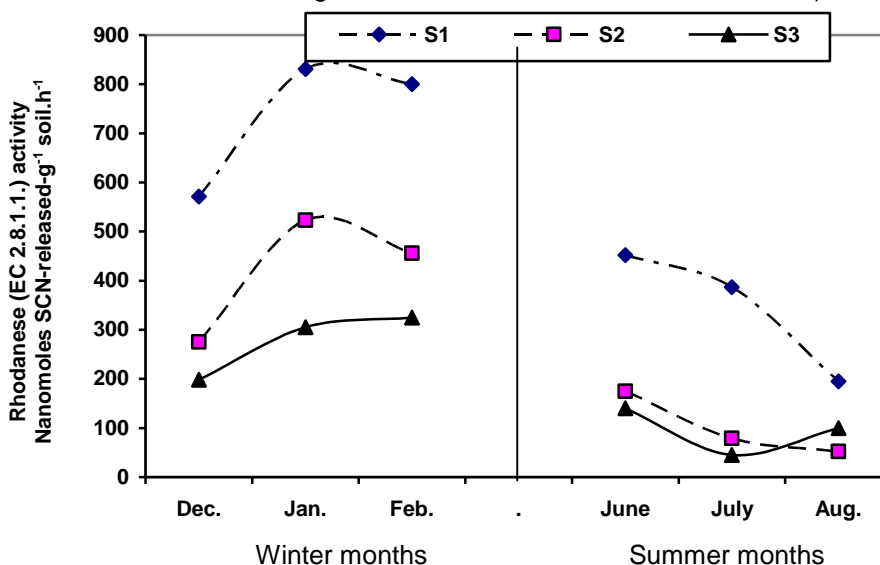
Fig. (6):   Seasonal courses of grand mean average of the soil rhodanese activity in studied soils.

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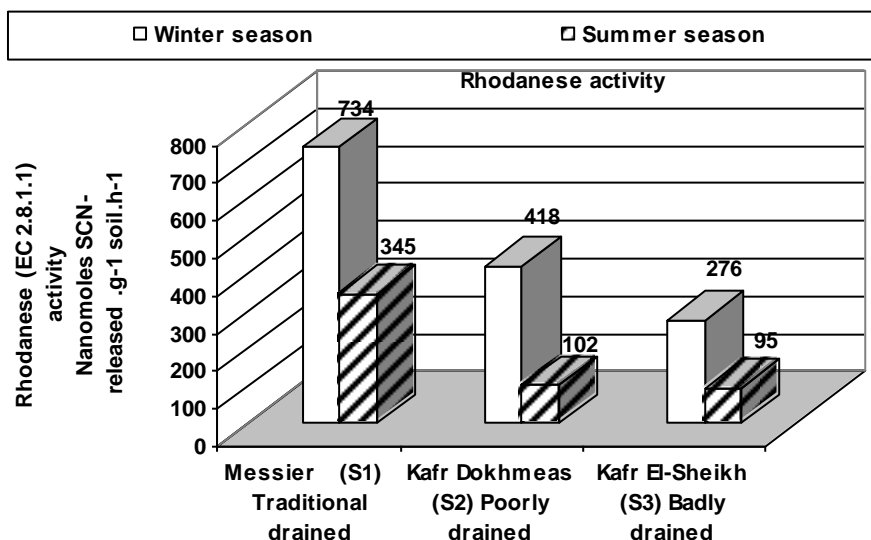
Fig. (7):   A schematic diagram illustrates rhodanese activity in the studied soils

Consequently, rhodanese activity reached its maximum values in traditional-drained soils in year 1999/2000, in winter seasons and chiefly on Feb. over the experimental period elongated 21 months. However, it reached its minimum values in poorly and badly drained soils, in year 2000/2001, in summer seasons and mainly on August as illustrated in Figs. (6 and 7). Rhodanese activity was positive significantly correlated with organic-C content ($r = 0.88^{**}$); total-N ($r = 0.86^{**}$); pH ($r = 0.95^{**}$) and water table depth ($r = 0.90^{**}$). Additionally, rhodanese activity also had positive correlations with total non sulfate-S ($r = 0.83^{**}$), thiosulfate plus tetrathionate ($r = 0.96^{**}$) and lowly oxidized plus reduced-S ($r = 0.56^{*}$). Its values was also negatively and significant correlated with ionic strength ($r = -0.78^{**}$), max. air temp.($r = -0.74^{**}$), soil temp. ($r = -0.69^{**}$) and mainly with total sulfate-S ($r = -0.76^{**}$) and soluble sulfate-S ($r = -0.96^{**}$). Negative significant correlation between rhadonese activity and soluble sulfate-S fraction indicates that soluble sulfate-S has a potential role in suppressing rhodanese activity. These observations were coincides with the results reported by Deng & Dick (1990). They demonstrated that soluble sulfate-S strongly inhibits rhodanese activity, since, synthesis of rhodanese enzyme in soils is reduced in the presence of sulfate-S

2.   Dehydrogenase enzymes activity:
Analytical results belong to dehydrogenases activity in studied soils shown in Figs. (8 and 9). Dehydrogenases activities on the average conditions of winter and summer seasons were 15.21, 9.44 and 3.56 µg TPF formed.g^{-1} soil. hour^{-1} (avg. 9.41) for S_1, S_2 and S_3 respectively.
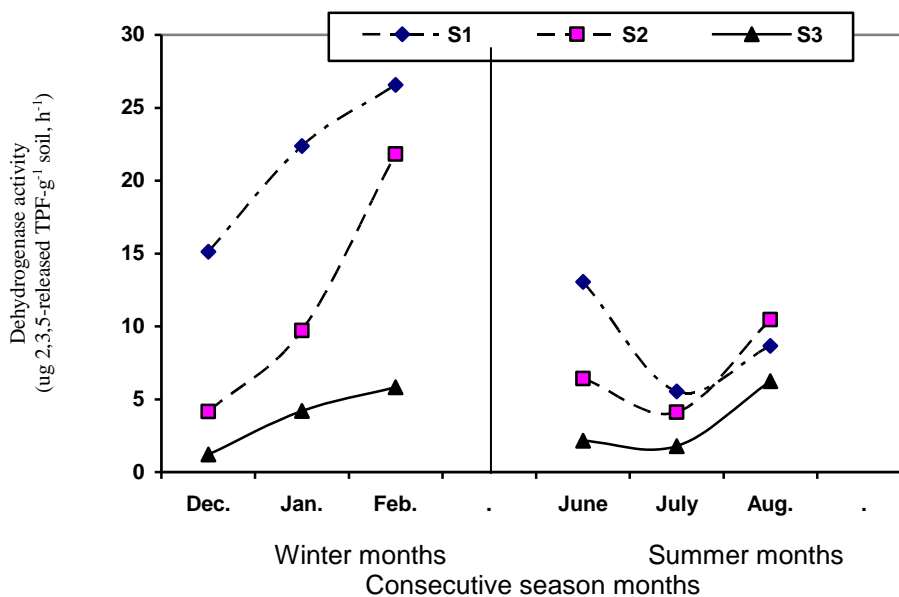
Fig. (8): Seasonal changes of grand mean average of soil dehydrogenase activity in studied soils.
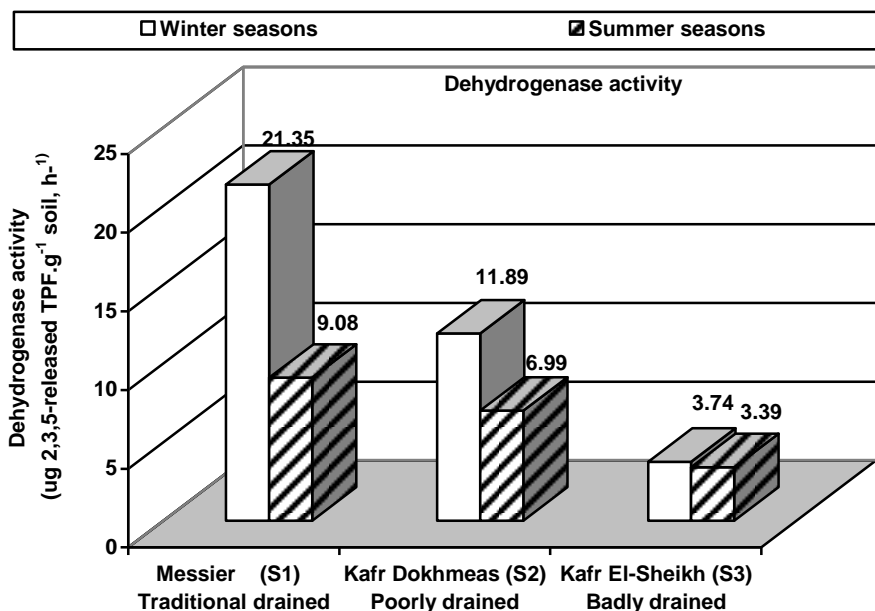

Fig. (9): A schematic diagram shows dehydrogenase enzyme activity in the studied soils.

Statistical results revealed that enzyme activity in winter seasons: (12.33) was highly significant and grater than those obtained in summer

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seasons: (6.47). On the other hand, monthly distribution of enzyme activities within winter seasons: were 6.83, 12.08 and 18.07 on winter months Dec., Jan. and Feb., respectively. Meanwhile within summer seasons: were 7.21, 3.77 and 8.45 on summer months June, July and August, respectively.

Dehydrogenase activity in year 1999/2000: (12.14) was highly significant and greater than those obtained in year 2000/2001: (6.676) over the experimental period belonged 21 months. Similar data were confirmed these observations reported by Tabatabai (1994). Commonly, dehydrogenase activity reached its maximum values in traditional drained soils in comparison with other drainage conditions; in year 1999/2000; in winter seasons and mainly on Feb. However, it reached its minimum values in badly drained soils; in year 2000/2001, in summer seasons and chiefly on July. Dehydrogenases activity had positive significant correlation with organic-C (r = 0.89**). However, it had a negative correlations with max. air temp. (r = -0.59**), soil temp. (= -0.82**) and ionic strength (r = -0.88**).

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نشـاط إنزيمـات تحـولات الكبريـت وعلاقتهـا التبادليـة بمحتـوى وتوزيـع مكونـات الكبريت المعدنية المختلفة فى الأراضى المتأثرة بالأملاح

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أقيمت هذه الدراسة الشاملة تحت الظروف التجريبية الحقلية فى ثلاث مواقع بكفرالشيخ تعكس خواص المناطق شبه الجافة ، تتصف الأراضى المختارة بأنها طينية متأثرة بالأملاح بدرجة خفيفة ، واقعة تحت ظروف صرف ومستوى أعماق ماء أرضى مختلفة ، وتروى لمدة طويلة بمياه ملوثة مختلفة المصادر. الهدف مـن البحـث هـو (1) دراسـة النشـاط البيولـوجى لـبعض إنزيمـات تحـولات الكبريـت: الرادونيـز *Rhadonese* ، الـدى هيـدروجينيز *Dehydrogenase* فى الأراضى المختـارة ، (2) تقدير المكونـات المختلفة للكبريت المعدنية ومركباتها وتوزيعاتها النسبية للحصول على معلومـات كاملة عن رصيدها الكمى Standing stocks، (3)) ربط المتغيرات الموسمية والبيئية بنشاط الإنزيمات وعلاقتها بالمكونات المختلفة للكبريت المعدنى ، ولتقدير هذه المكونات تم وضع تصور ديجرامى يتضمن كل الطرق التقليدية المستخدمة فى تقديرها وكيفية حسابها.

ويمكن تلخيص النتائج التحليلية والإحصائية المتحصل عليها فى الآتى:

*   طبقا للنشاط البيوكيميائى للإنزيمـات كمتوسط لتـأثير خـواص الأراضى الفيزيائيـة الكيميائيـة والعضـوية الكيميائيـة ، حالـة الصـرف ، عمـق مسـتوى المـاء الأراضـى ، والظـروف البيئيـة المحيطـة بمنطقة الدراسـة (درجة حرارة الهواء ودرجة حرارة الأراضى) وتذبذبتها الشهرية والموسمية والسنوية. فإن متوسط نشاط إنزيم الرادونيز 328.35 nano moles SCN- relased-g-1 soil. hr-1 ونشاط إنزيم الدى هيدروجينيز 9.408 µg TPF produced.g-1 soil. hr-1.

*   محتوى الأراضى من الكبريت الكلى Total-S والكبريت المعدنى الكلى Total inorganic-S هو 300 ، 111.34 مليجـرام كبريـت/كجم أرض ورصـيدهما الكمـى Standing stock 257.48 ، 96.61كجم كبريت/فدان ويمثل الكبريت المعدنى 37.77% من الكبريت الكلى بالتربة وأن قيمتـه النسبية فى الأراضى المدروسة أعلى من تلك المقدرة فى المناطق المناخية الأخرى (الرطبة والمعتدلة والشبة استوائية).

*   محتوى الأراضى من الكبريت المعدنى الكلى فى صـورة كبريتـات (الكبريتـات المعدنيـة الكليـة) Total inorganic sulfate-S 106.18 مليجرام كبريت/كجم أرض يمثل 95.61% من الكبريت المعدنى الكلى Total inorganic-S لذا يعتبر المكون السائد لصور الكبريت المعدنى الكلى بالأراضى ، وأن قيمتـه النسبية عاليـة بالمقارنة بأراضى المناطق المناخيـة الأخرى. ويـرتبط معنويـا مـع محتوى الطـين بالأراضى والكبريتات المعدنية الكلية تشتمل على ثلاثة مكونات معدنية هى: (1) الكبريتات المعدنية سهلة الذوبان Easily soluble sulfate-S: محتوى الأراضى منها 82.109 مليجرام كبريت/كجم أرض

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تمثل 77.16% من الكبريتات المعدنية الكلية حيث تعتبر المكون السائد لها ، (2) الكبريتات المعدنية المدمصة Adsorbed sulfate-S: محتوى الأراضى منها 1.804 مليجرام كبريت/كجم أرض تمثل 1.347% من الكبريتات المعدنية الكلية وترتبط ارتباطا معنويا سالبا مع pH وموجبا مع محتوى الأراضى من الطين ، (3) مجموعة الكبريتات المعدنية غير الميسرة (الكبريتات غير الذائبة ـ الكبريتات المترسبة ـ الكبريتات المرتبطة بللوريا بكربونات الكالسيوم: محتوى الأراضى منها 22.27 مليجرام كبريت/كجم أرض تمثل 21.05% من الكبريتات المعدنية الكلية. وهى ترتبط ارتباطا معنويا موجبا مع كربونات الكالسيوم لذا يتضح من النتائج أن الكبريتات المعدنية الذائبة تمثل المكون الرئيسى السائد للكبريتات المعدنية الكلية وهى تعتبر عالية بالمقارنة بأراضى النطاقات المناخية الأخرى وإن الكبريتات المدمصة تمثل أقل قيمة لمحتوى الأراضى من الكبريتات المعدنية.

محتوى الأراضى من الكبريت المعدنى الكلى فى صورة غير الكبريتات total inorganic non-sulfate-S هو 5.165 مليجرام كبريت/كجم أرض يمثل 4.38% من الكبريت المعدنى الكلى وهذه القيمة النسبية عالية بالمقارنة بأراضى المناطق الأخرى وترتبط ارتباطا إيجابياومعنويا مع محتوى الأراضى من كربونات الكالسيوم وأيضا سالبيا مع نسبة الـ C/S ratio وهذا المكون يتضمن: (1) مركبات أوكسجينية عالية الأكسدة (الثيوكبريتات والتتراثيونات): محتوى الأراضى منها 4.172 ملجرام كبريت/كجم أرض تمثل 84.21% ، (2) مركبات أوكسجين منخفضة الأكسدة بالإضافة إلى مركبات كبريت معدنية مختزلة: محتوى الأراضى منها 0.993 مليجرام كبريت/كجم أرض تمثل 15.79% ،

* عموما فإن محتوى الأراضى من الكبريت الكلى وجميع مكونات الكبريت المعدنى ومركباته المختلفة ، وتوزيعاتها النسبية بلغت أقصى قيمة لها فى الأراضى جيدة الصرف وفى مواسم الشتاء بينما وصلت إلى أدناها فى الأراضى الرديئة الصرف وفى مواسم الصيف وأن القيم المتحصل عليها عام 1999/2000م أكبر من تلك المتحصل عليها عام 2000/2001م وهى ترتبط مباشرة مع الظروف البيئية السائد بالمنطقة (درجة حرارة الهواء ودرجة حرارة التربة) وكذلك تذبذب خواص التربة وعمق المستوى المائى.

* النشاط البيوكيميائى لإنزيمات الرادونيز والدى هيدروجينيز كمتوسطات للمتغيرات الدراسية ، تأخذ نفس السلوك فقد بلغت أقصاها فى الأراضى جيدة الصرف ، وفى موسم الشتاء حيث وصلت أعلى قيمة فى شهر يناير ، بينما بلغت أقل نشاطها فى الأراضى رديئة الصرف وفى مواسم الصيف حيث وصلت أقصى انخفاض فى شهر يوليه.

* النشاط البيوكيميائى للإنزيمات يرتبط بعلاقات معنوية سالبة مع كل من: متوسط درجة حرارة الهواء السائدة بمنطقة الدراسة ، متوسط درجة حرارة الأرض بعمق 20سم ، القوة الأيونية لمستخلص عجينة التربة المشبعة ونسبة الكربون إلى الكبريت ، وترتبط أيضا بعلاقات معنوية موجبة مع كل من عمق مستوى الماء الأرضى ، رقم تفاعل الأرض ، الكربون العضوى والنيتروجين الكلى. ويرتبط النشاط أيضا ارتباطاً موجباً مع الكبريت المعدنى فى صورة غير الكبريتات وكذلك مع مركباته الأوكسجينية عالية ومنخفضة الأكسدة هذا بالإضافة إلى المركبات الكبريتية المعدنية المختزلة. بالاضافة الى ذلك فإنه يرتبط ارتباطا معنويا سالبا مع القوى الأيونية لمحلول التربة ونسبة الـ C/S ratio وأساسا مع الكبريتات المعدنية الكلية والكبريتات سهلة الذوبان.

Table (1.1): **Main analytical properties of studied soils under different drainage conditions**

Successive seasons from Dec. 1999 to August 2001 (21 months)		pH (1: 2.5)	ECe (dSm^{-1})	Ionic strength (mmoles L^{-1})	SAR ratio	Bulk density Mg.m^{-3}	Total porosity %	Hydraulic conductivity (cm.hour^{-1})	Organic-C (g.kg^{-1} soil)	Total-N (mg.kg^{-1}) soil	C/N (ratio)	C/S (ratio)	CaCO$_3$ (%)
				Saturation extracts (soil pastes)									
Messier (S$_1$):													
Winter seasons	1999/2000	7.94	4.17	60.3	4.75	1.25	52.7	1.582	20.0	1737	11.5	35.3	1.9
	2000/2001	7.55	3.86	56.7	4.90	1.28	51.4	1.560	17.6	1823	9.7	37.3	2.3
	Mean	(7.74)	(4.01)	(58.5)	(4.82)	1.26	(52.0)	(1.571)	(18.8)	(1780)	(10.5)	(36.3)	(2.1)
Summer seasons	2000	7.75	4.34	64.1	5.24	1.225	53.7	1.393	16.7	1374	12.2	40.3	2.3
	2001	7.69	4.68	67.3	4.81	1.36	48.5	1.365	14.5	1362	10.6	36.7	2.4
	Mean	(7.72)	(4.50)	(65.7)	(5.02)	1.29	(51.1)	(1.379)	(15.6)	(1368)	(11.4)	(38.5)	(2.3
Grand mean		7.73	4.26	62.1	4.92	1.282	51.6	1.475	17.2	1574	11.0	37.4	2.2
Kafr Dokhmeas (S$_2$):													
Winter seasons	1999/2000	7.86	4.82	66.2	6.35	1.23	53.2	1.243	12.9	975	13.2	43.7	3.3
	2000/2001	7.93	4.67	69.8	6.27	1.34	49.1	1.205	12.5	1051	11.9	51.3	3.7
	Mean	(7.89)	(4.74)	(68.0)	(6.31)	1.29	(51.2)	(1.224)	(12.7)	(1013)	(12.5)	(47.5)	(3.5)
Summer seasons	2000	7.68	5.12	71.4	6.74	1.41	46.5	1.000	8.8	579	15.2	41.0	4.0
	2001	7.75	4.58	72.9	6.57	1.42	46.2	0.892	8.4	531	15.9	43.5	3.8
	Mean	(7.71)	(4.85)	(72.2)	(6.65)	1.42	(46.3)	(0.946)	(8.6)	(555)	(15.6)	(42.2)	(3.9)
Grand mean		7.80	4.80	70.1	6.48	1.35	48.8	1.085	10.6	759	14.0	44.9	3.7
Kafr El-Sheikh (S$_3$):													
Winter seasons	1999/2000	8.36	6.54	82.67	6.85	1.53	42.0	0.933	10.6	723	14.7	42.66	3.501
	2000/2001	8.31	6.11	85.28	6.34	1.50	43.0	0.856	9.7	610	15.9	53.33	4.175
	Mean	(8.33)	(6.32)	(83.98)	(6.60)	1.52	(42.5)	(0.834)	(10.1)	(664)	(15.3)	(48.00)	(3.837)
Summer seasons	2000	8.13	6.92	87.98	7.24	1.62	38.8	0.634	8.3	466	17.8	40.16	3.929
	2001	8.24	6.83	89.73	7.55	1.63	38.3	0.609	7.7	418	18.4	47.95	4.997
	Mean	(8.18)	(6.88)	(88.84)	(7.40)	1.62	(38.5)	(0.622)	(8.0)	(441)	(18.1)	(44.06)	(4.463)
Grand mean		8.26	6.60	86.41	7.00	1.57	40.5	0.758	9.1	543	16.7	46.03	4.150

Table (3): Residual total-S and total inorganic-S fractions in the studied soils under different drainage conditions.

Successive seasons from December 1999 to August 2001 (21 months)	Residual total-S fraction (FRACTION 1.2)						Total inorganic sulfur fraction (Fractions 3.1 plus 3.2) (FRACTION 3)					
	Messier (S$_1$) Traditional drained		Kafr Dokhmeas (S$_2$) Poorly drained		Kafr El-Sheikh (S$_3$) Badly drained		Messier (S$_1$) Traditional drained		Kafr Dokhmeas (S$_2$) Poorly drained		Kafr El-Sheikh (S$_3$) Badly drained	
Seasons	Winter seasons (Dec., Jan., Feb.)						Winter seasons (Dec., Jan., Feb.)					
Relations	1999/2000	2000/2001	1999/2000	2000/2001	1999/2000	2000/2001	1999/2000	2000/2001	1999/2000	2000/2001	1999/2000	2000/2001
mg S fraction kg^{-1} soil	519.45	442.82	281.59	228.38	233.77	163.57	235.66	156.88	85.75	81.57	109.53	85.65
	(481.13)		(254.98)		(198.67)		(196.27)		(83.66)		(97.59)	
% of total-S fraction	91.61%	93.42%	95.13%	93.60%	93.51%	89.87%	41.56%	33.10%	28.97%	33.43%	43.81%	47.06%
	(92.51%)		(94.36%)		(91.69%)		(37.33%)		(31.07%)		(45.44%)	
Standing stock kg S. fed^{-1} (15 cm depth)	409.72	359.04	219.80	193.81	226.36	155.50	185.87	127.19	66.94	69.22	106.05	81.42
	(384.38)		(206.80)		(190.93)		(156.53)		(68.08)		(93.74)	
Seasons	Summer seasons (June, July, August)						Summer seasons (June, July, August)					
Relations	2000	2001	2000	2001	2000	2001	2000	2001	2000	2001	2000	2001
mg S fraction kg^{-1} soil	403.10	365.80	207.23	183.55	174.06	132.37	123.69	160.21	54.30	57.42	106.30	79.14
	(384.45)		(195.39)		(153.21)		(141.95)		(55.86)		(92.72)	
% of total-S fraction	96.90%	92.37%	96.39%	94.13%	84.09%	82.22%	29.73%	40.46%	25.26%	29.45%	51.35%	49.15%
	(94.63%)		(95.25%)		(83.15%)		(35.09%)		(27.35%)		(50.25%)	
Standing stock (kg S. fed^{-1}) (15 cm depth)	311.09	314.11	184.87	164.78	177.76	136.26	95.46	137.57	48.44	51.55	108.56	81.46
	(312.59)		(174.82)		(157.01)		(116.52)		(49.99)		(95.01)	
Grand mean mg sulfur. kg^{-1} soil	461.28	404.31	244.41	205.97	203.92	147.97	179.68	158.55	70.03	69.50	107.92	82.39
	(432.79)		(225.18)		(175.94)		(169.11)		(69.76)		(95.15)	