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Land Use Effect on the Profile Distribution of Sulfur in an Aquic Brown Soil

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Abstract: This study was aimed to investigate the dynamics of Soil Total Sulfur (STS), Available Sulfur (SAS) concentration, sulfur storage and Carbon/Sulfur (C/S) ratio in 0-150 cm depth of an aquic brown soil at the Shenyang Experimental Station of Ecology, Chinese Academy of Sciences under 14 years of four land use patterns, i.e., Paddy Field (PF), Maize Field (MF), Fallow Field (FF) and Woodland (WL). The results showed that the profile distribution of STS and SAS was different under different land uses, indicating the effect of land use on the biogeochemical cycling of sulfur. The STS concentration throughout the 150 cm depth was numerically greater of WL than of PF, MF and FF. Soil available S extracted with 0.01 mol L^{-1} $Ca(H_2PO_4)_2$ in profiles was not significantly correlated with that of the STS, indicating a different distribution mechanism of SAS from that of the STS. Although PF had the lower STS in profile than MF, it's SAS in layers above 60 cm was significantly greater than that in MF. The SAS in the deep layers was significantly greater in WL than in the other three land uses. The sequence of STS storage in 100 and 150 cm thickness was WL>MF>FF>PF, suggesting the effects of different root biomass and biological S cycling under various land uses. Soil total S was significantly related with soil organic carbon and total nitrogen and the correlation was slightly closer in nature ecosystems than in agroecosystems (with $R^2=0.974$ and 0.996 for FF, 0.953 and 0.931 for WL, 0.894 and 0.865 for PF, 0.833 and 0.851 for MF, respectively, $p<0.001$, $n=30$). Although the profile distribution of STS concentration was different among different land uses, the soil C/S ratio was comparatively constant in 0-80 cm layers, while it was tended to be lower in layers below 80 cm owing to the comparatively constant total S concentration and the decreasing total soil organic C with depth. It is suggested that woodland have the potential to make a significant contribution to STS storage.

Key words: Aquic brown soil, soil sulfur, C/S ratio, land use

INTRODUCTION

Sulfur (S), along with carbon, hydrogen, oxygen, nitrogen and phosphorus, is one of the major constituents of living tissue. In addition to its vital roles in plant and animal nutrition, sulfur is also responsible for several types of air, water and soil pollution and is therefore of increasing environmental interest[1,2]. The three major source of sulfur that can become available for plant uptake are organic matter decomposition, soil mineral weathering and atmospheric deposition. In natural ecosystems where most of the sulfur taken up by plants is eventually returned to the same soil, these three source combined are usually sufficiently to supply the need of growing plants[3]. Sulfate in soil is a direct S source for plants, generally more than 95% of soil S is organic bonded and divided into sulfate ester S and carbon-bonded S in surface soils in temperate, humid regions. Although not readily plant available, organic S compounds may potentially contribute to the S supply of plants via mineralization[3]. In the recent years, reductions in atmospheric S deposition and less fertilizer S input have created S deficiency in some agricultural soils. In such soils the release of S from organic matter may be important for the supply of S to plants[4,5]. Sulfur cycling has important analogies with both N and P, including both biological and geochemical reactions and gas-phase reactions[6], while land use practices alter C, N, P and S cycling in ecosystems[7,8]. Compared to cultivated lands, forests and grasses are often favorable to carbon sequestration because they can store large amount of organic matter in their woody biomass and decay-resistant litter[9]. Many studies have been done on the changes of soil organic carbon and nitrogen storage under different land uses[7-10], but a few were on soil sulfur changes. Just for this, we chose the Shenyang Experimental Station of Ecology, Chinese Academy of Sciences as the study site and investigated the sulfur

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Table 1: Description of sampling sites

No	Land use pattern	Years	Latitude(N)	Longitude (E)	Remark
1	Paddy field	>14	31'12"	22'11"	Annul application of urea, $(NH_4)_2HPO_4$ and KCl was 450, 150 and 112.5 kg ha^{-1}, respectively.
2	Paddy field	>14	31'07"	22'00"	
3	Paddy field	>14	31'06"	22'00"	
4	Maize field	14	31'09"	21'58"	Annul application of urea, $(NH_4)_2HPO_4$ and KCl was 300, 150 and 75 kg ha^{-}, respectively.
5	Maize field	14	31'10"	21'58"	
6	Maize field	14	31'08"	21'58"	
7	Fallow field	9	31'15"	21'59"	Maize was planted in 1990-1994 and fallowed after 1995.
8	Fallow field	9	31'16"	21'59"	
9	Fallow field	9	31'16"	21'58"	
10	Woodland	14	31'14"	22'04"	Litter layer was about 3 cm.
11	Woodland	14	31'14"	22'05"	
12	Woodland	14	31'15"	22'04"	

Table 2: Soil total sulfur content under different land uses (g kg^{-1})

Depth(cm)	Paddy field	Maize field	Fallow¡¡field	Woodland
0-5	0.26±0.06b	0.24±0.01b	0.35±0.02ab	0.47±0.13a
5-10	0.22±0.02ab	0.24±0.01a	0.22±0.02ab	0.21±0.01b
10-20	0.18±0.07a	0.23±0.01a	0.18±0.01a	0.20±0.01a
20-30	0.12±0.04b	0.22±0.03a	0.18±0.02a	0.19±0.01a
30-40	0.10±0.02a	0.16±0.04a	0.16±0.04a	0.16±0.02a
40-60	0.08±0.03c	0.14±0.02ab	0.11±0.02bc	0.16±0.01a
60-80	0.07±0.01c	0.15±0.02b	0.10±0.02c	0.20±0.03a
80-100	0.06±0.00c	0.14±0.03b	0.09±0.01c	0.19±0.04a
100-120	0.04±0.01c	0.11±0.01ab	0.08±0.01bc	0.16±0.05a
120-150	0.06±0.01b	0.10±0.03b	0.08±0.00b	0.17±0.05a

Mean values of 3 replicates, different letters followed in a line are significantly different by Duncan's multiple range test ($p<0.05$)

profile distribution and storage in different lands, aimed to understand the dynamics of sulfur under different land use patterns and to provide scientific basis for sulfur management.

MATERIALS AND METHODS

Site description: Shenyang Experimental Station of Ecology, Chinese Academy of Sciences is situated at the lower reaches of Liao River Plain (41°31'N, 123°22'E). It is located in the continental temperate monsoon zone, with a dry-cold winter and a warm-wet summer. The mean annual temperature is 7.0-8.0°C, annual precipitation is 650-700 mm and non-frost period is 147-164 days. The soil is classified as aquic brown soil (sandy loam Hapli-Udic Cambosols in Chinese Soil Taxonomy[11], with a deep thickness of pedon and Fe-Mn mottlings in it. Before the establishment of the Station in 1989, all the lands were paddy field and after 1989, part of the lands was turned into maize field, fallow field and woodland.

Soil sampling: In November 2003, soil samples were collected from four types of land use patterns, i.e., paddy field, maize field, fallow field and woodland (*Populus Canadensis* L.), respectively. Three replicated profiles for each land use pattern were excavated in 0-150 cm depth, which were divided into 0-5, 5-10, 10-20, 20-30, 30-40, 40-60, 60-80, 80-100, 100-120 and 120-150 cm layers. Descriptions of the sampling sites were showed in Table 1.

Soil analyses: Soil bulk density was determined by using stainless steel ring and oven-dried at 105°C, Soil Total Sulfur (STS) was digested by oxidation with Mg $(NO_3)_2$-HNO_3 solution and soil available sulfur (SAS) was extracted with 0.01 mol L^{-1} $Ca(H_2PO_4)_2$ and both STS and SAS were determined by turbidimetry. Total nitrogen was determined using semi-microkjeldahl method[12] and Soil Organic Carbon (SOC) was measured using SSM-5000A for TOC-5000 analyzer.

Data analysis and soil total sulfur storage calculation: The obtained data were analyzed with SPSS 10.0 statistical software, using one-way ANOVA and Duncan's pairwise comparison for means separation. A significance level of p = 0.05 was chosen for detecting significant differences.

Soil total sulfur storage was calculated through formula 1,

$$STS_s = \sum_{i=1}^{n}(S_i \times \rho_i \times T_i)/10 \qquad (1)$$

where STS_S is soil total sulfur storage (t ha^{-1}) at a given depth s, S_i is total sulfur concentration (g kg^{-1}) of layer i, ρ_i is soil bulk density (g cm^{-3}) of layer i, T_i is the thickness (cm) of layer i and n is the number of layers.

RESULTS AND DISCUSSION

Profile distribution of soil total sulfur: Soil Total Sulfur (STS) concentration throughout the 150 cm depth was numerically greater in woodland than in paddy, maize and fallow fields. All the profiles of paddy, maize and fallow fields showed a decreasing trend of STS concentration with depth Table 2.

In 0-5 cm layer, the STS was higher in woodland than in the other three land uses, while no significant difference was found among fallow, paddy and maize fields. The STN was significantly higher in maize field than in fallow field and woodland in 5-10 cm layer. The average STS contents in layers between 5-40 cm were higher in maize field than in the other three land uses and

Table 3: Relationships of Soil Total Sulfur (STS) with organic carbon (SOC) and Total Nitrogen (STN) (n = 30)

Land use	Regression model	R square	p value	Standard error
Paddy field	$STS=1.077\times10^{-3}+2.239\times10^{-2}SOC$	0.894	<0.001	2.604×10^{-2}
Maize field	$STS=5.301\times10^{-2}+1.709\times10^{-2}SOC$	0.833	<0.001	2.289×10^{-2}
Fallow field	$STS=4.776\times10^{-2}+1.525\times10^{-2}SOC$	0.974	<0.001	1.344×10^{-2}
Woodland	$STS=8.004\times10^{-2}+1.282\times10^{-2}SOC$	0.953	<0.001	2.159×10^{-2}
Paddy field	$STS=-4.310\times10^{-2}+0.285\times10^{-2}STN$	0.865	<0.001	2.929×10^{-2}
Maize field	$STS=1.453\times10^{-2}+0.214\times10^{-2}\ STN$	0.851	<0.001	2.161×10^{-2}
Fallow field	$STS=2.081\times10^{-2}+0.191\times10^{-2}\ STN$	0.966	<0.001	1.529×10^{-2}
Woodland	$STS=3.721\times10^{-2}+0.196\times10^{-2}\ STN$	0.931	<0.001	2.619×10^{-2}

Table 4: Soil C/S ratio under different land uses

Depth(cm)	Paddy field	Maize field	Fallow field	Woodland
0-5	42.55±7.16b	43.46±1.94b	55.91±1.47a	63.60±4.65a
5-10	43.43±4.47b	43.03±2.92b	50.07±0.70a	48.22±2.73ab
10-20	48.34±15.68a	44.07±2.03a	50.61±4.45a	48.88±2.91a
20-30	55.24±12.69a	41.38±5.84a	45.92±2.99a	46.27±4.55a
30-40	48.18±5.02a	42.79±6.05a	46.72±8.94a	50.55±3.95a
40-60	53.80±11.19a	51.62±7.16a	47.60±9.32a	45.18±3.55a
60-80	46.93±17.14a	44.16±4.16a	38.47±9.43a	45.16±5.11a
80-100	38.65±5.97ab	37.73±3.83ab	26.35±11.11b	44.35±0.77a
100-120	39.30±7.76a	27.49±4.04b	20.73±2.42b	39.03±4.02a
120-150	27.71±3.51a	18.56±4.43a	25.69±4.01a	25.79±6.00a

Mean values of 3 replicates, different letters followed in a line are significantly different by Duncan's multiple range test ($p<0.05$)

in the layers below 40 cm were significantly higher in woodland than in the other three land uses. In layers below 60 cm, no significant difference of STS was observed between paddy and fallow fields Table 2.

In the surface layer, STS was greater in woodland and fallow field than in paddy and maize fields, while in the layers 5-20 cm, it was less significantly different from the surface layer under the four land uses. The oxidation rate of Soil Organic Matter (SOM) would be considerably lower in the undisturbed woodland than in the cultivated fields because the litter would not be incorporated into the soil through tillage and the absence of physical disturbance would result in a weaker soil respiration. The litter may also be rich in phenolics and lignin, the factors that greatly slow down SOM decomposition and organic sulfur loss[3]. Moreover, the loss of SOM through soil erosion would be much smaller in woodland than in cultivated fields. Soil Organic Sulfur (SOS) concentration is the balance between plant material input and its loss mainly through heterotrophic decomposition. In natural ecosystems, litter fallen to the soil surface and turnover of fine roots were regarded as the main pathways of SOM input[13] and therefore increased SOS input [34].S values had been used to evaluate the downward movement of organic S applied to a grassland soil and the[34]. S values of the C-bonded organic S fraction indicated profile immigration of organic S in this form[14]. Mechanical tillage is an integral practice used on paddy and maize fields in the study region to prepare seedbed, control weeds and incorporate herbicide and other pesticides into soil. However, tillage encouraged the decomposition of SOM[15] and runoff of nutrients in soil surface[16] and hence, led to a lower concentration of C-bonded S in the surface layer of cultivated fields in contrast to woodland and fallow field during 14 years of different land uses. In contrast to the undisturbed soils, the high production of biomass in paddy and maize field may lead to SOS consumption in profile. Because of the accumulation of organic material at the soil surface, SOM level generally declined with soil depth[13] and so did STS Table 2.

Soil carbon/sulfur ratio under different land uses: Either in natural ecosystem or in agroecosystem, soil organic sulfur is closely correlated with Soil Organic Carbon (SOC) and Soil Total Nitrogen (STN). In this study, STS was significantly correlated with SOC and STN and the correlations were slightly closer in natural ecosystems (woodland and fallow field) than in agroecosystems (paddy and maize fields) Table 3. Because of the linkage among STS, SOC and STN, adequate SOM and N inputs are always requisite for adequate organic sulfur levels[3]. Kirchmann *et al.*[17] had conducted a long-term experiment on a clay loam soil (Typic Eutrochrept) at Uppsala of Sweden, the results showed that STS was correlated with both STN and SOC in soil, but SOC was less well correlated than STN. While in our study, the correlations of STS with STN and SOC had no significant difference Table 3.

Table 4 showed that in the top 0-5 and 5-10 cm layers soil C/S ratio was significantly higher in woodland and fallow field than in paddy and maize fields, but not significantly different in the 10-80 cm layers among the four land uses. As a whole, soil C/S in layers above 80 cm depth had a comparatively small variation, while it was tended to be lower in layers below 80 cm than in the above layers.

Sulfur in soil organic matter may be associated with organic C in a reasonable constant ratio[3]. The soil C/S ratio in the upper layers may be induced by comparatively higher SOC contents in fallow field and woodland where the S contents was not in accordance with SOC accumulation in these layers. Although SOC was significantly higher in profiles of woodland than the in the other three land uses[8], there was no significant difference of soil C/S ratio among the four land uses in 10-80 layers, indicating a comparatively constant value of soil C/S ratio

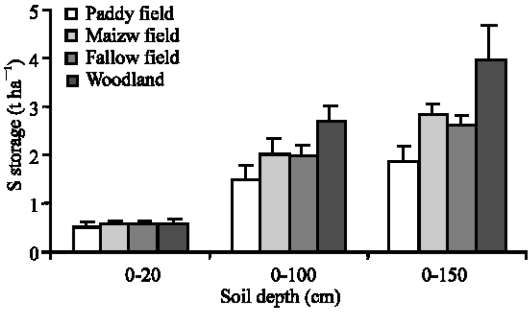

Fig. 1: Soil total sulfur storage under different land uses

in these layers among the four land uses. Sulfate leaching may reduce the long-term possibility of maintaining the S supply in topsoil in low input farming systems[4,18] and the leached S may increase the total S concentration in deep layers where SOC concentration was comparatively lower and hence led to the comparatively lower soil C/S ratio in layers below 80 cm. The profile distribution of soil C/S was as similar as the results conducted by Huang *et al.*[19] in a paddy soil in Hunan province of China.

Soil sulfur storage under different land uses: Calculations on the soil sulfur storage in different layers Fig. 1 showed that at the depth of 0-20 cm, the STS storage was not significantly different among different land uses. Post hoc tests showed that the mean difference of STS storage in woodland from paddy, maize and fallow fields were 0.091, 0.069 and 0.020 t ha^{-1}, with the p values of 0.112, 0.990 and 0.705, respectively. The STS storage at the depth of 0-100 cm was significant greater in woodland than in paddy, maize and fallow fields ($p = 0.001$, 0.022 and 0.015, respectively). It was also significant greater in maize field than in paddy field ($p = 0.043$), but there was no significant difference between maize and fallow fields ($p = 0.891$). A similar trend was found at the depth of 0-150 cm as at the depth of 0-100 cm.

In this study, soil tended to accumulated more sulfur in woodland than in the other three land uses, especially at the depth of 0-100 cm, *e.g.*, the annual sequestration of STS at the depth of 0-100 cm in woodland was 87.5, 47.3 and 79.7 kg ha^{-1} more, with the annual increasing rate being 5.94, 2.32 and 4.02% higher than that in paddy, maize and fallow fields, respectively.

The root biomass was greater in maize than in paddy field and hence, maize field tended to sequester more SOM than paddy field. Moreover, C_4 plant tends to sequester more SOM than C_3 plant[20]. Therefore, the SOS concentration was greater in maize (C_4 plant) field than in paddy (C_3 plant) field.

According to Brady and Weil[3], if the soil fertility of woodland being not too low, its annual total biomass production would probably be similar to that of maize field, while its standing biomass would be greater since the tree crop is not removed each year. Although a great part of the annual biomass production would remain stored in the trees, some of the litters would fall onto the soil surface. Intensifying land use through permanent or semi- permanent cultivation would cause a significant loss of the SOM. The shallower root system and the very low root biomass of the cropping systems could not provide the necessary SOM input, particularly at greater depth, to maintain SOM storage comparable to that of the woodland[21]. On the basis of enhanced biological production, the S storage in the vegetation and soil greatly increased, along with an enhanced N uptake by the plants.

It's assumed that fallow system would sequester more S than maize system, but the result showed that there was no significant difference between them Fig. 1, suggesting that fallow would not be an ideal system to sustain S as what have been thought to be an important way to improve soil fertility in cultivated fields in the study region. Because the weed roots in fallow field were not so deep to accumulate enough SOM in deep layer, the S storage in fallow field was not coincide with what we have assumed. Fallowing could accumulate SOM in surface soil[22], but the data about its profile distribution and its storage in layers deeper than 1 m are still lacking. Therefore, it is a strong argument for seeking means to maintain the fallow vegetation as part of the agricultural land-use system. The tree in woodland maintained a deep root system and sequestered SOM at greater depth and thus, stored more S than the fallow field.

Soil available sulfur under different land uses: 0.01 mol L^{-1} $Ca(H_2PO_4)_2$ extractable soil sulfur was regarded as plant available S in north China and hence it was determined as available S index. Soil available S concentration was tended to be higher in 0-30 cm layers in paddy and fallow field than in maize field and woodland, *e.g.*, it was significantly greater in 0-5 cm layer in paddy field than in maize field ($p = 0.003$) and woodland ($p = 0.036$). It was significantly greater in layers below 40 cm in woodland than in the other three land uses, with the mean differences were all significant with $p<0.001$. Soil available S content in maize field within 80 cm layers was lower as compared with the other three land uses Table 5.

No significant difference of SAS was observed in profiles of fallow field. Although paddy field had lower STS in profile than maize field Table 2, it's SAS in layers above 60 cm was significantly higher than that in maize field. The SAS was accumulated in layers below 80 cm of maize field and below 60 cm of woodland, which was

Table 5: Soil available sulfur content under different land uses (mg kg^{-1})

Depth(cm)	Paddy field	Maize field	Fallow¡¡field	Woodland
0-5	59.83±6.41a	37.31±4.75c	53.68±7.89ab	46.51±6.56bc
5-10	52.06±6.02ab	39.97±4.50b	59.37±9.52a	43.02±5.56b
10-20	49.61±2.30a	33.36±2.67b	52.64±9.28a	41.36±8.43ab
20-30	60.23±9.82a	30.54±0.95b	50.25±6.99a	34.17±7.35b
30-40	45.93±2.33a	26.85±3.12b	45.02±4.35a	50.48±12.10a
40-60	48.42±13.0ab	22.25±4.07c	37.67±1.24bc	63.34±11.50a
60-80	40.66±13.7b	28.09±1.84b	43.46±11.7b	100.80±7.20a
80-100	34.05±9.41c	40.25±6.13bc	50.18±5.10b	92.92±2.76a
100-120	32.46±4.51b	39.70±8.91b	50.18±4.57b	99.69±14.7a
120-150	35.30±7.97c	42.52±5.54bc	54.06±6.83b	115.50±3.85a

Mean values of 3 replicates, different letters followed in a line are significantly different by Duncan's multiple range test ($p<0.05$)

similar with the result carried out in a dry land farming system in Shaanxi Province of China by Fan and Hao[23], who owed this to fertilizer S leaching. However, highly concentrated N-P-K fertilizers with lower or no S was applied in the study site, fertilizer S leaching could not be regarded as the cause of SAS accumulation in the deep soil layers. Dissolved organic S leaching from the surface horizon and root exudation in the deep horizon would be considered as the main cause of SAS accumulation in both maize field and woodland. According to Zhang *et al.*[24], the soil pH in layers below 60 cm of the paddy field was slightly alkaline (about 7.5), in the maize and fallow field was about neutral (about 7.0), while in the woodland it was slightly acidic (about 6.5). The slightly acidic condition of the woodland soil may come from organic acid secreted by organic matter and the leaching of sulfate from the upper layers. No significant relation was found between STS and SAS under different land uses, indicating that SAS in profile was not dominated by STS.

CONCLUSION

The profile distribution of S in woodland and in paddy, maize and fallow fields showed that different land uses altered both total S and available S concentrations, indicating the effects of land use on soil S dynamics. Soil total S storage in the 0-20 cm depth was not significantly different among different land uses, while it was significant greater in 0-100 cm depth and in 0-150 cm depth in woodland than in paddy, maize and fallow fields. The variation of soil total S storage was mainly caused by the changes of SOM under different land uses. Owing to its higher underground biomass and enriched SOM, the woodland stored more S in its profile. As a C_4 plant and owing to its comparatively higher root biomass, maize might sequester more carbon and store more SOM and thus accumulate more S than C_3 plant paddy rice. Compared with maize field, fallow field showed no advantages in accumulating S in profile.

Soil total S was significantly related with soil organic C and soil total N, while the correlation was slightly closer in natural ecosystems than in agroecosystems. This indicated that S cycle had a considerable similarity to C and N cycle and the similarity was more significant without human disturbance under fallow field and woodland. The soil C/S ratio in above 80 cm layers was comparatively constant, while it was tended to be lower in layers below 80 cm owing to the comparatively constant total S concentration and the decreasing total soil organic C with depth. Soil available S in profiles was not significantly correlated with that of the soil total S, indicating a different distribution mechanism of soil available S from that of the soil total S.

As the study was conducted in a long-term experimental station where the soil type, land use pattern, cultivation and fertilization were comparatively homogenous before the station was established, the variation of S after 14 years of land use change may help us to understand soil S cycle in agroforestry ecosystems and enrich our knowledge about S management in agroecosystems and forestry ecosystems.

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