



2 Sulfur species behavior in soil organic matter 3 during decomposition

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7 [1] Soil organic matter (SOM) is a primary reservoir of terrestrial sulfur (S), but its role in
8 the global S cycle remains poorly understood. We examine S speciation by X-ray
9 absorption near-edge structure (XANES) spectroscopy to describe S species behavior
10 during SOM decomposition. Sulfur species in SOM were best represented by organic
11 sulfide, sulfoxide, sulfonate, and sulfate. The highest fraction of S in litter was organic
12 sulfide, but as decomposition progressed, relative fractions of sulfonate and sulfate
13 generally increased. Over 6-month laboratory incubations, organic sulfide was most
14 reactive, suggesting that a fraction of this species was associated with a highly labile pool
15 of SOM. During humification, relative concentrations of sulfoxide consistently decreased,
16 demonstrating the importance of sulfoxide as a reactive S phase in soil. Sulfonate
17 fractional abundance increased during humification irrespective of litter type, illustrating
18 its relative stability in soils. The proportion of S species did not differ systematically by
19 litter type, but organic sulfide became less abundant in conifer SOM during
20 decomposition, while sulfate fractional abundance increased. Conversely, deciduous SOM
21 exhibited lesser or nonexistent shifts in organic sulfide and sulfate fractions during
22 decomposition, possibly suggesting that S reactivity in deciduous litter is coupled to rapid
23 C mineralization and independent of S speciation. All trends were consistent in soils
24 across study sites. We conclude that S reactivity is related to speciation in SOM,
25 particularly in conifer forests, and S species fractions in SOM change during
26 decomposition. Our data highlight the importance of intermediate valence species
27 (sulfoxide and sulfonate) in the pedochemical cycling of organic bound S.

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31 1. Introduction

32 [2] The soil environment, particularly organic-rich sur-
33 face soil horizons, is a critical component of the global S
34 cycle [Schlesinger, 1997]. Soil organic matter represents
35 both a major source and sink of S, and its composition and
36 geochemical environment often influence S speciation,
37 which in turn could influence its mobility in soil systems
38 [Dhamala and Mitchell, 1995; Solomon *et al.*, 2003]. In
39 addition, S, depending on its chemical form, can be a highly
40 reactive element that has been suggested to influence metal
41 pollutant mobility and nutrient cation availability in soils
42 [Hamburg *et al.*, 2003; Martinez *et al.*, 2002]. Since many
43 toxic metals bind strongly to certain species of S (i.e., Pb,
44 Hg), a mechanistic understanding of S speciation dynamics

in soils is needed [Martinez *et al.*, 2002]. Furthermore, an 45
understanding of the factors controlling S reactivity in soil 46
organic matter (SOM) is vital to describe the S flux from 47
soil and as such the transfer of S between soil and other 48
reservoirs in the global S cycle. 49

[3] Organic S accounts for greater than 90% of total soil 50
S in temperate forest soils of the northeast [Likens *et al.*, 51
2002]. Sulfur in these and other soils is primarily associated 52
with SOM as ester and carbon-bonded organic S species 53
[McBride, 1994; McGill and Cole, 1981]. Until recently, 54
advances in our understanding of S speciation in organic 55
matter were associated with destructive methods of extract- 56
ing organic S compounds through preferential reduction of 57
S phases, which are indirect in their characterization and 58
thus limited in accuracy and detail of S species measure- 59
ments [Fitzgerald *et al.*, 1985; Morra *et al.*, 1997; Solomon 60
et al., 2003, 2001]. Sulfur K-edge X-ray absorption near 61
edge structure (XANES) spectroscopy has been used more 62
recently to measure speciation of organic S based on 63
characteristic spectral properties when samples are exposed 64
to synchrotron-sourced radiation [Morra *et al.*, 1997; Waldo 65
et al., 1991]. Sulfur XANES spectroscopy characterizes 66
S species present in a sample based on their 1s binding 67

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68 energy and $s \rightarrow p$ electron transitions, properties unique to
69 individual S species. Results gleaned from spectral data are
70 advantageous given that they are obtained in situ without
71 chemical alteration/destruction of the sample and that a far
72 greater level of detail of compound/valence-specific identi-
73 fication is possible than operationally defined S fractions
74 identified from selective extraction-based data. *Solomon et*
75 *al.* [2003] found that the S speciation results obtained
76 directly by XANES often do not compare well with indirect
77 extraction-based speciation data obtained from the same soil
78 samples (ester sulfate by XANES vs. HI fractionation $R^2 =$
79 0.23). Because of the evident limitations of operationally
80 defined S speciation in soil samples, direct measures of
81 S speciation by XANES analyses have considerable poten-
82 tial to enhance our understanding of the role of S species in
83 S cycling/reactivity in surface soils.

84 [4] The utility of K-edge XANES spectroscopy for
85 S species identification in SOM was first demonstrated by
86 *Morra et al.* [1997]. Subsequent work using this technique
87 has sought to further examine the nature of S speciation in
88 SOM, with the goal of understanding how organic matter
89 properties and pedochemical/physical conditions influence
90 S speciation and mineralization [*Hutchison et al.*, 2001;
91 *Solomon et al.*, 2003; *Xia et al.*, 1998]. *Hutchison et al.*
92 [2001] found that pH and redox conditions can influence the
93 stability of carbon-bonded S compounds, but only at rela-
94 tively extreme conditions not often encountered in temper-
95 ate forest soil environments. Land-use history impacts
96 S speciation and dynamics in soil systems, with natural
97 forest soils containing more reduced S phases relative to
98 plantation style forests, both of which contain more carbon-
99 bonded S than cultivated soil environments [*Solomon et al.*,
100 2003]. It has therefore been proposed that these carbon-
101 bonded phases could be the most labile fraction of organic
102 bound S in tropical soils [*Solomon et al.*, 2003]. If so, the
103 mineralization of carbon-bonded S species in soil could
104 control S export from surface soils and exert a strong
105 influence on the global S budget. Extraction-based studies
106 have also found that S speciation changes with depth in the
107 soil profile, with decreasing relative abundance of carbon-
108 bonded S with depth, which also suggests an influence of
109 S speciation in SOM on S mobility in soil, but is also
110 associated with the precipitation of ester-bonded sulfate at
111 depth [*Dhamala and Mitchell*, 1995; *Homann and Cole*,
112 1990]. Sulfur speciation is also impacted by the organic
113 matter source; aquatic dissolved organic C (DOC) contain-
114 ing more reduced S than organic soil samples, which
115 contain more reduced S than mineral soil samples, suggest-
116 ing a connection between S speciation and C pool reactivity
117 and SOM maturity [*Morra et al.*, 1997; *Xia et al.*, 1998].
118 Although intermediate oxidation state phases of S have been
119 identified in SOM and are known to comprise a significant
120 fraction of SOM associated S [*Xia et al.*, 1998], their
121 behavior during decomposition in the soil profile remains
122 completely unexplored. The XANES technique can identify
123 and differentiate such phases [*Morra et al.*, 1997] and could
124 provide significant insight into the unexplored role of
125 intermediate S phases in S cycling.

126 [5] Selective extraction-based studies indicate that tree
127 species and their associated communities impact organic
128 S mineralization and associated flux of dissolved S from
129 soil environments [*Homann and Cole*, 1990; *Zhang et al.*,

1999]. Previous work examining the composition of soil
130 solutions draining surface soils indicates that most organic
131 S leaving the forest floor and mineral soil was hydrophilic
132 (ester-bonded) and the fraction of mobile organic S that was
133 ester-bonded was higher under European beech forest floors
134 than Scots pine forest floors [*Kaiser and Guggenberger*,
135 2005]. The different microbial populations under conifer
136 and deciduous forests may also influence the reactivity of
137 organic S in associated SOM [*Vannier et al.*, 1993].
138

[6] Although organic S is a critical component to our
139 understanding of S storage and nutrient dynamics in soil
140 systems, a thorough understanding of the influence of SOM
141 decomposition on S cycling and speciation in surface soils
142 remains elusive. Organic S speciation and release during
143 decomposition and humification of leaf litter with unique
144 chemical properties have not been adequately characterized
145 by direct methodologies. This limitation has been exacer-
146 bated by the fact that most XANES-based studies of
147 S speciation in soils have been based on fractions of
148 extracted organic matter rather than whole soils. Here we
149 quantify S speciation in SOM of different forest types in
150 northern New England. We use XANES to identify
151 S species and their respective fractional contributions to
152 total S in bulk fresh and decomposed litter and their
153 associated soils to study the influence of S speciation and
154 quality of organic matter on S reactivity. We examine
155 S species in fast and slow pools of S in SOM and compare
156 their relative reactivity during decomposition of different
157 litter types.
158

2. Methods and Materials 159

2.1. Site Descriptions 160

[7] Organic soil horizon samples were collected from
161 three well-characterized northern forests, Marsh-Billings-
162 Rockefeller National Historical Park (MBRNHP) in the
163 piedmont of Vermont, Hubbard Brook Experimental Forest
164 (HBEF) in the White Mountains of New Hampshire, and
165 Whiteface Mountain in the Adirondack Mountains of New
166 York. Located near Woodstock, Vermont, MBRNHP con-
167 tains plantation-style stands of red pine (*Pinus resinosa*),
168 white pine (*Pinus strobes*), and Norway spruce (*Picea*
169 *abies*), with adjacent stands of northern hardwood forest
170 (primarily sugar maple (*Acer saccharum*), beech (*Fagus*
171 *grandifolia*), yellow birch (*Betula alleghaniensis*)) that are
172 50 to 100 years (a) old where soils are well characterized
173 [*Lautzenheizer*, 2002; *Schroth et al.*, 2007]. The Whiteface
174 Mountain site consists of > 100-a-old forests of balsam fir
175 (*Abies balsamea*) and red spruce (*Picea rubens*) typical of
176 high-elevation forests in the northeastern United States,
177 where extensive monitoring of ecosystem and soil chemis-
178 try has been performed [*Miller et al.*, 1993]. Samples from
179 HBEF, an extremely well characterized long-term ecologi-
180 cal research site [*Likens et al.*, 2002], were collected from
181 both low-elevation northern hardwood forests (same general
182 composition as those at MBRNHP) and high-elevation red
183 spruce and balsam fir forests that were also at least 100 a
184 old. Samples were collected and archived by researchers at
185 HBEF in watershed 5 in 1983 prior to tree harvesting efforts
186 within this watershed and sampling methods are fully
187 described by *Zhang et al.* [1999].
188

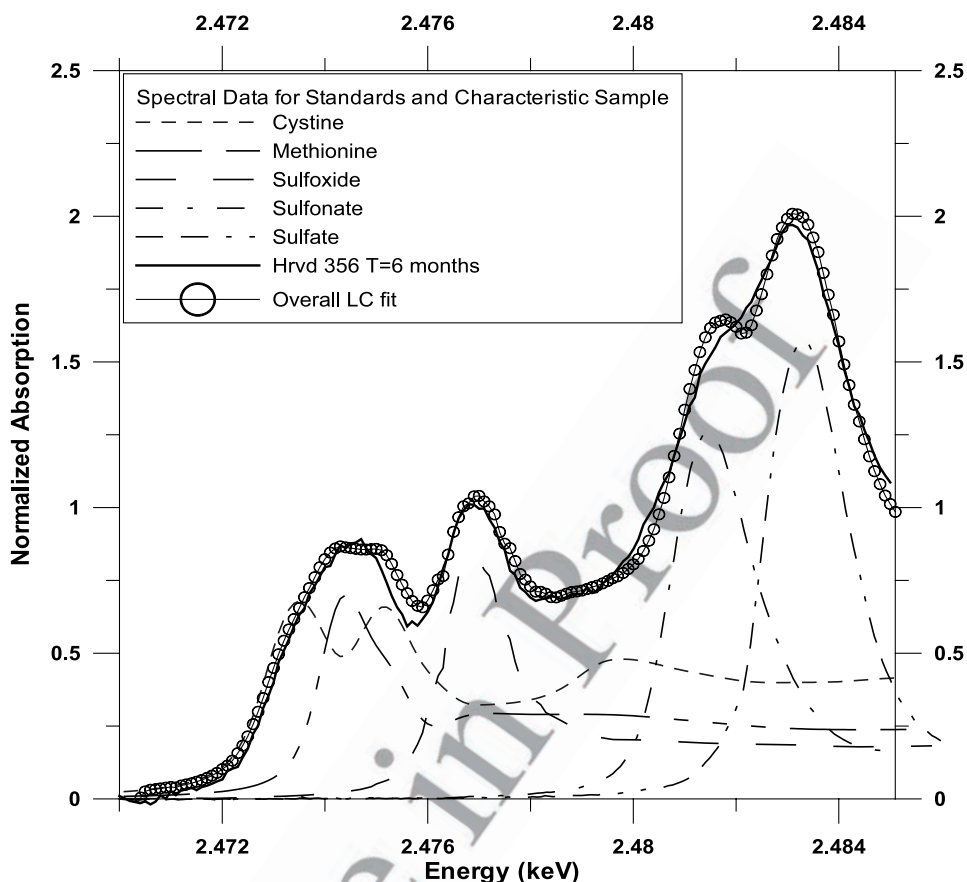


Figure 1. Spectral deconvolution of representative organic matter sample, showing the relative contribution of organic sulfides (cystine and methionine standards), sulfoxides, sulfonates, and ester sulfates (weighted standard spectra are shown in black dashed lines) based on linear combination fitting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

189 2.2. Litter Decomposition Study and Sectioned 190 Organic Soil Horizons

191 [8] Litter samples were collected from the surface of the
192 forest floor (O_i) from each forest type at MBRNHP. The
193 samples collected from MBRNHP consisted of litter from
194 red pine; white pine, northern hardwood, old Norway
195 spruce (~ 100 a) and young Norway spruce (~ 50 a) stands.
196 Litter samples were then allowed to decompose under moist
197 conditions in a closed system that prevented leaching losses
198 of dissolved and colloidal organic matter, with weekly
199 wetting (to the appearance of homogenous $\sim 50\%$ moisture
200 content by mass similar to that observed in O_i horizons after
201 a precipitation event) to enhance decomposition. Immediately
202 upon sampling organic matter from the experiment, samples
203 were refrigerated ($\sim 4^\circ\text{C}$) to limit further decomposition.
204 Two decomposition experiments were conducted at different
205 times for 6 month periods. The first began in winter of 2003
206 and the second began in summer of 2004. Samples were
207 collected from the same general sites at MBRNHP, but on
208 different sampling trips, so they provide us with some
209 perspective on variability in the system and experimental
210 replication. The only difference in experimental design was
211 that the second experimental litter samples were finely ground.
212 Carbon mineralization was measured by mass loss and changes
213 in C and N concentrations measured

with a Carlo Erba C-H-N analyzer. In addition, A horizon 214
soil samples were collected from soil pits within each forest 215
type at MBRNHP based on visual characterization. These 216
latter samples were assumed to represent highly decomposed 217
and hence humified organic matter from the same 218
initial litter source used for decomposition experiments, 219
which allowed us to examine S speciation along a decom- 220
position continuum beyond that available from the labora- 221
tory incubations (at least 100 a). 222

[9] Subhorizons (i.e., O_i , O_e , O_a) from the forest floor 223
were collected at Whiteface Mountain and HBEF in discrete 224
intervals corresponding with their extent of humification by 225
visual characterization. At Whiteface Mountain, ~ 10 cm 226
sections of the spruce/fir forest floors were sectioned in 227
centimeter-scale resolution and divided into O_i , O_e and O_a 228
subsamples. At HBEF, forest floor samples were collected 229
under high-elevation conifer forests primarily consisting of 230
red spruce and balsam fir and lower elevation northern 231
hardwood forests primarily consisting of sugar maple, 232
American beech, and yellow birch. These forest floors were 233
sectioned into two subsamples ($O_{i/e}$ and O_a), ground and 234
archived in 1983 as part of a previous study (see Zhang *et al.* 235
[1999] for a complete description of sampling protocol). 236
The goal of collecting sectioned forest floor samples was to 237
obtain S species data in soils that would represent a 238

t1.1 **Table 1.** Peak Maximum Energy Positions for Standards Used to Produce Linear Combination Fits

t1.2	Standard	Peak Position, eV
t1.3	Cystine	2473.2
t1.4	Methionine	2473.8
t1.5	Dimethylsulfoxide	2475.6
t1.6	Sulfonate	2481.5
t1.7	Organic Sulfate	2482.5

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

247 2.3. Sulfur Speciation

248 [10] All samples were analyzed by K-edge XANES
 249 spectroscopy to determine S speciation by fraction of total
 250 S. XANES spectra were collected at beam line X19A at the
 251 National Synchrotron Light Source (NSLS), Brookhaven
 252 National Laboratory, Brookhaven, New York. Soil samples
 253 were ground and homogenized with a mortar and pestle and

spread into a thin (~1 mm) layer on 25.4 × 38.1 mm 254
 sample holders with Whatman (No. 1) filter paper. On most 255
 samples, a thin (3-μm) Mylar film was added to prevent 256
 evaporation during analysis and preserve the sample oxida- 257
 tion state. The S analysis on X19A was performed under 258
 ambient (moist, He purged) conditions [Hutchison *et al.*, 259
 2001; Waldo *et al.*, 1991; Xia *et al.*, 1998]. Spectra were 260
 collected in fluorescence mode using a one-element passive 261
 implanted plana silicon (PIPS) detector. Spectra were cali- 262
 brated using a 28mmol sulfate standard solution (2483 eV). 263
 The background was subtracted, and the step-edge height 264
 normalized to unity for all samples prior to data processing. 265

[11] Sulfur speciation was identified and quantified using 266
 WinXAS [Ressler, 1998] for least squares fitting of spectra 267
 to known standards following Bostick *et al.* [2005]. Spectral 268
 components of each sample were identified by comparison 269
 to those of organic S standards and the fractional abundance 270
 of each component was then determined by linear combi- 271
 nations to yield theoretical spectra (Figure 1) [Bostick *et al.*, 272
 2005; Waldo *et al.*, 1991]. The quality of fit can be 273
 examined statistically by calculating the residual and 274
 χ^2 of each sample fit. Five standards were assumed to best 275
 represent organic S species found in these soils: cystine and 276
 methionine (representative of carbon-bonded sulfur sul- 277
 fides), dimethylsulfoxide (model intermediate oxidation 278
 state sulfoxide, R-SO-R), cysteic acid (a model sulfonate, 279

t2.1 **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

t2.3	Sample	Percent Organic Species				Fitting Residual	C:N	
		Sulfide	Sulfoxide	Sulfonate	Sulfate			
<i>First Decomposition Experiment</i>								
t2.4								
t2.5	White pine	t = 0	63.5	13.7	9.5	13.2	8.0	85.0
t2.6	White pine	t = 6 months	40.0	14.5	27.4	18.2	3.7	52.6
t2.7	White pine	A horizon	43.9	5.3	28.2	22.6	8.2	18.9
t2.8	Red pine	t = 0	56.3	11.9	21.0	10.8	4.4	71.6
t2.9	Red pine	t = 6 months	38.2	13.8	20.2	27.7	7.0	55.6
t2.10	Red pine	A horizon	49.5	8.9	24.2	17.3	3.2	28.1
t2.11	Young spruce	t = 0	47.2	15.4	22.9	14.5	5.1	37.9
t2.12	Young spruce	t = 6 months	45.1	15.1	22.1	17.7	6.4	33.7
t2.13	Young spruce	A horizon	48.8	9.7	26.2	15.3	3.6	18.5
t2.14	Old spruce	t = 0	57.5	13.0	16.0	13.6	6.6	39.7
t2.15	Old spruce	t = 6 months	32.3	7.6	25.2	34.9	7.8	39.0
t2.16	Old spruce	A horizon	40.6	4.1	30.8	24.5	6.1	14.9
t2.17	Hardwood	t = 0	54.0	13.7	13.5	18.8	9.8	51.7
t2.18	Hardwood	t = 6 months	42.7	12.5	21.3	23.6	8.5	41.8
t2.19	Hardwood	A horizon	55.9	9.5	21.9	12.7	5.4	15.8
<i>Second Decomposition Experiment</i>								
t2.21								
t2.22	White pine	t = 0	58.0	12.2	20.7	9.2	4.5	NA
t2.23	White pine	t = 6 months	53.7	11.5	21.0	13.8	4.3	NA
t2.24	White pine	A horizon	35.9	1.1	34.6	28.4	5.3	NA
t2.25	Red pine	t = 0	56.8	11.8	21.2	10.2	4.2	38.3
t2.26	Red pine	t = 6 months	53.8	11.7	23.4	11.1	3.2	31.5
t2.27	Red pine	A horizon	39.2	3.7	33.1	24.0	10.1	20.2
t2.28	Young spruce	A horizon	52.4	12.0	24.0	11.6	3.2	NA
t2.29	Young spruce	t = 0	49.2	10.6	27.7	12.6	8.3	NA
t2.30	Young spruce	t = 6 months	35.8	6.4	35.0	22.8	10.5	18.9
t2.31	Old spruce	t = 0	56.3	11.6	16.4	15.7	4.4	32.7
t2.32	Old spruce	t = 6 months	37.6	11.3	29.9	21.2	6.9	27.5
t2.33	Hardwood	t = 0	51.2	12.7	23.6	12.5	7.5	29.4
t2.34	Hardwood	t = 6 months	55.3	11.4	22.6	10.7	2.7	24.9
t2.35	Hardwood	A horizon	53.1	6.5	26.3	14.1	6.1	14.1

^aTypical uncertainties are 2%. 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.

280 R-SO₃-H) and dodecyl sulfate (a model ester sulfate)
281 (Table 1). It should be clearly noted here that the use
282 of these standards does not imply that the entire fraction
283 of S fit to each of the standards must exist as these exact
284 compounds, but that the bonding and valence of S in the
285 identified fraction is similar to the representative standard
286 that was used to fit that portion of the spectra.

287 [12] Linear combination (LC) fitting was used to deter-
288 mine relative proportions of each S species present in the
289 sample. Linear combinations of reference spectra, each of
290 which is representative of a class of S species were fit to
291 normalized spectra over the range of 2465 to 2488 eV
292 (Figure 1). Fit parameters with reasonable χ^2 values
293 typically ranged from 0.3 to 4.0. Residuals ranged from
294 2.7 to 10.5. The sum of linear coefficients determined by
295 fitting the data is ideally equal to 1 and is a useful
296 indicator of fit quality. Sums of all linear coefficients
297 were close to 1 with a range of 0.9 to 1.15; however, the
298 reported speciation is normalized to unity. The precision
299 of these analyses was estimated by analyzing known
300 mixtures of S reference materials. Precision is best for
301 ester sulfate because of its intense white line feature—
302 typically a 1–2% change in sulfate fraction was routinely
303 measured. Although XANES is less sensitive to sulfides
304 (which lack a strong white line), the method precision
305 was about 3% for sulfides for normalized spectra. Fitting
306 accuracy is similar, usually within a few percent for a
307 spectrum, and impacted most strongly by background
308 subtraction and normalization. Overall, statistical analysis
309 suggests an error of 2–3% for comparative purposes of
310 speciation data presented here between samples, and an
311 accuracy of 5% of S species composition in the litter.

313 3. Results

314 3.1. Degree of Decomposition

315 [13] Carbon to nitrogen ratios (by weight percent) all
316 decreased for both incubations and all litter types (Table 2).
317 C:N ratios in sectioned forest floor samples also decrease
318 with depth where older and more decomposed SOM was
319 collected (Table 2). Mass losses during the decomposition
320 experiments ranged from 8 to 15% with northern hardwood
321 litters losing more mass than Norway spruce litters, which
322 lost more mass compared to pine samples. Considering that
323 there was low mass loss during the experiment, it is
324 surprising that there were observed decreases in C:N of
325 over 30 in two samples over 6 months (Table 2).

326 3.2. Sulfur Species Identification

327 [14] In all litter samples analyzed by XANES, spectra
328 were characteristic of 4 species of organic S (Figure 1).
329 Optimized fits of the spectral data came with contributions
330 from standards of cystine, methionine, sulfoxide, sulfonate,
331 and sulfate with the peak positions shown in Table 1 (Figure
332 1). Low-energy spectral features of organic S were charac-
333 teristic of organic sulfides and disulfides and low-valence
334 intermediate organic sulfoxides based on spectral features at
335 2473–2475 and 2476–2477 eV, respectively (Table 1 and
336 Figure 1). Combined, spectral features fit with organic
337 sulfide and sulfoxide represent the majority of sulfur in
338 these samples (Table 2). Spectral features at higher energies
339 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).

345 3.3. Sulfur Speciation Dynamics on 6-month 346 Timescales

347 [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 frac-
tional abundances generally did not significantly change
over 6 months of decomposition in all litters (Table 2).

357 3.4. Sulfur Speciation Dynamics Over Humification

358 [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 O_i and O_a or T = 0 to A horizon
transitions (Table 2 and Figures 3–5).

4. Discussion

4.1. Sulfur Speciation

382 [17] In general, multiple pools of SOM are known to exist
383 in the soil profile, with labile fractions that are thought to
384 turn over on the order of months to years and more
385 recalcitrant, mature phases that are thought to break down
386 on the order of 100–1000 a during humification [Stevenson,
387 1986, 1994]. For this study, changes in S speciation in SOM
388 during the decomposition experiment were associated with
389 mineralization of labile organic matter fractions, while
390 speciation differences between litter decomposition samples
391 (O_i) and their underlying A horizon samples were associ-
392 ated with the mineralization or humification of more recal-
393 citrant SOM. Sectioned forest floor samples to some extent
394 bridge this time gap representing changes on the 1 to 100 a
395 timescale between O_i and O_a horizons and also provide
396 independent replication of our laboratory and field collected
397 samples from MBRNHP [Kaste *et al.*, 2007].

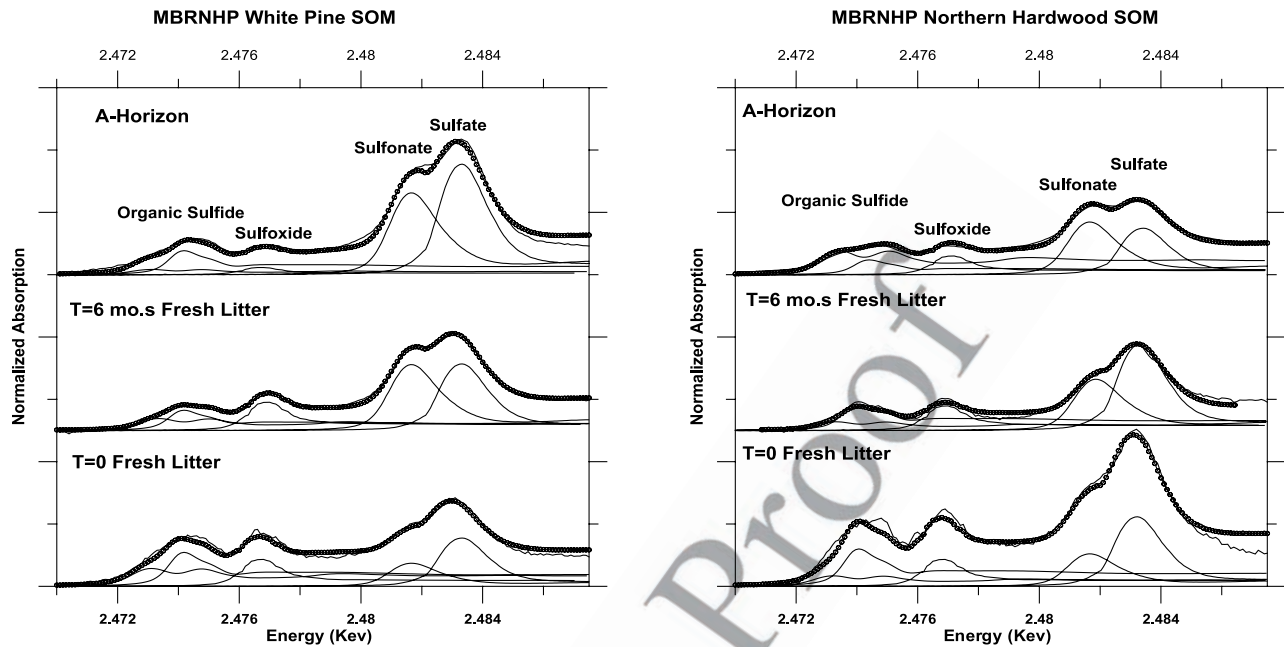


Figure 2. Representative normalized S K-edge XANES spectra of soil organic matter in white pine and northern hardwood forest types over the course of decomposition. LC fits for each sample's spectral data are shown with circles, and the components of each standard are shown as thin black lines below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

398 [18] Spectral features and associated S speciation
 399 observed in SOM of northern forest soils here were broadly
 400 consistent with those found by XANES in isolated fractions
 401 of SOM by other researchers, although sulfones have been
 402 observed in certain matrices and may represent a minor
 403 component here [Morra *et al.*, 1997; Solomon *et al.*, 2003;
 404 Xia *et al.*, 1998]. Organic S found in these soil samples
 405 contained somewhat higher (~20%) fractions of reduced
 406 S than those found by Solomon *et al.* [2003]. Part of the
 407 observed difference in S speciation may be attributed to the
 408 fact that our analyses are performed on whole soils rather
 409 than humic/fulvic acid extracts or size separate fractions.
 410 Our data builds upon past works by directly determining
 411 S species from bulk soils in situ along a decomposition
 412 continuum for these forest types. These analyses also
 413 include identification and quantification of multiple inter-
 414 mediate forms of S (sulfoxide and sulfonate), the behavior
 415 of which has not been described during decomposition.

416 4.2. Sulfur Transformations Linked to Labile SOM 417 Mineralization

418 [19] Carbon to N ratios and sample mass all decreased
 419 significantly during our experiment indicating that substan-
 420 tial C mineralization/humification occurred in the ground
 421 litter in a N-limited environment over these 6 months
 422 (Table 2). The decrease in organic sulfide abundance
 423 suggests that a substantial fraction of organic sulfide present
 424 in SOM was associated with labile SOM. A similar trend of
 425 a decreasing proportion of organic sulfide in SOM with
 426 depth/degree of decomposition was observed by Solomon *et al.*
 427 [2003] in organic matter derived from semitropical soils
 428 of the Ethiopian highlands. The decomposition of labile
 429 amino acids that would constitute a portion of this organic

sulfide pool may have contributed to the decline of this 430
 fraction in the oxidizing experimental environment. 431
 [20] Generally, intermediate oxidation state sulfoxide 432
 fractions did not significantly change over the 6-month 433

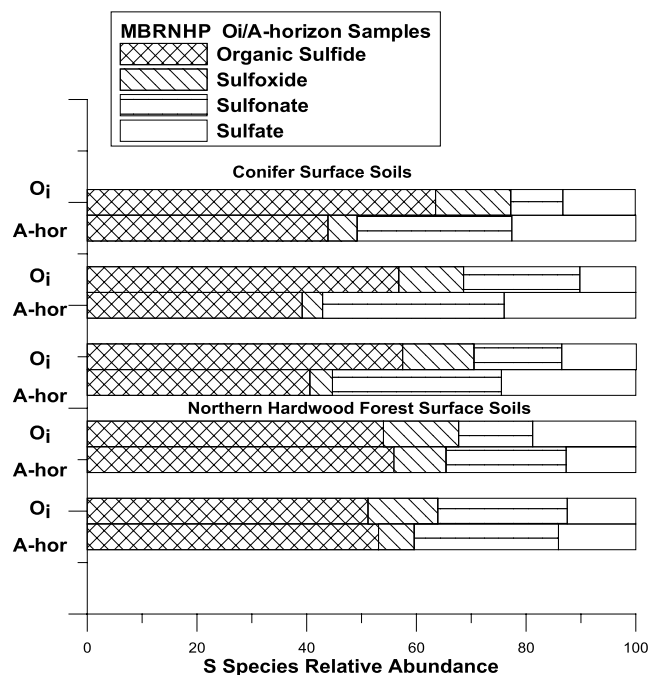


Figure 3. Organic sulfur speciation in sectioned forest floors collected at Whiteface Mountain, New York and HBEF, New Hampshire. Age of organic matter increases from Oi to A horizon samples and represents at least 100 a of decomposition in these soils.

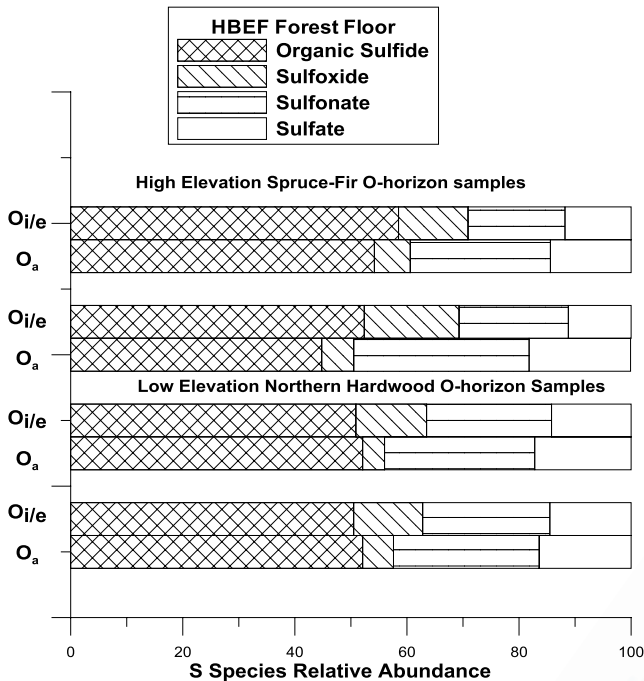


Figure 4. Organic sulfur speciation in sectioned forest floors collected at Hubbard Brook Experimental Forest, New Hampshire in 1983 (fully described by Zhang *et al.* [1999]). Age of organic matter increases from $O_{i/e}$ to O_a subhorizons representing a decomposition continuum of 50–100 a of pedogenesis 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, sulfide 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 and mineral soil 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 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 ($O_{i/e}$) 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

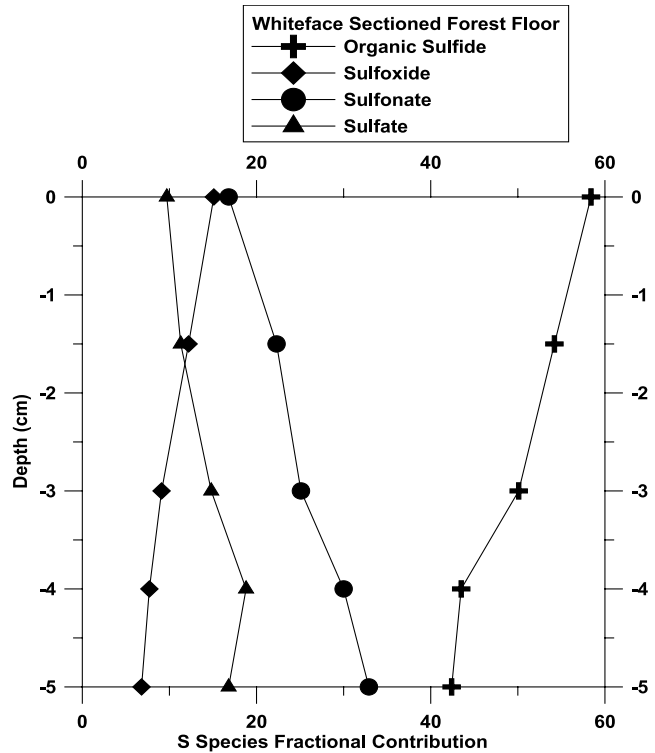


Figure 5. Organic sulfur speciation in sectioned forest floor collected in soil of the spruce/fir forest at Whiteface Mountain, New York. Age of organic matter increases with depth representing roughly 50–100 a of pedogenesis.

494 different than that observed during labile OM mineraliza- 555
495 tion. The consistent decline in sulfoxide relative abundance 556
496 in samples of all litter types at all sites during humifica- 557
497 SOM indicates that its role in the S cycle could change with 558
498 time and depth in the forest floor (Table 2 and Figures 3–5). 559
499 On labile SOM turnover timescales, sulfoxide appears 560
500 relatively inert, but on pedogenic timescales, this phase is 561
501 clearly a significant source of reactive S, which, based on the 562
502 this work, must now be considered as an integral part of the 563
503 soil S cycle. Our data indicate that during labile organic 564
504 matter decomposition, organic sulfide oxidation to soluble 565
505 sulfoxy species was initially the dominant process affecting 566
506 S speciation in our litter samples, but on humification 567
507 timescales with leaching processes incorporated, sulfoxide 568
508 phases were at least comparably reactive. It is likely that 569
509 there are a range of organic sulfide constituents in these 570
510 soils with some being highly reactive (e.g., amino acids) but 571
511 other forms being more recalcitrant to decomposition to 572
512 varying degrees (e.g., aromatics) [Likens et al., 2002]. Our 573
513 results suggest that intermediate valence sulfoxide is an 574
514 important reservoir of relatively reactive S in these soil 575
515 horizons and must play an important role in the S cycle of 576
516 soils of the northern forest, particularly as SOM undergoes 577
517 humification.

518 [23] The relative abundance of sulfonate in all MBRNHP 577
519 forests was higher in A horizons than in litter samples, and 578
520 this species also increased with degree of decomposition in 579
521 forest floors (Figures 3–5). These data indicate that much of 580
522 this form of S is associated with stable organic matter (as 581
523 inferred from short-term experiments), which is resistant to 582
524 mineralization or transformation, even on humification 583
525 timescales. This implies that within organic horizons, this 584
526 fraction of S represents an increasing fraction of the soil 585
527 solid phase S inventory as SOM matures with depth, and 586
528 that this more oxidized intermediate phase is a relatively 587
529 long-term reservoir of solid phase-sequestered S in organic 588
530 rich surface soils of the northern forest. It is important to 589
531 mention that S species behavior during humification at 590
532 MBRNHP was always consistent with the observed trends 591
533 in sectioned forest floors from Whiteface and HBEF sites 592
534 (Figures 3–5), suggesting that our results and related 593
535 conclusions pertaining to S species reactivity during pedo- 594
536 genesis are likely applicable across the large geographic 595
537 areas that contain similar ecosystems and soils.

538 4.4. Organic Sulfur Speciation by Forest Type

539 [24] In addition to significant differences in S speciation 601
540 in organic matter of differing maturity, forest type may 602
541 influence the reactivity of S species in SOM. Conifer and 603
542 deciduous trees each produce litter of differing quality 604
543 (usually estimated by the C:N and Lignin:N ratios), which 605
544 are thought to influence SOM's susceptibility to microbial 606
545 attack and related decomposition [Finzi et al., 1998]. 607
546 Despite these differences, initial litter proportions of S 608
547 species did not differ systematically between conifer and 609
548 deciduous litters, suggesting that there is not a specific forest 610
549 type effect on the initial S species distribution in litter of these 611
550 forests prior to decomposition (Table 2 and Figures 3–5). 612
551 Similarities in organic S species reactivity between forest 613
552 types were observed during SOM decomposition. Inter- 614
553 mediate oxidation state S phases reactivity did not appear 615
554 to differ by litter source, with a relative decrease in

555 sulfoxide abundance and increases in sulfonate abundance 556
556 through decomposition across all soils during humifica- 557
557 tion (Figures 3–5). This indicates that the reactivity of 558
558 intermediate S species is consistent across conifer and 559
559 hardwood litter types. Important differences in the behavior 560
560 of S species by forest type through SOM decomposition 561
561 were also observed. Although relatively reactive throughout 562
562 decomposition at all temporal and spatial scales in conifer 563
563 litter, organic sulfide did not appear to be preferentially reactive 564
564 in northern hardwood field-based decomposition continuums 565
565 that incorporated a leaching component (Figures 3–5). In 566
566 addition, conifer litters, with the exception of one of the young 567
567 Norway spruce experimental samples, consistently increased 568
568 in the fractional abundance of sulfate over pedogenic time- 569
569 scales (Figures 3–5). In contrast, sulfate maintained a rela- 570
570 tively constant fraction over decomposition of northern 571
571 hardwood litters in field-based samples (Figures 3–5). These 572
572 differences in S species behavior were consistent by forest 573
573 type in soils of MBRNHP, Whiteface, and HBEF during 574
574 humification, thus there appears to be a fundamental differ- 575
575 ence in these S species reactivity by forest type in soils of 576
576 the northern forest.

577 [25] On the basis of these data, we can speculate as to 577
578 possible causes for different trends between the conifer and 578
579 northern hardwood in S species reactivity during decompo- 579
579 sition SOM. Northern hardwood SOM organic sulfide 580
580 fractions did not appear to be preferentially reactive over 581
581 decomposition. This could indicate that decreases in organic 582
582 sulfide associated with labile SOM decomposition were also 583
583 associated with mineralization of sulfate that was not redox 584
584 sensitive in the oxidizing conditions of our experiment and 585
585 could not leach due to experimental design. Such trends are 586
586 somewhat counterintuitive, as high-quality deciduous litter 587
587 is thought to decompose at a greater rate than conifer litter, 588
588 thus one would anticipate reactive S fractions to decrease 589
589 more rapidly in high- than low-quality litter. A likely 590
590 explanation for the relatively stable S speciation in decid- 591
591 uous litter is that both reduced and oxidized S were 592
592 comparably reactive during decomposition of this litter 593
593 type, with a higher reactivity of ester-bonded sulfate in 594
594 deciduous litters relative to conifer litters. The direct cou- 595
595 pling of S and C mineralization may be enhanced by the 596
596 higher litter quality of deciduous species; as deciduous litter 597
597 would presumably have a larger fraction of reactive SOM, 598
598 which contains a broad range of S functional groups and 599
599 would be subject to facile decomposition. This explanation 600
600 is supported by the surface soil solution data of Kaiser and 601
601 Guggenberger [2005], who found ester-bonded S to be 602
602 more concentrated in deciduous forest floor solutions rela- 603
603 tive to conifer forest floor solutions and also observed 604
604 higher concentrations of DOC and DOS under the decidu- 605
605 ous forest floors in association with decomposition, con- 606
606 firming the relationship between C and S reactivity in these 607
607 forest soils. Alternatively, recent work has challenged the 608
608 convention of litter quality alone controlling the rate of 609
609 microbially mediated decomposition of SOM in some soils, 610
610 and indicates that conifer SOM on the short term can 611
611 decompose at a higher rate than deciduous litter [Giardina 612
612 et al., 2001]. If this was the case, rapid decomposition and 613
613 associated S mineralization of conifer litter relative to 614
614 deciduous litter is one mechanism by which the observed 615
615 trends could also be explained. It has been suggested that 616

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

630 5. Conclusions

631 [26] Using experimental and natural soil samples from
 632 multiple field sites, we conclusively demonstrate that
 633 S speciation in SOM is affected by stage of decomposition
 634 at greater level of temporal and species specific detail than
 635 previously known. We show that S speciation in litter is
 636 dynamic, and influenced by decomposition and a variety of
 637 SOM properties, but also is consistent in behavior across
 638 study sites of similar ecosystems. In temperate forest soils
 639 of the northeast studied here, spectral data from SOM
 640 indicates that S speciation in SOM is best represented by
 641 four species of sulfur; organic sulfides, low-valence sulfox-
 642 ide, sulfonates and sulfates, each of which has a unique
 643 reactivity during decomposition. As SOM decomposition
 644 progresses, the relative abundances of each fraction of
 645 S species changes, even within a few months of decompo-
 646 sition. Overall, the preferential reactivity of organic sulfide
 647 fractions in oxidizing podzolic environments accounts for
 648 much of this change in speciation of SOM-associated
 649 S during pedogenesis. Furthermore, a significant component
 650 of organic sulfides appear to be associated with a very labile
 651 fraction of SOM that is mineralized on the order of months
 652 during initial litter decay. This indicates that the initial rapid
 653 turnover of litter releases sulfide into oxic soil solutions,
 654 most likely associated with reactive S-bearing amino acids
 655 present in the decaying litter, where it can either oxidize or
 656 react with other species. The concentration of these com-
 657 pounds in young SOM must play an important role in forest/
 658 soil S cycling and other processes related to S speciation
 659 and concentration in soil solution (i.e., metal sequestration,
 660 nutrient cation depletion). Intermediate sulfoxides appear to
 661 be another labile fraction of S, particularly on longer time-
 662 scales associated with the humification of SOM and must
 663 play an important role in S cycling on this timescale in
 664 organic rich soil horizons. The consistent enrichment of
 665 sulfonate in SOM during decomposition suggests that this
 666 species is relatively stable and immobile during at least
 667 100 a of pedogenesis, and must be an important reservoir of
 668 solid phase S in the soil S cycle. The behavior of these
 669 intermediate S species during pedogenesis as demonstrated
 670 here reveals a component of S cycling in soils that was
 671 previously unknown, but now must be considered important
 672 forms of labile and solid phase-sequestered S in the soil
 673 S cycle over pedogenic time depending on the bonding
 674 environment and oxidation state of S.

675 [27] The S species composition of forest types studied
 676 here indicates that there is not a systematic difference in
 677 S speciation in litter of the studied forest types. We have

discovered similarities in the behavior of intermediate 678
 S species during SOM mineralization across litter types 679
 and demonstrated that these phases behave similarly within 680
 the studied forest types. The behavior of organic sulfide and 681
 sulfate in soil samples of conifer and northern hardwood 682
 forests indicates that S speciation could play a different role 683
 in S cycling/flux in spodic soils dependant on the quality of 684
 litter produced and its related susceptibility to microbial 685
 attack. At present we do not have a conclusive explanation 686
 for the similar behavior of intermediate S species but 687
 different behavior of organic sulfide and sulfate in SOM 688
 of different forests, and this should be an interesting area for 689
 additional research. Our data indicate that shifts in north- 690
 ern forest composition due to management decisions or 691
 environmental change would cause a distinct change in 692
 the distribution and form of S within organic-rich soil 693
 environments. 694

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References

- 704
 Bostick, B. C., K. M. Theissen, R. B. Dunbar, and M. A. Vairavamurthy 705
 (2005), Record of redox status in laminated sediments from Lake Titica- 706
 ca: A sulfur K-edge X-ray absorption near edge structure (XANES) 707
 study, *Chem. Geol.*, 219(1–4), 163–174. 708
 David, M. B., M. J. Mitchell, and J. P. Nakas (1982), Organic and inorganic 709
 sulfur constituents of a forest soil and their relationship to microbial 710
 activity, *Soil Sci. Soc. Am. J.*, 46(4), 847–852. 711
 Dhamala, B. R., and M. J. Mitchell (1995), Sulfur speciation, vertical- 712
 distribution, and seasonal-variation in a northern hardwood forest soil, 713
 USA, *Can. J. For. Res.*, 25(2), 234–243. 714
 Finzi, A. C., C. D. Canham, and N. Van Breeman (1998), Canopy tree-soil 715
 interactions within temperate forests: Species effects on pH and cations, 716
Ecol. Appl., 8(3), 905. 717
 Fitzgerald, J. W., J. T. Ash, T. C. Strickland, and W. T. Swank (1983), 718
 Formation of organic sulfur in forest soils: A biologically mediated pro- 719
 cess, *Can. J. For. Res.*, 13(6), 1077–1082. 720
 Fitzgerald, J. W., T. C. Strickland, and J. T. Ash (1985), Isolation and partial 721
 characterization of forest floor and soil organic sulfur, *Biogeochemistry*, 722
 1(2), 155–167. 723
 Giardina, C. P., M. G. Ryan, R. M. Hubbard, and D. Binkley (2001), Tree 724
 species and soil textural controls on carbon and nitrogen mineralization 725
 rates, *Soil Sci. Soc. Am. J.*, 65(4), 1272–1279. 726
 Hamburg, S. P., R. D. Yanai, M. A. Arthur, J. D. Blum, and T. G. Siccamo 727
 (2003), Biotic control of calcium cycling in northern hardwood forests: 728
 Acid rain and aging forests, *Ecosystems*, 6(4), 399–406. 729
 Homann, P. S., and D. W. Cole (1990), Sulfur dynamics in decomposing 730
 forest litter: Relationship to initial concentration, ambient sulfate and 731
 nitrogen, *Soil Biol. Biochem.*, 22(5), 621–628. 732
 Hutchison, K. J., D. Hesterberg, and J. W. Chou (2001), Stability of reduced 733
 organic sulfur in humic acid as affected by aeration and pH, *Soil Sci. Soc.* 734
Am. J., 65(3), 704–709. 735
 Kaiser, K., and G. Guggenberger (2005), Dissolved organic sulphur in soil 736
 water under *Pinus sylvestris* L. and *Fagus sylvatica* L. stands in north- 737
 eastern Bavaria, Germany: Variations with seasons and soil depth, *Bio-* 738
geochemistry, 72(3), 337–364. 739
 Kaste, J. M., A. J. Heimsath, and B. C. Bostick (2007), Short-term soil 740
 mixing quantified with fallout radionuclides, *Geology*, 35(3), 243–246. 741
 Lautzenheizer, T. (2002), Marsh-Billings-Rockefeller National Historical 742
 Park natural community report, pp.37, Univ. of Vt., Woodstock. 743
 Likens, G. E., C. T. Driscoll, D. C. Buso, M. J. Mitchell, G. M. Lovett, S. W. 744
 Bailey, T. G. Siccamo, W. A. Reiners, and C. Alewell (2002), The bio- 745
 geochemistry of sulfur at Hubbard Brook, *Biogeochemistry*, 60(3), 235– 746
 316. 747
 Martinez, C. E., M. B. McBride, M. T. Kandianis, J. M. Duxbury, S. J. 748
 Yoon, and W. F. Bleam (2002), Zinc-sulfur and cadmium-sulfur associa- 749

- 750 tion in metalliferous pleats evidence from spectroscopy, distribution coef-
 751 ficients, and phytoavailability, *Environ. Sci. Technol.*, 36(17), 3683–
 752 3689.
- 753 McBride, M. B. (1994), *Environmental Chemistry of Soils*, 406 pp., Oxford
 754 Univ. Press, New York.
- 755 McGill, W. B., and C. V. Cole (1981), Comparative aspects of cycling of
 756 organic C, N, S and P through soil organic-matter, *Geoderma*, 26(4),
 757 267–286.
- 758 Miller, E. K., A. J. Friedland, E. A. Arons, V. A. Mohnen, J. J. Battles, J. A.
 759 Panek, J. Kadlecek, and A. H. Johnson (1993), Atmospheric deposition to
 760 forests along an elevational gradient at Whiteface-Mountain, NY, USA,
 761 *Atmos. Environ. Part A*, 27(14), 2121–2136.
- 762 Morra, M. J., S. E. Fendorf, and P. D. Brown (1997), Speciation of sulfur in
 763 humic and fulvic acids using X-ray absorption near-edge structure
 764 (XANES) spectroscopy, *Geochim. Cosmochim. Acta*, 61(3), 683–688.
- 765 Ressler, T. (1998), WinXAS: A program for X-ray absorption spectroscopy
 766 data analysis under MS-Windows, *J. Synchrotron Radiat.*, 5, 118–122.
- 767 Schlesinger, W. H. (1997), *Biogeochemistry: An Analysis of Global*
 768 *Change*, 588 pp., Academic, San Diego, Calif.
- 769 Schroth, A. W., A. J. Friedland, and B. C. Bostick (2007), Macronutrient
 770 depletion and redistribution in soils under conifer and northern hardwood
 771 forests, *Soil Sci. Soc. Am. J.*, 71(2), 457–468.
- 772 Solomon, D., J. Lehmann, M. Tekalign, F. Fritzsche, and W. Zech (2001),
 773 Sulfur fractions in particle-size separates of the sub-humid Ethiopian
 774 highlands as influenced by land use changes, *Geoderma*, 102(1–2),
 775 41–59.
- 776 Solomon, D., J. Lehmann, and C. E. Martinez (2003), Sulfur K-edge
 777 XANES spectroscopy as a tool for understanding sulfur dynamics in soil
 778 organic matter, *Soil Sci. Soc. Am. J.*, 67(6), 1721–1731.
- Stevenson, F. J. (1986), *Cycles of Soil: Carbon, Nitrogen, Phosphorus, Sulfur, Micronutrients*, 380 pp., John Wiley, New York. 779
- Stevenson, F. J. (1994), *Humus Chemistry Genesis, Composition, Reactions*, John Wiley, New York. 780
- Vannier, C., J. F. Didonlescot, F. Lelong, and B. Guillet (1993), Distribution 781
 of sulfur forms in soils from beech and spruce forests of Mont-Lozere 782
 (France), *Plant Soil*, 154(2), 197–209. 783
- Waldo, G. S., R. M. K. Carlson, J. M. Moldowan, K. E. Peters, and J. E. 784
 Pennerhahn (1991), Sulfur speciation in heavy petroleum: Information 785
 from X-ray absorption near-edge structure, *Geochim. Cosmochim. Acta*, 786
 55(3), 801–814. 787
- Xia, K., F. Weesner, W. F. Bleam, P. R. Bloom, U. L. Skyllberg, and P. A. 788
 Helmke (1998), XANES studies of oxidation states of sulfur in aquatic 789
 and soil humic substances, *Soil Sci. Soc. Am. J.*, 62(5), 1240–1246. 790
- Zhang, Y. M., M. J. Mitchell, C. T. Driscoll, and G. E. Likens (1999), 791
 Changes in soil sulfur constituents in a forested watershed 8 years after 792
 whole-tree harvesting, *Can. J. For. Res.*, 29(3), 356–364. 793
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