ELSEVIER

Geoderma 102 (2001) 41–59

GEODERMA

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Sulfur fractions in particle-size separates of the sub-humid Ethiopian highlands as influenced by land use changes

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Received 21 February 2000; received in revised form 24 August 2000; accepted 2 October 2000

Abstract

Extensive deforestation of natural forests in the Ethiopian highlands and their conversion to low-input agriculture and plantations have caused severe soil degradation and significant changes in the ecosystem. We investigated the influence of land use changes on the amount, form and distribution of sulfur (S) in bulk soils and size separates of the sub-humid highlands of southern Ethiopian. Surface soil samples (0–10 cm) were collected from natural forest, tea plantation and 25 years cultivated fields at Wushwush and from *Podocarpus* dominated natural forest, *Cupressus* plantation and 30 years cultivated fields at Munesa sites. The total S contents ranged from 635 to 1082 mg kg^{-1} soil and from 520 to 1040 mg kg^{-1} soil at Wushwush and Munesa, respectively. Organic S represented on the average 98% of the total S, while inorganic SO_4–S accounted for only 2%. C-bonded S was the dominant organic S fraction at both sites comprising 77–84% of the total organic S pool, whereas ester SO_4–S constituted merely for 16–23%. Total S and C-bonded S were highly significantly correlated ($P < 0.001$) with soil organic C (SOC) and N. However, correlation between ester SO_4–S and total S, SOC and N were weak. The C/S and N/S ratios ranged from 58 to 99 and from 5.7 to 7.9, respectively, and decreased generally in the order: sand > silt > clay. Continuous cropping resulted in 41% and 50% depletion of total S at Wushwush and Munesa, respectively. In contrast, losses from the tea (34%) and *Cupressus* (13%) plantations were low. Sulfur depletions due to cultivation were lower than losses from SOC (55%, Wushwush; 63%, Munesa) and N (52%, Wushwush; 60%, Munesa), suggesting that S was more

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PII: S0016-7061(00)00103-8

resistant to mineralization compared to SOC and N. C-bonded S accounted for 88% and 73% of the total S depletion, whereas ester SO_4–S accounted only for 11% and 26% at Wushwush and Munesa, respectively. These results indicate that most of the S depletion occurred from C-bonded S. Based on our results, it is possible to conclude that S deficiency might occur in a foreseeable future, if the current depletion rate of SOM continues. Therefore, integrated soil and crop management practices have to be developed, which involve the use of organic materials of farm and non-farm origins and inorganic fertilizers to combat the ongoing nutrient depletion in the sub-humid highlands agroecosystems of southern Ethiopia.

Keywords: C-bonded S; Deforestation; Ester SO_4–S; Plantation; Tropical agroecosystem

1. Introduction

Sulfur (S) is highly reactive, existing in six oxidation states and moving among the lithosphere, hydrosphere and atmosphere. Within the biosphere, it is found in numerous chemical combinations and serves multiple biochemical functions. As a result, the pathways of S in any ecosystem are complex and intertwined with those of other elements (Janzen and Ellert, 1998).

Agriculture has claimed a large share of productive terrestrial environment in the tropics and sub-tropics by deforestation of natural forests. The concern over rapid deforestation has prompted studies to determine how the tropical ecosystem responds to this disturbance. These have included topics such as climate, hydrology, primary production as well as decomposition of soil organic matter (SOM) and nutrient cycling (Odum and Pigeon, 1970; Zech et al., 1996). An often neglected essential nutrient in these studies has been S. Although some researchers attempted to determine the status and form of S in tropical soils (Neptune et al., 1975; Acquaye and Kang, 1987; Stanko-Golden and Fitzgerald, 1991), almost all the information on S in soils have been derived from investigations of soils from temperate regions (Tabatabai and Bremner, 1972; Bettany et al., 1980; Zucker and Zech, 1985).

Extensive deforestation of natural forests from the Ethiopian highlands and their subsequent conversion into low-input agriculture has caused extensive soil degradation (physical, chemical and biological), and thereby a decline in agricultural land productivity. Moreover, the recent introduction of plantation crops such as tea further aggravated the destruction of remnant natural forests in the southwestern parts of the country resulting in significant changes in the ecosystem. Almost no quantitative information is available on the impact of such land use changes on the amount, form and transformation of organic and inorganic S species in bulk soils and particle-size separates of these sub-humid tropical highland agroecosystems. Soils of the tropics generally have low total S contents because of low S containing parent materials or extreme weathering and leaching losses (Acquaye and Kang, 1987). In addition, even soils that inherently contain sufficient S can often develop deficiencies after a period of intensive cultivation due to crop removal, SOM depletion, leaching and erosion losses and by the use of low-S containing fertilizers (Biederbeck, 1978; Acquaye and Kang, 1987). The changes in management practices imposed on agricultural lands affect S dynamics, not only within agroecosystems, but also among other terrestrial biomes (Janzen and Ellert, 1998). Therefore, there is a need to conduct a comparative study between the different land use systems in order to understand S pool sizes and transformations within these pools in tropical soils.

A number of methods exist for fractionation of soil S (Lowe and DeLong, 1963; Tabatabai, 1982). Recently, Kowalenko (1993a,b) introduced a faster and more versatile method for fractionation of soil S into organic S (C-bonded and ester SO_4–S) and inorganic SO_4–S forms using hydriodic acid reduction of SO_4^{2-}. Physical fractionation of soil according to particle-size separates combined with degradative chemical techniques offers a significant potential for evaluating the influence of land use changes on SOM (Anderson et al., 1981; Zech et al., 1996; Solomon et al., 2000). Thus, soil S fractionation combined with particle-size fractionation may permit to identify the nature, distribution and forms of S and follow S dynamics in tropical soils.

The objectives of this study were, therefore, to assess the impact of land use changes on the amount, form and distribution of organic and inorganic S fractions in bulk soils and particle-size separates in the sub-humid tropical highland ecosystems of southern Ethiopia.

2. Materials and methods

2.1. Site description

The study was conducted at the southwestern highlands (Wushwush) and the southern Rift Valley escarpment (Munesa) of Ethiopia. Wushwush is located at 7°19′N and 36°07′E. The altitude of the area is 1900 m above sea level. Mean annual temperature is 18°C with an average annual precipitation of 1800 mm. Geologically, the area is associated with Jimma volcanics with abundant rhyolites and trachybasalts. Soils of the area are classified as Plinthic Alisols (FAO, 1997), with clayey texture and dark reddish brown color. The Wushwush natural forest is mainly composed of *Olea africana* (Mill.), *Syzygium guineense* (Guill. and Perr. Gmel.), *Cordia africana* (Lam.), *Croton macrostachys* (Hochst. ex Rich.) and *Ficus vasta* (Hayne.). The Munesa site is located at 7°35′N and 38°45’E. Mean annual temperature is 19°C with an average annual precipitation of 1250 mm. Parent materials of the Munesa area are of volcanic origin, principally trachytes and basalts with ignimbrites and pumices at the rift valley floor. The escarpment extends from about 2100–3200 m and the plain descends gradually to the Rift Valley lakes at about 1600 m above sea level. The soils of the area are classified as Humic Nitisols (FAO, 1997), with clayey texture and very dark reddish brown color. Basic physical and chemical characteristics of the soils at both sites are shown in Table 1. The natural vegetation of the Munesa forest ranges from the *Arundinaria alpina* (Schun.), *Hagenia abyssinica* (J.F. Gmel.), *Croton macrostachys* (Hochst. ex Rich.), *Podocarpus falcatus* (Thunb. Mirb.), *Olea hochstetteri* (Baker.) dominated forest on the escarpment to *Acacia* woodlands (*Acacia tortilis* (Hayne), *Acacia abyssinica* (Hochst. ex Benth.) and *Acacia seyal* (Delile) in the semi-arid lowlands.

The land use systems studied at the Wushwush site were natural forest, tea plantations (*Camellia sinensis* O. Kuntze) (35 years old) and fields cultivated for 25 years, while at the Munesa site, *Podocarpus* dominated natural forest, *Cupressus* plantations (*Cupressus lusitanica* Mill.) (25 years old) and 30 years cultivated fields were investigated. At the Wushwush site, land preparation for cultivation or establishment of the tea plantations was done by clear-cutting of the indigenous forest, whereas at the Munesa site, clear-cutting was accompanied by burning. In the cultivated fields of both sites, maize (*Zea mays* L.) was grown without fertilizer inputs. However, during the intermittent dry periods, sorghum (*Sorghum bicolor* L. Moench) was grown at Munesa. Crop residues were normally collected and used as animal feed.

We used a core sampler and collected composite samples in three replicates from the upper 10 cm of the different land use systems in April, 1998. We selected three representative sites from each land use and collected three sub-samples (200 cm^3 core volume at each sub-site) in a radial sampling scheme (Wilding, 1985). The three sub-samples were then bulked into one sample. The spacing between the sub-sites on the radii ranged from 5 to 10 m depending on the size of the patches. The samples were air-dried and sieved (< 2 mm) prior to fractionation and chemical analysis.

2.2. Particle-size fractionation

Particle-size fractionation was done on < 2 mm material (bulk soil) according to Amelung et al. (1998). After removing visible root remnants, 30 g of soil was ultrasonically treated with an energy input of 60 J ml^{-1} using a probe type sonicator (Branson Sonifier W-450) in a soil/water ratio of 1:5 (w/v). The coarse sand fraction (250–2000 μm) was isolated by wet sieving. In order to completely disperse the remaining material in the < 250 μm suspension, ultrasound was again applied with an energy input of 440 J ml^{-1} in a soil/water ratio of 1:10 (w/v). The clay fraction (< 2 μm) was separated from the silt (2–20 μm) and fine sand (20–250 μm) fractions by repeated centrifugation. The silt fraction was separated from the fine sand fractions by wet sieving. Coarse and fine sand fractions were combined and all fractions were dried at 40°C before grinding them for chemical analysis. The recovery of size separates after ultrasonic dispersion, wet sieving and centrifugation ranged from 968 to 979 g kg^{-1} of the initial soil mass (Table 1).

Table 1

Selected physical and chemical characteristics of surface soils (0–10 cm) in the sub-humid highlands of southern Ethiopia

Land use	Sand	Silt	Clay	Bulk density (Mg m^{-3})	pH		SOC[a]	N	C/N	CEC (cmol kg^{-1} soil)	BS[b] (%)	Fe$_d$[c]	Fe$_o$[d]	Al$_d$[c]	Al$_o$[d]
	(g kg^{-1} soil)				(H_2O)	(KCl)		(g kg^{-1} soil)				(g kg^{-1} soil)			
Wushwush															
Natural forest	103	327	570	0.69	6.4	5.5	82	7.7	10.8	37.0	69	6.7	0.60	0.96	0.25
Tea plantation	102	330	568	0.87	5.7	4.5	42	4.0	10.4	24.7	35	6.5	0.70	0.97	0.32
Cultivation	70	337	593	0.89	5.7	4.7	38	3.7	10.2	26.4	46	5.8	0.83	0.77	0.30
Munesa															
Natural forest	130	347	523	0.62	7.6	6.8	98	7.9	12.6	52.2	98	2.5	0.30	0.38	0.15
Cupressus plantation	231	326	443	0.77	7.4	6.6	71	7.1	10.0	40.4	96	2.5	0.36	0.32	0.18
Cultivation	229	285	486	1.04	5.6	4.5	38	3.3	11.8	26.5	51	3.4	0.71	0.40	0.21

[a] SOC, soil organic C.

[b] BS, base saturation.

[c] Fe$_d$ and Al$_d$, dithionite–citrate–bicarbonate extractable Fe and Al.

[d] Fe$_o$ and Al$_o$, oxalate extractable Fe and Al.

2.3. Chemical analysis

Carbon and nitrogen contents of bulk soils and particle-size separates were analyzed by dry combustion with a C/H/N/S-analyzer (Elementar Vario EL). The pH–H_2O and pH–KCl were determined in 1:2.5 soil/water (w/v) suspension using a glass electrode. Cation-exchange capacity (CEC) was determined with 1 M NH_4OAc (pH = 7.0) according to Avery and Bascomb (1974) (Table 1). Dithionite–citrate–bicarbonate extractable aluminum and iron (Al_d, Fe_d) were determined after double extractions at 70°C for 15 min as described by Mehra and Jackson (1960). Oxalate-extractable aluminum and iron (Al_o, Fe_o) were determined using atomic absorption spectrometer (Varian AAS-400) after extraction for 2 h with 0.2 M ammonium oxalate at pH = 3 in the darkness (Blume and Schwertmann, 1969).

The analysis of S fractions was carried out as follows: soil solution and adsorbed SO_4^{2-} was extracted with KH_2PO_4 (500 ppm P) and quantified by hydriodic acid (HI) reduction of SO_4^{2-} to sulfide and subsequent determination of S as bismuth sulfide by spectroscopy at 400 nm as described by Kowalenko (1993a). Total organic S was estimated as the difference between the total S and inorganic S extracted by KH_2PO_4. HI-reducible S, consisting primarily of ester SO_4–S and inorganic SO_4–S was analyzed by direct reduction with 4 ml of the hydriodic acid reducing mixture and measured on a spectrophotometer according to Kowalenko (1993b). The difference between HI-reducible S and inorganic SO_4–S (KH_2PO_4 extractable) was considered as ester SO_4–S. Because HI will not reduce the C–S (amino acid) or C–SO_3 (sulfonate) linkage (Strickland et al., 1987), C-bonded S was considered to be that fraction of the total organic S that was not reduced by HI. All extractions were made on triplicate samples.

2.4. Statistics

Statistical analysis of the data was carried out by one-way analysis of variance (ANOVA). If the main effects were significant at $P < 0.05$, a post hoc separation of means was done by univariate LSD test. Correlation coefficients showing the relationship between the different S fractions and total soil organic C (SOC) and N were run by Pearson product moment correlation. All statistical analyses were conducted using the software package Statistica for Windows (1995).

3. Results and discussion

3.1. Soil S status and forms in bulk soils and particle-size separates

3.1.1. Total S

The total S contents ranged from 635 to 1082 mg kg^{-1} soil and from 520 to 1041 mg kg^{-1} soil at the Wushwush and Munesa sites, respectively (Table 2).

Table 2
Amounts of the different S forms, ester SO_4–S and C-bonded S as the proportion of total organic S and C/S and N/S ratios in bulk soils of different land use systems

Land Use	Total S ($mg\ kg^{-1}$ soil)	Inorganic S ($mg\ kg^{-1}$ soil)	Organic S ($mg\ kg^{-1}$ soil)	HI-reducible S ($mg\ kg^{-1}$ soil)	Ester S ($mg\ kg^{-1}$ soil)	C-bonded S ($mg\ kg^{-1}$ soil)	Ester S (%)	C-bonded S (%)	C/S	N/S
Wushwush										
Natural forest	1082a[a]	17a	1065a	191a	174a	891a	16	84	78	7.2
Tea Plantation	719b	14a	705b	175a	161a	544b	23	77	58	5.7
Cultivation	635b	11b	624b	133b	122b	502b	20	80	60	5.9
Munesa										
Natural forest	1041a	16a	1025a	237a	221a	804a	22	78	99	7.9
Cupressus plantation	903b	11b	892b	191b	180b	712a	20	80	79	7.9
Cultivation	520c	11b	509c	95c	84c	425b	17	83	74	6.3

[a] Within one site, different letters along the column indicate significant differences between the mean values of S fractions of the different land use systems at $P < 0.05$ ($n = 3$).

These results are inline with the ranges reported for tropical soils by Stanko-Golden and Fitzgerald (1991) from Puerto Rico (353–1231 mg kg^{-1} soil). However, these values are higher compared to ranges reported by Kang et al. (1981) for forest zones of Nigerian (117–489 mg kg^{-1} soil) and by Acquaye and Kang (1987) for Ghanaian soils (44–281 mg kg^{-1} soil). The difference between these soils may be attributed to differences in SOM levels resulting from differences in vegetation, climate, depth of sampling and soil type. For example, the amounts of SOM at our sites were two to four times higher than the amounts reported for Nigerian and Ghanaian soils.

The total S content was highly significantly correlated ($P < 0.001$) with organic S ($r = 0.99$), total SOC ($r = 0.98$) and total N ($r = 0.98$), indicating that most of the S in the surface layer of these tropical soils is present in organic form (Table 3). These relationships agree with those reported for Brazilian (Neptune et al., 1975) and Ghanaian soils (Acquaye and Kang, 1987). The C/S and N/S ratios of the bulk soils ranged from 58 to 99 and from 5.7 to 7.9, respectively (Table 2) and are in good agreement with the ranges reported for a variety of temperate and tropical soils (Tabatabai and Bremner, 1972; Neptune et al., 1975).

The amount of total S in particle-size separates decreased in the order: clay > silt > sand (Tables 4 and 5), the highest being in the clay size separates

Table 3
Correlation coefficients (r) for paired relationships between different forms of S and total soil organic C (SOC) and N in soils of the sub-humid highlands of southern Ethiopia

Relationship	Correlation coefficient (r)		
	Bulk soil	Silt	Clay
Total S vs. organic S	0.99***	0.99***	0.99***
Total S vs. inorganic S	0.53ns[a]	0.42ns	0.45ns
Total S vs. total SOC	0.98***	0.98***	0.96***
Total S vs. total N	0.98***	0.98***	0.99***
Organic S vs. total SOC	0.97***	0.97***	0.95***
Organic S vs. total N	0.93***	0.95***	0.97***
Ester S vs. total S	0.72*	0.63ns	0.45ns
Ester S vs. total SOC	0.66ns	0.68*	0.41ns
Ester S vs. total N	0.63ns	0.65ns	0.47ns
C-bonded S vs. total S	0.99***	0.97***	0.95***
C-bonded S vs. total SOC	0.93***	0.97***	0.94***
C-bonded S vs. total N	0.97***	0.98***	0.97***

***, ** and * indicate significant differences at $P < 0.001$, $P < 0.01$ and $P < 0.05$, respectively ($n = 18$).

[a] ns, not significant at $P < 0.05$.

Table 4
Amounts of the different S forms, ester SO_4–S and C-bonded S as the proportion of total organic S and C/S and N/S ratios in particle-size separates of different land use systems at the Wushwush site

Separate	Land use	Total S (mg kg^{-1} soil)	Inorganic S (mg kg^{-1} soil)	Organic S (mg kg^{-1} soil)	HI-reducible S (mg kg^{-1} soil)	Ester S (mg kg^{-1} soil)	C-bonded S (mg kg^{-1} soil)	Ester S (%)	C-bonded S (%)	C/S	N/S
Clay	Natural forest	849a[a]	8a	841a	112ns	104ns	737a	12	88	47	5.4
	Tea Plantation	635b	7b	628b	84ns	77ns	551b	12	88	41	4.5
	Cultivation	577b	6b	571b	90ns	84ns	487b	15	85	41	4.6
Silt	Natural forest	280a	5ns[b]	275a	38a	33a	242a	12	88	110	8.5
	Tea Plantation	142b	4ns	138b	34ab	30ab	108b	22	78	87	7.1
	Cultivation	145b	3ns	142b	22b	19b	123b	13	87	80	6.5
Sand	Natural forest	72a	n.d.[c]	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	148	9.3
	Tea Plantation	30a	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	133	7.6
	Cultivation	20b	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	129	6.9

[a] Different letters along the column indicate significant differences between the means of the different land use systems at $P < 0.05$ ($n = 3$).
[b] ns, not significant at $P < 0.05$.
[c] n.d., not determined.

Table 5

Amounts of the different S forms, ester SO_4–S and C-bonded S as the proportion of total organic S and C/S and N/S ratios in particle-size separates of different land use systems at the Munesa site

Separate	Land use	Total S (mg kg^{-1} soil)	Inorganic S (mg kg^{-1} soil)	Organic S (mg kg^{-1} soil)	HI-reducible S (mg kg^{-1} soil)	Ester S (mg kg^{-1} soil)	C-bonded S (mg kg^{-1} soil)	Ester S (%)	C-bonded S (%)	C/S	N/S
Clay	Natural forest	991a[a]	7ns[b]	983a	117a	110a	873a	11	89	41	4.5
	Cupressus plantation	882a	6ns	876a	115a	109a	767a	12	88	36	4.4
	Cultivation	560b	7ns	553b	44b	37b	516b	7	93	40	4.1
Silt	Natural forest	356a	5ns	351a	33b	28b	323a	8	92	146	8.8
	Cupressus plantation	333a	4ns	329a	48a	44a	285a	13	87	95	7.8
	Cultivation	174b	4ns	170b	21b	17b	153b	6	94	106	7.1
Sand	Natural forest	50a	n.d.[c]	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	173	7.6
	Cupressus plantation	25b	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	105	6.1
	Cultivation	13c	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	132	6.7

[a] Different letters along the column indicate significant differences between the means of the different land use systems at $P < 0.05$ ($n = 3$).

[b] ns, not significant at $P < 0.05$.

[c] n.d., not determined.

with the largest SOC and N contents and with the lowest C/S, N/S and C/N ratios (C/N data not presented).

3.1.2. Inorganic SO_4–S

Sulfate (SO_4^{2-}) is the main inorganic form of S present in most soils, although some reduced S forms (e.g., elemental S, thiosulfate or sulfide) may be present in soils under predominantly anaerobic conditions (Biederbeck, 1978; Kowalenko, 1993a). Since the reduced S forms are transitory in aerobic soils and their concentrations are usually negligible (Biederbeck, 1978; Janzen and Ellert, 1998), in the present study, inorganic S was estimated by the solution and adsorbed SO_4^{2-}. The inorganic SO_4–S ranged from 11 to 17 mg kg^{-1} soil at Wushwush and from 11 to 16 mg kg^{-1} soil at Munesa (Table 2). These values accounted on the average for 2% of the total S content of the bulk soils and compared favorably with the results from other tropical soils (Neptune et al., 1975; Acquaye and Kang, 1987).

According to the data shown in Tables 4 and 5, the amount of inorganic S in the clay was 1.5–2 times greater than the amount extracted from the silt size separates. This may be attributed to adsorption of SO_4^{2-} to clay size separates and to the higher clay content of these soils. A positive correlation between the relative SO_4^{2-} adsorption capacity and the clay content of tropical soils was reported by Acquaye and Kang (1987).

3.1.3. Organic S

The major proportion of total S in most agricultural soils is present in organic forms (Janzen and Ellert, 1998; Saggar et al., 1998), mainly because, unlike inorganic SO_4^2–S, soil organic S is mostly insoluble in water and not susceptible to leaching losses. Organic S was also the dominant S pool in the upper 10 cm of these tropical soils. Its amount varied from 624 to 1065 mg kg^{-1} soil at Wushwush and from 509 to 1025 mg kg^{-1} soil at Munesa, representing on the average 98% of the total S in bulk soils of the two sites (Table 2). The percentage of organic S in these soils is of similar magnitude as those quoted for other tropical soils (Neptune et al., 1975; Stanko-Golden and Fitzgerald, 1991). Table 3 shows that the organic S was highly significantly correlated ($P < 0.001$) with total SOC ($r = 0.97$) and with N ($r = 0.93$), indicating the close coupling between these parameters. Similar relationships were reported for soils from Brazil (Neptune et al., 1975), Nigeria (Kang et al., 1981) and Ghana (Acquaye and Kang, 1987). The close association of organic S with SOC and N in these soils is due to the fact that SOM provides the major non-leachable reserve of S and N in most surface soils. Therefore, based on the above results, it is possible to suggest that SOM content could be taken as a fair indicator of the S status in these tropical soils.

Examination of particle-size separates of both sites showed that significantly higher amounts of organic S ($P < 0.05$, data not presented) were present in the clay than in the silt size separates (Tables 4 and 5). The values of the clay size separates were two to three times greater than the values of silt size separates. This was also demonstrated by the C/S and N/S ratios, which were markedly lower in the clay than in the silt size separates. The observed pattern of organic S distribution in particle-size separates of these tropical soils is similar to the pattern observed in temperate soils by Anderson et al. (1981).

Organic S originates mainly from plant and animal residues, which are subsequently decomposed and remetabolized by soil microorganisms. The main forms of organic S in soils include sulfonates, in which S is directly bonded to C ($C–SO_3$), S-containing amino acids (C–S) and the esters of sulfuric acid (C–O–S), where S is bonded to oxygen in the form of $C–O–SO_3^-$ linkages. Sulfamates may also be found in soils where S occurs in the form of $N–O–SO_3^-$ and $N–SO_3^-$ groups (Saggar et al., 1998).

Biederbeck (1978) reported that in most mineral soils of temperate and tropical ecosystems, ester SO_4–S is the dominant form of organic S, constituting between 33% and 78% of total soil organic S. However, the distribution of the different organic forms of S shown in Tables 2, 4 and 5 indicate that C-bonded S was the largest constituent of the total organic S pool compared to ester SO_4–S in bulk soils and size separates of these sub-humid tropical highland ecosystems. It accounted for 77–84%, whereas ester SO_4–S constituted merely for 16–23% of the organic S pool in bulk soils of both sites. The dominance of C-bonded S in forest-derived tropical soils was also reported by Stanko-Golden and Fitzgerald (1991). Ester SO_4–S is generated predominantly through biochemical processes by soil microflora, which metabolize organic residues and is controlled by supply of S. On the contrary, C-bonded S is directly derived from leaf litter and root inputs (sulfonate-S), as well as microbial protein synthesis (amino acid-S) (Saggar et al., 1998). Stanko-Golden and Fitzgerald (1991) demonstrated that sulfonates are the dominant components of C-bonded S pool representing as much as 68% of the total S content of soils from Puerto Rico. Thus, the abundance of C-bonded S in these forest-derived surface soils may be attributed to the higher amount of SOM and increased microbial activity under the sub-humid tropical environment.

Comparisons of organic S fractions in particle-size separates indicate that significantly higher ($P < 0.05$, data not presented) amounts of both C-bonded S and ester SO_4–S fractions were found in the clay than in the silt size separates (Tables 4 and 5). This could be ascribed to stabilization of organic S compounds and microbial metabolites produced during decomposition of SOM by the clay size separates. C-bonded S was highly significantly ($P < 0.001$) correlated with the total S, SOC and N in bulk soils and size separates further indicating the close link between C-bonded S and SOM (Table 3). In contrast, the correlation between the ester SO_4–S and total S, SOC and N were generally weak. These results might also explain the prevalence of C-bonded S over ester SO_4–S in these tropical soils.

3.2. Land use effects on the status and forms of S in bulk soils and particle-size separates

3.2.1. Total S

Deforestation of the natural forests and subsequent cultivation both at Wushwush and Munesa sites invariably led to large losses of SOM from the soils under study (Table 2). These losses of SOM were associated with concomitant losses of S. In the present study, continuous cropping resulted in a 41% and 50% depletion of the total sulfur contents in bulk soils of Wushwush and Munesa sites, respectively (Figs. 1 and 2). In comparison, the reductions from the tea (34%) and *Cupressus* (13%) plantations were relatively low. In these sub-humid tropical agroecosystems, the depletion of S was lower than the losses of SOC (55% at Wushwush; 63% at Munesa) and N (52% at Wushwush; 60% at Munesa) from the cultivated fields. These results are consistent with the findings of McLaren and Swift (1977) and Bettany et al. (1980) for a variety of cultivated temperate soils. The above results, coupled with the relatively narrow C/S and N/S ratios of the soils from the plantations and the cultivated fields (Table 2), suggest that despite the relatively higher decomposition rate of SOM under the sub-humid tropical environment, S is more resistant to mineralization

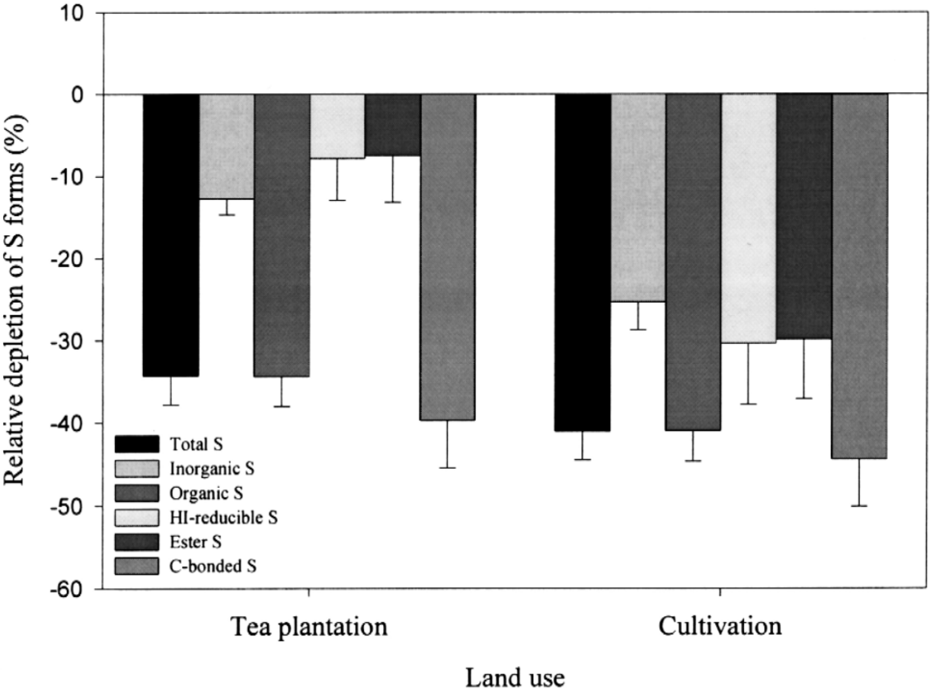

Fig. 1. Average depletion of the different S fractions in bulk soils of the different land use systems relative to the natural forest at the Wushwush site. Bars indicate standard deviations ($n = 3$).

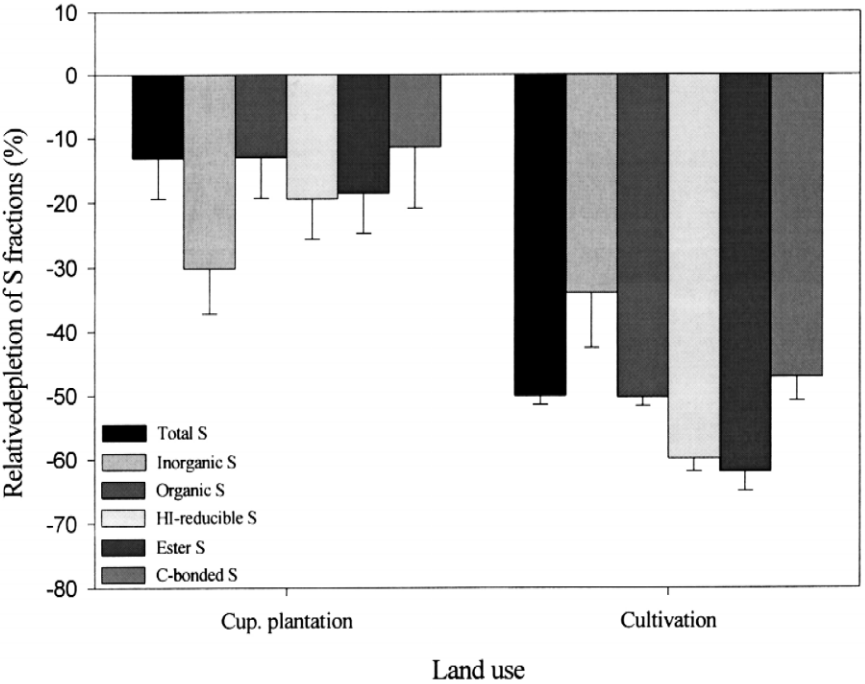

Fig. 2. Average depletion of the different S fractions in bulk soils of the different land use systems relative to the natural forest at the Munesa site. Bars indicate standard deviations ($n = 3$). Cup. plantation, *Cupressus* plantation.

than SOC and N. Alternatively, the higher retention of S relative to the SOC or N may also reflect the lower susceptibility of S to losses from the ecosystem.

The amount of total S in particle-size separates consistently decreased in the order: natural forest > plantations > cultivated fields (Tables 4 and 5). The C/S and N/S ratios of size separates of the natural forests were higher than the C/S and N/S ratios from corresponding plantations and cultivated field. These results indicate that S losses from the size separates due to soil disturbance caused by land use changes were lower than the depletions of SOC and N.

3.2.2. Inorganic SO_4–S

In arable ecosystems, significant amount of inorganic SO_4–S is removed by crops. However, much of the S assimilated by the crops is retained in the system in fields where crop residues are effectively incorporated into the soil (Janzen and Ellert, 1998). Removal or burning of crop residues, which is usually practiced in the cultivated fields of the southwestern Ethiopia, appreciably increases the loss of inorganic SO_4–S from the agroecosystem.

In the soils under study, a significantly higher ($P < 0.05$) amount of inorganic SO_4–S was found in bulk soils of the natural forests compared to the corresponding cultivated fields (Table 2). According to Figs. 1 and 2, the relative losses of inorganic SO_4–S from bulk soils of the cultivated fields were higher than from soils of the corresponding plantations. Depletion of inorganic SO_4–S as a result of cultivation was also reported by Bettany et al. (1980) for Canadian soils and by Tracy et al. (1990) for soils from North America. Tracy et al. (1990) demonstrated that in addition to crop removal, in areas of high precipitation, leaching could also cause a substantial amount of inorganic SO_4–S depletion in conventionally cultivated fields. However, with the exception of clay size separates from the Wushwush sites, a pronounced difference in the inorganic S fractions of the different land use systems was not observed in the finer particle-size separates. This indicates that leaching of inorganic SO_4–S from the finer separates may not be a very serious problem in these soils. Therefore, the differences in the amount of inorganic SO_4–S in the bulk soils might be attributed to losses from coarse size separates as a result of continuous cropping.

3.2.3. Organic S

Continuous cultivation under arable management breaks up soil clods and exposes previously inaccessible SOM to microbial attack (Haynes and Williams, 1992). As a result, organic matter contents considerably decline in cropped fields. Any change in SOM is likely to be reflected as a change in S status since more than 90% of S in most noncalcareous soils is present in organic form (Biederbeck, 1978). Clear-cutting and subsequent cultivation resulted in significantly higher ($P < 0.05$) depletion of organic S in the bulk soils of these tropical agroecosystems (Table 2). These results are in line with the results of Bettany et al. (1980) for arable Canadian soils and Haynes and Williams (1992) for cultivated soils from New Zealand. According to Figs. 1 and 2, the relative depletion of organic S fractions as a result of continuous cropping were higher at the Munesa (50%) than at the Wushwush site (41%). This could be attributed to the initial burning of forest-derived organic matter after clear-cutting of the natural forests, to the relative difference in duration of cultivation and to the slightly lower clay content of the cultivated than the natural forest soils. Compared to the cultivated fields, lower losses of organic S were observed at the tea (34%) and *Cupressus* (13%) plantations. This may be ascribed to better crop residue management through the use of pruned tea plant parts as a mulch at the tea plantations and to the surface litter accumulation after senescence observed at the *Cupressus* plantations, which helps to return S removed by the crops to the soils. In addition, pumping-up and recycling of S from the lower soil layer to the surface soil through the relatively deep rooted tea plants and *Cupressus* trees may also contribute to the lower loss of S observed at the plantation sites.

Although several researchers have observed qualitative changes in soil organic S as a result of cultivation, no consistent trends with regard to the interchange between different organic forms of S are yet apparent (Saggar et al., 1998). There is a conflicting evidence on the globally dominant labile form of organic S fraction. In mineralization studies using Canadian soils, Lowe (1964) considered C-bonded S to be of little value as a source of mineralizable S. In contrast, Ghani et al. (1991) using New Zealand soils, found that most of the SO_4^{2-} generated from soil incubation studies originated from C-bonded S. Freney et al. (1975), also showed that over 9 months, most of the available S (60%) removed by plants in a pot experiment came from C-bonded S, although there were changes in all organic fractions. In the present study, cultivation of the native forests at the Wushwush site resulted in a 41% and 30% reduction of C-bonded S and ester SO_4–S, respectively (Figs. 1 and 2). At the Munesa site, 47% of the C-bonded S and 62% of the ester SO_4–S were lost as a result of converting the natural forest to cultivated fields. However, when the depletions of the two organic S fractions were expressed as proportions of the total S, the losses of C-bonded S accounted for 88% and 73% of the total S depletion from bulk soils of the Wushwush and Munesa, while the depletions in ester SO_4–S accounted only for 11% and 26% of the total S reduction observed at the two sites, respectively. McLaren and Swift (1977) also demonstrated that C-bonded S contributed to 75% of S loss, while only 25% of this loss derived from the ester SO_4–S due to cultivation of Scottish soils. Compared to the cultivated fields, the relative depletions of both C-bonded and ester SO_4–S were lower at the two plantation sites (Figs. 1 and 2). The results of the present study show that most of the soil S depletion in these sub-humid tropical highland agroecosystems occurred from the C-bonded S than the ester SO_4–S, supporting the results of Freney et al. (1975), McLaren and Swift (1977) and Ghani et al. (1991). McLaren and Swift (1977), McGill and Cole (1981) and Saggar et al. (1998) suggested that ester SO_4–S has a more transitory nature and its mobilization is controlled by the end-product supply. On the other hand, since C-bonded S is mineralized as a result of C oxidation to provide energy, the increased microbial activity associated with cultivation of soils could result in an accelerated transformation of the C-bonded S, which passes through ester SO_4–S prior to release as inorganic SO_4–S. This mechanism would tend to maintain the level of ester SO_4–S fraction in these soils, while the C-bonded fraction being continually diminished.

Comparisons of the particle-size separates from different land use systems indicate that highest amounts of both C-bonded and ester SO_4–S were generally found in clay and silt size separates of the natural forests (Tables 4 and 5). Cultivation resulted in 34% and 19% depletions of C-bonded S and ester SO_4–S in clay size separates of the Wushwush site, while the losses of these organic S fractions from the silt size separates were 49% and 42%, respectively. At Munesa, the clay separate lost 41% and 66% of C-bonded and ester SO_4–S, whereas losses from the silt separate were 53% and 39%, respectively. The results of the size separates also indicate that among the two organic S fractions, generally higher losses as a result of continuous cultivation occurred from the C-bonded S than the ester SO_4–S. The losses of C-bonded S and ester SO_4–S from clay and silt size separates of the two plantations were generally low. This could be associated to the higher input of plant residue, thus increasing the SOM levels of soils at the tea and *Cupressus* plantations.

4. Conclusions

In southern Ethiopia, deforestation of the natural forests and subsequent cultivation or establishment of plantations resulted in significant S depletion from bulk soils and particle-size separates. The reduction was associated with the improved aeration and microbial activity, which led to accelerated decomposition of the native SOM following clear-cutting and cultivation. Lower losses of S were observed from the plantations compared with those from the continuously cultivated fields. This indicates the importance of better crop residue management and recycling of S from the sub-soil to the surface layer by the relatively deep rooted plantation crops in minimizing S-losses from these tropical agroecosystems.

The lower depletion of S compared to SOC and N coupled with narrow C/S and N/S ratios of soils from the cultivated fields and plantations suggest that despite the higher decomposition rate of SOM under sub-humid tropical environments, S is more resistant to mineralization compared to SOC and N. Alternatively, the higher retention of S relative to SOC or N may also reflect the lower susceptibility of S to losses from the ecosystem.

C-bonded S was the dominant organic S fraction compared to ester SO_4–S both in bulk soils and size separates in these forest-derived tropical soils. In addition, most of organic S depletion from bulk soils and size separates due to land use changes occurred from C-bonded S than ester SO_4–S.

Based on our results, it is possible to conclude that S deficiency might occur in a foreseeable future, if the current depletion rate of SOM continues, since organic matter is the major source of S in the region. Therefore, integrated crop and soil management practices have to be developed which involve the use of organic materials of farm and non-farm origins as well as inorganic fertilizers to combat the ongoing nutrient depletion in these sub-humid tropical highland agroecosystems of southern Ethiopia.

Acknowledgements

We wish to express our gratitude for the German Academic Exchange Service (DAAD) for providing a fellowship for D. Solomon and for the Wushwush Tea and Munesa Forest Enterprises for their co-operation in providing the research sites. The authors would like also to thank D.L. Sparks, M.A. Tabatabai and the unanimous reviewer for their valuable comments and suggestions, which helped to improve this manuscript.

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