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ORIGINAL PAPER

Sequential transformation rates of soil organic sulfur fractions in two-step mineralization process

Toko Tanikawa · Kyotaro Noguchi · Kenichi Nakanishi · Hidetoshi Shigenaga · Junko Nagakura · Hisao Sakai · Akio Akama · Masamichi Takahashi

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Abstract To understand the organic sulfur (S) stabilization in volcanic soils, we investigated organic S transformation rates and their relationships to soil properties in incubation experiments using forest soils from the Nikko volcanic region, central Japan. We hypothesized that carbon (C)-bonded S would first be transformed into ester sulfate-S and then into inorganic sulfate-S. We separately calculated the rates of decrease of C-bonded S (velocity 1, v_1) and ester sulfate-S (velocity 2, v_2) concentrations. During incubation, the ester sulfate-S concentration increased in two soils characterized by a high concentration of both ammonium oxalate-extractable aluminum (Al_o) and pyrophosphate-extractable Al (Al_p), whereas the C-bonded S concentration decreased in all soils. A large proportion of the S that was lost in the incubation experiments consisted of C-bonded S rather than ester sulfate-S. Velocity 2 was negatively correlated with both of Al_o and Al_p contents when soils were incubated at 20 °C. These results suggest that when C-bonded S is transformed into ester sulfate-S, complete mineralization to inorganic sulfate is inhibited, because ester sulfate-S is stabilized due to organo–mineral association. Incubation temperatures significantly affected v_2. Thus, production of inorganic sulfate by mineralization of ester sulfate-S appeared to be regulated by soil Al contents and temperatures. Velocity 1 was proportional to soil pH ranging from 4.5 to 5.5, indicating that the degradation of C-bonded S is pH dependent.

Keywords Aggregate · Aluminum–humus complex · Mineralization · Organic sulfur transformation · Pyrophosphate-extractable aluminum · Sulfur stabilization

Introduction

Sulfur, an essential element for plants and microorganisms, is continuously cycled between organic and inorganic forms (Castellano and Dick 1990). Mineralization of organic S is a key process for regulating the S cycling in forest soils.

Kenichi Nakanishi Deceased

T. Tanikawa (✉)
Kansai Research Center, Forestry and Forest Products Research Institute, Nagai-kyutaro, Momoyama, Fushimi,
Kyoto 612-0855, Japan
e-mail: tanikawa@affrc.go.jp

K. Noguchi · H. Sakai
Shikoku Research Center, Forestry and Forest Products Research Institute, 2-915 Asakura-Nishimachi, Kochi 780-8077, Japan

K. Noguchi
e-mail: kyotaro@affrc.go.jp

H. Sakai
e-mail: sakai03@affrc.go.jp

K. Nakanishi
Mie University, 1577 Kurimamachiya, Tsu, Mie 514-8507, Japan

H. Shigenaga
Kyushu Research Center, Forestry and Forest Products Research Institute, 4-11-16 Kurokami, Kumamoto 860-0862, Japan
e-mail: shige1@affrc.go.jp

J. Nagakura · A. Akama · M. Takahashi
Forestry and Forest Products Research Institute, Matsunosato,
Tsukuba, Ibaraki 305-8687, Japan

J. Nagakura
e-mail: kurya@affrc.go.jp

A. Akama
e-mail: akama@affrc.go.jp

M. Takahashi
e-mail: masamiti@affrc.go.jp

Traditionally, soil organic S has been fractionated into hydriodic acid (HI)-reducible and non-reducible S, which are thought to represent ester sulfates and C-bonded S, respectively (Freney 1986). The former contains the C–O–S bonds (ester sulfate) and the C–N–S bonds (sulfamate) along with some organic sulfites (Freney 1961) and corresponds to highly oxidized soil organic S (Solomon et al. 2011). The latter contain organic S directly bonded to C (C–S) and correspond to highly reduced S (e.g., organic sulfides and thiols) and S with intermediate oxidation states (e.g., sulfonates and sulfoxides) (Solomon et al. 2011). Mineralization process of C-bonded S is different from that of ester sulfates (McGill and Cole 1981), and it is a two-step process in which C-bonded S is first converted into ester sulfates, followed by hydrolysis of the ester sulfates (McGill and Cole 1981; Ghani et al. 1991, 1992; Norman et al. 2002; Solomon et al. 2003, 2011; Churka Blum et al. 2013). Nevertheless, the sequential transformation rates, i.e., "change rates of S from C-bonded S to ester sulfate-S" and "change rates from ester sulfate-S to inorganic sulfate-S," have not been separately estimated yet; furthermore, influence of soil properties on mineralization of C-bonded S and ester sulfate-S are poorly known. The occurrence of the ester sulfate-S mineralization can be obscured by the C-bonded S mineralization to sulfate and subsequent transformation to ester sulfate-S (Ghani et al. 1991). If the sequential transformation rates are estimated separately, the mineralization rate of ester sulfate-S is deleted from S mineralized from C-bonded S form and this can allow studying effects of climate and soil properties on both S mineralization rates.

The ester sulfate-S fraction is believed to consist primarily of organic compounds with widely different solubility, ranging from protected clay-associated forms to highly soluble ester sulfates (Eriksen et al. 1998). Clays can physically and chemically stabilize organic S directly or indirectly due to strong association of organic C with aluminum (Al) and iron (Fe) oxides and hydroxides covering clays. The direct interaction depends on specific charge characteristics and surface area of clays (Solomon et al. 2003). Particularly volcanic soils have surface-active (highly reactive) Al/Fe solid compounds (Yagasaki et al. 2006). We previously observed that Japanese forest soils derived from volcanic materials contained large amount of HI-reducible S, acid ammonium oxalate-extractable S (S_{oxa}), and pyrophosphate-soluble S (S_{pyp}) (Tanikawa et al. 2009a, 2013). Each fraction accounted for more than 60 % of total S concentration, and they were significantly ($p<0.001$) correlated with one another, and thus overlapped. Because HI-reducible S comprise of ester sulfate-S and inorganic sulfate-S, the predominant organic S form in both S_{oxa} and S_{pyp} was postulated to be ester sulfate-S. Organically bound S extracted with pyrophosphate was significantly correlated with oxalate-extractable Al (Al_o) concentration. The oxalate-extractable Al/Fe act as aggregating agents (Igwe et al. 2009), and pyrophosphate reagent can dissolve Al/Fe–humus complex (McKeague 1967; Wada 1989) with a little portion of the other active Al/Fe forms (Kaiser and Zech 1996; García-Rodeja et al. 2004). Based on the previous studies, the occlusion of ester sulfate-S in soil aggregate and the formation of complexes between ester sulfate-S and metal–humus are probably high in soils containing high amounts of active Al/Fe during organic S transformation.

The aim of the present study was (1) to separately estimate the transformation rates of organic S from C-bonded S into ester sulfate-S (v_1) and of ester sulfate-S into inorganic sulfate-S (v_2), and (2) to evaluate the influence both of site-specific soil properties and incubation temperatures on the transformation rates (v_1 and v_2). It was hypothesized that ester sulfate-S is derived from C-bonded, and then the inhibition of ester sulfate-S mineralization is observed at soil with high contents of active Al. Since stable soil organic matter (SOM) is characterized by low activation energies in the Arrhenius function (Lützow and Kögel-Knabner 2009), v_2 is hypnotized to be more temperature sensitive than v_1. Japanese subalpine soils tend to accumulate high amounts of decomposable SOM, because of their cool temperatures. We predict that these soils contain a high amount of substrates (organic S), and that both long incubation periods and a high temperature can increase the mineralization of organic S as described by Ghani et al. (1991).

The mineralization of organic S is very low at 10 °C but increases by increasing temperature from 20 to 40 °C and then it decreases (Stevenson and Cole 1999). Sulfite oxidase activities have an optimal pH of 8.0 and increase by increasing temperature up to 35 °C (Bilen and Dick 2011). Arylsulfatase activities that hydrolyze of ester sulfate showed an optimal pH at about 6.2, and increase by increasing the temperature up to about 60 °C, with inactivation temperatures ranging from 60 to 70 °C (Tabatabai 1996). Considering all these reports, we chose 20 and 35 °C temperatures sufficiently high for mineralization of ester sulfate-S. The discrete temperature step was chosen to evaluate the temperature dependency of the sequential transformation rates: v_1 and v_2. To investigate the influence of site-specific properties on S transformations, three soils with different chemical properties were selected to have a variation in soil pH and in Al–humus complex concentrations according to our previous study (Tanikawa et al. 2009b).

Materials and methods

Soils

Soils were sampled from subalpine forest sites in the Nikko volcanic region of Tochigi Prefecture, central Japan and the relative chemical properties are reported by Tanikawa et al. (2009b). There are no active fumaroles in this region. We studied soils from three sites, designated as DC, HL, and NA (Table 1). The dominant vegetation at the DC site was

Table 1 Site characteristics and soil chemical properties

Soil	Location	Altitude (m)	MAT (°C)	MAP (mm)	pH(H_2O)	Organic C (g kg^{-1})	Organic N	Al_o	Al_p	Saturated hydraulic conductivity (cm s^{-1})	Total S (mg S kg^{-1})	Total organic S	Ester sulfate-S	Carbon-bonded S	Phosphate-extractable sulfate-S
DC	36°47′ N,139°31′ E	1,800	3.7	2,100	4.9	134	8.3	25.6	11.6	1.06×10^{-2}	1,270	1,190	769	426	79
HL	36°47′ N,139°31′ E	1,800	3.7	2,100	4.5	145	9.0	8.9	9.0	1.79×10^{-2}	940	924	433	490	17
NA	36°45′ N,139°30′ E	2,100	1.9	2,100	5.5	126	7.7	13.2	11.2	4.18×10^{-2}	820	803	301	502	17

Data were obtained at a nearest weather station (AMeDAS Oku-Nikko station of Japan Meteorological Agency)

MAT mean annual air temperature, *MAP* mean annual precipitation

bamboo shrubs (*Sasa nipponica*), which has recently replaced the original coniferous forest of *Tsuga diversifolia*. The dominant vegetation at the NA site was *T. diversifolia*, whereas *T. diversifolia* and *Betula ermanii* were dominant at the HL site. The soils were classified as Andic Dystrudepts according to the USDA Soil Taxonomy (Soil Survey Staff 2010). Three soil samples were randomly collected at each site with an approximate distance of 10 m among them. Each sample consisted of four pooled subsamples. Subsamples were taken from the A1 horizon by a trowel and had a size of 50 cm× 50 cm. The litter layer was removed before soil sampling. All coarse plant materials were removed, and then subsamples were thoroughly mixed to give the composite sample. Then, field-moist soils were sieved (2 mm) and stored in polyethylene bags at 4 °C until they were used in the incubation experiment.

Fresh soil was analyzed for soil pH (H_2O) and the phosphate-extractable sulfate-S concentration (Tabatabai 1996), oven-dried to calculate water content, or air-dried before being ground, sieved (149-μm) and analyzed for the initial total S, initial HI-reducible S (which includes the ester sulfate-S and the inorganic sulfate-S), and the organic C and N concentrations.

Microbial incubation experiments

The incubation experiments were performed according to Tabatabai and Al-Khafaji (1980). We placed a layer of fine glass beads (each 350 to 710 μm in diameter) and a thin glass wool pad (about 5 mm thick) in the bottom of a 100-mL plastic syringe (JS-S00S, JMS Co. Ltd., Tokyo, Japan). A field-moist soil sample equivalent to 20 g dry weight was thoroughly mixed with 20 g of coarse glass beads (2.0 to 2.8 mm in diameter) in order to avoid compaction of soils during leaching, maintain aeration, and enhance leaching (Ghani et al. 1991). The mixture was transferred into the syringe. Another glass wool pad was used to prevent dispersal of soil when the KCl solution (described below) was poured over the soil–glass beads column. A silicon tube was attached to the lower end of the syringe for collecting the leachate. When the incubation experiment was started, the soil–glass beads mixture was leached with 100 ml 0.01 M KCl in four to five times to remove inorganic sulfate-S from soil, and excess water was removed under vacuum at 67 kPa. The concentration of the KCl solution was chosen considering that microbial (e.g., fungi) biomass and growth rates did not significantly decrease at salt concentrations lower than 0.2 M (e.g., Matsuda et al. 2006). The top of the syringe was then covered with a piece of plastic film (Saran Wrap) having several holes created with a wooden pick to provide aeration; the syringe was set in an upright position in a rack.

We prepared a total of nine syringes (three soil samples at each the site) for incubation at both 20 and 35 °C. The incubation lasted for 2 weeks from the initial preparation and leaching of the syringes; then the soil mixture was leached again with 0.01 M KCl solution, the plastic film was removed, and suction was applied to produce a vacuum of 67 kPa. The syringe was again covered with the plastic film, placed vertically in the rack, and incubated at the chosen temperature. The leaching procedure was repeated every 2-week intervals and the incubation lasted for 40 weeks. The water contents of soils in the incubation syringes were adjusted by weighing them every week and adding deionized water to maintain a constant weight. At the end of the incubation experiment, a portion of each subsample incubated was oven-dried to calculate the water content.

Before incubation, the gravimetric soil water content was 58, 53, and 57 % in the DC, HL, and NA soils, respectively. After the first leaching and the removal of excess water by vacuum, the water content increased to 67, 64, and 66 % in the DC, HL, and NA soils, respectively. After the second leaching procedure, the water content decreased to levels similar to those before the beginning of incubation: 59 % for the DC soil, 53 % for the HL soil, and 57 % for the NA soil. The stable water contents were then maintained until the end of the incubation period. During the incubation period, the average water contents ($n=3$) were 59±2 % for the DC soil, 54±3 % for the HL soil, and 58±2 % for the NA soil at 20 °C and 60±2 % for the DC soil, 55±3 % for the HL soil, and 58±2 % for the NA soil at 35 °C. The soil water content at the end of the incubation was similar to the initial water content; 59, 53, and 58 % in the DC, HL, and NA soils, respectively.

The leachates were filtered (0.45 μm Chromato Disk, 13AI, Kurabo Industries Ltd., Osaka, Japan), then we measured the sulfate-S concentrations by ion chromatography (IC 7000 Series II, Yokogawa Analytical Systems, Tokyo, Japan).

Chemical analysis

Table 2 lists the methods used to determine the soil S fractions. The soil S concentrations were measured as described by Tabatabai (1996). The ground soil sample was oxidized with an HNO_3–$HClO_4$ mixture, and then the initial total S concentration in the digested material was determined by inductively coupled plasma atomic emission spectrometry (ICP-AES) (Maxim, Fisons Instruments, Ecublens, Switzerland). The final total S was calculated by subtracting "the cumulative S mass leached from soil" from the initial total S concentration to avoid an overestimation of mineralized S amount due to soluble organic S.

The ester sulfate-S of the ground soil samples was directly reduced with HI (Freney 1961). After reduction to sulfide, the concentration of S was colorimetrically determined by the methylene blue method (Johnson and Nishita 1952). Because the soil solution and the adsorbed sulfate-S are also reduced by HI (Tabatabai 1996), the ester sulfate-S fraction was obtained by subtracting S_{phos}, determined as described below, from the HI-reducible S.

The C-bonded S concentration was obtained by subtracting the initial ester sulfate-S and the initial S_{phos} from the initial total S (Freney 1967). Because the adsorbed S and the soil solution sulfate-S are usually extracted with phosphate solution (Kowalenko 1993), we determined S_{phos} by shaking field-moist soil samples (5 g of oven-dried soil) with 50 ml 500 mg P $Ca(H_2PO_4)_2$ H_2O L^{-1} for 30 min (Maynard et al. 1987); then the mixture was filtered through no. 6 filter paper (Advantec, Dublin, CA, USA). The concentration of sulfate-S in the extract was determined by ion chromatography (IC 7000 Series II). The pH of the phosphate solvent never exceeded 7, so the extraction of organic S was minimized (Kowalenko 1993).

Sulfate-S is the main inorganic form in most soils, with elemental and sulfide forms present in soils under predominantly anaerobic conditions (Kowalenko 1993). In an analysis of well-drained, well-aerated soils, reduced inorganic S compounds are not expected (Tabatabai 1996). Therefore, we estimated the total concentration of soil inorganic sulfate-S of the soil solution and adsorbed sulfate-S, which are the dominant S_{phos} fractions. Organic S concentration was calculated by subtracting S_{phos} concentration from total S concentration.

The total C and N concentrations were measured using a CN analyzer (MT600 CN Corder, Yanaco Ltd., Kyoto, Japan). Because the amount of inorganic C is negligible in noncalcareous soils (Nelson and Sommers 1996), we regarded total C as the organic C fraction of our samples. Soil pH (H_2O) was determined with a glass electrode using fresh soil samples (soil:water=1:2.5 w/w). Extractable Al was determined following the methods of the International Soil Reference and Information Centre (ISRIC 1993). Al_o was extracted with 0.2 M acid ammonium oxalate solution by shaking air-dried soil (pH 3; soil:solution=1:50 w/w) for 4 h in the dark. The Al concentrations in the extracts were determined by ICP-AES after centrifugation (8,000–9,000×g for 1 h) with three drops of Superfloc and filtration through a 0.45-μm membrane filter. Oxalate extracts Al in hydrous amorphous to paracrystalline aluminosilicate minerals (allophane, allophane-like minerals, and imogolite) and in humus complex. The pyrophosphate-extractable Al (Al_p) was extracted with 0.1 M $Na_4P_2O_7$ $10H_2O$ by shaking air-dried soil (soil:solution=1:100 w/w) for 16 h. Pyrophosphate extraction can be used to extract Al from Al–humus complexes (Higashi and Shinagawa 1981), and strong correlation between Al_p and total organic carbon is observed in volcanic soils (e.g., Matus et al. 2008). However, the solvent can extract small amount of aluminous goethite (Andriesse 1979), amorphous Al hydroxides and gibbsite (Kaiser and Zech 1996), some interlayer complexed Al in the silt plus clay, or relatively labile forms of surface-precipitated Al-OM (García-Rodeja et al. 2004). These overestimations of Al–humus complexes might be serious when the suspension is low-speed centrifuged without Superfloc

Table 2 Methods used for the assessment of various soil sulfur fractions

Sulfur fraction	Assessment	Main S fraction / Definition	Method
Initial total S	Determination	Total S	Acid digestion and determination by ICP-AES for subsample of initial soil
Initial organic S	Calculation	Organic S	Initial organic S=initial total S−initial S_{phos}
Initial HI-reducible S	Determination	Ester sulfate-S, adsorbed and soil solution sulfate-S	Johnson and Nishita reduction method for subsample of initial soil
Initial S_{phos}	Determination	Adsorbed and soil solution sulfate-S (inorganic forms)	Batch extraction with $Ca(H_2PO_4)_2$ H_2O, determination by IC for subsample of initial soil
Initial ester-S	Calculation	Ester sulfate-S, and so on	Initial ester-S=initial HI-reducible S−initial S_{phos}
Initial C-bonded S	Calculation	Organic sulfide-S, and so on	Initial C-bonded S=initial total S−initial HI-reducible S
Final total S	Calculation	Total S	Final total S=initial total S−"the cumulative S mass leached from soil"
Final organic S	Calculation	Organic S	Final organic S=final total S−final S_{phos}
Final HI-reducible S	Determination	Ester sulfate-S, adsorbed and soil solution sulfate-S	Johnson and Nishita reduction method for subsample gained after incubation experiment
Final S_{phos}	Determination	Adsorbed and soil solution sulfate-S (inorganic forms)	Batch extraction with $Ca(H_2PO_4)_2$ H_2O, determination by IC for subsample gained after incubation experiment
Final ester-S	Calculation	Ester sulfate-S, and so on	Final ester-S=final HI-reducible S−final S_{phos}
Final C-bonded S	Calculation	Organic sulfide-S, and so on	Final C-bonded S=final total S−final HI-reducible S
Δtotal S	Calculation	The decrease in the total S concentration after incubation	Δtotal S=initial total S−final total S
ΔS_{phos}	Calculation	"the increment of dissolved and adsorbed sulfate-S in soils after the incubation"	ΔS_{phos}=final S_{phos}−initial S_{phos}
Δester-S	Calculation	Mineralization mass of ester sulfate-S	Δester-S=initial ester-S−final ester-S
ΔC-bonded S	Calculation	Degradation mass of C-bonded S	ΔC-bonded S=initial C-bonded S−final C-bonded S

and then the supernatant is not adopted for ultrafiltration (Schuppli et al. 1983). Therefore, the suspensions were centrifuged at high speed for a long time (8,000–9,000×*g* for 1 h) with three drops of Superfloc and then passed through a 0.025-μm Millipore filter (Schuppli et al. 1983) in the present study. All values are reported on an oven-dry mass basis.

Calculations and statistical analyses

In this study, we defined words related to "transformation" as follows: "S mineralization" for ultimate formation of inorganic sulfate-S from ester sulfate-S and C-bonded S; "transformation of C-bonded S" for change of C-bonded S into ester sulfate-S; "degradation of C-bonded S" for change of C-bonded S into ester and inorganic sulfate-S; "mineralization of ester sulfate-S" for change of ester sulfate-S into inorganic sulfate-S. "The total mass of sulfate-S produced during the incubation" was calculated as the sum of "the cumulative S mass leached from soil" and "the increment of dissolved and adsorbed sulfate-S in soils after the incubation (ΔS_{phos}, determined as described below)." The overall mineralization rate of organic S (OMR) was obtained by dividing "the total mass of sulfate-S produced during the incubation" by 280 days. The results are reported as the average of three replicates on an oven-dry basis. The leached sulfate-S at the beginning of the incubation period after the first application of the KCl solution accounted for 8 to 29 % of total leaching mass of sulfate-S, and was excluded from "the cumulative S mass leached from soil." The decrease in the S fractions after incubation (Δtotal S, ΔC-bonded S, and Δester sulfate-S) was calculated by subtracting the final concentration of a given fraction from the initial concentration of that fraction. The increment of S_{phos} (ΔS_{phos}) was calculated by subtracting the initial S_{phos} from the final S_{phos}.

The transformation rate of C-bonded S (v_1) was calculated by the following equation:

$$\Delta\text{C−bonded S} = v_1 \times t \tag{1}$$

where t is time.

The mineralization of ester sulfate-S (v_2) was calculated by the following equation:

$$\Delta\text{ester sulfate−S} = (v_2 - v_1) \times t \tag{2}$$

By rearranging both equations, v_1 and v_2 can be calculated as:

$$v_1 = \Delta\text{C−bonded S}/t \tag{3}$$

$$v_2 = (\Delta\text{ester sulfate−S}/t) + v_1 \tag{4}$$

Immobilization of inorganic sulfate-S and conversion of ester sulfate-S into C-bonded S have been observed in previous studies (e.g., McLaren et al. 1985; Castellano and Dick 1990). Therefore, the transformation rates v_1 and v_2 are *net* but not *gross* rates. If the conversion rates from ester sulfate-S and inorganic sulfate-S into C-bonded S are higher than degradation of C-bonded S into ester sulfate-S and inorganic sulfate-S, v_1 would be negative. Similarly, v_1 and v_2 would be negative when net immobilization of inorganic S occurs. Direct mineralization of C-bonded S into inorganic sulfate-S would lead to overestimation of v_1 and subsequent overestimation of v_2. Therefore, v_1 and v_2 likely represent the maximum net rates.

To test whether the concentrations of the initial total S and initial S fractions differed significantly among soils, we used the χ^2 test. Paired *t* test was performed for detecting differences between initial C-bonded S concentrations and initial ester sulfate-S concentrations of soils. We tested for significant differences among sites and incubation temperatures in terms of their effects on OMR, Δester sulfate-S, ΔC-bonded S, v_1, and v_2 using a split-plot ANOVA design, with the site as the main plot and temperature as the subplot. We used regression analysis to determine whether the relationships between v and soil pH, between v and Al_p, and between v and Al_o were statistically significant. All statistical analyses were performed using version 06 J of the STATISTICA software (StatSoft, Tulsa, OK, USA).

Results

Initial soil S fractions

The initial total S concentration ranged from 820 to 1,270 mg S kg^{-1}. The dominant S fraction was organic S ranging from 803 to 1,190 mg S kg^{-1}. The initial ester sulfate-S concentration ranged from 301 to 769 mg S kg^{-1}, as same as the initial C-bonded S concentration from 426 to 502 mg S kg^{-1}. The initial S_{phos} was a minor fraction since values ranged from 17 to 79 mg S kg^{-1}. The concentrations of total S, ester sulfate-S, C-bonded S, and S_{phos} differed significantly among soils ($p < 0.05$). The initial total S, organic S, ester sulfate-S, and S_{phos} concentrations of the DC soil were the highest. The C:S ratio ranged from 112 to 157 and Al_p was from 9.0 to 11.6 g Al kg^{-1} (Table 1).

The overall mineralization rates of organic S, v_1 and v_2

"The cumulative S mass leached from soil" increased with incubation period (Fig. 1) as previously reported (Pirela and Tabatabi 1988; Ghani et al.1991). In our study, OMR ranged from 0.03 to 0.45 mg S kg^{-1} day^{-1} and fell within the range of values of previous studies (Tables 3 and 4). Among our soils and data of previous studies (Tables 3 and 4), the DC soil had the lowest OMR value at 20 °C. The v_1 values can be ranked as NA>DC>HL at both temperatures, whereas the rank order of v_2 values was HL>NA >>DC at both temperatures (Table 5). All rates were of the same order of magnitude, except for v_2 at 20 °C in the DC soil, which was an order of magnitude smaller than the other rates. The difference between v_1 and v_2 values was not significant at each temperature.

Influence of site

While the site influence on OMR was not significant, ΔC-bonded S, Δester sulfate-S, v_1, and v_2 differed significantly among sites ($p < 0.05$).

The C-bonded S concentration decreased in all soils during incubation (Fig. 2a), whereas the ester sulfate-S concentration increased during incubation in the DC and NA soils (Fig. 2b), which had a high Al_p. The ΔC-bonded S concentration ranged from 68 to 139 mg S kg^{-1} at 20 °C and from 62 to 145 mg S kg^{-1} at 35 °C. The Δester sulfate-S concentration ranged from −79 to 58 mg S kg^{-1} at 20 °C and from −9.2 to 82 mg S kg^{-1} at 35 °C. A large proportion of the S that was lost in the incubation experiments consisted of C-bonded S rather than ester sulfate-S, because the ratio of ΔC-bonded S/Δtotal S was higher (89 to 185 % at 20 °C, 52 to 103 % at 35 °C) at both incubation temperatures than the ratio of Δester sulfate-S/Δtotal S (−151 to 75 % at 20 °C and from −6 to 66 % at 35 °C).

Relationships between the sequential transformation rates of organic S and soil properties

Velocity 1 but not v_2 was directly proportional to soil pH (Fig. 3a, b), as shown by the following regression equations at both incubation temperatures:

At 20 °C:

$$v_1 = 0.243\ \mathrm{pH}–0.844 \quad R^2 = 0.90, p = 0.000 \tag{5}$$

At 35 °C:

$$v_1 = 0.278\ \mathrm{pH}–1.010 \quad R^2 = 0.76, p = 0.001 \tag{6}$$

Velocity 2 was also significantly correlated with Al_o at the 20 °C incubation temperature:

$$v_2 = –0.022\ \mathrm{Al_o} + 0.621 \quad R^2 = 0.71, p = 0.004 \tag{7}$$

Similarly, a significant regression equation was obtained between v_2 and Al_p at the 20 °C incubation temperature:

$$v_2 = –0.118\ \ \mathrm{Al_p} + 1.517 \quad R^2 = 0.54, p = 0.024 \tag{8}$$

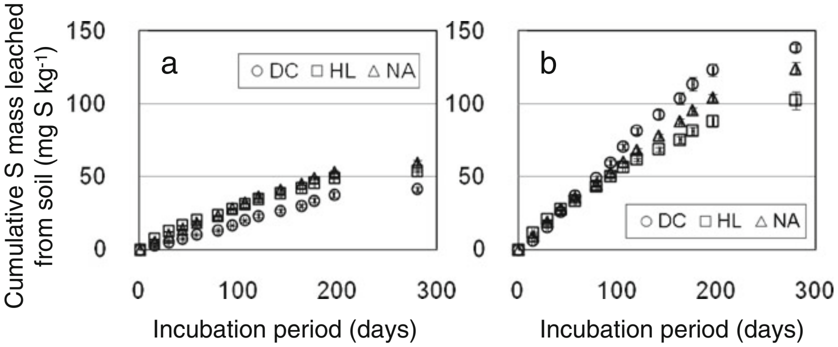

Fig. 1 The cumulative S mass leached from the soil during the incubation experiments (mean± SE; $n=3$). **a** 20 °C; **b** 35 °C

Influence of temperature

In all three soils, OMR was significantly higher during incubation at 35 °C than at 20 °C ($p=0.002$, Table 3). Although Δester sulfate-S concentration differed significantly between the two temperatures ($p=0.012$), that of ΔC-bonded S did not (Fig. 2a, b). Likewise, v_1 did not differ significantly between the two temperatures, but v_2 at 20 °C was significantly lower than at 35 °C ($p=0.003$) (Table 5).

Discussion

Transformation pathways

Increases of ester sulfate-S concentrations and decreases of C-bonded S concentrations during the incubation in the DC and NA soils suggested that C-bonded S is first transformed to ester sulfate-S before formation of inorganic sulfate-S, as described by McGill and Cole (1981), Ghani et al. (1991, 1992), and Solomon et al. (2003, 2011). The fact that the ratio of ΔC-bonded S/Δtotal S was higher than the ratio of Δester sulfate-S/Δtotal S indicated that the total mass of sulfate-S produced during incubation was derived almost exclusively from C-bonded S, being consistent with earlier studies (e.g., Ghani et al. 1991; Zhao et al. 2006; Solomon et al. 2011). In forests, plants absorb S mostly sulfate-S (Kertesz and Mirleau 2004) and synthesize organic S in the leaves, and the organic S is released into soils via litter and root exudates. Schroth et al. (2007) revealed that most of S present in plant litter is C-bonded S, accounting for more than 80 % of organic S. Roots exude amino acids, aliphatic acids, and proteins (Badri et al. 2009), being C-bonded S the predominant organic S form. During litter decomposition process, oxidation of organic S occurs and enriches this pool with oxidized compounds (Schroth et al. 2007); this process is accelerated by anthropogenic activities such as cultivation (Solomon et al. 2011). Our result also supported that the degradation of soil organic S originated from plants (C-bonded S) is generally assumed to represent a shift from reduced to oxidized forms (ester sulfate-S).

Because v_2 was positive in all soils (Table 5), the immobilization of inorganic sulfate-S into ester sulfate-S was probably a minor pathway. In addition, v_1 was also positive in all soils (Table 5). Therefore, mineralization was superior to immobilization even if immobilization/mineralization turnover was likely rapid as shown by radioisotope ^{35}S experiments (e.g., Eriksen 2005).

Velocity 1 in this study was higher than that calculated from Ghani et al. (1991, 1992) (ranging from 0.1 to 0.3 mg S kg^{-1} day^{-1} at 30 °C) who performed a comparable experiment to that of this study using New Zealand soils. The higher rates of v_1 may be explained by the higher amounts of substrates (C-bonded S) in our volcanic soils (ranging from

Table 3 Mineralized organic S (mean±SE; $n=3$) in soil incubated at 20 °C or 35 °C for 280 days

Soil	20 °C				35 °C				Percentage of organic S mineralized	
	Leached (mg S kg^{-1})	ΔS_{phos}	Total[a]	OMR[b] (mg S kg^{-1} day^{-1})	Leached (mg S kg^{-1})	ΔS_{phos}	Total[a]	OMR[b] (mg S kg^{-1} day^{-1})	20 °C	35 °C
DC	42±2	−34±14	7±13	0.03±0.05	139±3	−53±15	85±13	0.30±0.05	0.6±1.1	7.1±1.1
HL	54±1	50±29	104±29	0.37±0.10	103±7	24±27	127±32	0.45±0.12	11.2±3.2	13.7±3.5
NA	60±2	4±1	63±3	0.23±0.01	124±5	2±2	127±3	0.45±0.01	7.9±0.4	15.8±0.3

[a] "The total mass of sulfate-S produced during the incubation" was calculated as the sum of "the cumulative S mass leached from soil" and "the increment of soil solution and adsorbed sulfate-S (ΔS_{phos}) in soil after the incubation"

[b] Overall mineralization rate of organic S (OMR) was obtained by dividing "the total mass of sulfate-S produced during incubation" by incubation time

Table 4 Net mineralization rates of organic S in aerobic soils of previous studies

Vegetation/land use	Incubation temperature (°C)	Moisture condition of soil sample	S mineralization rate (mg S kg^{-1} day^{-1})	Reference
Forest	20	Air-dried and rewetted	0.04[a]	Calculated value after McLaren et al. (1985)
Forest	30	Field-moist	0.75	Calculated value after Ellert and Bettany (1992)
Forest	25	75 % of water holding capacity	0.17	Knights et al. (2001)
Grassland, pasture	20	Field-moist	0.09–0.18	Calculated value after Tabatabai and Al-Khafaji (1980)
Grassland, pasture	25	75 % of water holding capacity	0.12	Knights et al. (2001)
Grassland, pasture[b]	30	Field-moist	0.06–0.77	Calculated value after Nguyen and Goh (1992)
Grassland, pasture[c]	30	Air-dried and rewetted	0.04–0.37	Calculated value after Ghani et al. (1991)
Grassland, pasture	35	Field-moist	0.23–0.45	Calculated value after Tabatabai and Al-Khafaji (1980)
Arable[d]	18	Field-moist	0.04–0.05	Calculated value after Boye et al. (2009)
Arable	20	Field-moist	0.10–0.15	Calculated value after Tabatabai and Al-Khafaji (1980)
Arable[e]	25	75 % of water holding capacity	0.06–0.11	Knights et al. (2001)
Arable	35	Field-moist	0.26–0.47	Calculated value after Tabatabai and Al-Khafaji (1980)
Cleared field	30	Field-moist	0.12	Calculated value after Ellert and Bettany (1992)
Fallow wheat field	30	Field-moist	0.09	Calculated value after Ellert and Bettany (1992)

[a] Excluding a result of a sample with glucose application, because addition of glucose enhance S immobilization (McLaren et al. 1985; Knights et al. 2001) resulting in repression of net S mineralization rates. The values of gley soil were not presented, because its land use and aerobic/anaerobic condition had not been described in the reference

[b] Including two type of soils (camp and non-camp soils) with several levels of superphosphate application

[c] Majority of soils was sampled from pasture sites

[d] Including farmyard manure and crop residues plots

[e] Including control, N application, nutrient mixture (N, P, K, Mg, S) application, farmyard manure plots

430 to 500 mg S kg^{-1}) than in New Zealand soils (ranging from 83 to 368 mg S kg^{-1}).

Influence of active Al on transformation rates

To our knowledge, this is the first study to estimate the sequential S transformation rates, v_1 and v_2. By the estimation of v_1 and v_2 separately, significant site influences on both v_1 and v_2 were observed. Velocity 2 was significantly ($p < 0.05$) and negatively correlated with both of Al_o and Al_p contents at 20 °C (Fig. 3d, f), suggesting that ester sulfate-S is occluded in soil aggregates and adsorbed onto mineral surface (incorporation into Al–humus complexes). Bettany et al. (1979) suggested that ester sulfate-S is associated with the active side chain components of fulvic and humic materials. Ester-bonded sulfate groups can serve as complexation sites for metals such as Al and Fe (Sollins et al. 1996). Due to these characteristics, ester sulfate-S might be suitable for the occlusion and complexation reactions.

Table 5 Velocity 1 (v_1, in milligrams of sulfur per kilogram per day) and velocity 2 (v_2, in milligrams of sulfur per kilogram per day) in the incubation experiments (mean±SE; $n=3$)

Soil	Rate	20 °C	35 °C
DC	v_1[a]	0.35±0.03	0.38±0.07
HL	v_1[a]	0.24±0.03	0.22±0.03
NA	v_1[a]	0.50±0.02	0.52±0.02
DC	v_2[b]	0.06±0.05	0.35±0.05
HL	v_2[b]	0.45±0.11	0.52±0.11
NA	v_2[b]	0.30±0.02	0.51±0.01

[a] Calculated using Eq. (3)

[b] Calculated using Eq. (4)

Even though ester sulfate-S is often a minor organic S form in forest soils (e.g., Fitzgerald et al. 1988; Schroth et al. 2007), there was no significant difference between initial ester sulfate-S concentrations and initial C-bonded S concentrations in this study. Furthermore, initial ester sulfate-S concentration in our soils was higher than those reported in bibliography (Mitchell et al. 1992). Because great amounts of Al/Fe are released by the weathering of volcanic ash, a large amount of them is accumulated as hydroxides or metal–humus complexes (Yoshinaga 1986). The accumulation of ester sulfate-S appeared to be a unique characteristic of Japanese volcanic soils due to the high concentration of active Al. Keer et al. (1990) indicated that ester sulfates were mainly present in the high molecular weight compounds, whereas Lou and Warman (1992) stated that the ester sulfate-S associated with the low molecular weight fraction of SOM can be defolded by enzymatic hydrolysis. Estimation of both molecular weight of

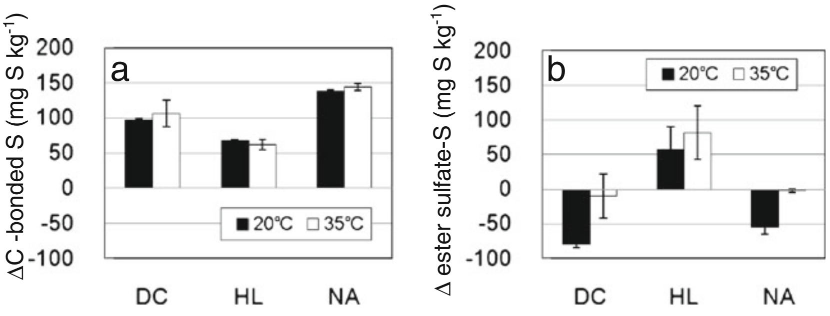

Fig. 2 The amounts of the organic S fractions decreased during the incubation experiments (mean±SE; n=3). *DC*, *HL*, and *NA* are names of the study sites (see Table 1). **a** C-bonded S; **b** ester sulfate-S

organic compounds including ester sulfates and transformation rates (v_1 and v_2) in soils with various textures may resolve this contradiction and supply information on various residence times of ester sulfate-S. The information can help to predict both plant available S and watersheds acidification both due to mobilization of soil organic S.

Influence of soil pH on transformation rates

Velocity 1 was positively correlated with soil pH, which ranged from 4.5 to 5.5 (Fig. 3a), suggesting that a decrease of soil pH suppress the degradation of C-bonded S. This result was similar to previous studies for the overall mineralization rate of organic S

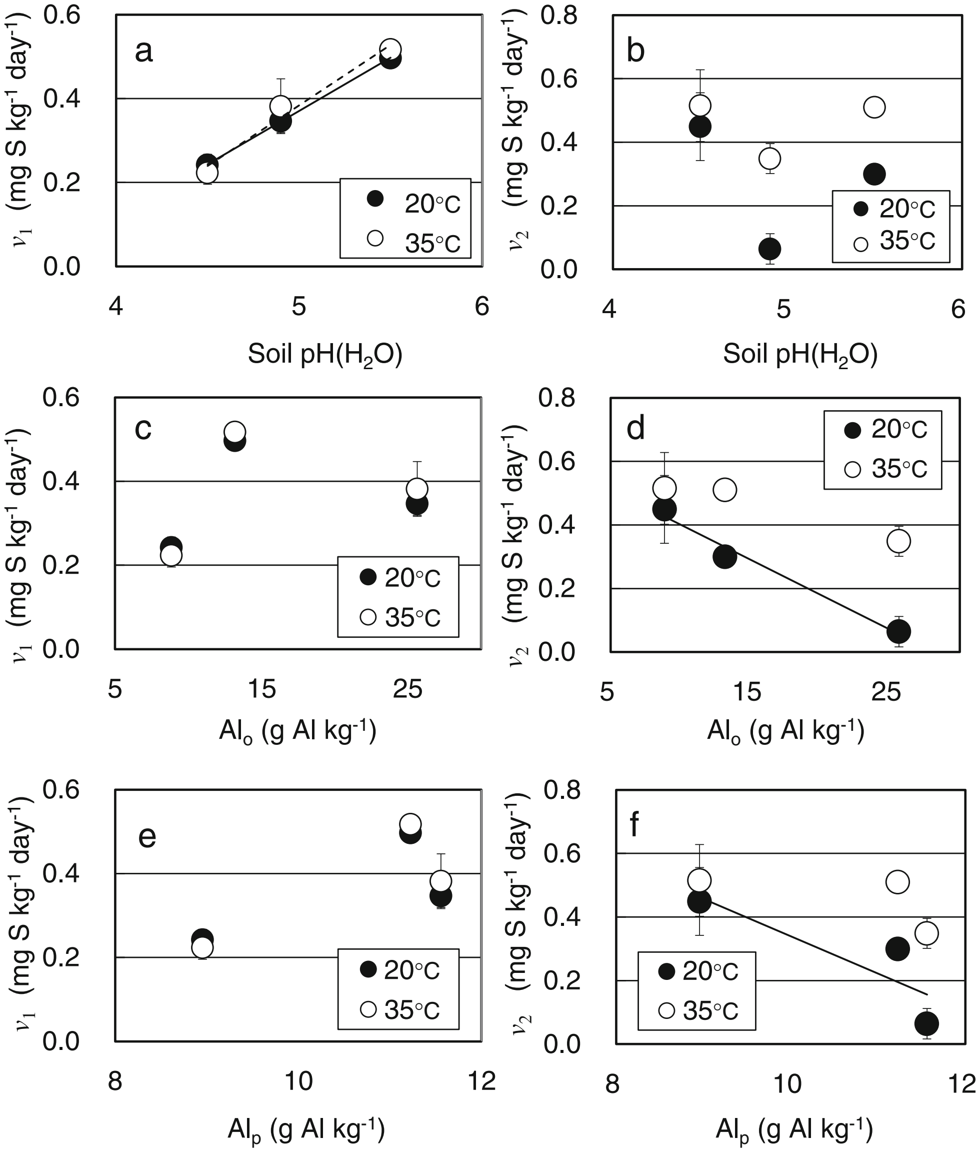

Fig. 3 Relationships between site-specific properties and v_1 or v_2 (mean±SE; n=3). **a** soil pH (H_2O) and v_1; **b** soil pH (H_2O) and v_2; **c** Al_o content and v_1; **d** Al_o content and v_2; **e** Al_p content and v_1; **f** Al_p content and v_2

but not for C-bonded S; OMR was most rapid at pH ranging from 5.5 to about 7.5 (Stevenson and Cole 1999), and was correlated to pH at values lower than pH 7.5 (Williams 1967). Our result might be caused by pH dependency of microbial activity as shown by Haynes (1986), Pietri and Brookes (2008) and by the pH dependency of enzyme activities in soils such as sulfite oxidase activity (Bilen and Dick 2011).

In contrast, v_2 was not related to soil pH (Fig. 3b). Two reasons for the different reactions between C-bonded S and ester sulfate-S to soil pH can be postulated. First, C-bonded S and ester sulfate-S may have heterogeneous quantitative distributions at hierarchical aggregate structures (e.g., Tisdall and Oades 1982; O'Brien and Jastrow 2013). Since plant residues, living roots, and fungal hypha were distributed in the outer part of the hierarchical aggregate structures (non-aggregated material and macroaggregate), a large portion of C-bonded S may be located in the outer part of the structures. In contrast, ester sulfate-S is mainly generated through biochemical process by soil microorganisms, metabolizing organic residues (Solomon et al. 2001), and most of ester sulfate-S is often found in the clay fraction rather than in the silt fraction (e.g., Bettany et al. 1979; Wang et al. 2006; Prietzel et al. 2007). These observations agree with the idea that ester sulfate-S is distributed in the inner part of the microaggregates. Therefore, C-bonded S may be located and biologically transformed into ester sulfate-S in the outer part of macroaggregates. Then, ester sulfate-S produced may reach the inner part of the aggregate structures due to its affinity to minerals, or be absorbed onto the surface of other organic materials, which are associated to minerals, like the onion layer model proposed for SOM stabilization by Sollins et al. (2006). Because microaggregates provide a unique microenvironment that selects specific microbial species in different soils (Mummey et al. 2006), pH dependency of transformation/mineralization processes may be different between C-bonded S and esters sulfate-S. In addition, different kinds of sulfatase, such as aryl-, alkyl-, steroid, gluco-, condro- and mycosulphatase activities can be active in these processes but only arylsulfatase activity has been investigated in soil (Eriksen 2008). Activities of enzymes interacting with mineral fraction and organo–mineral complexes can have different pH profiles compared to non-immobilized enzyme (Rao et al. 2000; Kelleher et al. 2004), and generally enzyme–mineral complexes have a broad pH optimum (Nannipieri et al. 1988). If several enzymes and the mineral complexes with different pH optimums contribute to the mineralization of ester sulfate-S, synergistically, linear relationships between soil pH and ester sulfate-S mineralization rate cannot be obtained.

Influence of temperature on transformation rates

Temperature is one of the most important factors governing the turnover of soil organic S pool (Wang et al. 2006). In the present study, v_2 is hypnotized to be more temperature sensitive than v_1. This hypothesis was consistent with observations that the temperature significantly affected v_2 and that the relationship between v_2 and Al_p was significant at 20 °C but not at 35 °C, suggesting that the ester sulfate-S stabilization of soils is greater at lower than at higher temperatures. Rasmussen et al. (2006) also indicated that the negative correlation between Al hydroxide (including Al–humus complexes) content and C mineralization increased as temperature decreased, suggesting that Al species were important in controlling C mineralization at low temperature. Probably this depended on the changes in microbial community structure and rates of enzyme production with temperature, as indicated by Dalias et al. (2001) and Waldrop and Firestone (2004), or by a greater Al-toxicity effect to microbial communities at low temperatures. It must be noted that SOM decomposition rates depend on microbial "functional diversity" rather than taxonomic diversity (Nannipieri et al. 2003; Bonkowski and Roy 2005; Chaparro et al. 2012). Based on ideas of these previous studies, increase in microbial activity, enzyme production rates, and microbial functional diversity may be higher at higher than at lower temperature.

Heterogeneous distribution of both microbes and organic S fractions in aggregates can also be noteworthy. The large particle size fractions contained higher levels of fungal biomass than the smaller particles (Chiu et al. 2006), whereas 90 % of heterotrophic bacteria preferentially located in the inner part of aggregates (Ranjard et al. 2000). If this is the case, ester sulfate-S may be located in the inner part of the structures where bacteria are predominantly located, whereas C-bonded S may be distributed in the outer part of the macroaggregates where higher abundances of fungi are expected than in the inner part. Fungal activity is often lower than bacterial activity at high temperature (e.g., Pietikäinen et al. 2005). Thus, it is possible that a larger amount of ester sulfate-S was mineralized by bacteria in the inner part of the hierarchical aggregate structures at 35 °C than 20 °C.

In addition, activities of enzymes interacting with minerals and/or organo–mineral complexes vary widely with the temperature (Rao et al. 2000; Kelleher et al. 2004). If enzymes activities mineralized ester sulfate-S have different optimal temperature than those for degradation of C-bonded S, the relationships between the transformation/mineralization rates of these two types of organic S fractions and temperature might also differ.

Conclusions

We performed an incubation experiment to estimate the sequential transformation rates of C-bonded S to ester sulfate-S (velocity 1, v_1) and of ester sulfate-S to sulfate-S (velocity 2, v_2) and the stabilization of ester sulfate-S in volcanic soils. By separating the sequential transformation rates, we showed that the transformation rate of C-bonded S and mineralization of ester sulfate-S depended on temperature and site-specific soil properties; v_2 was significantly ($p < 0.05$) correlated with active Al concentrations when soils were incubated at 20 °C, and it was sensitive to incubation temperatures. Thus, mineralization of ester sulfate-S would be governed by soil mineral properties and climate. Velocity 1 was significantly ($p < 0.01$) positively correlated with soil pH at both temperatures, suggesting that a decrease in soil pH suppress the degradation of C-bonded S. Further studies are needed for evaluating the distribution of both ester sulfate-S and C-bonded S in aggregates by using nondestructive methods, and studying ester sulfate-mineral occlusion in soil aggregates and/or adsorption onto mineral surface. In addition, the study of enzyme structures and their association with soil colloids can help to better understand S turnover in volcanic soils.

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