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Sulfur species behavior in soil organic matter during decomposition

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[1] Soil organic matter (SOM) is a primary reservoir of terrestrial sulfur (S), but its role in the global S cycle remains poorly understood. We examine S speciation by X-ray absorption near-edge structure (XANES) spectroscopy to describe S species behavior during SOM decomposition. Sulfur species in SOM were best represented by organic sulfide, sulfoxide, sulfonate, and sulfate. The highest fraction of S in litter was organic sulfide, but as decomposition progressed, relative fractions of sulfonate and sulfate generally increased. Over 6-month laboratory incubations, organic sulfide was most reactive, suggesting that a fraction of this species was associated with a highly labile pool of SOM. During humification, relative concentrations of sulfoxide consistently decreased, demonstrating the importance of sulfoxide as a reactive S phase in soil. Sulfonate fractional abundance increased during humification irrespective of litter type, illustrating its relative stability in soils. The proportion of S species did not differ systematically by litter type, but organic sulfide became less abundant in conifer SOM during decomposition, while sulfate fractional abundance increased. Conversely, deciduous SOM exhibited lesser or nonexistent shifts in organic sulfide and sulfate fractions during decomposition, possibly suggesting that S reactivity in deciduous litter is coupled to rapid C mineralization and independent of S speciation. All trends were consistent in soils across study sites. We conclude that S reactivity is related to speciation in SOM, particularly in conifer forests, and S species fractions in SOM change during decomposition. Our data highlight the importance of intermediate valence species (sulfoxide and sulfonate) in the pedochemical cycling of organic bound S.

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1. Introduction

[2] The soil environment, particularly organic-rich surface soil horizons, is a critical component of the global S cycle [*Schlesinger*, 1997]. Soil organic matter represents both a major source and sink of S, and its composition and geochemical environment often influence S speciation, which in turn could influence its mobility in soil systems [*Dhamala and Mitchell*, 1995; *Solomon et al.*, 2003]. In addition, S, depending on its chemical form, can be a highly reactive element that has been suggested to influence metal pollutant mobility and nutrient cation availability in soils [*Hamburg et al.*, 2003; *Martinez et al.*, 2002]. Since many toxic metals bind strongly to certain species of S (i.e., Pb, Hg), a mechanistic understanding of S speciation dynamics in soils is needed [*Martinez et al.*, 2002]. Furthermore, an understanding of the factors controlling S reactivity in soil organic matter (SOM) is vital to describe the S flux from soil and as such the transfer of S between soil and other reservoirs in the global S cycle.

[3] Organic S accounts for greater than 90% of total soil S in temperate forest soils of the northeast [*Likens et al.*, 2002]. Sulfur in these and other soils is primarily associated with SOM as ester and carbon-bonded organic S species [*McBride*, 1994; *McGill and Cole*, 1981]. Until recently, advances in our understanding of S speciation in organic matter were associated with destructive methods of extracting organic S compounds through preferential reduction of S phases, which are indirect in their characterization and thus limited in accuracy and detail of S species measurements [*Fitzgerald et al.*, 1985; *Morra et al.*, 1997; *Solomon et al.*, 2003, 2001]. Sulfur K-edge X-ray absorption near edge structure (XANES) spectroscopy has been used more recently to measure speciation of organic S based on characteristic spectral properties when samples are exposed to synchrotron-sourced radiation [*Morra et al.*, 1997; *Waldo et al.*, 1991]. Sulfur XANES spectroscopy describes S

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species present in a sample based on their ls binding energy and s → p electron transitions, properties unique to individual S species. Results gleaned from spectral data are advantageous given that they are obtained in situ without chemical alteration/destruction of the sample and that a far greater level of detail of compound/valence-specific identification is possible than operationally defined S fractions identified from selective extraction-based data. *Solomon et al.* [2003] found that the S speciation results obtained directly by XANES often do not compare well with indirect extraction-based speciation data obtained from the same soil samples (ester sulfate by XANES vs. HI fractionation R^2 = 0.23). Because of the evident limitations of operationally defined S speciation in soil samples, direct measures of S speciation by XANES analyses have considerable potential to enhance our understanding of the role of S species in S cycling/reactivity in surface soils.

[4] The utility of K-edge XANES spectroscopy for S species identification in SOM was first demonstrated by *Morra et al.* [1997]. Subsequent work using this technique has sought to further examine the nature of S speciation in SOM, with the goal of understanding how organic matter properties and pedochemical/physical conditions influence S speciation and mineralization [*Hutchison et al.*, 2001; *Solomon et al.*, 2003; *Xia et al.*, 1998]. *Hutchison et al.* [2001] found that pH and redox conditions can influence the stability of carbon-bonded S compounds, but only at relatively extreme conditions not often encountered in temperate forest soil environments. Land-use history impacts S speciation and dynamics in soil systems, with natural forest soils containing more reduced S phases relative to plantation style forests, both of which contain more carbon-bonded S than cultivated soil environments [*Solomon et al.*, 2003]. It has therefore been proposed that these carbon-bonded phases could be the most labile fraction of organic bound S in tropical soils [*Solomon et al.*, 2003]. If so, the mineralization of carbon-bonded S species in soil could control S export from surface soils and exert a strong influence on the global S budget. Extraction-based studies have also found that S speciation changes with depth in the soil profile, with decreasing relative abundance of carbon-bonded S with depth, which also suggests an influence of S speciation in SOM on S mobility in soil, but is also associated with the precipitation of ester-bonded sulfate at depth [*Dhamala and Mitchell*, 1995; *Homann and Cole*, 1990]. Sulfur speciation is also impacted by the organic matter source; aquatic dissolved organic C (DOC) containing more reduced S than organic soil samples, which contain more reduced S than mineral soil samples, suggesting a connection between S speciation and C pool reactivity and SOM maturity [*Morra et al.*, 1997; *Xia et al.*, 1998]. Although intermediate oxidation state phases of S have been identified in SOM and are known to comprise a significant fraction of SOM associated S [*Xia et al.*, 1998], their behavior during decomposition in the soil profile remains completely unexplored. The XANES technique can identify and differentiate such phases [*Morra et al.*, 1997] and could provide significant insight into the unexplored role of intermediate S phases in S cycling.

[5] Selective extraction-based studies indicate that tree species and their associated communities impact organic S mineralization and associated flux of dissolved S from soil environments [*Homann and Cole*, 1990; *Zhang et al.*, 1999]. Previous work examining the composition of soil solutions draining surface soils indicates that most organic S leaving the forest floor and mineral soil was hydrophilic (ester-bonded) and the fraction of mobile organic S that was ester-bonded was higher under European beech forest floors than Scots pine forest floors [*Kaiser and Guggenberger*, 2005]. The different microbial populations under conifer and deciduous forests may also influence the reactivity of organic S in associated SOM [*Vannier et al.*, 1993].

[6] Although organic S is a critical component to our understanding of S storage and nutrient dynamics in soil systems, a thorough understanding of the influence of SOM decomposition on S cycling and speciation in surface soils remains elusive. Organic S speciation and release during decomposition and humification of leaf litter with unique chemical properties have not been adequately characterized by direct methodologies. This limitation has been exacerbated by the fact that most XANES-based studies of S speciation in soils have been based on fractions of extracted organic matter rather than whole soils. Here we quantify S speciation in SOM of different forest types in northern New England. We use XANES to identify S species and their respective fractional contributions to total S in fresh and decomposed litter and their associated soils to study the influence of S speciation and quality of organic matter on S reactivity. We examine S species in fast and slow pools of S in SOM and compare their relative reactivity during decomposition of different litter types.

2. Methods and Materials

2.1. Site Descriptions

[7] Organic soil horizon samples were collected from three well-characterized northern forests, Marsh-Billings-Rockefeller National Historical Park (MBRNHP) in the piedmont of Vermont, Hubbard Brook Experimental Forest (HBEF) in the White Mountains of New Hampshire, and Whiteface Mountain in the Adirondack Mountains of New York. Located near Woodstock, Vermont, MBRNHP contains plantation-style stands of red pine (*Pinus resinosa*), white pine (*Pinus strobes*), and Norway spruce (*Picea abies*), with adjacent stands of northern hardwood forest (primarily sugar maple (*Acer saccharum*), beech (*Fagus grandifolia*), yellow birch (*Betula alleghaniensis*)) that are 50 to 100 years (a) old where soils are well characterized [*Lautzenheizer*, 2002; *Schroth et al.*, 2007]. The Whiteface Mountain site consists of > 100-a-old forests of balsam fir (*Abies balsamea*) and red spruce (*Picea rubens*) typical of high-elevation forests in the northeastern United States, where extensive monitoring of ecosystem and soil chemistry has been performed [*Miller et al.*, 1993]. Samples from HBEF, an extremely well characterized long-term ecological research site [*Likens et al.*, 2002], were collected from both low-elevation northern hardwood forests (same general composition as those at MBRNHP) and high-elevation red spruce and balsam fir forests that were also at least 100 a old. Samples were collected and archived by researchers at HBEF in watershed 5 in 1983 prior to tree harvesting efforts within this watershed and sampling methods are fully described by *Zhang et al.* [1999].

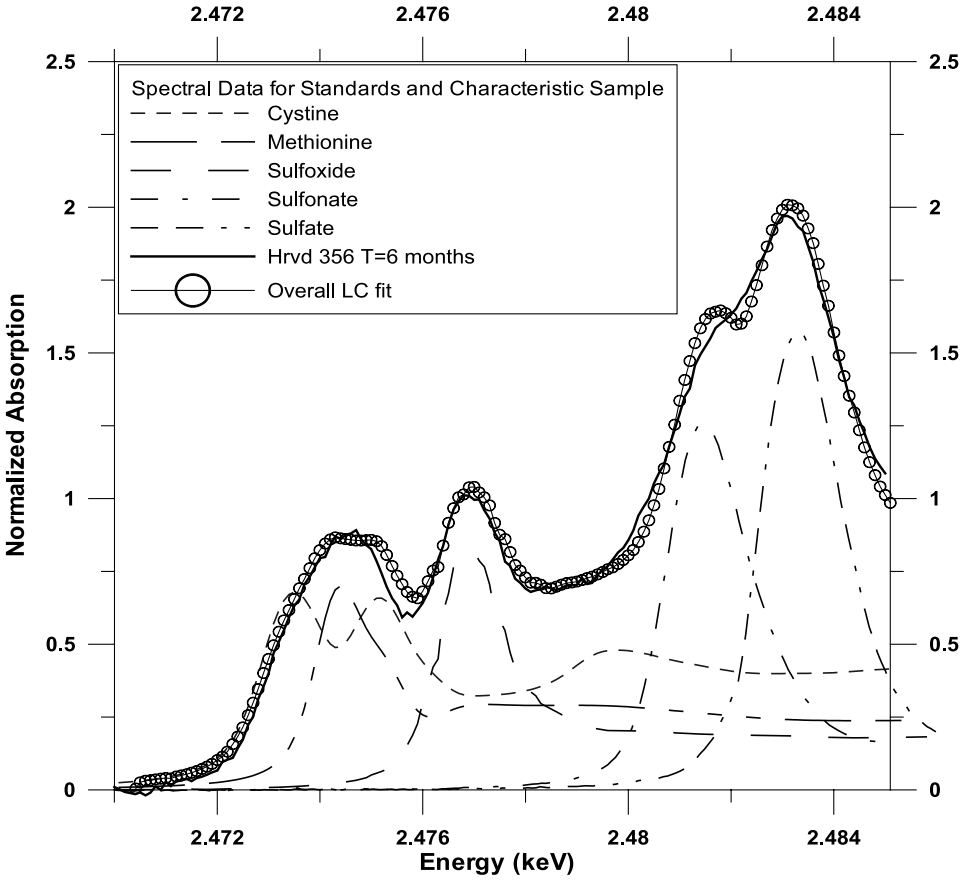

Figure 1. Spectral deconvolution of representative organic matter sample, showing the relative contribution of organic sulfides (cystine and methionine standards), sulfoxides, sulfonates, and ester sulfates (weighted standard spectra are shown in black dashed lines) based on linear combination fitting to observed sample spectra. The best fit (dotted black line) of the data (solid black line) has a residual of 4.9.

2.2. Litter Decomposition Study and Sectioned Organic Soil Horizons

[8] Litter samples were collected from the surface of the forest floor (Oi) from each forest type at MBRNHP. The samples collected from MBRNHP consisted of litter from red pine; white pine, northern hardwood, old Norway spruce (~100 a) and young Norway spruce (~50 a) stands. Litter samples were then allowed to decompose under moist conditions in a closed system that prevented leaching losses of dissolved and colloidal organic matter, with weekly wetting (to the appearance of homogenous ~50% moisture content by mass similar to that observed in O_i horizons after a precipitation event) to enhance decomposition. Immediately upon sampling organic matter from the experiment, samples were refrigerated (~4°C) to limit further decomposition. Two decomposition experiments were conducted at different times for 6 month periods. The first began in winter of 2003 and the second began in summer of 2004. Samples were collected from the same general sites at MBRNHP, but on different sampling trips, so they provide us with some perspective on variability in the system and experimental replication. The only difference in experimental design was that the second experimental litter samples were finely ground. Carbon mineralization was measured by mass loss and changes in C and N concentrations measured with a Carlo Erba C-H-N analyzer. In addition, A horizon soil samples were collected from soil pits within each forest type at MBRNHP based on visual characterization. These latter samples were assumed to represent highly decomposed and hence humified organic matter from the same initial litter source used for decomposition experiments, which allowed us to examine S speciation along a decomposition continuum beyond that available from the laboratory incubations (at least 100 a).

[9] Subhorizons (i.e., O_i, O_e, O_a) from the forest floor were collected at Whiteface Mountain and HBEF in discrete intervals corresponding with their extent of humification by visual characterization. At Whiteface Mountain, ~10 cm sections of the spruce/fir forest floors were sectioned in centimeter-scale resolution and divided into Oi, Oe and Oa subsamples. At HBEF, forest floor samples were collected under high-elevation conifer forests primarily consisting of red spruce and balsam fir and lower elevation northern hardwood forests primarily consisting of sugar maple, American beech, and yellow birch. These forest floors were sectioned into two subsamples ($O_{i/e}$ and O_a), ground and archived in 1983 as part of a previous study (see *Zhang et al.* [1999] for a complete description of sampling protocol). The goal of collecting sectioned forest floor samples was to obtain S species data in soils that would represent a

Table 1. Peak Maximum Energy Positions for Standards Used to Produce Linear Combination Fits

Standard	Peak Position, eV
Cystine	2473.2
Methionine	2473.8
Dimethylsulfoxide	2475.6
Sulfonate	2481.5
Organic Sulfate	2482.5

decomposition continuum under field conditions that allow for leaching of labile S, and bridge some of the time gap between experimental (6 month) and A horizon (>100 a) data from MBRNHP. These samples also provide replication for processes observed in experimental and A horizon data from similar pedochemical systems to MBRNHP, but at different sites with slightly different environmental conditions specific to their site locations.

2.3. Sulfur Speciation

[10] All samples were analyzed by K-edge XANES spectroscopy to determine S speciation by fraction of total S. XANES spectra were collected at beam line X19A at the National Synchrotron Light Source (NSLS), Brookhaven National Laboratory, Brookhaven, New York. Soil samples were ground and homogenized with a mortar and pestle and spread into a thin (~1 mm) layer on 25.4 × 38.1 mm sample holders with Whatman (No. 1) filter paper. On most samples, a thin (3-μm) Mylar film was added to prevent evaporation during analysis and preserve the sample oxidation state. The S analysis on X19A was performed under ambient (moist, He purged) conditions [*Hutchison et al.*, 2001; *Waldo et al.*, 1991; *Xia et al.*, 1998]. Spectra were collected in fluorescence mode using a one-element passive implanted plana silicon (PIPS) detector. Spectra were calibrated using a 28mmol sulfate standard solution (2483 eV). The background was subtracted, and the step-edge height normalized to unity for all samples prior to data processing.

[11] Sulfur speciation was identified and quantified using WinXAS [*Ressler*, 1998] for least squares fitting of spectra to known standards following *Bostick et al.* [2005]. Spectral components of each sample were identified by comparison to those of organic S standards and the fractional abundance of each component was then determined by linear combinations to yield theoretical spectra (Figure 1) [*Bostick et al.*, 2005; *Waldo et al.*, 1991]. The quality of fit can be examined statistically by calculating the residual and χ^2 of each sample fit. Five standards were assumed to best represent organic S species found in these soils: cystine and methionine (representative of carbon-bonded sulfur sulfides), dimethylsulfoxide (model intermediate oxidation state sulfoxide, R-SO-R), cysteic acid (a model sulfonate,

Table 2. Organic Sulfur Speciation in Litter, Decomposed Litter, and Mineral Soils (A Horizons) Under Different Forest Types as Determined by Linear Combination Fitting of XANES Spectra[a]

		Percent Organic Species					
	Sample	Sulfide	Sulfoxide	Sulfonate	Sulfate	Fitting Residual	C:N
			First Decomposition Experiment				
White pine	t = 0	63.5	13.7	9.5	13.2	8.0	85.0
White pine	t = 6 months	40.0	14.5	27.4	18.2	3.7	52.6
White pine	A horizon	43.9	5.3	28.2	22.6	8.2	18.9
Red pine	t = 0	56.3	11.9	21.0	10.8	4.4	71.6
Red pine	t = 6 months	38.2	13.8	20.2	27.7	7.0	55.6
Red pine	A horizon	49.5	8.9	24.2	17.3	3.2	28.1
Young spruce	t = 0	47.2	15.4	22.9	14.5	5.1	37.9
Young spruce	t = 6 months	45.1	15.1	22.1	17.7	6.4	33.7
Young spruce	A horizon	48.8	9.7	26.2	15.3	3.6	18.5
Old spruce	t = 0	57.5	13.0	16.0	13.6	6.6	39.7
Old spruce	t = 6 months	32.3	7.6	25.2	34.9	7.8	39.0
Old spruce	A horizon	40.6	4.1	30.8	24.5	6.1	14.9
Hardwood	t = 0	54.0	13.7	13.5	18.8	9.8	51.7
Hardwood	t = 6 months	42.7	12.5	21.3	23.6	8.5	41.8
Hardwood	A horizon	55.9	9.5	21.9	12.7	5.4	15.8
			Second Decomposition Experiment				
White pine	t = 0	58.0	12.2	20.7	9.2	4.5	NA
White pine	t = 6 months	53.7	11.5	21.0	13.8	4.3	NA
White pine	A horizon	35.9	1.1	34.6	28.4	5.3	NA
Red pine	t = 0	56.8	11.8	21.2	10.2	4.2	38.3
Red pine	t = 6 months	53.8	11.7	23.4	11.1	3.2	31.5
Red pine	A horizon	39.2	3.7	33.1	24.0	10.1	20.2
Young spruce	t = 0	49.2	10.6	27.7	12.6	8.3	NA
Young spruce	t = 6 months	35.8	6.4	35.0	22.8	10.5	18.9
Young spruce	A horizon	52.4	12.0	24.0	11.6	3.2	NA
Old spruce	t = 0	56.3	11.6	16.4	15.7	4.4	32.7
Old spruce	t = 6 months	37.6	11.3	29.9	21.2	6.9	27.5
Hardwood	t = 0	51.2	12.7	23.6	12.5	7.5	29.4
Hardwood	t = 6 months	55.3	11.4	22.6	10.7	2.7	24.9
Hardwood	A horizon	53.1	6.5	26.3	14.1	6.1	14.1

[a]Typical uncertainties are 3%. The model compounds used for each species of organic sulfur are described in the methods. Organic sulfide is fit with contributions from cystine + methionine standards. Differences between t = 0 and t = 6 month samples are indicative of labile SOM decomposition, while differences between t = 0 and A horizon samples refer to decomposition on pedogenic timescales.

R-SO_3-H) and dodecyl sulfate (a model ester sulfate) (Table 1). It should be clearly noted here that the use of these standards does not imply that the entire fraction of S fit to each of the standards must exist as these exact compounds, but that the bonding and valence of S in the identified fraction is similar to the representative standard that was used to fit that portion of the spectra.

[12] Linear combination (LC) fitting was used to determine relative proportions of each S species present in the sample. Linear combinations of reference spectra, each of which is representative of a class of S species were fit to normalized spectra over the range of 2465 to 2488 eV (Figure 1). Fit parameters with reasonable χ^2 values typically ranged from 0.3 to 4.0. Residuals ranged from 2.7 to 10.5. The sum of linear coefficients determined by fitting the data is ideally equal to 1 and is a useful indicator of fit quality. Sums of all linear coefficients were close to 1 with a range of 0.9 to 1.15; however, the reported speciation is normalized to unity. The precision of these analyses was estimated by analyzing known mixtures of S reference materials. Precision is best for ester sulfate because of its intense white line feature—typically a 1–2% change in sulfate fraction was routinely measured. Although XANES is less sensitive to sulfides (which lack a strong white line), the method precision was about 3% for sulfides for normalized spectra. Fitting accuracy is similar, usually within a few percent for a spectrum, and impacted most strongly by background subtraction and normalization. Overall, statistical analysis suggests an error of 2–3% for comparative purposes of speciation data presented here between samples, and an accuracy of 5% of S species composition in the litter.

3. Results

3.1. Degree of Decomposition

[13] Carbon to nitrogen ratios (by weight percent) all decreased for both incubations and all litter types (Table 2). C:N ratios in sectioned forest floor samples also decrease with depth where older and more decomposed SOM was collected (Table 2). Mass losses during the decomposition experiments ranged from 8 to 15% with northern hardwood litters losing more mass than Norway spruce litters, which lost more mass compared to pine samples. Considering that there was low mass loss during the experiment, it is surprising that there were observed decreases in C:N of over 30 in two samples over 6 months (Table 2).

3.2. Sulfur Species Identification

[14] In all litter samples analyzed by XANES, spectra were characteristic of 4 species of organic S (Figure 1). Optimized fits of the spectral data came with contributions from standards of cystine, methionine, sulfoxide, sulfonate, and sulfate with the peak positions shown in Table 1 (Figure 1). Low-energy spectral features of organic S were characteristic of organic sulfides and disulfides and low-valence intermediate organic sulfoxides based on spectral features at 2473–2475 and 2476–2477 eV, respectively (Table 1 and Figure 1). Combined, spectral features fit with organic sulfide and sulfoxide represent the majority of sulfur in these samples (Table 2). Spectral features at higher energies from 2480 to 2483 eV were characteristic of and fit with contributions of sulfonate and sulfate (Figure 1). The intermediate S species sulfonate is identified based on the low-energy shoulder of this peak (Figure 1). Fit residual data indicates that our fits are in good agreement with the normalized spectral data (Table 2).

3.3. Sulfur Speciation Dynamics on 6-month Timescales

[15] During the mineralization of labile OM fractions in the 6-month decomposition experiment, measurable changes in the S speciation of litter samples were observed (Figure 2 and Table 2). Organic sulfides consistently declined after the 6-month incubation (Table 2). Sulfonate and sulfate species increased in fractional abundance over 6 months of decomposition or in a few cases did not significantly change (Table 2). Intermediate sulfoxide fractional abundances generally did not significantly change over 6 months of decomposition in all litters (Table 2).

3.4. Sulfur Speciation Dynamics Over Humification

[16] Fractional abundances of S species in SOM also change on the longer humification timescales associated with sectioned forest floor samples and fresh litter to A horizon transitions (Figures 3, 4, and 5). As observed for the incubation experiments, organic sulfide was a smaller fraction of the total S pool in the more mature O_a/A horizons relative to the S composition in O_i litter from conifer soils, which was not observed in northern hardwood soils (Figures 3 and 4). The pattern of decreases in organic sulfide was generally coupled with increases in the relative abundance of sulfonate and sulfate in these litter types (Figures 3, 4, and 5). Sulfonate always significantly increased in fractional abundance over decomposition irrespective of litter type, but sulfate increases were generally nonexistent or very low in northern hardwood litters (Figures 3, 4, and 5). Although sulfoxide abundance did not change over 6 months of decomposition, in every case independent of site or litter type, substantial decreases in sulfoxide fractional abundance occurred in SOM over humification with often over 50% reduction between Oi and Oa or T = 0 to A horizon transitions (Table 2 and Figures 3–5).

4. Discussion

4.1. Sulfur Speciation

[17] In general, multiple pools of SOM are known to exist in the soil profile, with labile fractions that are thought to turn over on the order of months to years and more recalcitrant, mature phases that are thought to break down on the order of 100–1000 a during humification [*Stevenson*, 1986, 1994]. For this study, changes in S speciation in SOM during the decomposition experiment were associated with mineralization of labile organic matter fractions, while speciation differences between litter decomposition samples (Oi) and their underlying A horizon samples were associated with the mineralization or humification of more recalcitrant SOM. Sectioned forest floor samples to some extent bridge this time gap representing changes on the 1 to 100 a timescale between O_i and O_a horizons and also provide independent replication of our laboratory and field collected samples from MBRNHP [*Kaste et al.*, 2007].

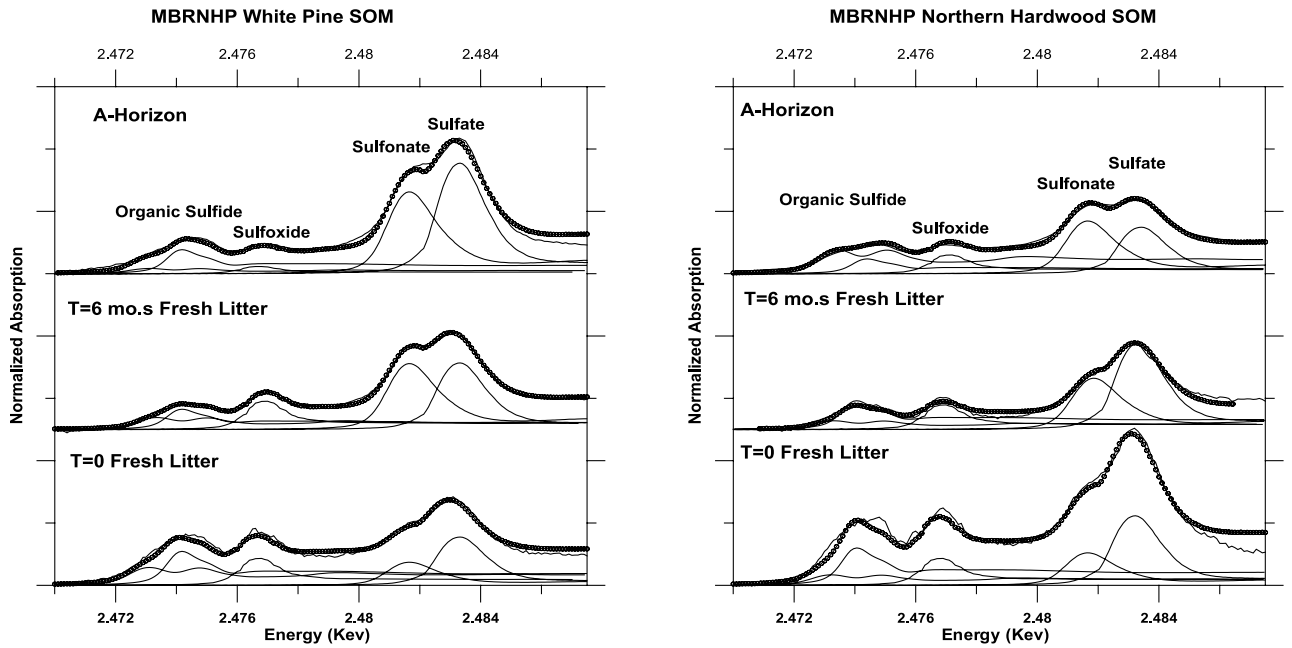

Figure 2. Representative normalized S K-edge XANES spectra of soil organic matter in white pine and northern hardwood forest types over the course of decomposition. LC fits for each sample's spectral data are shown with circles, and the components of each standard are shown as thin black lines below the spectra and its LC fit.

[18] Spectral features and associated S speciation observed in SOM of northern forest soils here were broadly consistent with those found by XANES in isolated fractions of SOM by other researchers, although sulfones have been observed in certain matrices and may represent a minor component here [*Morra et al.*, 1997; *Solomon et al.*, 2003; *Xia et al.*, 1998]. Organic S found in these soil samples contained somewhat higher (~20%) fractions of reduced S than those found by *Solomon et al.* [2003]. Part of the observed difference in S speciation may be attributed to the fact that our analyses are performed on whole soils rather than humic/fulvic acid extracts or size separate fractions. Our data builds upon past works by directly determining S species from bulk soils in situ along a decomposition continuum for these forest types. These analyses also include identification and quantification of multiple intermediate forms of S (sulfoxide and sulfonate), the behavior of which has not been described during decomposition.

4.2. Sulfur Transformations Linked to Labile SOM Mineralization

[19] Carbon to N ratios and sample mass all decreased significantly during our experiment indicating that substantial C mineralization/humification occurred in the ground litter in a N-limited environment over these 6 months (Table 2). The decrease in organic sulfide abundance suggests that a substantial fraction of organic sulfide present in SOM was associated with labile SOM. A similar trend of a decreasing proportion of organic sulfide in SOM with depth/degree of decomposition was observed by *Solomon et al.* [2003] in organic matter derived from semitropical soils of the Ethiopian highlands. The decomposition of labile amino acids that would constitute a portion of this organic sulfide pool may have contributed to the decline of this fraction in the oxidizing experimental environment.

[20] Generally, intermediate oxidation state sulfoxide fractions did not significantly change over the 6-month

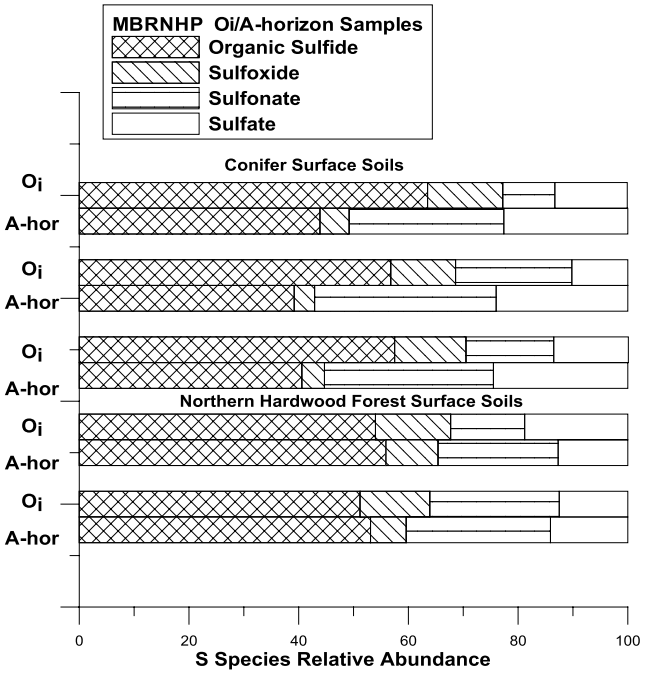

Figure 3. Organic sulfur speciation in sectioned forest floors collected at Whiteface Mountain, New York and HBEF, New Hampshire. Age of organic matter increases from Oi to A horizon samples and represents at least 100 a of decomposition in these soils.

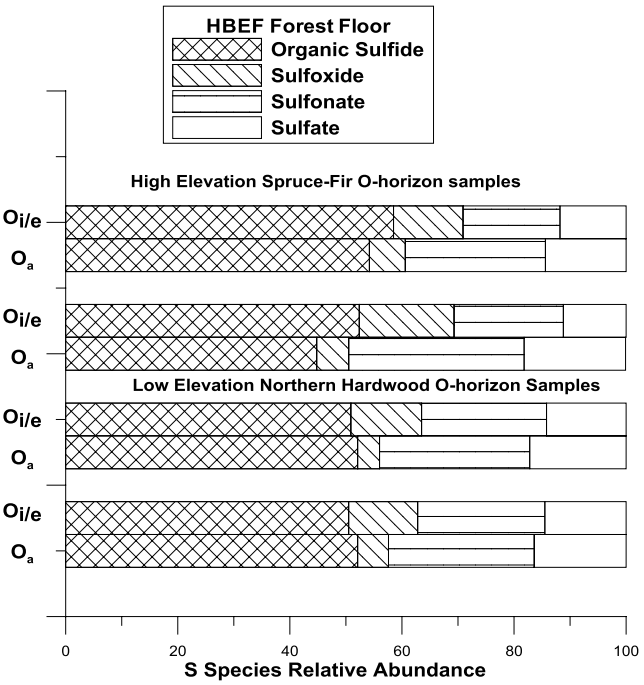

Figure 4. Organic sulfur speciation in sectioned forest floors collected at Hubbard Brook Experimental Forest, New Hampshire in 1983 (fully described by *Zhang et al.* [1999]). Age of organic matter increases from Oi/e to Oa subhorizons representing a decomposition continuum of 50–100 a of pedogenesis in these soils.

decomposition experiment (Figure 2 and Table 2) suggesting that this phase was relatively stable during initial phases or was in steady state during the early periods of decomposition. In the latter case, some of the sulfoxide could have been produced by the oxidation of organic sulfides. Unfortunately, our experimental design does not allow us to distinguish between the two scenarios.

[21] The laboratory incubation experiments do not allow leaching and hence differ from natural soil processes. However, these data from a closed system do indicate that the decreases in abundance of organic sulfide phases were balanced by comparable and concurrent increases in sulfonate, sulfate or both species over the continuum (Table 2). This trend suggests that on very short carbon turnover timescales (6 months), organic sulfide is oxidized within soils. Unfortunately, our experimental design does not allow us to extensively examine the reactivity of oxidized phases in the litter since a leaching component is not incorporated in the experiment. With acknowledgment of experimental limitations, it is interesting to note that sulfonate never decreases in abundance over this timescale, suggesting that this fraction could be most resistant to the short-term oxidation processes (Table 2). More information concerning the reactivity of oxidized sulfur forms in SOM can be gleaned through comparison of fresh litter speciation to that of humified SOM present in associated A horizons and sectioned forest floor samples. Sulfur speciation dynamics in sectioned forest floor and mineral soil samples capture the effects of S mineralization and associated leaching from these soil horizons.

4.3. Sulfur Species Behavior During the Mineralization/Humification of Recalcitrant SOM

[22] Organic matter sampled from soil profiles represents a gradation of young (surficial) organic litter to humified SOM at depth. Substantial C mineralization through the transformation of fresh litter to O_a/A horizon material can be assumed due to large changes in litter C:N (Table 2) and the noticeable change in appearance of the SOM to that characteristic of humified litter in the O_a/A horizon of each forest type. Differences between S speciation in litter from surficial horizons ($O_{i/e}$) and that of SOM in the O_a/A horizon of soils that were sampled below the litter layer of each forest type represent the dynamics of long-term S transformations associated with humification (Figure 2 and Table 2). Sulfur speciation in samples also reflects the loss of mineralized S species and dissolved organic matter because leaching occurred in these samples that underwent decomposition in the solum. Differences in organic S speciation between these samples should incorporate the mineralization of more recalcitrant phases of SOM during pedogenesis. Interestingly, some trends in S species reactivity are different, while others are similar when comparing S species distribution over labile C turnover timescales to those observed over humification timescales. There remained a consistent decrease in the fractional abundance of organic sulfide between fresh (Oi/e) conifer litters and more mature (O_a/A) horizons, suggesting that in these litters organic sulfide remains an important source of reactive S during conifer SOM humification (Figures 3–5). The behavior of sulfoxide on humification timescales is quite

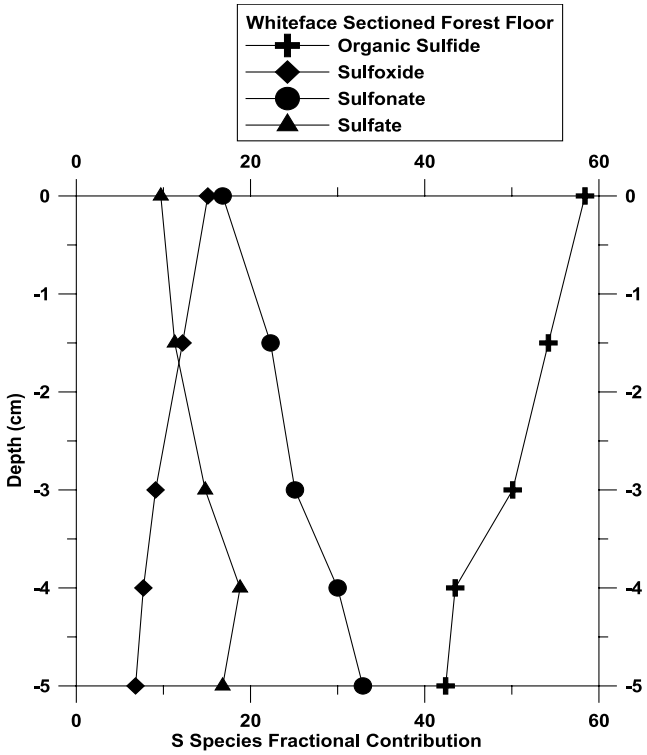

Figure 5. Organic sulfur speciation in sectioned forest floor collected in soil of the spruce/fir forest at Whiteface Mountain, New York. Age of organic matter increases with depth representing roughly 50–100 a of pedogenesis.

different than that observed during labile OM mineralization. The consistent decline in sulfoxide relative abundance in samples of all litter types at all sites during humification of SOM indicates that its role in the S cycle could change with time and depth in the forest floor (Table 2 and Figures 3–5). On labile SOM turnover timescales, sulfoxide appears relatively inert, but on pedogenic timescales, this phase is clearly a significant source of reactive S, which, based on this work, must now be considered as an integral part of the soil S cycle. Our data indicate that during labile organic matter decomposition, organic sulfide oxidation to soluble sulfoxy species was initially the dominant process affecting S speciation in our litter samples, but on humification timescales with leaching processes incorporated, sulfoxide phases were at least comparably reactive. It is likely that there are a range of organic sulfide constituents in these soils with some being highly reactive (e.g., amino acids) but other forms being more recalcitrant to decomposition to varying degrees (e.g., aromatics) [*Likens et al.*, 2002]. Our results suggest that intermediate valence sulfoxide is an important reservoir of relatively reactive S in these soil horizons and must play an important role in the S cycle of soils of the northern forest, particularly as SOM undergoes humification.

[23] The relative abundance of sulfonate in all MBRNHP forests was higher in A horizons than in litter samples, and this species also increased with degree of decomposition in forest floors (Figures 3–5). These data indicate that much of this form of S is associated with stable organic matter (as inferred from short-term experiments), which is resistant to mineralization or transformation, even on humification timescales. This implies that within organic horizons, this fraction of S represents an increasing fraction of the soil solid phase S inventory as SOM matures with depth, and that this more oxidized intermediate phase is a relatively long-term reservoir of solid phase-sequestered S in organic rich surface soils of the northern forest. It is important to mention that S species behavior during humification at MBRNHP was always consistent with the observed trends in sectioned forest floors from Whiteface and HBEF sites (Figures 3–5), suggesting that our results and related conclusions pertaining to S species reactivity during pedogenesis are likely applicable across the large geographic areas that contain similar ecosystems and soils.

4.4. Organic Sulfur Speciation by Forest Type

[24] In addition to significant differences in S speciation in organic matter of differing maturity, forest type may influence the reactivity of S species in SOM. Conifer and deciduous trees each produce litter of differing quality (usually estimated by the C:N and Lignin:N ratios), which are thought to influence SOM's susceptibility to microbial attack and related decomposition [*Finzi et al.*, 1998]. Despite these differences, initial litter proportions of S species did not differ systematically between conifer and deciduous litters, suggesting that there is not a specific forest type effect on the initial S species distribution in litter of these forests prior to decomposition (Table 2 and Figures 3–5). Similarities in organic S species reactivity between forest types were observed during SOM decomposition. Intermediate oxidation state S phases reactivity did not appear to differ by litter source, with a relative decrease in sulfoxide abundance and increases in sulfonate abundance through decomposition across all soils during humification (Figures 3–5). This indicates that the reactivity of intermediate S species is consistent across conifer and hardwood litter types. Important differences in the behavior of S species by forest type through SOM decomposition were also observed. Although relatively reactive throughout decomposition at all temporal and spatial scales in conifer litter, organic sulfide did not appear to be preferentially reactive in northern hardwood field-based decomposition continuums that incorporated a leaching component (Figures 3–5). In addition, conifer litters, with the exception of one of the young Norway spruce experimental samples, consistently increased in the fractional abundance of sulfate over pedogenic timescales (Figures 3–5). In contrast, sulfate maintained a relatively constant fraction over decomposition of northern hardwood litters in field-based samples (Figures 3–5). These differences in S species behavior were consistent by forest type in soils of MBRNHP, Whiteface, and HBEF during humification, thus there appears to be a fundamental difference in these S species reactivity by forest type in soils of the northern forest.

[25] On the basis of these data, we can speculate as to possible causes for different trends between the conifer and northern hardwood in S species reactivity during decomposition SOM. Northern hardwood SOM organic sulfide fractions did not appear to be preferentially reactive over decomposition. This could indicate that decreases in organic sulfide associated with labile SOM decomposition were also associated with mineralization of sulfate that was not redox sensitive in the oxidizing conditions of our experiment and could not leach due to experimental design. Such trends are somewhat counterintuitive, as high-quality deciduous litter is thought to decompose at a greater rate than conifer litter, thus one would anticipate reactive S fractions to decrease more rapidly in high- than low-quality litter. A likely explanation for the relatively stable S speciation in deciduous litter is that both reduced and oxidized S were comparably reactive during decomposition of this litter type, with a higher reactivity of ester-bonded sulfate in deciduous litters relative to conifer litters. The direct coupling of S and C mineralization may be enhanced by the higher litter quality of deciduous species; as deciduous litter would presumably have a larger fraction of reactive SOM, which contains a broad range of S functional groups and would be subject to facile decomposition. This explanation is supported by the surface soil solution data of *Kaiser and Guggenberger* [2005], who found ester-bonded S to be more concentrated in deciduous forest floor solutions relative to conifer forest floor solutions and also observed higher concentrations of DOC and DOS under the deciduous forest floors in association with decomposition, confirming the relationship between C and S reactivity in these forest soils. Alternatively, recent work has challenged the convention of litter quality alone controlling the rate of microbially mediated decomposition of SOM in some soils, and indicates that conifer SOM on the short term can decompose at a higher rate than deciduous litter [*Giardina et al.*, 2001]. If this was the case, rapid decomposition and associated S mineralization of conifer litter relative to deciduous litter is one mechanism by which the observed trends could also be explained. It has been suggested that

ester-bonded sulfate is highly susceptible to microbial attack in northern hardwood SOM [*David et al.*, 1982]. Different reactivity of ester sulfate, possibly related to different microbial populations associated with different forest types could produce the observed differences in S species behavior and would produce trends in soil solution chemistry observed by *Kaiser and Guggenberger* [2005]. Different microbial populations in soils under different tree types could be an important factor influencing S dynamics [*David et al.*, 1982; *Fitzgerald et al.*, 1983], but their role is not examined in this study and should be an active area of future research.

5. Conclusions

[26] Using experimental and natural soil samples from multiple field sites, we conclusively demonstrate that S speciation in SOM is affected by stage of decomposition at greater level of temporal and species specific detail than previously known. We show that S speciation in litter is dynamic, and influenced by decomposition and a variety of SOM properties, but also is consistent in behavior across study sites of similar ecosystems. In temperate forest soils of the northeast studied here, spectral data from SOM indicates that S speciation in SOM is best represented by four species of sulfur; organic sulfides, low-valence sulfoxide, sulfonates and sulfates, each of which has a unique reactivity during decomposition. As SOM decomposition progresses, the relative abundances of each fraction of S species changes, even within a few months of decomposition. Overall, the preferential reactivity of organic sulfide fractions in oxidizing podzolic environments accounts for much of this change in speciation of SOM-associated S during pedogenesis. Furthermore, a significant component of organic sulfides appear to be associated with a very labile fraction of SOM that is mineralized on the order of months during initial litter decay. This indicates that the initial rapid turnover of litter releases sulfide into oxic soil solutions, most likely associated with reactive S-bearing amino acids present in the decaying litter, where it can either oxidize or react with other species. The concentration of these compounds in young SOM must play an important role in forest/soil S cycling and other processes related to S speciation and concentration in soil solution (i.e., metal sequestration, nutrient cation depletion). Intermediate sulfoxides appear to be another labile fraction of S, particularly on longer timescales associated with the humification of SOM and must play an important role in S cycling on this timescale in organic rich soil horizons. The consistent enrichment of sulfonate in SOM during decomposition suggests that this species is relatively stable and immobile during at least 100 a of pedogenesis, and must be an important reservoir of solid phase S in the soil S cycle. The behavior of these intermediate S species during pedogenesis as demonstrated here reveals a component of S cycling in soils that was previously unknown, but now must be considered important forms of labile and solid phase-sequestered S in the soil S cycle over pedogenic time depending on the bonding environment and oxidation state of S.

[27] The S species composition of forest types studied here indicates that there is not a systematic difference in S speciation in litter of the studied forest types. We have discovered similarities in the behavior of intermediate S species during SOM mineralization across litter types and demonstrated that these phases behave similarly within the studied forest types. The behavior of organic sulfide and sulfate in soil samples of conifer and northern hardwood forests indicates that S speciation could play a different role in S cycling/flux in spodic soils dependant on the quality of litter produced and its related susceptibility to microbial attack. At present we do not have a conclusive explanation for the similar behavior of intermediate S species but different behavior of organic sulfide and sulfate in SOM of different forests, and this should be an interesting area for additional research. Our data indicate that shifts in northern forest composition due to management decisions or environmental change would cause a distinct change in the distribution and form of S within organic-rich soil environments.

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