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Evaluation of Sulphate Adsorption and Release Properties in Selected Soils from Malawi

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The soils selected for this study represented major soil types in Malawi. They exhibited a wide range of physical and chemical properties. Their pH values ranged from 4.7 to 6.7 and their contents of clay fraction (<0.002 mm) ranged from 170 to 500 g kg^{-1}, organic matter from 6.7 to 39.3 g kg^{-1}, free Fe_2O_3 from 18.9 to 44.7 g kg^{-1}, and free Al_2O_3 from 17.8 to 45.6 g kg^{-1}. The soils varied widely in their SO_4 sorption behaviour. Soil pH was negatively and significantly correlated (P<0.05) with the bonding energy (k) of SO_4 by the soil, Langmuir sulphate sorption maximum (b) and maximum buffering capacity (MBC). Soil organic matter was positively and significantly related with k, b and MBC at the same level of significance ($P<0.05$). Free Al_2O_3 and Fe_2O_3 were positively and significantly related ($P<0.001$) with b and MBC. Free Fe_2O_3 and Al_2O_3 were positively and significantly correlated with k at $P<0.01$ and $P<0.001$ respectively. About 90 and 91% of the total variations in the sulphate sorption maxima were accounted for by free Al_2O_3 and Fe_2O_3 respectively.

Key words: Sulphate, sorption, desorption, Langmuir, hysteresis, affinity.

INTRODUCTION

Because crop yields were widely observed to be related to levels of N and P bioavailability in soils, these two elements featured prominently in mineral fertilisers used by smallholder farmers prior to the early 1980s. Among the fertilisers smallholder farmers in Malawi were then advised to use were single superphosphate [$Ca(H_2PO_4)_2.CaSO_4$] or 20:20:0 granular fertilizer as a basal dressing, and low analysis fertilisers including ammonium sulphate [$(NH_4)_2SO_4$] as a topdressing. During this period, some crop responses to S additions were observed only in few parts of the country where soils were coarse-textured and highly weathered (Jones, 1977).

Early reports about S deficiencies observed in some parts of Malawi are those reviewed by Bolle-Jones (1964). Bolton and Bennett (1974) observed crop responses to fertiliser S applications in the South Rukuru Valley, the Mzimba Hills, Kasungu Plain, Dzalamanja Hills, and Dedza Hills. The crop responses to S supplementation were observed on newly opened land with course-textured soils and on smallholder farmers' fields that had not received dressings of S-containing

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fertilizers. Jones (1977) observed that the soils that were coarse-textured and highly weathered were low in their total and available S contents and that maize (*Zea mays*), groundnut (*Arachis hypogaea* L.) and tea (*Camellia sinensis*) grown on these soils showed variations in their responses to fertiliser S applications. Severe S deficiency symptoms on maize were also observed by MacColl (1984) from investigations conducted on land that had been acquired from smallholder farmers by the Department of Crop and Soil Sciences, Lilongwe University of Agriculture and Natural Resources, Malawi.

Workers in other parts of the sub-Saharan Africa (SSA) also observed crop responses to S additions. Increases in crop yields ranging from 12 to 20% due to S additions, for example, were observed during this period by Kang and Osiname (1976) in Nigeria, Shenkalwa (1986) in Tanzania, and Grant and Rowell (1976) in Zimbabwe. The S deficiencies in the SSA, however, were not widely observed on smallholder farmers' fields and this can be ascribed to several reasons principal amongst which are three. First, N and S deficiency symptoms are similar. Sulphur deficiency symptoms can therefore be easily confused with those of N symptoms. Secondly, S might have been supplied following the biodegradation of soil organic matter during the growing season of the crop. The mineralisation of organically bound S serves as a source of S which plants manage to use to meet their nutritional demands when effective S concentration is too low to meet such demands. Ester sulphates, for example, which are not as likely to become bonded covalently to humic compounds as is C-bonded S (McGill and Cole, 1981), are mineralised more easily than C-bonded S, thus releasing S that can be used by growing plants. Soil microorganisms and plant roots are able also to hydrolyse ester sulphates when S is needed to meet immediate nutritional demands (McGill and Cole, 1981).

The third possible reason for the absence of S deficiency symptoms then observed on smallholder farmers' fields is the incidental supply of S following the supplementation of single superphosphate [$Ca(H_2PO_4)_2.CaSO_4$] as basal dressing and ammonium sulphate [$(NH_4)_2SO_4$] as topdressing. The fortuitous supply of 24% S and 12% S following the application of $Ca(H_2PO_4)_2.CaSO_4$ and $(NH_4)_2SO_4$ could have counteracted S deficiencies in the plant. These three reasons may explain why S received very little attention from agronomists during the period when low-analysis fertilizers were used by smallholder farmers. Following the introduction of high-analysis fertilizers such as urea and diammonium phosphate (DAP), however, some S deficiency symptoms started to be widely observable in Malawi.

Sulphur is one of the elements that are essential for plant growth and crop production. It is essential for nodule development in legumes and for fruiting in some of the other crops (Tandon, 1991). Plants take up sulphur as SO_4^{2-} ions, and the availability of the sulphate ions for crop nutrition causes crop yields to increase; the quality of cereals for milling and baking to improve; both the quality and quantity of protein in cereals, oilseeds, pulses and tubers to improve; the quality, colour, and uniformity of vegetable crops to improve; the content of oilseeds and other oil-producing crops to increase; and an increase in the content of, and a decrease in the N:S ratio and nitrate levels in, forages. As the S deficiencies are becoming more widespread with the increasing use of high-analysis fertilizers and increasing decline in the content of soil organic matter, the economic importance of S is increasing recognised.

The widespread recognition of the role of S in accelerating food production in most of the developing countries now increasingly calls for the addition of this macronutrient to soils. It is due to increased recognition of the contribution S makes towards increased crop production per unit area that S-containing granular fertilizers such as 23:21:0 + 4%S have been introduced in Malawi. Because of soil heterogeneity, blanket application of S-containing fertilizers recommended to smallholder farmers in Malawi is so uneconomical that farmers may fail to get value for money they invest in the purchase of fertilizers and consequently dissuade smallholder farmers from utilising fertilizers for their crop production. Economic fertiliser use is based on a number of factors one of which is fertiliser use efficiency, which in turn is dependent on several factors including root S influx rate, inherent capacity of soils to replenish S taken up by living biota, and sulphate adsorption/desorption processes.

The word "adsorption" refers removal of a solute from solution to a contiguous solid phase and is used specifically to refer to the two-dimensional accumulation of an adsorbate at a solid surface. "Surface precipitation" is used to refer to a three-dimensional accumulation of sorbate at the solid surface. When the specific removal mechanism is not known, the word "sorption" is used as a general term. Sulphate (SO_4^{2-}) is one of the important adsorptive, non-polymeric anions that are present in soil solution. When S-containing fertilizers are incorporated into the soil, some of the S in this ionic form is therefore sorbed. Hydrous oxides of Fe and Al are ubiquitous in the Ultisols, Alfisols, and Oxisols where they often exist as coatings on clay-size minerals causing these soils to have a high sorption capacity. The effective concentration of SO_4^{2-} ions in soil solution as predicted by adsorption/desorption curves provides valuable information on S bioavailability. Central among the sorption isotherms that have been used to obtain parameters useful for the description of a substrate sorption in soils are the Temkin, Freundlich and Langmuir isotherms (Hinz, 2001).

Langmuir and Freundlich adsorption equations have been used extensively by different workers to obtain parameters useful for the description of S and P sorption

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in soils (Sanyal et al., 1993; Sami et al., 2001; Ghosh and Dash, 2012; Uzoho et al., 2014). The parameters obtained from the isotherms include sorption maximum (*b*) which describes the maximum amount of sorbate that can be sorbed by a sorbent, the bonding energy (*k*) that explains the tenacity with which sorbates are sorbed to the sorbents, the equilibrium solution concentration (*C*) that shows the concentration of the sorbate in equilibrium solution concentration at which the amount sorbed is equal to that desorbed (Litaor et al., 2005; Brand-Klibanski et al., 2007).

One of the mechanisms of SO_4^{2-} sorption, which involves inner-sphere surface complexes, entails ligand exchange in which SO_4^{2-} ions enter into direct coordination with Fe or Al ions of the oxide surfaces as OH- groups are displaced, resulting in an alteration of the point of zero charge (PZC) of the oxide minerals (Marcono-Martinez and McBride, 1989; Zhang and Sparks, 1990), and a release of hydroxyl (OH^-) ions into soil solution that cause a decrease in soil acidity, an increase in the negative charge of the soil colloidal surface, and therefore an increase in CEC (Dolui and Mustaffi, 1997).

It has been suggested that these effects of SO_4^{2-} sorption can be of benefits to highly weathered, acidic soils that abound in the tropics (Ghosh and Dash, 2012). There is, however, a lack of information regarding the SO_4^{2-} sorption/desorption characteristics of Malawi acid soils. The present study was therefore conducted to determine the SO_4^{2-} sorption/desorption characteristics of selected acid soils of Malawi.

MATERIALS AND METHODS

Soil sample collection

Selected for the present study were ten soil samples randomly collected at a depth of 0 to 0.15 m. The representative soil samples were collected in bulk quantities from Mphelero in Mchinji district; Bunda in Lilongwe district; Bembeke in Dedza district; Manjawila in Ntcheu district; Lisasadzi in Kasungu district; Chipoka in Salima district; Champhira in Mzimba district; Malula in Balaka district; Nkhate in Chikhwawa district; and Masenjere in Nsanje district. Soils at each site have been classified by Brown and Young (1965) and Lancini, 1991). The samples were randomly collected from 20 spots from a square area of 1 km^2 at each site and mixed together to form a composite sample. The soil samples were air-dried at room temperature (25 ± 2°C) and sieved to pass through a 2 mm sieve mesh.

Physical and chemical properties

The sieved samples were analyzed for pH in a 1:2.5 soil to water slurry using a pH electrode as outlined by described by Blakemore et al. (1987) and particle size distribution using the Bouyoucos hydrometer method (Day, 1965) as described by Anderson and

Ingram (1993). The organic carbon contents of the soils were determined by the potassium dichromate ($K_2Cr_2O_7$) oxidation method of Walkley and Black (1934) as described by Anderson and Ingram (1993). Organic matter was estimated by multiplying the total soil organic carbon with 1.724.

Phosphate sorption procedures

Three grams of soil were shaken for 24 h with 15 ml solution of K_2SO_4 varying in SO_4 concentrations from 20 to 120 mg S dm^{-3}. The sulphate sorption studies were carried out in triplicate. The suspension was filtered through Whatman No. 42 filter paper and the amount of S remaining in the solution was determined turbidimetrically (Chesnin and Yien, 1951). The amount of SO_4 sorbed was estimated as the difference between equilibrium SO_4 concentration and initial SO_4 added. The sorption data were fitted to the linear form of the Langmuir equations given as follows.
Langmuir equation:

$$C/x/m = 1/kb + C/b$$

Where, C = the concentration of SO_4^{2-} in the equilibrium solution (mg SO_4 dm^{-3}), x/m = the amount of SO_4 sorbed per unit weight of soil (mg SO_4 kg^{-1} soil); b = is the Langmuir sorption maximum (mg SO_4 kg^{-1} soil). k = is a constant related to bonding energy or the affinity of the soil by SO_4.

The Langmuir equation gave a good fit for all the soils when equilibrium S concentration (C) was plotted against *C/x/m*. This equation enabled the computation of Langmuir sorption maximum (*b*) and the constant relating to the bonding energy (*k*).

Sulphate desorption study

In the desorption experiment, soils were allowed to sorb sulphate as in the sorption studies and the sorbed sulphate was extracted by shaking for 24 h with 15 ml KH_2PO_4 solution containing 500 mg P dm^{-3}. Sulphate desorption studies were conducted in triplicate. The amount of sulphate desorbed was calculated with respect to the sorbed SO_4.

Statistical analysis

The relationship between sulphate sorption parameters with selected soil chemical properties was determined using simple regressions and correlations, and tested for significance at 0.01 and 0.05 probability levels using the 16th edition of GenStat statistical software. The contribution of soil properties to sorption parameters was examined using the stepwise model-building procedure.

RESULTS AND DISCUSSION

Soil properties

The soils used in the present study are representative of the major soil types in Malawi and exhibit a wide range of physical and chemical properties (Table 1). The clay fraction (<0.002 mm) ranged 170 g kg^{-1} in the soil collected from Masenjere in Nsanje district to 500 g kg^{-1} in the soil collected from Bunda, in Lilongwe district. The organic matter contents ranged from 6.7 g kg^{-1} in the soil collected from Masenjere to 39.3 g kg^{-1} in the soil collected from Mphelero in Mchinji district. Total S

Table 1. Physical and chemical properties.

Site	Soil taxonomy (USDA)*	pH	OM	Sand	Silt	Clay	Free Fe2O3	Free Al2O3	Available	Total
			(g kg^{-1})--------------------------------------						-----S(mg kg^{-1})	
Mphelero	Ustalfs	4.9	39.3	530	170	300	44.7	45.6	24.7	350.7
Bunda	Ustults	5.0	36.3	270	230	500	39.7	44.5	26.1	398.3
Bembeke	Ustults	4.7	25.6	470	230	300	33.9	35.9	21.6	287.6
Manjawila	Ustalfs	5.7	14.1	530	200	270	32.7	27.7	25.7	356.9
Lisasadzi	Ustults	5.2	23.9	570	170	270	30.9	23.9	23.5	347.9
Chipoka	Fluvents	6.7	6.7	400	130	470	29.6	21.6	23.1	288.6
Champhila	Ustalfs	5.6	20.8	400	170	430	22.4	20.9	25.3	367.5
Malula	Ustults	5.3	12.1	530	200	270	20.2	18.7	26.7	299.4
Nkhate	Vertisols	6.3	29.6	430	170	400	19.3	17.8	27.9	345.3
Masenjere	Vertisols	6.2	9.4	600	230	170	18.9	18.8	28.9	378.1

*Soil Taxonomy (1999), USDA.

contents ranged from 287.6 to 398.3 mg kg^{-1} while extractable S ranged from 21.6 to 28.9 mg kg^{-1}. The soils had pH values that ranged from 4.7 to 6.7, free Fe2O3 that ranged from 18.9 to 44.7 g kg^{-1}, and free Al2O3 that ranged from 17.8 to 45.6 g kg^{-1} (Table1). The contents of Fe2O3 and Al2O3 observed in this study are of the order of magnitude similar to that of aluminium and ferric oxide contents observed previously (Ghosh and Dash, 2012). In general, most of the soils were acidic in their reaction and low in their fertility.

Sulphate adsorption and desorption behaviour

The SO4 sorption and desorption pattern of the soils containing the various amounts of SO4 is presented in Table 2. Within the solution SO4 concentration range considered in this study, the pattern of SO4 adsorption showed a linear relationship between SO4 adsorption and the SO4 concentration (Figures 1 and 2), which is consistent with previous observations (Dolui and Nandi, 1989; Ghosh and Dash, 2012). At higher SO4 concentrations, however, the rate of adsorption has been observed to gradually decrease though not proportionally, thus giving hyperbolic shapes of curve (Ghosh and Dash, 2014). In this study the mean sorbed SO4-S was highest (98%) in soils collected from Chipoka, Champhila, Malula, and Masenjere while the lowest (94%) amount of sorbed SO4-S was in Nkhate (Table 2).

Desorption of adsorbed SO_4^{2-} from soil and clays has been observed to be irreversible leading to a large hysteresis effect (Reddy et al., 2001). During desorption, the amount of sorbed SO_4^{2-} at a given equilibrium concentration was always higher than that during desorption (Table 2). The adsorption isotherm was thus displaced to the left of the desorption isotherm. This was in accord with the findings of Reddy et al. (2001) and

Ghosh and Dash (2014). The percentages of sorbed SO_4^{2-} that was desorbed were in the same order of magnitude as those observed in earlier studies, for example, by Dolui and Jana (1997) who obtained the desorption of 72 to 80% of the sorbed sulphate and Reddy et al. (2001) who reported the desorption of 73 to 80% of the sorbed sulphate, indicating an effect of hysteresis which may be defined as a deviation of a substrate desorption isotherm from adsorption isotherm.

After SO_4^{2-} ions have been sorbed on a solid phase, their desorption process is very often irreversible, leading to a large hysteric effect (Sammi et al., 2001). The extent of hysteresis effect involved in SO_4^{2-} sorption-desorption process, as observed in this study, is shown in Figures 1 and 2. Barrow (1985) has observed that hysteresis effect leads to an over estimation of the replacing ability of soil to an overestimation of the replacing ability of soil to supply sulphur to the solution, when sulphur solution isotherms are used for the purpose.

Affinity between the sulphate and soil colloidal surfaces

The data presented in Table 2 reinforce the notion that most of the removal of sulphate ions from solution to a contiguous solid phase is via an electrostatic (outer-sphere) adsorption mechanism (Peak et al., 1999, 2001; Bohn et al., 2001; Ghosh and Dash, 2012). Microscopic and spectroscopic investigations have, however, demonstrated sulphate inner-sphere surface complexation (Peak et al., 1999, 2001). It has been observed that (SO_4^{2-}) ions form outer-sphere surface complexes only at pH above 6.0 and a mixture of outer- and inner-sphere surface complexes is formed at pH less than 6.0 (Peak et al., 1999). Among the soils used for the

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Table 2. Adsorbed and desorbed sulphate (**μg g^{-1}**) in soils treated with different levels of sulphur

Soil collected from	Reaction observed	SO₄ conc. (μg g^{-1})				
		40	60	80	100	120
Mphelero[1] (Mchinji)[2]	Adsorbed	36.0 (90)[3]	56.5(94)	76.7(96)	97.(97)	117.5(98)
	Desorbed	25.7(71)[3]	43.5(77)	63.7(83)	86.9(89)	98.0(83))
Bunda (Lilongwe)	Adsorbed	39.4(99)	59.4(99)	76.0(95)	96.4(96)	116.7(97)
	Desorbed	26.10(66)	48.6(82)	61.8(81)	87.0(90)	81.6(70)
Bembeke (Dedza)	Adsorbed	36.1(90)	56.5(94)	56.5(94)	97.3(97)	117.7(98)
	Desorbed	23.98(66)	49.6(88)	41.3(73)	88.3(91)	85.8(73)
Manjawila (Ntcheu)	Adsorbed	36.7(92)	57.2(95)	77.7(97)	98.2(98)	118.3(99)
	Desorbed	29.1(79)	49.2(86)	66.7(86)	80.1(82)	88.1(74)
Lisasadzi (Kasungu)	Adsorbed	37.6(94)	58.0(97)	78.4(98)	98.9(99)	119.3(99)
	Desorbed	25.3(67)	43.6(75)	66.6(85)	83.5(84)	89.6(75)
Chipoka (Salima)	Adsorbed	38.1(95)	58.2(97)	78.8(98)	99.2(99)	119.5(99)
	Desorbed	26.3(69)	47.5(82)	68.3(87)	83.9(85)	82.1(69)
Champhila (Mzimba)	Adsorbed	38.2(95)	58.6(98)	78.7(98)	98.8(99)	119.5(99)
	Desorbed	29.6(77)	44.4(76)	61.6(78)	85.9(87)	86.7(73)
Malula (Balaka)	Adsorbed	38.6(96)	58.8(98)	79.0(99)	99.0(99)	119.4(99)
	Desorbed	23.7(61)	47.6(81)	60.3(76)	84.8(86)	88.8(74)
Nkhate (Chikwawa)	Adsorbed	38.1(95)	58.6(79)	79.1(99)	99.5(99)	119.5(99)
	Desorbed	20.9(55)	46.8(80)	69.8(88)	89.6(90)	96.0(80)
Masenjere (Nsanje)	Adsorbed	37.8(94)	58.6(98)	79.0(99)	99.4(99)	119.6(99)
	Desorbed	29.9(79)	44.5(76)	61.3(78)	80.6(81)	88.1(74)

[1]Denotes the site and [2]district from which the soil sample was collected; [3]the figures in parenthesises denote adsorption or desorption percentage.
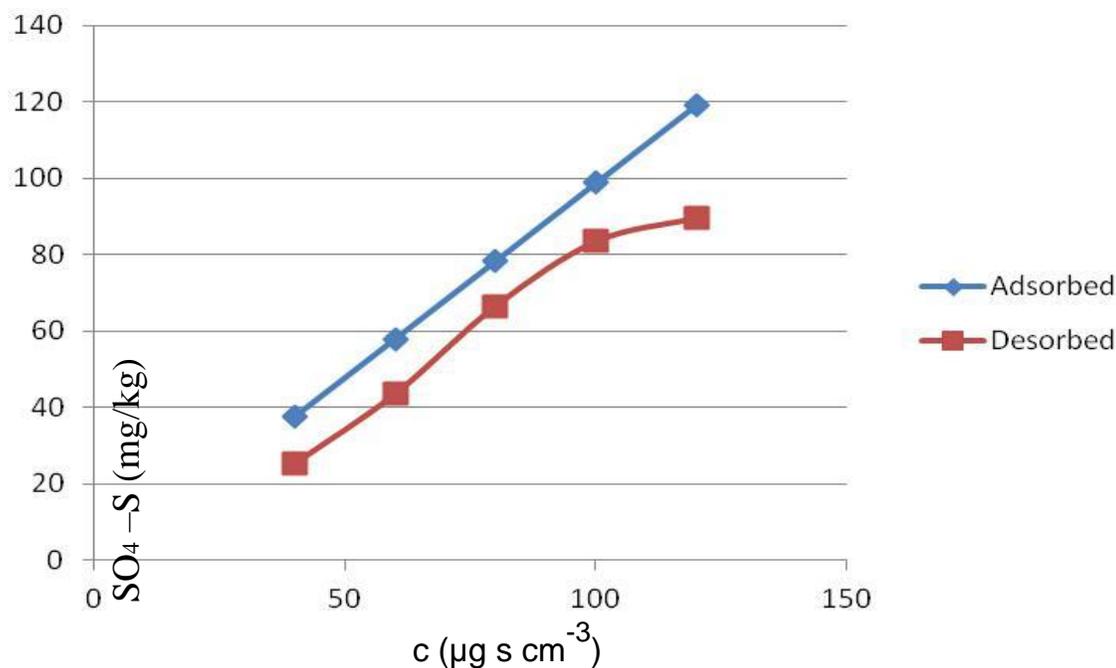

Figure 1. Relationship between sulphate sorbed or desorbed and equilibrium s concentrations in soil solution (lisasadzi, kasungu).
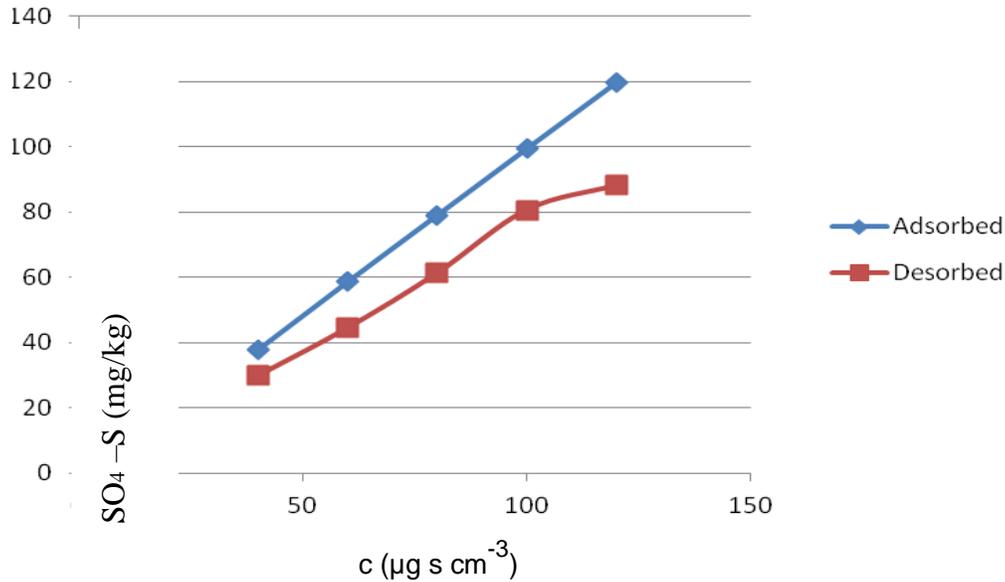
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Figure 2. Relationship between sulphate sorbed or desorbed and equilibrium S concentrations in soil solution (Bunda, Lilongwe).

present study, there were only three soils that had pH values above 6, thus suggesting that the SO_4^{2-} adsorbed by these soils was labile, and therefore, bioavailable. This may explain why, of the soils whose pH values were above 6, compared to all soils studies, have the highest extractable SO_4^{2-} (Table 2)

There is some evidence that suggests that interactions between SO_4^{2-} and the mineral surface are more complex and that SO_4^{2-} ions do participate in ligand exchange reactions with hydroxylated Fe and Al surfaces (Parfitt, 1980). The adsorption of SO_4^{2-} on the hydroxylated Al and Fe surfaces ($M_{oxide}]OH^0$) may be illustrated as follows:

$$M_{oxide}]OH^0 + SO_4^{2-} \rightleftharpoons M_{oxide}]SO_4^- + OH^- \qquad (1)$$
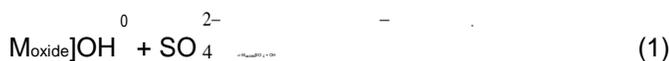
Reaction (1) shows that following the displacement of the OH ligand on the metal oxide surface results in the metal surface that is electrostatically neutral becoming negatively charged thus increasing the capacity of the surface to coulombically attract cations. When the adsorption of SO_4^{2-} results in the displacement of a water ligand, the surface of the metal oxide also becomes negatively charged as the following reaction illustrates:

$$M_{oxide}]OH_2^+ + SO_4^{2-} \rightleftharpoons M_{oxide}]SO_4^- + H_2O \qquad (2)$$

A simple ligand exchange has been shown at low pH where two adjacent -OH ligands are replaced by one

SO_4^{2-} (Rajan, 1978). Because of the amphoteric properties of the sorption sites on the oxide surfaces, sulphate sorption increases with decreasing pH (Nodvin et al., 1986b; Fuller et al., 1987) due to the protonation of the adsorption sites on oxide surfaces which results in the surfaces becoming positively charged and able to electrostatically attract SO_4^{2-}.

The Langmuir sulphate sorption maxima (*b*) and the constant relating to bonding energy (*k*), computed from the Langmuir equation and shown in Table 3, further reinforce the extent to which the soils vary in their SO_4^{2-} sorption behaviour.

The soil collected from Mphelero in Mchinji district, which had the highest organic matter and free ferric and aluminium oxide contents, had the highest sulphate sorption capacity and a pH value of 4.9. The highest maximum buffering capacity (MBC) was observed in the soil of Mphelero in Mchinji district (37.6 dm^3 kg^{-1}) followed by that of Bunda in Lilongwe district (23.8 dm^3 kg^{-1}), Bembeke in Dedza district (17.8 dm^3 kg^{-1}), Manjawila (16.3 dm^3 kg^{-1}) in Ntcheu district and Lisasadzi in Kasungu district (13.1 dm^3 kg^{-1}).

Since the higher the MBC, the greater the soil's resistance to changes in the concentration of SO_4^{2-} ions in soil solution is, the present observations appear to suggest that the effectiveness of S fertiliser applied at the same rate to these soils (blanket application) will vary with MBC, with the soil collected from Mphelero requiring much more additional S fertiliser than that required by the soil collected from Lisasadzi to obtain a similar crop yield with other growth factors being invariant.

Table 3. Langmuir constants of sulphate sorption.

Soil collected from		Langmuir constants		
			Sulphate sorption	Maximum
		Bonding	maximum	buffering capacity
		energy (k)	(b)	($b \times k$)
Site	District	$dm^3\ mg^{-1}$	$mg\ kg^{-1}$	$dm^3\ kg^{-1}$
Mphelero	Mchinji	9.9	3.8	37.6
Bunda	Lilongwe	8.2	2.9	23.8
Bembeke	Dedza	7.4	2.3	17.0
Manjawila	Ntcheu	6.8	2.4	16.3
Lisasadzi	Kasungu	6.9	1.9	13.1
Chipoka	Salima	5.8	1.4	8.1
Champhila	Mzimba	5.9	1.5	8.9
Malula	Balaka	6.9	1.2	8.3
Nkhate	Chikwawa	5.8	1.0	5.8
Masenjere	Nsanje	6.7	1.2	8.0

Table 4. Relationship between sulphate sorption and soil properties

Parameter	k	b	MBC	Fe_2O_3	Al_2O_3	pH
b	0.9048***					
MBC	0.9554***	0.9814***				
Fe_2O_3	0.8045*	0.9530***	0.9101***			
Al_2O_3	0.8773***	0.9482***	0.9293***	0.9319***		
pH	-0.7171*	-0.6757^	-0.6569*	-0.5931 ns	-0.7028^	
OM	0.6737*	0.6856*	0.7164*	0.6167 ns	0.7417*	-0.6219 ns
Clay	-0.1563 ns	0.0554 ns	0.0130 ns	0.2037 ns	0.2015 ns	0.1457 ns
P_{ex}	-0.1538 ns	-0.3570 ns	-0.2714 ns	-0.5376 ns	-0.3632 ns	0.3904 ns
Silt	0.2912 ns	0.1625 ns	0.1364 ns	0.0395 ns	0.3005 ns	-0.4774 ns
	OM	Clay	P_{et}			
Clay	0.2863 ns					
P_{et}	-0.1092 ns	-0.2079 ns				
Silt	0.1295 ns	-0.3739 ns	0.2580 ns			

*, ** and *** denote significant at $P = 0.05$, 0.01 and 0.001 respectively, while ns denotes not significant, k denotes bonding energy (affinity coefficient), MBC denotes maximum buffering capacity; number of observations = 10.

of the total variation in the sulphate sorption maximum was accounted for by free aluminium oxide while free ferric oxide accounted for about 91% of the total variation in the sulphate sorption maxima (Figure 4).

Soil pH was observed in this study to be negatively and significantly correlated (P<0.05) with the bonding energy or the affinity (k) of sulphate by the soil, Langmuir sulphate sorption maximum (b) and maximum buffering.

Relationship between sulphate adsorption parameters and soil properties

The use of soil physical and chemical properties to explain the Langmuir sorption parameters showed the best relationships between free aluminium and ferric oxides and b and MBC each of which was positive and significant at the same level of significance (P<0.001). While free Fe_2O_3 was positively and significantly correlated with the bonding energy (k) at P<0.01, the free Al_2O_3 showed a better affinity for k at P<0.001 (Table 4).

Barreal et al. (2003) have also demonstrated a positive correlation between Al and SO_4^{2-} sorption, and have related the relationship to an increase in surface area associated with the substitution of Al into otherwise crystalline Fe minerals (García-Rodeja et al., 1986; Curi and Franzmeier, 1984). Potter and Yong (1999) have shown such substitutions to raise the point of zero net
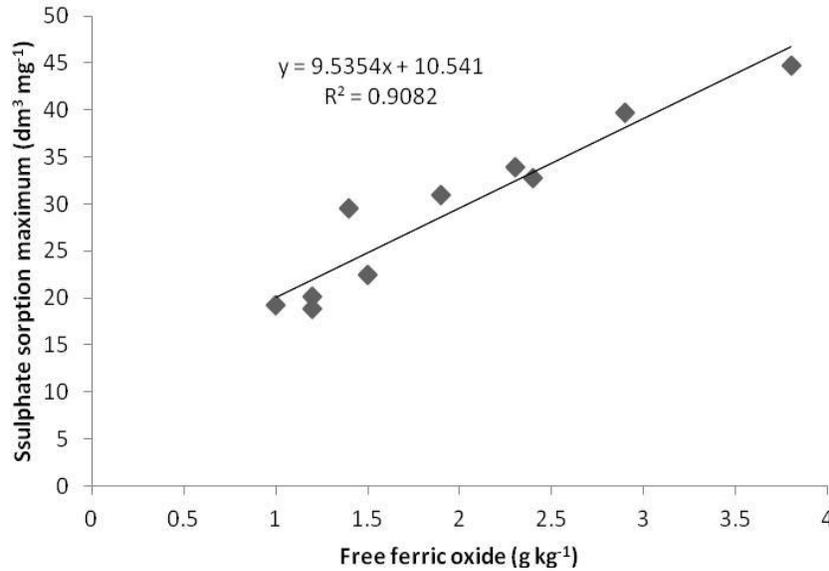
Figure 3. Relationship between the Langmuir sulphate adsorption maximum and free aluminium oxide
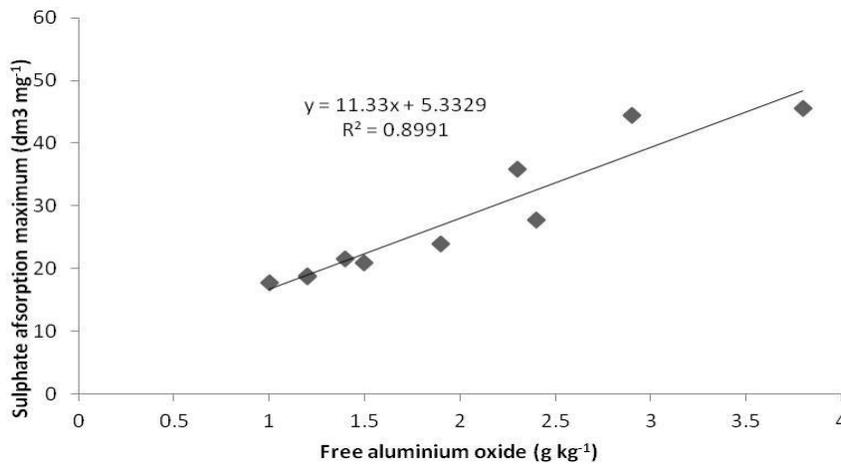
The figure shows: $y = 9.5354x + 10.541$, $R^2 = 0.9082$. Y-axis: Ssulphate sorption maximum ($dm^3\ mg^{-1}$). X-axis: Free ferric oxide ($g\ kg^{-1}$).

Figure 4. Relationship between the Langmuir sulphate adsorption maximum and free ferric oxide.

The figure shows: $y = 11.33x + 5.3329$, $R^2 = 0.8991$. Y-axis: Sulphate afsorption maximum ($dm3\ mg^{-1}$). X-axis: Free aluminium oxide ($g\ kg^{-1}$).

charge (PZNC) of the mineral surface and increase ion exchange capacities. Other workers have observed relationships between anion sorption and the development of Al-humus complexes that inhibit crystalline formation and result in an increase in mineral surface area (Alves and Lavorenti, 2004; Camps et al., 1999a, 2001; Barreal et al., 2001) and the formation of short-range-order Al oxides with a potential positive surface charge under acidic conditions (Inoue and Huang, 1986). The present study showed that about 90 per cent of the total variation in the sulphate sorption maximum was accounted for by free aluminium oxide (Figure 3) while free ferric oxide accounted for about 90%

of the total variation in the sulphate sorption maxima (Figure 4). The present study showed that about 90% capacity (MBC). In the sorption of the sorptive, non-polymeric anions such as SO_4^{2-}, the effect of soil pH is, as has been noted earlier, associated with the amphoteric properties of reactive soil colloidal particles which predominate in soils with variable charge. The fact that surfaces of the amphoteric properties of the oxide surfaces increasingly become positive with increasing effective hydrogen concentration explains the inverse relationship between soil pH and each of the Langmuir sulphate sorption parameters at $P<0.05$ (Table 4). Previous workers such as Dolui and Nandi (1989) also

observed statistically significant relationship between sulphate sorption maximum.

Whereas Sposito (1984) has suggested that sulphate sorption might be of an intermediate nature, sorbing under different conditions as an outer-sphere complex versus an inner-sphere complex, other authors (Turner and Kramer, 1991; Eggleston et al., 1998; Rietra et al., 1999; Sparks, 1999) have observed that as pH is lowered and the concentration of SO_4^{2-} increased, a higher percentage of inner-sphere complexes are formed by SO_4. Peak et al. (2001) have also observed that sulphate forms inner-sphere monodentate surface complexes on hematite from pH 8.0 to 3.5 and across a wide range of surface loadings, whereas on goethite, SO_4^{2-} forms only outer-sphere surface complexes at pH 6.0 and forms a mixture of outer-sphere and inner-sphere complexes at pH < 6.0. It has also been shown that SO_4^{2-} forms predominantly outer-sphere surface complexes on ferrihydrite and on the basis of these observations it has been concluded that it is important to consider not only the effects of pH, ionic strength, and reaction concentration on SO_4^{2-} sorption, but also the nature of the sorbent under study (Peak et al., 2001).

The results given in Table 4 showed that soil organic matter was positively and significantly related with each of the Langmuir sulphate adsorption parameters at the same level of significance (P<0.05). The effect of organic matter on the sorption of non-polymeric anions including SO_4^{2-}

can either promote or reduce the adsorption of these anions. In aqueous solution, organic ligands reduce the effective concentration of Al and Fe by complexing these cations thus hindering the crystallization of Al and Fe oxides. It has been demonstrated that organic acids such as malic, citric, aspartic, oxalic, and tannic acid, promote formation of active sites for the sorption of phosphate by distorting the structure of precipitation products of aluminium and enhancing their specific surface Huang and Violante, 1986; Violante et al., 1996). Maintenance of the short-range structure of the precipitates with a large specific surface area by the presence of critical concentrations of some bio-molecules helps to promote a high sulphate retention capacity of organomineral complexes. The competition of organic ligands with sulphate for sorption sites of variable charge mineral such as aluminium and ferric oxides can result in the reduction of sulphate adsorption.

It has been observed that the amount of sulphate (SO_4^{2-}) adsorbed is dependent on the surface area of the clay and the surface charge, and that the higher the Al content the soil has, the greater the anion adsorption (Bohn et al., 1986). This clearly suggests that soil reaction and type of clay minerals are the main factors that influence the adsorption of SO_4^{2-} ions on the surfaces of aluminium and iron oxides. The soils used in the present study had been subjected to varying degree of intensive weathering and, as a consequence, kaolinitic clay minerals, which usually adsorb higher amounts of SO_4^{2-} ions than the 2:1 clay minerals, predominate in these soils.

Conclusion

The soils varied in their physical and chemical properties, and their SO_4 sorption behaviour also varied widely. Since the higher the MBC, the greater the soil's resistance to changes in the concentration of SO_4^{2-} ions in soil solution is, the present observations show that the effectiveness of fertiliser S applied at the same rate (blanket application) to these soils will vary with MBC. The soil collected from Mphelero in Mchinji district, for example, requiring much more additional S fertiliser than that required by the soil collected from Lisasadzi in Kasungu district to obtain a similar level of crop yield under similar pedo-climatic conditions. This observation is reinforced by the SO_4^{2-} desorption percentages that ranged from 55 to 91%, suggesting differences in the lability of sulphate sorbed by these soils. These observations emphasise the need for fertiliser S application, like the application of any of the other essential nutrients, to be based on indices of soil fertility obtained using well-calibrated soil test methods in order to maximise economic fertilise use and to avoid environmental pollution.

Conflict of interests

The authors hereby declare that no conflict of interest exists among them.

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