Anthropogenic and climate influences on biogeochemical dynamics and molecular-level speciation of soil sulfur

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Abstract. The soil environment is a primary component of the global biogeochemical sulfur (S) cycle, acting as a source and sink of various S species and mediating oxidation state changes. However, ecological significance of the various S forms and the impacts of human intervention and climate on the amount and structural composition of these compounds are still poorly understood. We investigated the long-term influences of anthropogenically mediated transitions from natural to managed ecosystems on molecular-level speciation, biogeochemical dynamics, and the apparent temperature sensitivity of S moieties in temperate, subtropical, and tropical environments with mean annual temperature (MAT) ranging from 5°C to 21°C, using elemental analysis and X-ray absorption near-edge structure (XANES) spectroscopy. Land-use and land-cover changes led to the depletion of total soil S in all three ecoregions over a period of up to 103 years. The largest decline occurred from tropical forest agroecosystems (67% Kakamega and 76% Nandi, Kenya), compared to losses from temperate (36% at Lethbridge, Canada, and 40% at Pendleton, USA) and subtropical (48% at South Africa) grassland agroecosystems. The total S losses correlated significantly with MAT. Anthropogenic interventions profoundly altered the molecular-level composition and resulted in an apparent shift in oxidation states of organic S from native ecosystems composed primarily of S moieties in intermediate and highly reduced oxidation states toward managed agroecosystems dominated by organic S rich in strongly oxidized functionalities. The most prominent change occurred in thiols and sulfides, the proportion of which decreased by 46% (Lethbridge) and 57% (Pendleton) in temperate agroecosystems, by 46% in subtropical agroecosystems, and by 79% (Nandi) and 81% (Kakamega) in tropical agroecosystems. The proportion of organic S directly linked to O increased by 81%, 168%, 40%, 92%, and 85%, respectively. Among the various organic S functionalities, thiols and sulfides seem to have higher apparent temperature sensitivity, and thus these organic S moieties may become prone to losses due to land-use changes, even from the cooler regions of the world if MAT of these regions rise in the future.

Key words: C-bonded S; ester-bonded S; land use; organic S; oxidized S; reduced S; sulfates; sulfides: sulfonates; synchrotron radiation; XANES.

INTRODUCTION

Sulfur is the fifth most abundant element (by mass) in the universe and the 13th most abundant element in Earth's crust (Stevenson and Cole 1999, Likens et al. 2002). Electronic expansions into *d* orbitals allow S to exhibit by far the greatest range in oxidation state (S^{-2} to S^{+6}) of the geochemically abundant elements. This characteristic hetrovalent nature makes S highly redox sensitive and allows it to form a series of chemically active oxyanions and compounds at the different intermediate oxidation states (Janzen and Ellert 1998,

Fleet 2005). Because of its range in oxidation states and a diverse geochemical affinity, S moves freely between the lithosphere, hydrosphere and atmosphere; and its pathways within any ecosystem are highly complex and intricately intertwined with other elements.

The soil environment is a primary component of the global biogeochemical S cycle, acting as a source and sink of various S species and mediating changes in oxidation states. The estimated total mass of global S reserve in soils amounts to 250×10^{15} g (Zhao et al. 1996, Stevenson and Cole 1999) and each year it contributes about 208×10^{12} g to runoff into oceans and about 5 to 77×10^{12} g to the Earth's atmosphere as biogenic emission (Morra et al. 1997). Sulfur in terrestrial ecosystems is found in inorganic and organic forms, each of which may play characteristic biological

DAWIT SOLOMON ET AL.

TABLE 1. Selected climate, physical, and chemical characteristics of the ecological reference sites from temperate (Lethbridge, Canada, and Pendleton, USA), subtropical (Harrismith, Kroonstad, and Tweespruit, South Africa), and subhumid tropical (Nandi and Kakamega, Kenya) ecosystems.

Site	Ecosystem	Longitude	Latitude	Altitude (m)	MAT (°C)	MAP (mm)	Sand (g/kg soil)	Silt (g/kg soil)	Clay (g/kg soil)
Temperate									
Lethbridge	grassland	49°42′ N	112°50′ W	951	5.0	404	420	330	250
Pendleton	grassland	46°43′ N	118°39′ W	438	10.0	406	120	700	180
Subtropical									
Harrismith	grassland	28°16′ S	29°07′ E	1753	13.8	625	750	100	150
Kroonstad	grassland	27°38′ S	27°13′ E	1416	16.6	563	830	50	120
Tweespruit	grassland	29°46′ S	26°10′ E	1379	16.0	516	770	100	130
Tropical									
Nandi	forest	00°04′ N	34°58′ E	1800	19.0	2000	240	180	570
Kakamega	forest	00°14′ N	34°57′ E	1700	21.0	2080	380	210	400

Note: Key to abbreviations: MAT, mean annual temperature; MAP, mean annual precipitation; BD, bulk density; SOC, soil organic carbon.

and chemical roles. Inorganic S occurs in both oxidized (e.g., sulfates) and reduced (e.g., elemental S, thiosulfates, sulfides) forms in soils. Reduced inorganic S forms are transitory in aerobic soils and their concentrations are usually negligible (Kowalenko 1993a, Saggar et al. 1998). The bulk of soil S ($>95\%$), both in temperate and tropical agroecosystems, however, is found in organic forms (Biederbeck 1978, Janzen and Ellert 1998, Solomon et al. 2001). In undisturbed ecosystems, the biogeochemical cycling of soil S is essentially in balance with minimal short-term losses or gains. In these ecosystems, internal cycling reactions are responsible for maintaining a supply of biologically available soil S through mineralization of S-containing organic substrates and subsequent redox transformations. However, during the past 150 years alone, anthropogenic land-use and land-cover changes through clearing of natural forests and native grasslands for agricultural purposes have claimed a large share of productive terrestrial environment in temperate and tropical ecosystems and dramatically altered not only the physical and biological nature of the land surface and thus the Earth's climate system but also the rates and processes underlying the biogeochemical cycling of elements (Janzen and Ellert 1998, Houghton et al. 1999, 2003). The steady state attained in undisturbed ecosystems and thereby the amount, structural composition and stability of soil organic S pools, could thus be considerably influenced by these interventions until new steady state is eventually established.

The concern over rapid conversion of natural forests and grasslands has prompted several studies to determine how natural ecosystems respond to anthropogenic perturbations. These include topics such as climate, hydrology, net primary production as well as decomposition of soil organic matter (SOM) and biogeochemical cycling of organically associated elements such as C, N, and P (Schlesinger 1997, Vitousek et al. 1997, Houghton 2003). In contrast, studies about the molecular-level speciation, long-term turnover dynamics and ecological

significance of specific S compounds in temperate and tropical ecosystems have received little attention (McGill and Cole 1981, Scherer 2001, Solomon et al. 2001). Moreover, although climate is an important attribute governing organic S accumulation in soils (Ellert and Bettany 1992, MacDonald et al. 1995, Wang et al. 2006) and it is expected to accentuate the impacts of anthropogenic perturbations on S biogeochemical cycling, detailed studies on the "intrinsic" and "apparent" temperature sensitivity (Davidson and Janssens 2006) are largely lacking.

Therefore, we investigated the influences of anthropogenically mediated transitions from natural to managed ecosystems on biogeochemical dynamics, oxidative state and accompanying functional group chemistry of soil S and apparent temperature sensitivity of the various organic S moieties in soils using carefully selected long-term chronosequences and real-time series (up to 103 years old) in temperate (Canada and USA), subtropical (South Africa) and subhumid tropical (Kenya) environments with mean annual temperature (MAT) ranging from 5°C to 21°C.

MATERIALS AND METHODS

Study sites and chemical analysis

The present study was conducted using soil samples collected from the (1) prairie grassland agroecosystems of North America, (2) subtropical Highveld grassland agroecosystems of South Africa, and (3) subhumid tropical forest agroecosystems of Kenya (Table 1). The study sites were located in regions that are away from major urban and industrial development, historically exposed to almost no atmospheric S deposition, and where S seems to be deficient in soils and crops were shown to respond to S fertilization.

Canada.—The prairie grassland agroecosystem at Lethbridge is part of the long-term experimental site of Agriculture and Agri-Food Canada established in 1906. The experimental site is located at Lethbridge, Alberta

TABLE 1. Extended.

BD (g/cm^3)	pH (H$_2$0)	pH (KCl)	SOC (g/kg soil)	N (g/kg soil)	C:N (g/kg soil)
1.24	7.0	6.2	26.0	0.26	9.9
1.20	7.0	6.6	21.0	0.21	10.0
1.28	5.2	4.5	20.6	1.60	12.9
1.39	6.0	5.0	8.0	0.85	9.4
1.30	5.9	5.0	11.7	1.12	10.5
0.65	6.5	6.0	95.1	9.5	10.1
0.76	5.9	5.3	118.7	10.8	11.0

(49°42′ N and 112°50′ W). The altitude of the area is 951 m above sea level, with a MAT of 5°C and a mean annual precipitation (MAP) of 404 mm. The original species compositions are characteristic of the *Stipa comata* Trin. and Rupr. and *Agropyronsmithii* faciation of the mixed Prairie. The soils are well drained, dark brown in color, and have a clay loam texture. They are developed under native grassland vegetation on alluvial-lacustrine parent material and are classified as Haplic Chernozems (FAO-UNESCO 1997). The long-term "ABC" rotation experiment at Lethbridge was started in 1911. It consists of undisturbed grassland areas that have been maintained as a benchmark site since 1911 for comparison with three original cultivation treatments (unfertilized continuous wheat [*Triticum aestivum* L.] cultivation [rotation A], fallow–wheat–fallow rotation [rotation B], and fallow–wheat–oat [*Avena sativa* L.]–fallow rotation [rotation C]) aimed to determine whether spring wheat can be grown on a grassland soil indefinitely without depleting the soil or harming the environment. Archived composite soil samples collected from unfertilized continuous wheat cultivation (rotation A) in 1956, 1967, 1995, and 2001 were compared with soil samples from the control grassland sites. The archived samples were composed of up to four replicate subsamples bulked together into one composite sample. The samples were air-dried, ground to pass through a 2-mm sieve, and stored in sealed glass jars.

United States.—The Columbia Basin Agricultural Research Center is home to some of the oldest agricultural experiments in western United States, with experiments dating back to 1931. This site includes virgin grassland that has not been cultivated since 1931 with *Pseudoroegneria spicata* (Pursh) Á. Löve and *Festuca idahoensis* Elmer as the dominant species that serve as a baseline for evaluating changes in managed systems. The research center is located at Pendleton, Oregon (46°15′ N and 119°58′ W) in the Columbia Plateau physiographic province. The research center is 438 m above sea level, with a MAT of 10°C and MAP of 406 mm. The soils are derived from loess overlying cobbly caliche and basalt rock. They are well drained,

dark grey in color, silty loam in texture and are classified as Haplic Kastanozems (FAO-UNESCO 1997). Carefully collected and archived composite soil samples (composed of up to four subsamples) from the upper 15-cm layer of grass pasture and from conventionally tilled winter wheat (*Triticum aestivum* L.)–fallow rotation fields established in 1931 were used in the present experiment. Archived samples from the cultivated fields were collected in 1976, 1986, 1994, and 2002, air-dried, ground to pass through a 2-mm sieve, and stored in sealed glass containers.

South Africa.—The three study sites in South Africa (Harrismith, 29°7′ E and 28°16′ S; Kroonstad, 27°13′ E and 27°38′ S; and Tweespruit, 26°10′ E and 29°46′ S) are located in the summer rainfall region with MAP ranging from 516 to 625 mm and MAT ranging from 14° to 17°C. The elevation of these sites ranges from 1350 to 1800 m above sea level. The sites belong to the Highveld grassland biome, which is dominated by *Themeda triandra* Forssk. and *Eragrostis curvula* Nees at Harrismith; *Eragrostis lehmanniana* Nees and *Panicum coloratum* L. at Kroonstad and *Themeda triandra* Forssk. at Tweespruit. The soils have medium to coarse texture and are classified as Dystric to Eutric Plinthosols (FAO-UNESCO 1997). The agricultural fields were plowed to a depth of 20 cm and wheat and maize (*Zea mays* L.) were grown. In South Africa, we sampled soils from fields cultivated for about 3, 8, 10, 20, 30, 40, 60, and 90 years and from adjacent native grasslands sites from the three agroecosystems. At each field, we collected nine subsamples from the upper 20 cm in a radial sampling scheme, which were later combined to one composite sample. Due to limitations in instrument and beam-time allocation, we pooled samples from each conversion time from the three sites together and prepared one representative sample per site for each age group.

Kenya.—The Kakamega forest is the eastern-most remnant of the Guineo–Congolian rainforest, which in the past millennium stretched across the entire expanse of West and central Africa to the East African highlands. It is one of the last remnants of pristine subhumid tropical rainforests currently existing in this intensely cultivated region. The Kakamega forest was a contiguous forest until 1895; since then the forested area has been constantly decreasing through deforestation to a number of peripheral fragments among which the Nandi highland forests are the largest ones. The altitude of the Kakamega and Nandi sites range from 1700 to 1800 m above sea level. Mean annual temperature range from 19°C to 21°C, with MAP of about 2000 mm. The soils of Kakamega forest are well-drained, deep red to yellowish red, friable sandy clay to sandy loam texture. They are developed from undifferentiated Basement System rocks and are classified as Ferralo-Chromic Acrisols (FAO-UNESCO 1997). The soils at the southern Nandi forest are composed of well drained, extremely deep dark to reddish brown with friable clay

and thick humic top layer principally developed on biotite-gneisses parent material. They are classified as Humic Nitosols (FAO-UNESCO 1997). The natural vegetation of these two sites is composed of tropical rainforest of Guineo-Congolian species, including *Aningeria altissima* (A.Chev.) Aubrév. and Pellegr., *Antiaris toxicaria* Lesch. and *Chrysophyllum albidum* G. Don. The soils at Kakamega and Nandi were plowed to 10 to 12 cm depth and maize was grown as the main crop without fertilizer inputs with an occasional inclusion of finger millet (*Eleusine coracana* Gaertn.) or sorghum (*Sorghum bicolor* (L.) Moench. In Kenya, we selected fields from natural forests and from fields cultivated for different durations (Nandi for 2, 4, 20, 30, 50, 80, and 100 years and Kakamega for 2, 4, 18, 45, 73, and 103 years). We collected nine subsamples from the upper 10 cm soil from each field, which were later combined to one composite sample. The soil samples from Kenya and South Africa were air-dried and sieved (<2 mm) prior to chemical analysis. Total soil organic carbon (SOC), N and S concentrations were determined by a C/H/N/S-analyzer (Elementar Analysensysteme GmbH, Hanau, Germany). The pH-H_2O and pH-KCl were determined in 1:2.5 soil : water (m/v, mass : volume) suspension.

X-ray absorption near-edge structure (XANES) spectroscopy

Solid-state characterization of S oxidation states of the humic fractions extracted from the native grassland, natural forest, and cultivated soils was conducted using S K-edge XANES spectroscopy at beam-line X-19A of the National Synchrotron Light Source (NSLS), Brookhaven National Laboratory. The sieved soil samples were extracted three times with a mixture of 0.1 mol/L NaOH and 0.4 mol/L NaF solutions in a 1:5 soil to extraction solution ratio (w/v) under N_2 environment. The extraction procedure followed the outline of Schnitzer (1982), as modified by Sumann et al. (1998). Replacement of 0.1 mol/L $Na_4P_2O_7$ by 0.1 mol/L NaOH–0.4 mol/L NaF mixture improves extraction yield compared with extraction using only 0.1 mol/L $Na_4P_2O_7$ (Sumann et al. 1998). The F^- ion was introduced to dissolve silicate impurities and reduce the influence of paramagnetic metals on XANES spectra (Solomon et al. 2003, 2007). The extracts were filtered twice through 0.2-μm pore-size membrane filter (Pall Gelman Laboratory, Ann Arbor, Michigan, USA) to remove fine clay that may interfere with XANES measurements (Solomon et al. 2003), transferred into dialysis tubes (MWCO 12 000 to 14 000 Da, Spectrum Laboratories, Gardena, California, USA), dialyzed against deionized water to eliminate soluble salts and lyophilized using a freeze dryer (Kinetics Thermal Systems, Stone Ridge, New York, USA). Schoenau and Bettany (1987) suggested that artificial changes such as autooxidation and alkaline hydrolysis of SOM could occur following NaOH extraction of humic substances. However, recent studies using S K-edge XANES (Hutchison et al. 2002) failed to detect any change in the oxidation states, as well as accompanying structural composition of organic S in humic substances extracts aerated at various pH levels for up to 44 hours.

The S XANES measurements of the humic fractions were conducted under standard operating conditions. The X-ray energy was calibrated to the K-edge of elemental S at 2472 eV and scans ranging from 150 eV below to 300 eV above the absorption edge of S were collected with step size of 0.2 eV. We used a monochromator consisting of double-crystal Si (111) with an entrance slit of 0.5 mm and a minimum energy resolution of 2×10^{-4} (~0.5 eV) at the S K-edge. The monochromator was detuned to 70% at the S K edge in order to reduce fluorescence induced by high-order harmonics (Xia et al. 1998). The spectra were recorded in fluorescence mode using a passivated implanted planar silicon (PIPS) detector (Canberra Industries, Meriden, Connecticut, USA). The beam path from incident ion chamber to the sample chamber was purged with He gas. The samples were pressed into a 0.5 mm thick acrylic holder and covered with 2.5 μm thick Mylar film (Chemplex Industries, Palm City, Florida, USA). Each XANES spectrum represents the average of three scans. Background correction, normalization, and deconvolution of XANES spectra for each sample into pseudo-components were done using the nonlinear least square fitting routine solver supplied by MS-Excel according to Xia et al. (1998), Martínez et al. (2002), Solomon et al. (2003), and Einsiedl et al. (2007). The linear part of the spectral baseline was removed and the spectrum was normalized prior to fitting to avoid spectral dependence on the total organic S content; therefore, spectral properties are indicative of changes in S chemistry. The XANES spectra were fitted using a series of Gaussian peaks (G1, G2, G3, G4, and G5) that represent the white-lines ($1s \rightarrow 3p$ photoelectron transition peaks). To obtain meaningful fits, the following assumptions were made in the fitting process: (1) all $s \rightarrow p$ transition peaks have a Gaussian shape, (2) the full width at half-maximum (FWHM) of each Gaussian components for S in low and intermediate oxidation states ($\leq 4^+$) was loosely constrained between 0.2 and 1.0 eV, whereas the FWHM of Gaussian components for high-valence S ($\geq 4^+$) was tightly constrained at 1.4 and 2.2 eV, respectively, and (3) the X-ray absorption step heights (background) of the spectra were approximated by the sum of two arctangent functions. The first (AT1) and the second (AT2) arctangent functions represent the transition of ejected photoelectrons to the continuum for the unoxidized S (white-lines located between 0 and 5 eV above the elemental S K-edge) and for the oxidized S forms (white-lines located between 5 and 12 eV above the elemental S K-edge), respectively. Additional justifications and assumptions made for the fitting procedure, as well as details of the fitting and other data collections procedures were described by Xia et al. (1998). The energy positions (eV) of the Gaussian curves were used to

identify the oxidation states of S present in the sample, and the percentages of S functionalities present at each oxidation state in a sample were determined from the area under the respective Gaussian peak relative to the total area under the five Gaussian peaks after correcting for the change in absorption cross section with increasing oxidation state (Xia et al. 1998). Because XANES reflects the distribution of electrons in the valence shell of S atoms in their actual bonding environment, the difference between electronic and formal oxidation states can be substantial, especially for reduced S species in complex organic materials, depending on whether S is bonded to S, H, C or metals (Xia et al. 1998, Martínez et al. 2002). Due to the higher electronegativity of O, the differences are not significant for higher-valence ($\geq 4^+$) S species and for S atoms bound to multiple O atoms. Therefore, we reported the electronic oxidation states rather than formal oxidation states as they reflect the actual electron density in the valence shell of S. Integer values were used to report the electronic oxidation states of the high-valence S species ($\geq 4^+$), while non-integer values were used for the low-valence ($\leq 4^+$) S compounds.

RESULTS AND DISCUSSION

Total soil S contents in undisturbed temperate, subtropical, and tropical ecosystems

The concentration of total S in the surface soils of undisturbed temperate prairie grassland ecosystems of North America varied from 246 mg S/kg soil (Pendleton, USA) to 399 mg S/kg soil (Lethbridge, Canada), while the concentration of total soil S in the native subtropical Highveld grassland ecosystems of South Africa was 241 mg S/kg soil. These values fall within the range reported for a variety of soils from native temperate (Tabatabai and Bremner 1972, Neptune et al. 1975, Wang et al. 2006) and tropical (Acquaye and Kang 1987) grassland ecosystems. Total soil S in the surface layers of the native subhumid tropical forest ecosystems of Kenya ranged from 2916 mg S/kg soil (Kakamega) to 3706 mg S/kg soil (Nandi) and was considerably higher than the values from grassland-derived soils of temperate and subtropical ecosystems. However, these results are in line with the values reported for a variety of forest-derived soils from tropical ecosystems (Stanko-Golden and Fitzgerald 1991, Solomon et al. 2001, Möller et al. 2002). The higher concentration of S in the subhumid tropical forest ecosystems of Kenya compared with the native temperate and subtropical grassland ecosystems could be broadly attributed to differences in climate, vegetation, and soil type.

Total soil S was significantly correlated with both total SOC ($r = 0.93$, $P < 0.05$, $n = 5$ samples at Lethbridge; $r = 0.99$, $P < 0.01$, $n = 5$ at Pendleton; $r = 0.98$, $P < 0.001$, $n = 9$ at the South African sites; $r = 0.98$, $P < 0.001$, $n = 9$ at Nandi; and $r = 0.97$, $P < 0.01$, $n = 7$ at Kakamega) and with total N ($r = 0.96$, $P < 0.01$, n
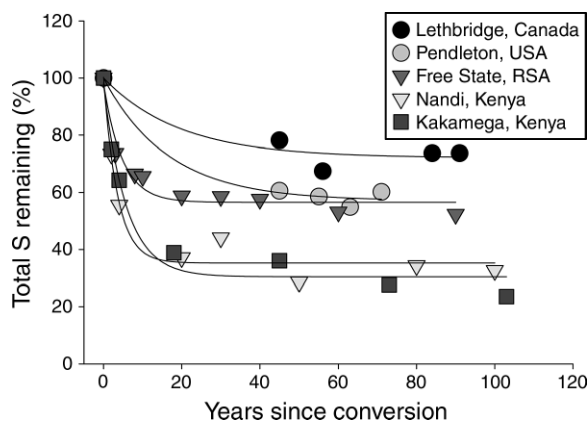

FIG. 1. Long-term impacts of human-induced land-use and land-cover changes on the percentage of total S in the surface layers of soils from temperate (Canada and USA) and subtropical (South Africa [RSA]) grassland and subhumid tropical forest (Nandi and Kakamega, Kenya) ecosystems.

$= 5$ at Lethbridge; $r = 0.99$, $P < 0.001$, $n = 5$ at Pendleton; $r = 0.97$, $P < 0.001$, $n = 9$ at the South African sites; $r = 0.98$, $P < 0.001$, $n = 9$ at Nandi; and $r = 0.94$, $P < 0.01$, $n = 5$ at Kakamega) concentrations of the soils from the three ecosystems. These results indicate a close association between C, N, and S in the investigated ecosystems and provide a clear indication that for the most part, the total S in the surface layers of the soils under investigation was present in organic forms. Similar observations have been made for a variety of grassland- and forest-derived soils by Tabatabai and Bremner (1972), Neptune et al. (1975), Acquaye and Kang (1987), and Wang et al. (2006).

The soils from the three investigated native ecosystems showed distinct differences in their total SOC to total S (C/S) and total N to total S (N/S) ratios. Generally, the C/S and N/S ratios of soils from temperate (66 and 6.6 at Lethbridge and 86 and 8.6 at Pendleton) and subtropical (68 and 5.7 at the South African sites) grassland ecosystems were much higher than the values from the native tropical forest (26 and 2.6 at Nandi and 41 and 3.7 at Kakamega) ecosystems.

Anthropogenic and temperature impacts on biogeochemical dynamics of total soil S

The concentration of total S decreased exponentially to 74% (Lethbridge), 60% (Pendleton), 52% (South African sites), 33% (Kakamega), and 24% (Nandi) of the original amount following clearing of the natural vegetation and continuous cultivation over a period of up to 103 years (Fig. 1). These results show larger decline in total S concentration following human intervention in soils from subhumid tropical agroecosystem than from cooler subtropical and temperate agroecosystems. This was also confirmed by a positive correlation observed between average total soil S loss and MAT ($r = 0.98$; $P < 0.01$, $n = 5$; Fig. 2). The higher organic S loss from the subhumid tropical forest
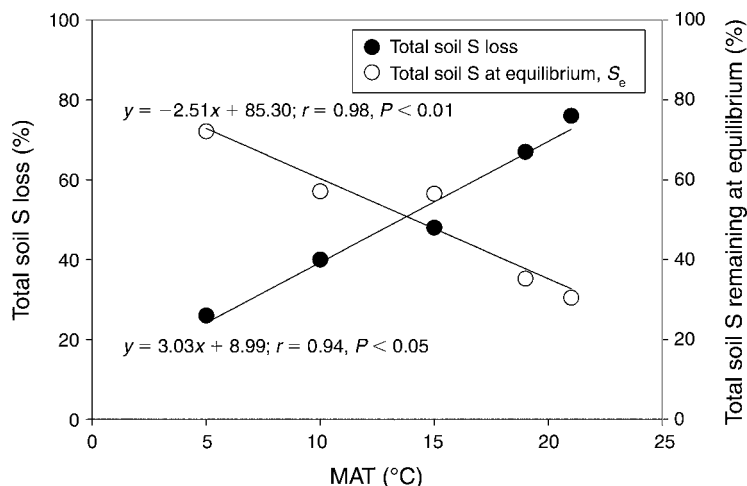
FIG. 2. Relationship between the total soil S loss and percentage of total soil S concentration at equilibrium (S_e) following the conversion of native grassland and forest ecosystems to agricultural land and mean annual temperature (MAT) in the soils collected from temperate, subtropical, and subhumid tropical ecosystems.

agroecosystems might be attributed to their larger initial organic matter content (Solomon et al. 2007) accompanied by the relatively warm temperature, which create more conducive environment for decomposers and may lead to increased susceptibility of organic S to oxidative mineralization and subsequent loss of soil S through various means upon human intervention.

The above results are also supported by an inverse relationship observed between the total soil S concentration at equilibrium (S_e) and MAT of the investigated sites (Fig. 2). The average S concentration at equilibrium was significantly but negatively correlated with MAT ($r = -0.94$, $P < 0.05$, $n = 5$), implying that, compared to warm and moist subhumid tropical ecosystems, new quasi-equilibrium conditions can be achieved at much higher total soil S levels in cooler temperate and subtropical grassland ecosystems. These results corroborate our earlier findings (Wang et al. 2006), where significantly negative correlation between MAT and total organic S concentration was observed for a variety of soils from native grassland and cultivated sites along temperature gradient in the Great Plains of North America. The decrease in total soil organic S with an increase in MAT was attributed to an increase in soil temperature, which may lead to accelerated soil organic S decomposition and may further reflect the enhanced sensitivity of organic S to climatic variables such as temperature (Wang et al. 2006). A linear relationship between cumulative soil S mineralized and temperature has also been reported by Tabatabai and Al-KhafaJi (1980).

Speciation of soil organic S in temperate, subtropical, and tropical ecosystems

Soil organic S is a heterogeneous mixture of complex organic molecules representing substrates released from living plants and animals (e.g., extracellular enzymes, surface-active proteins, chelating compounds, and so on), as well as plant and animal detritus transformed by microbial degradation ranging in size and complexity from simple monomers to mixtures of complex biopolymers (Zhao et al. 1996, Solomon et al. 2003). The chemical complexity and variation along the decomposition and size continuum creates significant analytical problems for routine biochemical characterization techniques; thus very little is known about the precise form and chemical characteristics of soil organic S. The standard analytical techniques largely rely on differential reduction of S compounds to hydrogen sulfide (H_2S) and permits only a broad classification of organic S compounds into two operationally defined principal groups: (1) C-bonded S in which S is directly bonded to C in either C-S or C-S-O linkages as in the case of S-containing amino acids and sulfonates, respectively, and (2) organic sulfates in which S is linked to C mostly through an O atom in the form of C-O-S linkage as in the case of true ester-SO_4-S (Maynard et al. 1984, Kowalenko 1993a, b, Saggar et al. 1998). XANES spectroscopy, however, is a powerful nondestructive solid-state tool that employs synchrotron-radiation and helps to directly determine the various oxidation states of S based on the energy position of the white-line. The intensity and energy dependence of white-line features of the S K-edge spectra also allow probing and determining the various S functionalities in complex matrixes such as soils (Morra et al. 1997, Xia et al. 1998, Solomon et al. 2003). Our baseline-corrected and normalized XANES spectral features recorded from soil humic fractions consistently showed several white-lines in the energy range of 0 to 10 eV above the S K-edge (spectra not shown). We grouped the different oxidation states identified by our XANES spectra and the organic S functionalities associated with them into three major groups: (1) organic S in strongly reduced oxidation (S^0

TABLE 2. Structures of representative organic S compounds, their relative energy positions (peak maxima), and predicted oxidation states of the humic fractions extracted from temperate, subtropical, and tropical ecosystems.

Organic S compounds[†]	Structure	Gaussian curve	Peak maxima (eV)	Electronic oxidation state[‡]
Most reduced S				
Thiols	R-SH			
Organic monosulfides	R-S-R′	G1	0.43–0.63	0.14–0.30
Organic disulfides	R-S-S-R′			
Organic polysulfides	R-S-S-S-R′			
Thiophenes	(structure)	G2	1.5–1.8	0.80–0.96
Intermediate S				
Sulfoxides	R-SO-R′	G3	2.3–3.2	1.3–1.8
Sulfonates	$R-S(O)_3-H$	G4	7.7–8.4	5
Highly oxidized S				
Ester-SO_4-S	$R-O-SO_3-H$	G5	9.5–10.2	6

† Representative organic S compounds were compiled from literature data collected from Vairavamurthy et al. (1993), Morra et al. (1997), Xia et al. (1998), Prietzel et al. (2003), and Solomon et al. (2003).

‡ Integer values were used to report the electronic oxidation states of the high-valence S species ($\geq 4^+$), while non-integer values were used for the low-valence ($\leq 4^+$) S compounds.

to S^{+1}) states, which include polysulfides, disulfides, thiols, monosulfides (G1) and thiophenes (G2); (2) organic S in intermediate oxidation (S^{+2} to S^{+5}) states, which include sulphoxides (G3) and sulfonates (G4); and (3) organic S in strongly oxidized (S^{+6}) state, which represents ester-SO_4-S (G5). The first two groups of organic S compounds (organic S in strongly reduced and intermediate oxidation states [G1, G2, G3, and G4]) represent the organic S directly linked to C, commonly referred to as C-bonded S in the conventional classification systems (Table 2).

Previous studies on S speciation using differential reduction techniques indicate that ester-SO_4-S is the most prevalent organic S form, accounting for 33 to 93% of the total organic S in mineral soils and humic acid from temperate and tropical ecosystems (Fitzgerald 1976, Biederbeck 1978). The remaining organic S is attributed to C-bonded S, consisting mainly of sulfolipids and S-containing amino acids (Harwood and Nicholls 1979). Contrary to these results, the relative proportions of organic S functional groups resolved by XANES spectroscopy (Fig. 3) indicate that S directly linked to C is the predominant form of organic S in the studied humic fractions from surface soils of undisturbed temperate prairie grassland ecosystems of North America (77%), subtropical Highveld grassland ecosystems of South Africa (60%) and subhumid tropical forest ecosystems of Kenya (70%). Organic S in highly oxidized state, where S is directly bonded to O in the form of R-OSO_3–H linkage, constituted only for smaller fraction of the total soil organic S identified by XANES spectroscopy (23% in temperate, 40% in subtropical and 30% in tropical ecosystems). These results concur positively with the XANES analysis of organic S in humic fractions extracted from peat (Morra et al. 1997) and forest-derived soils (Xia et al. 1998, Solomon et al. 2003), as well as with XANES spectra taken directly from peat (Martínez et al. 2002) and organic layers of forest soils (Prietzel et al. 2003). Our results agree also with those of Bettany et al. (1980) and Möller et al. (2002), who reported higher proportions of C-bonded S (70–84% of the total organic S) in the humic fractions of variety of temperate and tropical soils using conventional wet-chemical techniques. The dominance of organic S directly bonded to C in the surface layers of grassland-derived temperate and subtropical soils and forest-derived tropical soils could be attributed to the fact that this organic S fraction originates directly from plant exudates, root and leaf litterfall, animal residues, as well as microbial metabolites; which make up the bulk of soil organic matter input to the surface layers of these undisturbed ecosystems. This agrees with earlier suggestion by Maynard et al. (1984) and Autry et al. (1990), who stated that a significant fraction of the intrinsic organic S comprising mainly of amino acids and sulfolipids in mineral horizons of native grassland and forest soils may originate from direct accumulation of litter and foliage in the organic horizons and through subsequent translocation of this organic S fraction into the mineral horizons. In contrast, although some amount of ester-SO_4-S is known to occur in plant and animal residues in the form of aryl, alkyl, phenol, and polysaccharide sulfates and may be deposited in soils to a smaller extent along with detritus input (Maynard et al. 1984, Houle and Carignan 1992); for the most part this organic S fraction is believed to be a transitory product synthesized in situ predominantly through biochemical processes by microflora in the presence of adequate inorganic SO_4^{-2} and usually its contribution to the total soil organic S pool in undisturbed ecosystems is

Temperate grassland   Subtropical grassland   Tropical forest
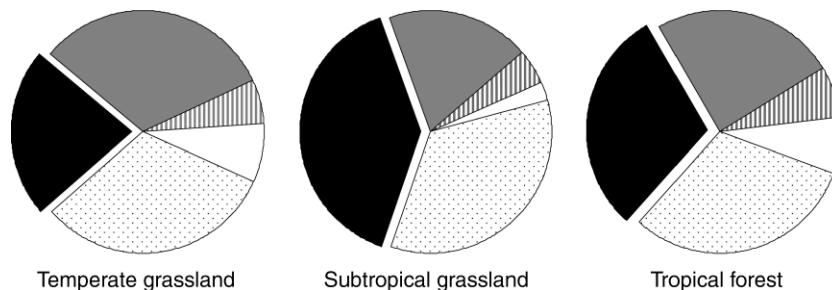
FIG. 3. Speciation of soil organic S in temperate and subtropical grassland and subhumid tropical forest ecosystems. The organic S composition is shown as sulfides and thiols (gray), thiophenes (hatched), sulfoxides (open), sulfonates (stippled), and ester sulfates (black). The relative proportions of the various organic S functional groups from the Lethbridge, Canada, and Pendleton, USA, sites were averaged to represent temperate grassland ecosystems; values from South Africa represent subtropical grassland, and values from the Nandi and Kakamega sites in Kenya were averaged to represent the values for the tropical forest ecosystems.

minimal (McGill and Cole 1981, Houle and Carignan 1992, Saggar et al. 1998, Solomon et al. 2003). Our investigation also provides evidence that the majority of C-bonded S in the undisturbed soils originated from soil organic S in intermediate oxidation states (51% in temperate grassland, 60% in subtropical grasslands, 55% in subhumid tropical forest). Albeit small variability, sulfonates (R-SO_3–H) were the major forms of soil organic S, constituting 80%, 93%, and 81% of the S in the intermediate oxidation states in the three ecosystems, respectively (Fig. 3). These results are consistent with XANES analysis of the high-valence S species in organic soils (Martínez et al. 2002), in humic fractions extracted from soil, peat, and sediments (Morra et al. 1997), organic horizon (Xia et al. 1998), and clay (Solomon et al. 2003). These authors showed that spectra of humic fractions produce white-lines indicative of high-valence organic S predominantly in S^{+5} oxidation state, indicating the prevalence of sulfonate S in the surface layers of undisturbed ecosystems. Our results are also in line with the results of wet-chemical analysis, which shows sulfonates to be the major component of soil organic S in undisturbed ecosystems (Harwood and Nicholls 1979, Autry and Fitzgerald 1990, Stanko-Golden and Fitzgerald 1991). The sulfonate S linkage is found in the sulfoquinovose component of the plant sulfolipids, which is a primary constituent of leaves and photosynthetic tissues and, to a smaller extent, of other tissues (Harwood and Nicholls 1979). Additionally, sulfocarbohydrates possessing the sulfonate linkage are also widely distributed in green plants and to a lesser extent in bacterial membranes and spores in soils (Fitzgerald 1976). During leaf fall, substantial amount of these organic S compounds enter the soil system and could lead to accumulation of sulfonate S in undisturbed grassland and forest soils. Biogenic sulfonates might also be derived from oxidation products of cysteine (Kertesz 1999), a major S-containing amino acid, which might explains why higher sulfonate levels were found in the surface horizons of these undisturbed ecosystems. Stanko-Golden et al. (1994) stated that the dominance of sulfonates in the surface layers of undisturbed soils is

more evident in soils derived from grassland ecosystems than the ones from forest ecosystem; since grassland vegetation typically has shallower root systems than forest vegetation and tend to concentrate plant material above ground. However, such trends were not apparent in the investigated ecosystems as we recovered almost similar proportions of sulfonate S (32% from temperate grassland, 34% from subtropical grassland and 31% from tropical forest ecosystems) as percentage of the total organic S.

Organic S in the most reduced oxidation states represented 49%, 40%, and 45% of the total C-bonded S in surface soils of the undisturbed ecosystems, respectively, and was almost entirely (78–85%) due to contributions from polysulfide, disulfide, monosulfide, and thiol (R-S) containing S moieties (Fig. 3). This is not surprising because both plants and microorganisms are capable of taking SO_4^{-2} as a primary source of S and reducing it to sulfides, its lowest oxidation state through a reductive assimilation pathway (Leustek 2002). The process is assimilative because sulfides are exclusively used for the synthesis of highly reduced organic S compounds such as cysteine, cystine, methionine, and other metabolites. In higher plants, this process takes place mostly in the chloroplasts of green leaves, where the enzymes for assimilatory SO_4^{-2} reduction are mainly localized, resulting in localization of S-containing amino acids in the leaf protein, perhaps explaining the higher concentration of these organic S moieties in the upper horizons of undisturbed soils (Autry and Fitzgerald 1990).

Anthropogenic and temperature impacts on molecular-level dynamics of organic S

Land-use and land-cover changes.—Clearing of natural vegetation and subsequent cultivation induce drastic change in the equilibrium status attained under undisturbed conditions and affect the amounts of organic S in soils (Solomon et al. 2001). Considerable efforts have been made in the past to characterize the sources of mineralized organic S following anthropogenic disturbances in temperate and tropical soils. These studies
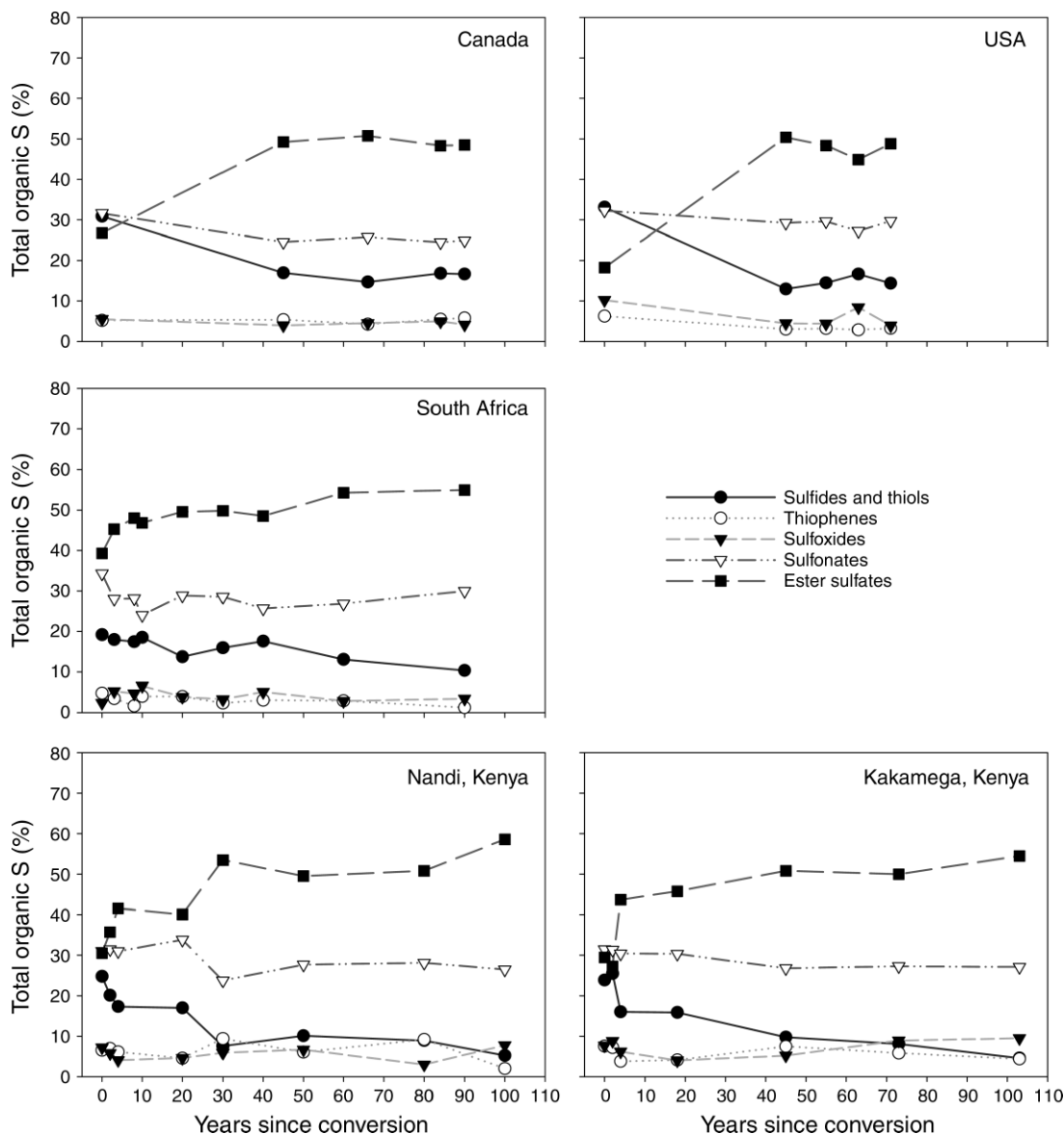
FIG. 4. Long-term impacts of human-induced land-use and land-cover changes on the relative proportions of organic S functional groups resolved by S K-edge XANES spectroscopy of humic fractions extracted from soils of temperate (Canada and USA), subtropical (South Africa), and tropical (Nandi and Kakamega, Kenya) ecosystems.

have observed both qualitative and quantitative changes in soil organic S fractions due to land-use and land-cover changes (McLaren and Swift 1977, Ghani et al. 1991, Solomon et al. 2001). Despite intensive study, however, no consistent trend in molecular-level reactivity, dynamics, as well as the interchange between the different organic S functionalities in soils is yet apparent (Wang et al. 2006). Thus, there is still conflicting evidence about the globally dominant labile form of organic S fraction, which can be taken as a major source of mineralizable S in various agroecosystems.

Examination of the molecular-level dynamics of the various organic S moieties suggested that the largest loss of organic S as a result of land-use and land-cover

changes in all the three agroecosystems occurred from S directly bonded to C in the form of thiols and sulfides (Fig. 4). The relative proportions of these organic S moieties decreased by 46% (Lethbridge) and 57% (Pendleton) in the temperate grassland agroecosystems of North America, by 46% in the subtropical grassland agroecosystems of South Africa and by 79% (Nandi) and 81% (Kakamega) in the subhumid tropical forest agroecosystems of Kenya over a period of up to 103 years. These results suggest that S directly linked to C in the form of thiols and sulfides may represent the most labile components of soil organic S pool and might be the major source of mineralizable S in all three agroecosystems. We attribute the rapid decline of thiols

and sulfides to (1) direct biological oxidation of the C-S linkage and/or (2) the conversion of the C-S linkage in thiols and sulfides to ester-SO_4-S linkage (McGill and Cole 1981, Edwards 1998, Schroth et al. 2007). According to McGill and Cole (1981), the release of S from organic S moieties directly linked to C is a biological process, occurring when the C to which they are attached to is oxidized to CO_2 by soil microorganisms. This process occurs internally and is strictly catabolic controlled primarily by the requirement for energy and C skeletons than the need for S. Several studies have demonstrated that various soil fungi and bacteria can convert cysteine ($HS-CH_2-CH(NH_2)-COOH$) and cystine ($(S-CH_2-CH(NH_2)-COOH)_2$) to inorganic SO_4^{-2} aerobically using oxidative enzymatic degradation mechanisms (Fitzgerald 1976). Sulfur present in methionine ($CH_3-S-(CH_2)_2-CH(NH_2)-COOH$) has been also shown to be converted aerobically to this anion by a mixed population of soil microorganisms (Hesse 1957). In fact, biological oxidation is thought to be the principal pathway for mineralization of organic S, whereby SO_4^{-2} is co-mineralized or released as a byproduct of the oxidation process (McGill and Cole 1981, Zhao et al. 1996). On the other hand, improved soil aeration and exposure of physically protected organic materials due to physical disruption of aggregates could lead to an increased microbial activity and thereby accelerated transformation of C-bonded S functionalities to ester-SO_4-S as an intermediate product, prior to being released as inorganic SO_4-S (McGill and Cole 1981, Saggar et al. 1998, Solomon et al. 2001). This mechanism will tend to increase or maintain the level of ester-SO_4-S (Fig. 5), while continually diminishing the level of thiols and sulfides, a finding in line with the results of the study by McLaren and Swift (1977).

Since its discovery nearly half a century ago, the plant sulfolipid (sulfoquinovosyl diacylglycerol) is increasingly recognized as a major component of the biological S cycle in terrestrial ecosystems (Harwood and Nicholls 1979). However, the pathways for the catabolism of this major form of sulfonates are poorly delineated (Roy et al. 2000). Our results show that long-term anthropogenic interventions led to small but consistent decreases in the relative proportion of these organic S functionalities (22% at Lethbridge, 8% at Pendleton, 13% at the South African sites, 15% at Nandi, and 14% at Kakamega). These results are somewhat surprising because sulfonates are thought to be biologically very labile (Autry and Fitzgerald 1990). For example, Strickland and Fitzgerald (1983) found that 6-sulfoquinovose, was subject to rapid biological mineralization when incubated with forest soil and litter indicating the dynamic nature of these organic S moieties. Focht and Williams (1970) showed that arylsulfonates, including ρ-toluene sulfonate and benzene sulfonate, are rapidly degraded by bacteria in pure cultures. In a study involving microbial degradation of the plant sulpholipids, Roy et al. (2000) isolated five bacterial strains (four from forest leaves and one from activated sewage sludge) that grew on sulfoquinovose as a sole source of C. Two of these strains achieved complete mineralization of sulfoquinovose to inorganic SO_4-S. The results of investigations conducted on the mobilization of sulfonate S from the outset seem to indicate that the liberation of SO_4^{-2} ion from sulfonates is primarily due to biological processes and not due to chemical catalysis (Strickland and Fitzgerald 1983, Autray and Fitzgerald 1990, Roy et al. 2000).

In contrast to S directly bonded to C, the relative proportion of organic S linked to O as a fraction of the total organic S increased considerably upon land-use changes by 81% (Lethbridge) and 168% (Pendleton) in the temperate grassland agroecosystems of North America, by 40% in the subtropical grassland agroecosystems of South Africa and by 85% (Kakamega) and 92% (Nandi) in the subhumid tropical forest agroecosystems of Kenya. These results show a shift in oxidation states from organic S moieties in highly reduced and intermediate states toward organic S functionalities in strongly oxidized states. This was further illustrated by the ratios of organic S in strongly reduced states (thiols, monosulfides, disulfides, polysulfides and thiophenes) to organic S in strongly oxidized state (ester-SO_4-S) (R-S/O-S) and organic S in intermediate states (sulfoxides and sulfonates) to strongly oxidized S (I-S/O-S) (Fig. 5). The ratio of R-S/O-S decreased from 1.35 to 0.46 at Lethbridge, from 2.16 to 0.36 at Pendleton, from 0.61 to 0.21 at the South African sites and from 1.03 to 0.12 at Nandi and 1.07 to 0.16 at Kakamega sites. Similarly, the ratio of I-S/O-S declined from 1.39 to 0.60 (Lethbridge) and from 2.33 to 0.69 (Pendleton) in the temperate grassland agroecosystems, from 0.93 to 0.61 in the subtropical grassland agroecosystems, and from 1.25 to 0.58 (Nandi) and 1.33 to 0.67 (Kakamega) in the subhumid tropical forest agroecosystems. The relative shift in oxidation state toward high-valence (S^{+6}) state and the accompanying apparent change in the functional group chemistry of S toward organic S compounds directly linked to O following land-use changes could be explained by several processes occurring simultaneously within the soils system. The first process could be through direct biological oxidation of organic S linked to C and subsequent removal of S as inorganic SO_4-S from the soil system or due to the formation of a more transient but strongly oxidized form of soil organic S. The second reason stems from the distinct mobilization mechanism of ester-SO_4-S. These organic S forms are mineralized in soils through a biochemical process involving extracellular hydrolysis of ester sulfates by sulfohydrolases. This catalytic process occurs independently from the biological need for energy and C. However, laboratory investigations indicated that the formation of sulfohydrolases such as sulfatase in soils could be repressed by the presence of sulfites, cysteine, cystine and methionine (Dodgson and
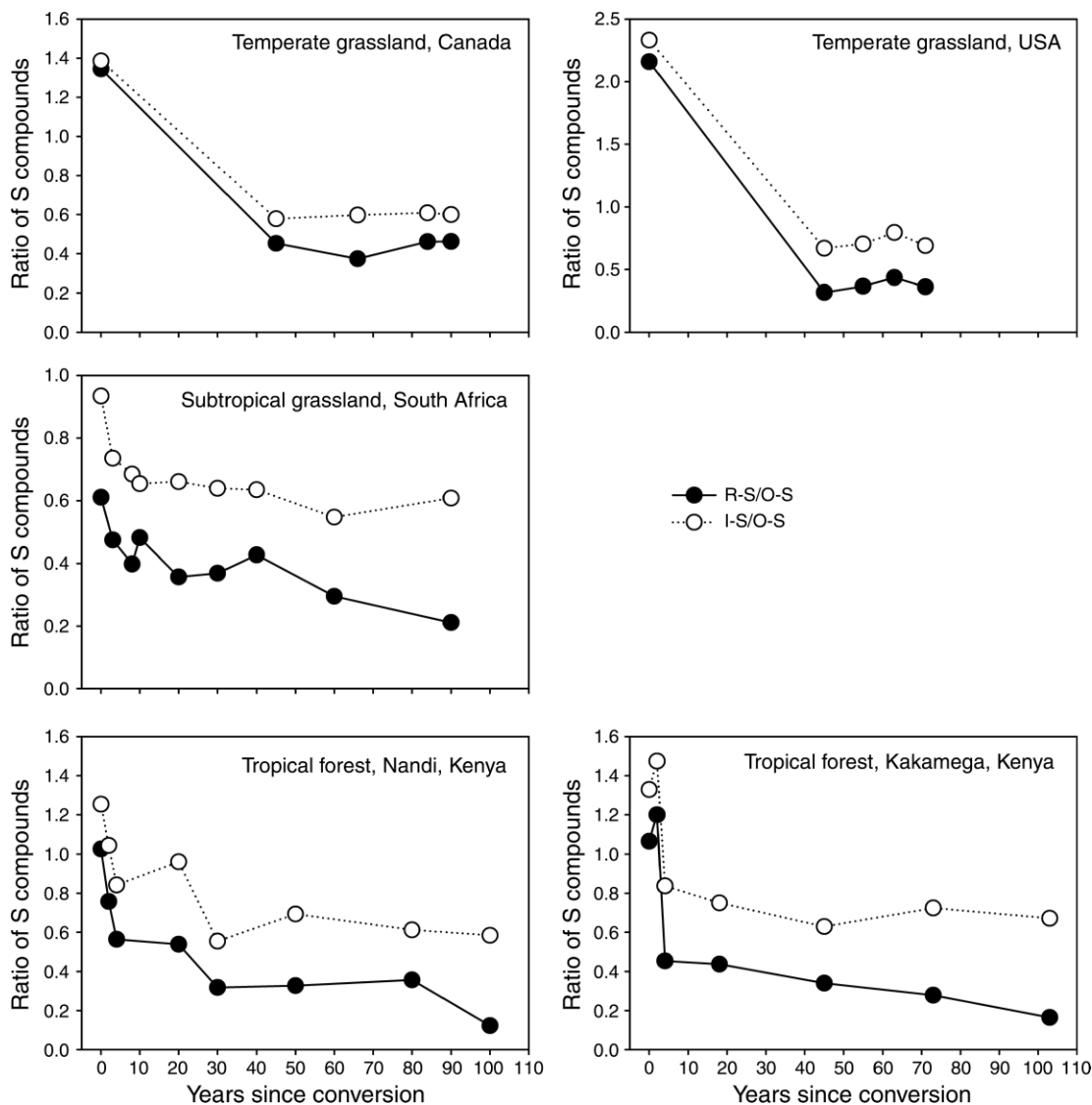
FIG. 5. Ratios of highly reduced S (thiols, monosulfides, disulfides, and polysulfides) to highly oxidized S (ester sulfates) (R-S/O-S) and organic S in the intermediate oxidation state (sulfoxides and sulfonates) to highly oxidized S (I-S/O-S) measured using S K-edge XANES spectroscopy of humic fractions extracted from temperate, subtropical, and tropical soils.

Rose 1975). Hence, the supply of substrates containing large amounts of C-bonded S could suppress the formation of these enzymes and may inhibit the biochemical mineralization of organic S directly linked to O leading to accumulation of ester-SO_4-S in the studied soils (McGill and Cole 1981). These enzymes are also subject to end product inhibition by SO_4^{-2} ion, which may further control their formation and activity in soils (Cooper 1972, Edwards 1998). Cooper (1972) reported that addition of inorganic $SO4^{-2}$ could lead to inhibition of sulfatase activity and overall reduction of S mineralization from ester-SO_4-S, resulting in the accumulation of these organic S moieties in soils. The third possible explanation comes from the fact that sulfate ester production may also be a safe mechanism used by

soil microbes to store S without altering the pH of their surroundings (Fitzgerald 1976). Ghani et al. (1991) suggested that in some cases, the occurrence of any short-term biochemical mineralization of ester-SO_4-S could be obscured by the much larger biological mineralization of C-bonded S to inorganic SO_4^{-2} and with subsequent transformation of this anion to ester-SO_4-S by soil microorganisms. The fourth mechanism arises from the stabilization pattern of elements existing in ester forms. In general, those elements existing in ester forms may be stabilized independent of the main organic matter moiety through reactions of esters with soil components such as clays, sesquioxides or even free cations present in soil solution, reducing their mobilization by extracellular enzymes (Lou and Warman 1992).
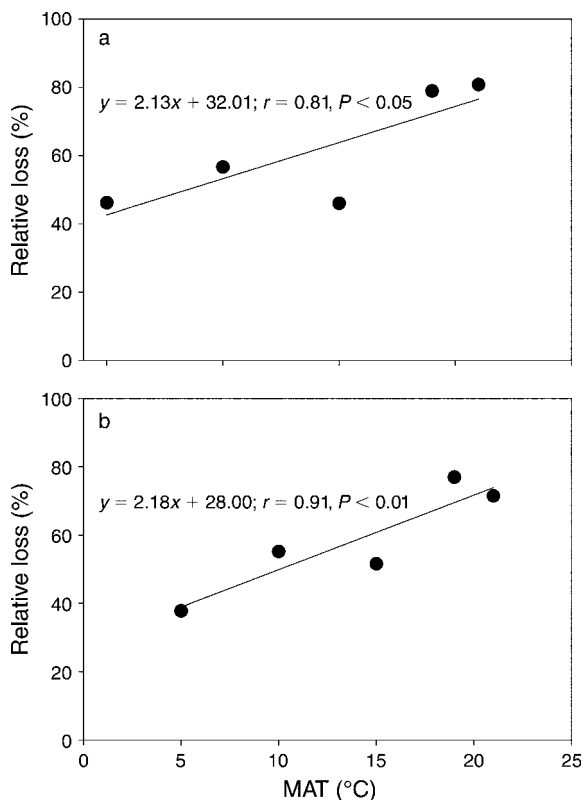
FIG. 6. Relationship between the relative losses of (a) organic S moieties directly bonded to C in C-S linkage (thiols and sulfides) as well as (b) the total organic S in highly reduced oxidation states (S^0 to S^{+1}) following land-use and land-cover changes with mean annual temperature (MAT).

Temperature.—Temperature is considered as a primary rate determinant of mineralization processes and more often than not, the impacts of management are imparted through changes in this parameter (Dalias et al. 2001, Wang et al. 2006). Temperature responses of organic S mineralization rates have been extensively investigated in soils (Tabatabai and Al-Khafaji 1980, Ellert and Bettany 1992, Jaggi et al. 1999). For example, MacDonald et al. (1995) and Jaggi et al. (1999) showed that organic S mineralization markedly increased with increasing temperature. Similarly, Strickland et al. (1984) found mobilization of organic S to be strongly affected by this parameter. These authors indicated that the mineralization rate of organic S at 5°C is only one-fifth of its level at 20°C or 30°C and they attributed this response to different enzymes achieving optimal activity levels at different temperatures. Despite the progress, however, relatively little information is available about the impact of temperature on the molecular-level dynamics of the various soil organic S. Hence, we compared the relative loss (gain in the case of S in highly oxidized state) of the various S moieties associated with the different oxidation states following land-use changes with MAT of the three ecoregions (Fig. 6). The relative loss of thiols and sulfides ($r = 0.81$, $P < 0.05$) and

organic S in highly reduced oxidation states ($r = 0.91$, $P < 0.01$) correlated positively ($P < 0.05$) with the MAT. These results indicate that the largest loss of organic S directly linked to C in a C-S linkage occurred upon human intervention in soils from agroecosystems with the higher MAT, possibly due to enhanced metabolism of these organic moieties through enzymatic oxidative processes by microorganisms. Our results concur positively with the results of Fitzgerald and Andrew (1984) who reported temperature dependent rapid conversion of methionine S to inorganic SO_4-S. In contrast, the relative loss of organic S in sulfonate S linkage ($r = 0.31$), as well as the increase in the proportion of organic S moieties directly bonded to O in the form of ester-SO_4-S linkage ($r = 0.25$), poorly correlated with MAT ($P < 0.05$, $n = 5$) and did not show any consistent trend with MAT. Although our results might provide an early indication about lower apparent temperature sensitivity for organic S with a C-S-O linkage, since the inherent kinetic properties of decomposition of these organic substrates can be suppressed by various environmental constraints within the soil system, they do not necessarily imply that the intrinsic temperature sensitivity of sulfonates is in any way different from organic S forms directly linked to C in a C-S linkage. Overall, the results of our investigation, however, seem to suggest that among the various organic S functionalities the turnover dynamics of organic S moieties directly linked to C in a C-S linkage appears to have higher apparent temperature sensitivity or they seem to be more responsive to this climatic variable.

CONCLUSIONS

Soils from undisturbed temperate grassland ecosystems of North America, subtropical grassland ecosystems of South Africa and subhumid tropical forest ecosystems of Kenya have different total soil S concentrations, the contents of the tropical forest soils being higher almost by an order of magnitude. However, the molecular-level information generated by XANES spectroscopy revealed that structural composition of soil organic S in all the three undisturbed ecosystems was remarkably similar. Organic S in highly reduced and intermediate oxidation states, where S is directly bonded to C in C-S and C-S-O linkages, respectively, was the predominant form of organic S in all the three ecoregions. Organic S in a highly oxidized state, where S is directly bonded to O in C-O-S linkage represents a smaller fraction of the total soil organic S pool, suggesting that C-bonded S may be the globally dominant organic S fraction. The majority of the C-bonded S in all the three ecoregions was present in C-S-O linkage as sulfonates, followed by organic S in a C-S linkage, as in thiols and sulfides. Thiophenes and sulfoxides accounted for only a small fraction of the total C-bonded S in all the three ecosystems.

Human-induced land-use and land-cover changes have persistent and multi-decadal effects on the amount

of total soil S in all three agroecosystems and could invariably lead to depletion of this organically bound element in soils. Anthropogenic disturbances also markedly altered the molecular-level composition and led to a shift in the apparent oxidation state of organic S with time from native ecosystems primarily composed of S moieties in intermediate and highly reduced oxidation states toward managed agroecosystems dominated by organic S rich in strongly oxidized or high-valence S. Sulfur directly bonded to C in the form of thiols and sulfides seems to be the most biologically dynamic or reactive organic S pool to anthropogenic perturbations and may represent the major source of biologically mineralizable S. Temperature was linearly related to total soil S loss following ecosystem disturbances and our results from the outset seem to suggest that an increase in this climatic variable could intensify the influence of human interventions on soil S loss from undisturbed ecosystems. Among the various organic S functionalities, thiols and sulfides seem to have higher apparent temperature sensitivity and may become more prone to losses due to human–induced land-use and land-cover changes even from the cooler regions of the world, if MAT of these regions rises. Since, the sensitivity of organic S dynamics to land-use changes under various temperature regimes is critical to the understanding of global S cycling; such detailed structural information can be used to further our understanding of factors regulating the biogeochemistry of S in terrestrial ecosystems and provide process-oriented data for ecosystem models of organic S transformations across the globe.

LITERATURE CITED

Acquaye, D. F., and B. T. Kang. 1987. Sulfur status and forms in some surface soils of Ghana. Soil Science 144:43–52.

Autry, A. R., and J. W. Fitzgerald. 1990. Sulfonate S: a major form of forest soil organic sulfur. Biology and Fertility of Soils 10:50–56.

Autry, A. R., J. W. Fitzgerald, and P. R. Caldwell. 1990. Sulfur fractions and retention mechanisms in forest soils. Canadian Journal of Forest Research 20:337–342.

Bettany, J. R., S. Saggar, and J. W. R. Stewart. 1980. Comparison of the amounts and forms of sulfur in soil organic matter fractions after 65 years of cultivation. Soil Science Society of America Journal 44:70–75.

Biederbeck, V. O. 1978. Soil organic sulfur and fertility. Pages 273–310 in M. Schnitzer and S. M. Khan, editors. Soil organic matter. Elsevier, Amsterdam, The Netherlands.

Cooper, P. J. M. 1972. Arylsulphatase activity in northern Nigeria soils. Soil Biology Biochemistry 4:333–337.

Dalias, P., J. M. Anderson, P. Bottner, and M. M. Couteaux. 2001. Temperature responses of carbon mineralization in conifer forest soils from different regional climates incubated under standard laboratory conditions. Global Change Biology 7:181–192.

Davidson, E. A., and I. A. Janssens. 2006. Temperature sensitivity of soil carbon decomposition and feedbacks to climate change. Nature 440:165–173.

Dodgson, K. S., and F. A. Rose. 1975. Sulfohydrolases. Pages 359–431 in D. M. Greenberg, editor. Metabolic pathways. Third edition, Volume VII. Metabolism of sulfur compounds. Academic Press, New York, New York, USA.

Edwards, P. J. 1998. Sulfur cycling, retention, and mobility in soils: a review. General Technical Report NE-250. United States Department of Agriculture Forest Service, Northeastern Research Station, Newtown Square, Pennsylvania, USA.

Ellert, B. H., and J. R. Bettany. 1992. Temperature dependence of net nitrogen and sulfur mineralization. Soil Science Society of America Journal 56:1133–1141.

Einsiedl, F., T. Schäfer, and P. Northrup. 2007. Combined sulfur K-edge XANES spectroscopy and stable isotope analyses of fulvic acids and groundwater sulfate identify sulfur cycling in a karstic catchment area. Chemical Geology 238:268–276.

FAO-UNESCO. 1997. Soil map of the world, revised legend. International Soil Reference and Information Centre, Wageningen, The Netherlands.

Fitzgerald, J. W. 1976. Sulfate ester formation and hydrolysis: a potentially important yet often ignored aspect of the sulfur cycle of aerobic soils. Bacteriological Reviews 40:698–721.

Fitzgerald, J. W., and T. L. Andrew. 1984. Mineralization of methionine sulfur in soils and forest floor layers. Soil Biology and Biochemistry 16:565–570.

Fleet, M. E. 2005. XANES spectroscopy of sulfur in earth materials. Canadian Mineralogist 43:1811–1838.

Focht, D. D., and F. D. Williams. 1970. The degradation of ρ-toluenesulfonate by a *Pseudomonas*. Canadian Journal of Microbiology 16:309–316.

Ghani, A., R. G. Mclaren, and R. S. Swift. 1991. Sulfur mineralization in some New Zealand soils. Biology and Fertility of Soils 11:68–74.

Harwood, J. L., and R. G. Nicholls. 1979. The plant sulfolipid: a major component of the sulfur cycle. Biochemical Society Transactions 7:440–447.

Hesse, P. R. 1957. Sulfur and nitrogen changes in forest soils of East Africa. Plant and Soil 9:86–96.

Houghton, R. A. 1999. The annual net flux of carbon to the atmosphere from changes in land use 1850–1990. Tellus 51B: 298–313.

Houghton, R. A. 2003. Why are estimates of the terrestrial carbon balance so different? Global Change Biology 9:500–509.

Houle, D., and R. Carignan. 1992. Sulfur speciation and distribution in soils and aboveground biomass of a boreal coniferous forest. Biogeochemistry 16:63–82.

Hutchison, K. J., D. Hesterberg, and J. W. Chou. 2002. Stability of reduced organic sulfur in humic acid as affected by aeration and pH. Soil Science Society of America Journal 65:704–709.

Jaggi, A. C., M. S. Aulakh, and R. Sharma. 1999. Temperature effects on soil organic sulfur mineralization and elemental sulfur oxidation in subtropical soils of varying pH. Nutrient Cycling in Agroecosystems 54:175–182.

Janzen, H. H., and B. H. Ellert. 1998. Sulfur dynamics in cultivated temperate agroecosystems. Pages 11–43 in D. G. Maynard, editor. Sulfur in the environment. Marcel Dekker, New York, New York, USA.

Kertesz, M. A. 1999. Riding the sulfur cycle: metabolism of sulfonates and sulfate esters in Gram-negative bacteria. FEMS Microbiology Reviews 24:135–175.

Kowalenko, C. G. 1993a. Extraction of available sulfur. Pages 65–74 in M. R. Carter, editor. Soil sampling and methods of analysis. Lewis Publishers, Boca Raton, Florida, USA.

Kowalenko, C. G. 1993b. Total and fractions of sulfur. Pages 231–246 in M. R. Carter, editor. Soil sampling and methods of analysis. Lewis Publishers, Boca Raton, Florida, USA.

Leustek, T. 2002. Sulfate metabolism. Pages 1–16 in C. R. Somerville and E. M. Meyerowitz, editors. The Arabidopsis book. American Society of Plant Biologists, Rockville, Maryland, USA.

Likens, G. E., C. T. Driscoll, D. C. Buso, M. J. Mitchell, G. M. Lovett, S. W. Bailey, T. G. Siccama, W. A. Reiners, and C. Alewell. 2002. The biogeochemistry of sulfur at Hubbard Brook. Biogeochemistry 60:235–316.

Lou, G., and P. R. Warman. 1992. Enzymatic hydrolysis of ester sulfate in soil organic matter extracts. Biology and Fertility of Soils 14:112–115.

MacDonald, N. W., D. R. Zak, and K. S. Pregitzer. 1995. Temperature effects on kinetics of microbial respiration and net nitrogen and sulfur mineralization. Soil Science Society of America Journal 59:233–240.

Martínez, C. E., M. B. McBride, M. T. Kandianis, J. M. Duxbury, S. Yoon, and W. F. Bleam. 2002. Zinc–sulfur and cadmium–sulfur association in metalliferous peats: evidence from spectroscopy, distribution coefficients, and phytoavailability. Environmental Science and Technology 36:3683–3689.

Maynard, D. G., W. B. Stewart, and J. R. Bettany. 1984. Sulfur cycling in grassland and parkland soils. Biogeochemistry 1: 97–111.

McGill, W. B., and C. V. Cole. 1981. Comparative aspects of cycling of organic C, N, S and P through soil organic matter. Geoderma 26:267–286.

McLaren, R. G., and R. S. Swift. 1977. Changes in soil organic sulfur fractions due to the long term cultivation of soils. Journal of Soil Science 28:445–453.

Möller, A., K. Kaiser, N. Kanchanakool, C. Anecksamphant, W. Jirasuktaveekul, A. Maglinao, C. Niamskul, and W. Zech. 2002. Sulfur forms in bulk soils and alkaline soil extracts of tropical mountain ecosystems in northern Thailand. Australian Journal of Soil Research 40:161–175.

Morra, M. J., S. E. Fendorf, and P. D. Brown. 1997. Speciation of S in humic and fulvic acids using X-ray absorption near-edge structure (XANES) spectroscopy. Geochimica et Cosmochimica Acta 61:683–688.

Neptune, A. M. L., M. A. Tabatabai, and J. J. Hanway. 1975. Sulfur fractions and carbon–nitrogen–phosphorus–sulfur relationship in some Brazilian and Iowa soils. Soil Science Society of America Proceedings 39:51–55.

Prietzel, J., J. Thieme, U. Neuhäusler, J. Susini, and I. Kögel-Knabner. 2003. Speciation of sulfur in soils and soil particles by x-ray spectroscopy. European Journal of Soil Sciences 54: 423–433.

Roy, A. B., A. J. Ellis, G. F. White, and J. L. Harwood. 2000. Microbial degradation of the plant sulpholipid. Biochemical Society Transactions 28:781–783.

Saggar, S., M. J. Hedley, and S. Phimsarn. 1998. Dynamics of sulfur transformations in grazed pastures. Pages 45–94 in D. G. Maynard, editor. Sulfur in the environment. Marcel Dekker, New York, New York, USA.

Scherer, H. W. 2001. Sulfur in crop production. European Journal of Agronomy 14:81–111.

Schlesinger, W. H. 1997. Biogeochemistry. Academic Press, San Diego, California, USA.

Schnitzer, M. 1982. Organic matter characterization. Pages 581–594 in A. L. Page, B. L. Miller, and R. H. Keeney, editors. Methods of soil analysis. Part 2. American Society of Agronomy, Soil Science Society of America, Madison, Wisconsin, USA.

Schoenau, J. J., and J. R. Bettany. 1987. Organic matter leaching as a component of carbon, nitrogen, phosphorus, and sulfur cycles in a forest, grassland, and gleyed soil. Soil Science Society of America Journal 51:646–651.

Schroth, W., B. C. Bostick, M. Graham, J. M. Kaste, M. J. Mitchell, and A. J. Friedland. 2007. Sulfur species behavior in soil organic matter during decomposition. Journal of Geophysical Research 112:G04011.

Solomon, D., J. Lehmann, J. Kinyangi, W. Amelung, I. Lobe, A. Pell, S. Riha, S. Ngoze, L. Verchot, D. Mbugua, J. Skjemstad, and T. Schäfer. 2007. Long-term impacts of anthropogenic perturbations on dynamics and speciation of organic carbon in tropical forest and subtropical grassland ecosystems. Global Change Biology 13:511–530.

Solomon, D., J. Lehmann, and C. E. Martínez. 2003. Sulfur K-edge x-ray absorption near-edge structure (XANES) spectroscopy as a tool for understanding S dynamics. Soil Science Society of America 67:1721–1731.

Solomon, D., J. Lehmann, M. Tekalign, F. Fritzsche, and W. Zech. 2001. Sulfur fractions in particle-size separates of the subhumid Ethiopian highlands as influenced by land use changes. Geoderma 102:42–59.

Stanko-Golden, K. M., and J. W. Fitzgerald. 1991. Sulfur transformation and pool size in tropical forest soils. Soil Biology and Biochemistry 23:1053–1058.

Stanko-Golden, K. M., W. T. Swank, and J. W. Fitzgerald. 1994. Factors affecting sulfate adsorption, organic sulfur formation, and mobilization in forest and grassland Spodosols. Biology and Fertility of Soils 17:289–296.

Stevenson, F. J., and M. A. Cole. 1999. Cycles of the soil: carbon, nitrogen, phosphorus, sulfur, micronutrients. John Wiley and Sons, New York, New York, USA.

Strickland, T. C., and J. W. Fitzgerald. 1983. Mineralization of sulfur in sulphoquinovose by forest soils. Soil Biology and Biochemistry 15:347–349.

Strickland, T. C., J. W. Fitzgerald, and W. T. Swank. 1984. Mobilization of recently formed forest soil organic sulfur. Canadian Journal of Forest Research 14:63–67.

Sumann, M., W. Amelung, L. Haumaier, and W. Zech. 1998. Climatic effects on soil organic phosphorus in the North American Great Plains identified by phosphorus-31 nuclear magnetic resonance. Soil Science Society of America Journal 62:1580–1586.

Tabatabai, M. A., and A. A. Al-Khafaji. 1980. Comparison of nitrogen and sulfur mineralization in soils. Soil Science Society of America Journal 44:1000–1006.

Tabatabai, M. A., and J. M. Bremner. 1972. Forms of sulfur and carbon, nitrogen and sulfur relationships in Iowa soils. Soil Science 114:380–386.

Vairavamurthy, A., B. Manowitz, G. W. Luther III, and Y. Jeon. 1993. Oxidation state of sulfur in thiosulfate and implications for anaerobic energy metabolism. Geochimica Cosmochimica Acta 57:1619–1623.

Vitousek, P. M., J. D. Aber, R. W. Howarth, G. E. Likens, P. A. Matson, D. W. Schindler, W. H. Schlesinger, and D. G. Tilman. 1997. Human alteration of the global nitrogen cycle: sources and consequences. Ecological Applications 7:737–750.

Wang, J., D. Solomon, X. Zhang, J. Lehmann, and W. Amelung. 2006. Organic sulfur forms in soils of the Great Plains of North America. Geoderma 133:160–172.

Xia, K., F. Weesner, W. F. Bleam, P. R. Bloom, U. L. Skyllberg, and P. A. Helmke. 1998. XANES studies of oxidation states in aquatic and soil humic substances. Soil Science Society of America Journal 62:1240–1246.

Zhao, F. J., J. Wu, and S. P. McGrath. 1996. Soil organic sulfur and its turnover. Pages 467–506 in A. Piccolo, editor. Humic substances in terrestrial ecosystems. Elsevier, Amsterdam, The Netherlands.