



Peer review status:

This is a non-peer-reviewed preprint submitted to EarthArXiv.

Mineral stabilization of soil organic sulfur at the continental scale

Zhuojun Zhang^{1,2}, M. Francesca Cotrufo³, Benjamin L. Turner⁴, Hai-Ruo Mao¹, Chao Liang⁵,
Mohsen Shakouri⁶, and Mengqiang Zhu^{1,7*}

¹ Department of Ecosystem Science and Management, University of Wyoming, Laramie, Wyoming
82071, United States

² State Key Laboratory of Lake and Watershed Science for Water Security, Nanjing Institute of
Geography and Limnology, Chinese Academy of Sciences, Nanjing, Jiangsu 211135, China

³ Department of Soil and Crop Science and Natural Resource Ecology Laboratory, Colorado State
University, Fort Collins, Colorado 80523, United States

⁴ Institute of Agriculture and Life Sciences, Gyeongsang National University, 501 Jinju-Daero,
Jinju 52828, South Korea

⁵ Institute of Applied Ecology, Chinese Academy of Sciences, Shenyang, Liaoning 110016, China

⁶ Canadian Light Source Inc., University of Saskatchewan, Saskatoon, Saskatchewan S7N 2V3,
Canada

⁷ Department of geological, Environmental, and Planetary Sciences, University of Maryland,
College Park, Maryland 20740, United States

* Corresponding author: Mengqiang Zhu

Email: mqzhu@umd.edu

Running Title: Mineral stabilization of soil organic sulfur

1 **Abstract**

2 Declining atmospheric sulfur (S) deposition makes S an emerging limiting macronutrient to
3 plants, yet the stability and dynamics of soil organic S - the largest terrestrial S pool supplying
4 plant-available sulfate via mineralization - remain unclear. Across North American soils, mineral-
5 associated organic S (MAOS), a stabilized pool by mineral protection, dominates ($61 \pm 26\%$ of the
6 total soil S) but saturates at $\sim 600 \mu\text{g S g}^{-1}$ soil. Compared with labile particulate organic S (POS)
7 that does not saturate, MAOS is more decomposed, chemically diverse, and climate-sensitive.
8 Projected global warming accelerates S mineralization in both pools, but shifting moisture regimes
9 drive their divergence in supplying available S, with MAOS stabilizing in wetter soils while POS
10 remains labile. This comprehensive reassessment of soil S cycle at the continental scale reveals a
11 mineral “gatekeeper” that both shields organic S and retains sulfate, providing a mechanistic basis
12 for nutrient management and carbon sequestration in response to climate change in a S-scarce
13 future.

14 **Keywords:** organic S mineralization, mineral stabilization, S availability, soil S cycle, climate
15 change, organic matter fractions

16 **1 Introduction**

17 Sulfur (S) is a vital macronutrient essential for all life, yet global soils are becoming
18 increasingly deficient in S due to a worldwide decline in atmospheric S deposition (Silvia
19 Haneklaus, Bloem, & Schnug, 2008; Hinckley, Crawford, Fakhraei, & Driscoll, 2020). Soil parent
20 materials are typically low in S, so anthropogenic SO_2 and SO_4^{2-} deposition has served as a major
21 external source since the industrial revolution (S. Haneklaus, Bloem, & Schnug, 2003). However,
22 global S emissions have declined by $\sim 40\%$ since 1990, driven by air quality improvements, with
23 reductions approaching 90% in North America and Europe (Feinberg et al., 2021; Ritchie & Roser,
24 2021). This decline has led to widespread S limitation across natural and agricultural ecosystems,

25 particularly in arable soils (Hinckley et al., 2020; Messick, Fan, & De Brey, 2005), prompting
26 growing reliance on supplemental S fertilizers to sustain food production (Gerson & Hinckley,
27 2023; Hinckley et al., 2020). As atmospheric contributions diminish, microbial mineralization of
28 soil organic S – the largest terrestrial S pool and accounting for over 95% of the total soil S (Jørgen
29 Eriksen, 2009; Kovar & Grant, 2011; Niknahad-Gharmakher, Piutti, Mchet, Benizri, & Recous,
30 2012) – has become increasingly important for sustaining plant-available sulfate (Barnard et al.,
31 2025; Churka Blum, Lehmann, Solomon, Caires, & Alleoni, 2013; Fakhraee, Li, & Katsev, 2017;
32 Kovar & Grant, 2011; Tolu et al., 2022). Yet, organic S compounds are not uniformly accessible:
33 associations with soil minerals can stabilize organic S, limiting microbial access and constraining
34 mineralization (J. Eriksen, Murphy, & Schnug, 1998; Solomon, Lehmann, & Martínez, 2003;
35 Tanikawa, Hashimoto, et al., 2014; Tanikawa et al., 2022). The balance between microbial
36 mineralization and mineral stabilization has thus emerged as a central, yet poorly understood,
37 control on terrestrial S cycling.

38 Traditionally, soil organic S has been categorized by biochemical reactivity into labile ester
39 sulfates (C–OSO₃) and more recalcitrant carbon-bonded S (C–S), with the former presumed more
40 readily mineralized to meet microbial demand (Churka Blum et al., 2013; Edwards, 1998; J.
41 Eriksen et al., 1998; Singh, Rengel, & Bowden, 2006) (Fig. 1). However, mineral associations can
42 strongly modulate these dynamics by physically protecting both compound types from microbial
43 and enzymatic attack (J. Eriksen et al., 1998; Solomon et al., 2003; Tanikawa, Hashimoto, et al.,
44 2014; Tanikawa et al., 2022). Recent developments in soil carbon research offer a mechanistic
45 framework: dividing SOM into particulate organic matter (POM) and mineral-associated organic
46 matter (MAOM) better predicts organic carbon turnover and stability, nitrogen cycling and their
47 responses to climate change (Averill & Waring, 2018; Cotrufo, Ranalli, Haddix, Six, & Lugato,
48 2019; Lavalley, Soong, & Cotrufo, 2020; Lugato, Lavalley, Haddix, Panagos, & Cotrufo, 2021).
49 Particulate organic matter consists mainly of plant structural residues that decompose on average

50 on decadal timescales and are stabilized by biochemical and microbial constraints, while MAOM
51 comprises largely of mineral-bound soluble or insoluble compounds of either plant or microbial
52 origin with C turnover times ranging on average from centuries to millennia (Heckman et al.;
53 Lavallee et al., 2020). This conceptual framework has enhanced our understanding of soil carbon
54 persistence and nitrogen availability (Averill & Waring, 2018; Jilling et al., 2018), yet its relevance
55 to soil organic S remains largely unexplored. Although some studies have demonstrated mineral
56 controls on S dynamics in specific soil types (J. Eriksen et al., 1998; Solomon et al., 2003; Tanikawa,
57 Hashimoto, et al., 2014; Tanikawa et al., 2022), the quantities, chemical forms, and environmental
58 sensitivities of mineral-associated organic S (MAOS) versus particulate organic S (POS) remain
59 uncharacterized across disparate ecosystems at broad spatial scales.

60 Here we present the first continental-scale assessment of physical and chemical nature of soil
61 organic S, extending the MAOM–POM framework to S using samples from 40 sites across 20 U.S.
62 ecoclimatic domains in the National Ecological Observatory Network (NEON). Consistent with
63 the most recent understanding of SOM physical fractions (Leuthold, Lavallee, Haddix, & Cotrufo,
64 2024), we fractionated SOM by density and size and considered POM as the light (LPOM, < 1.85
65 g cm^{-3}) and heavy fraction (HPOM, $> 1.85 \text{ g cm}^{-3}$ & $> 53\text{mm}$), and MAOM as the fine heavy
66 fraction ($> 1.85 \text{ g cm}^{-3}$ & $< 53\text{mm}$). LPOM and MAOM were directly characterized but HPOM
67 was not due to its low concentration of S. We measured organic S concentrations in the LPOM
68 (LPOS) and MAOM fractions (MAOS) and the bulk soil (TOS). Hereafter, the total particulate
69 organic matter, defined as HPOM + LPOM, is termed POM. Similarly, total particulate organic S
70 contained in combined HPOM and LPOM is denoted as POS, which was estimated as the difference
71 between MAOS and TOS. Further, we characterized S speciation in the MAOM (i.e., MAOS) and
72 LPOM (i.e., LPOS) fractions and the bulk soil using S K-edge X-ray absorption near-edge structure
73 (XANES) spectroscopy. We used average S oxidation state as a proxy for the extent of OS
74 decomposition and applied path analyses to identify climatic, mineralogical, and other edaphic

75 drivers of S stabilization and decomposition (see Methods for details). Our findings provide new
76 insights into the geochemical architecture of soil organic S and its sensitivity to environmental
77 factors, advancing our ability to manage S fertility and availability in a changing climate.

78 **2 Materials and Methods**

79 **2.1 Soil samples and analysis**

80 We used the subsamples of A and B horizons from 40 sites in the NEON Megapit archive.
81 Detailed soil profile descriptions for the NEON sites we studied are provided in Supplementary
82 Table S1. To obtain different fractions of OM, we utilized a physical soil organic matter
83 fractionation scheme as described by Soong and Cotrufo (Soong & Cotrufo, 2015). Briefly, a 5 g
84 subsample of oven-dried bulk soil was dispersed with glass beads in 25 mL of 1.85 g cm^{-3} sodium
85 polytungstate solution (SPT) to disperse all aggregates. Then, the samples were centrifuged, and
86 the light particulate OM (LPOM $< 1.85 \text{ g cm}^{-3}$) was aspirated from the sample and rinsed to remove
87 SPT. The remaining heavy fraction was rinsed thoroughly to remove SPT and then sieved through
88 a $53\text{-}\mu\text{m}$ screen to separate the heavy sand-sized OM (HPOM $> 1.85 \text{ g cm}^{-3}$ and $> 53 \mu\text{m}$) and
89 mineral associated organic matter (MAOM $> 1.85 \text{ g cm}^{-3}$ and $< 53 \mu\text{m}$). All fractions were oven-
90 dried at $60 \text{ }^\circ\text{C}$ prior to the analysis. The total mass recovery from the fractions was within $\pm 5\%$ of
91 the initial mass.

92 We directly characterized the LPOM and MAOM fractions, but the HPOM fraction was not
93 directly characterized due to its low S concentration. Organic S concentrations in the LPOM and
94 MAOM fractions and the bulk soil (TOS) were measured using a Thermo Flash Elemental Analyzer.
95 The MAOS concentration in bulk soil was calculated by multiplying the S concentration in MAOM
96 by the mass percentage of MAOM material over total bulk soil. The total particulate organic matter,
97 defined as HPOM + LPOM, is termed POM. Similarly, total particulate organic S contained in
98 combined HPOM and LPOM is denoted as POS, which was estimated as the difference between

99 MAOS and TOS. The close correlation between LPOS and POS in the topsoil, as indicated by the
100 regression line (Fig. S1), suggests that POS is predominantly derived from LPOS.

101 Exchangeable S in soils, considered as available S here, was extracted using a 0.016 M
102 KH_2PO_4 solution at a 1:20 ratio. After agitation on a reciprocal shaker for 2 hours, the samples
103 were centrifuged and then filtered through 0.45 μm syringe filters. The filtrates were then analyzed
104 for the SO_4^{2-} concentration by ion chromatography (Dionex ICS-90, Thermo Scientific,
105 Massachusetts, USA).

106 **2.2 Sulfur K-edge XANES spectroscopy**

107 Sulfur K-edge XANES spectra were collected from bulk soil, LPOM and MAOM in the top
108 A and B horizons at the Soft X-ray Micro-Characterization Beamline (SXRMB) at the Canadian
109 Light Source, Saskatoon, Canada. XANES spectra for all samples were recorded in fluorescence
110 yield using a 7-element SDD detector (RaySpec Inc.) over the energy range of 2442–2542 eV.
111 Measurements were conducted in three segments: 2442–2466 eV with 2 eV steps, 2466–2497 eV
112 with 0.15 eV steps, and 2497–2542 eV with 0.75 eV steps. The X-ray energy was calibrated to the
113 K-edge of elemental S at 2472.7 eV. The XANES spectra data were merged and normalized using
114 the software ATHENA. The spectra were further fitted using a series of Gaussian functions (G1,
115 G2, G3, G4, and G5) and two arctangent functions (step height) following the approach by Wojdyr
116 (2010) using Fityk. The five Gaussian curves correspond to different S species: exocyclic S (G1),
117 heterocyclic S (G2), sulfoxide (G3), sulfonate (G4), and inorganic and ester SO_4^{2-} (G5) (Prietz et
118 al., 2011). The relative abundance of each S functional group was calculated from the area under
119 the respective Gaussian peak relative to the total area under all the Gaussian peaks. The areas were
120 corrected for energy-dependent absorption cross section using the generic calibration curve
121 (Manceau & Nagy, 2012):

$$122 \quad y = 0.36841x - 909.97$$

123 where x is the white-line peak energy and y is the scaling factor normalized to y = 1 at the energy
124 of elemental S (E 2472.70 eV). It has been reported that the error for the OS fraction with the
125 Gaussian curve fit is 4-8% for reduced and < 5% for oxidized S species (Huffman et al., 1991;
126 Manceau & Nagy, 2012).

127 The electronic oxidation state (EOS) of each S species was calculated using the equation (Zeng,
128 Arnold, & Toner, 2013):

$$129 \quad \text{EOS} = 0.6179x - 1529$$

130 where x is the white-line peak energy. In this study, EOS values were reported as calculated
131 for the low-valent S species (EOS $\leq +4$) and EOS values were rounded to integer values for the
132 high-valent S species (EOS $> +4$). The average electronic oxidation state (ASOX) of S was
133 calculated using the following equation:

$$134 \quad \text{ASOX} = \text{EOS}_{G1} \times F_{G1} + \text{EOS}_{G2} \times F_{G2} + \text{EOS}_{G3} \times F_{G3} + \text{EOS}_{G4} \times F_{G4} + \text{EOS}_{G5} \times F_{G5}$$

135 where F represents the proportion of each fraction.

136 **2.3 Statistical analyses**

137 Structural equation modeling (SEM) was used to explore the direct and indirect effects of
138 climatic and edaphic variables on the concentrations of MAOS and POS, exchangeable S
139 concentration and percentage, as well as average S oxidation states (ASOX) in bulk soil, LPOM
140 and MAOM. Multiple goodness-of-fit tests were applied, including the Chi-square/degree of
141 freedom (χ^2/df) test ($p > 0.05$), the comparative fit index (CFI > 0.9), and the root mean square
142 error of approximation (RMSEA < 0.08). The path coefficient (l) for each environmental factor
143 indicated its effects on the target variable. The R² values represented the proportion of the variance
144 explained by the variables. The total effects were obtained by multiplying the l values along the
145 related effect paths and summing them. The SEM analyses were conducted using AMOS 22.0
146 (Amos Development Co.).

147 All the correlation analyses in this study were conducted using Origin 2018. To evaluate the
148 significance of these relationships, a one-way analysis of variance (ANOVA) method was applied.
149 The relationships between TOS and concentrations of MAOS and POS were fitted using asymptotic
150 and ExpDec models, respectively. All other correlations were fitted using ordinary least squares
151 linear regression.

152 **3 Results and Discussion**

153 **3.1 Distributions of MAOS and POS**

154 We find that MAOS constitutes a substantial fraction of total organic S across North American
155 soils, though its contribution varied considerably across sites (Figs. 2a–b). In the surface (A)
156 horizon, mean (\pm SD) concentrations of TOS, MAOS, and POS were 312 ± 294 , 155 ± 124 , and
157 157 ± 259 $\mu\text{g/g}$ soil, respectively, declining to 187 ± 231 , 88 ± 84 , and 99 ± 199 $\mu\text{g/g}$ soil in the B
158 horizon (Fig. 2a). The fraction of MAOS relative to TOS (f_{MAOS}) averaged $57 \pm 21\%$ in the A
159 horizon soil and $64 \pm 28\%$ in the B horizon (subsurface), without significant difference between
160 the two horizons (Fig. 2b). On average, mineral-associated S accounted for $61 \pm 26\%$ of total
161 organic S across all samples, underscoring the widespread role of mineral stabilization in shaping
162 soil organic S pools and MAOM as a major S reservoir larger than POM on average. Notably, the
163 concentrations of TOS, MAOS, and POS as well as f_{MAOS} did not differ significantly among
164 ecosystem types (Figs. S2a–d), suggesting common underlying mechanisms governing S
165 partitioning across ecosystems although the different numbers of data points for each ecosystem
166 type may obscure the finding.

167 Despite this broad prevalence, the capacity of soils to stabilize organic S through mineral
168 associations appears finite. MAOS concentrations exhibit a saturation response with increasing
169 TOS: at low TOS levels, sulfur was primarily stored as MAOS (Fig. 2c), but beyond ~ 600 $\mu\text{g/g}$
170 soil, MAOS reached an apparent upper limit, and further increases in TOS occurred exclusively via

171 POS accumulation (Fig.2d). This saturation pattern closely parallels that of mineral-associated
172 organic carbon (MAOC; Fig. S3) (Cotrufo & Lavelle, 2022; Cotrufo et al., 2019), as expected
173 given the consistently narrow carbon-to-sulfur (C/S) ratios in MAOM (Fig. 2h). However,
174 confirming the saturation threshold requires future empirical work, such as isotopic tracing and
175 controlled S enrichment studies, to assess incorporation rates and stabilization capacity.

176 Our findings reveal that S availability and mineral interactions may jointly stabilize organic C
177 in soils, underscoring the potential biogeochemical coupling of OS to OC. A comparison of C/S
178 ratios between MAOM and POM suggests that S availability might constrain the formation of
179 MAOC. Similar to C/N, MAOM consistently exhibited lower and less variable C/S ratios than
180 POM (Figs. 2h–i), reflecting more advanced microbial processing, a higher S demand for MAOM
181 formation (Kirkby et al., 2013), and a stronger affinity for S-rich organic molecules for soil mineral
182 surfaces (Spohn, 2024). Soils with higher f_{MAOC} tended to show higher C/S ratios in MAOM (Fig.
183 S8), suggesting more efficient S use in carbon stabilization under S-limited conditions. These
184 patterns imply that, like nitrogen and phosphorus (Favaro, Carrillo, Singh, Warren, & Dijkstra,
185 2025; Lieberman, von Sperber, & Kallenbach, 2025; Spohn, 2020), sulfur can act as a limiting
186 factor in long-term SOC stabilization — an effect likely to intensify as atmospheric S inputs
187 continues to decline. The close relationship between organic C and S is further supported by strong
188 correlations between MAOC and MAOS, and between POC and POS (Figs. 2e–f, 3a–b). MAOS
189 and POS concentrations were elevated in soils with higher C/N ratios of MAOM and POM and in
190 cooler climates (Figs. 3a–b), suggesting potential S enrichment in less decomposed organic matter.
191 This likely reflects the relative stability of C-bonded S in fresher material compared to ester-bound
192 S in more processed compounds. Mineralogical controls were especially important for MAOS: both
193 silt/clay content and oxalate-extractable Fe and Al were positively associated with MAOS
194 concentrations (Fig. 3a), highlighting the role of secondary minerals in organic S accumulation and
195 stabilization. Higher effective soil moisture may further enhance MAOS accrual, likely by

196 stimulating mineral weathering and plant productivity, while lower pH may suppress microbial
197 processing and necromass stabilization. Among all variables, the fraction of MAOC (f_{MAOC})
198 emerged as the strongest predictor of the proportion of MAOS in total organic S (f_{MAOS} ; Fig. 3c),
199 reinforcing the conclusion that C and S are potentially co-stabilized through mineral associations
200 under warm, moist, and mineral-rich conditions. Future studies are warranted to determine the
201 specific mechanisms by which S availability and mineral interactions drive organic C stabilization.

202 **3.2 Oxidation states and decomposition of MAOS and POS**

203 The chemical composition of organic S varied widely across the continent and differed
204 significantly between MAOS and LPOS, though not among ecosystems (Figs. 4A; Figs. S2j–r).
205 Light POS in the A horizon was dominated by C-bonded S ($89\% \pm 4\%$) with little ester sulfate ($11\% \pm 4\%$),
206 whereas MAOS exhibited lower C-bonded S ($73\% \pm 13\%$) and higher ester sulfate ($27\% \pm 13\%$)
207 with greater variability (as shown by higher standard deviations) than POS, reflecting a more
208 oxidized and decomposed state of MAOS. This greater variability suggests that MAOS is more
209 chemically sensitive than LPOS to environmental conditions. Our finding is consistent with that
210 organic S is more oxidized in clay fractions than in bulk soils (Prietzl, Thieme, Salomé, & Knicker,
211 2007). Despite being closer to complete mineralization on average, MAOS is expected to be more
212 stable due to mineral protection, particularly for ester sulfate through strong adsorption of its SO_4^{2-}
213 group onto mineral surfaces, slowing further mineralization (Prietzl et al., 2007; Tanikawa,
214 Noguchi, et al., 2014; Yang et al., 2016).

215 The contrasting compositions of MAOS and LPOS reflect differences in the origin and
216 transformation of MAOM and LPOM. The high C-bonded S content in LPOM aligns with its
217 predominantly plant-derived origins, as plants primarily contribute C-bonded S. Oxidation of this
218 C-bonded S produces ester sulfate, which can then hydrolyze rapidly to release inorganic sulfate
219 without subsequent mineral protection, which further enriches C-bonded S in LPOM relative to

220 ester sulfate. Microbial residues, especially those from fungi that are rich in ester sulfate (Heinze
221 et al., 2021), may also contribute to the ester sulfate content of LPOM. In contrast, MAOM accrues
222 more ester sulfate, likely due to multiple mechanisms such as preferential adsorption of ester sulfate
223 to mineral surfaces via its SO_4^{2-} group, greater microbial decomposition, and higher microbial
224 (fungal) residue inputs. The higher ester sulfate proportion in B horizon soils (Fig. 4Ab) further
225 supports the role of mineral surfaces, particularly secondary minerals abundant in deeper layers, in
226 concentrating and stabilizing ester sulfate.

227 Environmental conditions, especially temperature and effective soil moisture, appear to
228 further shape the chemical state and stability of organic S pools. Path analyses identified MAT,
229 MAP – PET, and soil pH (itself influenced by MAP – PET; Fig. S7b) as potential key drivers. MAT
230 positively correlated with the oxidation states of both MAOS and LPOS, with stronger effects in
231 the B horizon than the A horizon (Figs. 4Ba–e, Figs. 3d–h), consistent with evidence that warming
232 accelerates organic matter decomposition more in subsoils (Jia et al., 2019; Ofiti et al., 2021). In
233 contrast, MAP – PET had divergent effects on the two S pools (Figs. 4Bf–j, Figs. 3d–h). LPOS
234 oxidation increased slightly with MAP – PET, likely due to enhanced decomposition in wetter but
235 oxygen-rich macropores hosting LPOM, though this effect might be tempered by lower pH at high
236 moisture. MAOS oxidation, however, declined markedly with increasing MAP – PET, especially
237 in the A horizon. This trend reflects enhanced anoxia and acidification in micropores hosting
238 MAOM, which limit microbial oxidation and preserve reduced S forms (Keiluweit, Wanzek,
239 Kleber, Nico, & Fendorf, 2017; Zhu et al., 2026). Increased leaching under wetter conditions also
240 transports less-decomposed, plant-derived compounds into mineral soils, further enriching MAOM
241 in reduced organic S (Chakrawal, Lindahl, Qafoku, & Manzoni, 2024; Christ & David, 1996).
242 Compared to the A horizon, the B horizon showed weaker correlations with MAP – PET, likely
243 due to lower SOC and water concentration that disfavor development of reducing soil conditions.
244 Overall, these results demonstrate how climate-driven variations in temperature and moisture

245 modulate organic S oxidation and stabilization, with implications for the persistence of organic S
246 and release of plant-available sulfate in soils.

247 **3.3 Sulfate availability in soils**

248 Sulfur availability in soils, typically measured as exchangeable S, averaged $12 \pm 13 \mu\text{g/g}$ soil
249 in the A horizon and $41 \pm 80 \mu\text{g/g}$ soil in the B horizon (Fig. 5a). The proportion of exchangeable
250 S relative to total S ($f_{\text{exc S}}$) was also higher in the B horizon ($20 \pm 21\%$) than in the A horizon ($5 \pm$
251 6%) (Fig. 5b). Both the concentration and proportion of exchangeable S were consistently greater
252 in forest ecosystems compared to grasslands (Figs. S2e, f), suggesting enhanced S availability
253 under forest cover.

254 Exchangeable S in soils is influenced by climatic conditions and soil mineralogy, with positive
255 correlations with MAP – PET and oxalate-extracted Fe and Al (Fig. 5c). The strong association
256 with Fe and Al underscores the role of sulfate adsorption to metal oxides, which explains the higher
257 exchangeable S levels in the B horizon and in forest soils, where these oxides are more abundant
258 (Figs. 5a; S2e). MAP – PET likely enhances exchangeable S by promoting Fe/Al oxide formation
259 and increasing wet atmospheric sulfate deposition, though dry deposition, which may also
260 contribute (Luo et al., 2016), was not considered in this study.

261 Beyond environmental drivers, the size and oxidation state of organic S pools may play key
262 roles in S availability. Exchangeable S was positively correlated with LPOS concentration and the
263 oxidation state of MAOS, but negatively with the oxidation state of LPOS (Fig. 5c). The link to
264 LPOS may reflect its high lability and rapid turnover, which readily releases sulfate into the
265 exchangeable pool. The negative correlation with the oxidation state of LPOS likely reflects loss
266 of ester sulfate through hydrolysis, which both lowers its oxidation state and contributes sulfate to
267 the exchangeable pool. That is, oxidative decomposition of LPOS is an important source of
268 exchangeable sulfate. In contrast, the positive correlation with the oxidation state of MAOS

269 suggests that ester sulfate-rich MAOS, although stabilized by mineral associations, can gradually
270 release sulfate over time through enzymatic mineralization following MAOM destabilization. The
271 same factors and mechanisms influencing exchangeable S concentrations also apply to its
272 proportion relative to total S, except that POS concentration and Fe/Al oxides showed much weaker
273 effects (Fig. 5d). Overall, oxidation states of organic S seem to exert a stronger influence than pool
274 sizes on exchangeable sulfate. This finding suggests that the degree of organic matter
275 decomposition is a more critical regulator of S availability than the absolute amount of organic S
276 although atmospheric deposition of sulfate may obscure the conclusion.

277 **3.4 Role of minerals in sustaining sulfur fertility in soils**

278 Our findings indicate that minerals in the silt and clay fractions exert dual control on soil S
279 availability. On one hand, mineral associations concentrate organic S in MAOM and protect it from
280 microbial decomposition, particularly organic sulfate, presumably slowing down the release of
281 inorganic sulfate for biological uptake. On the other hand, the same minerals adsorb sulfate with
282 moderate binding strength, reducing leaching while maintaining its plant availability (J. Eriksen &
283 Askegaard, 2000). Elevated exchangeable sulfate in clay-rich soils therefore indicates that, despite
284 protection, MAOS continues to mineralize slowly because of MAOM destabilization and
285 subsequent mineralization (Bölscher et al., 2025; Jilling et al., 2025); the released sulfate is
286 efficiently retained on mineral surfaces and accumulates over time. Inorganic sulfate from
287 mineralization of POS and atmospheric deposition also enhances the adsorbed sulfate pool in soils.
288 Consequently, sulfate deficiency is common in sandy soils where low adsorption capacity
289 facilitates organic S mineralization and subsequent sulfate leaching, but rare in fine-textured soils
290 (Edwards, 1998). Thus, minerals function as sustained slow-release agents of plant-available
291 sulfate in soils.

292 **3.5 Implications for sulfur nutrient management**

293 Our results predict that projected warming accelerates S mineralization in both organic S pools
294 but shifting moisture regimes drive their divergence in supplying available S. Ignoring these
295 differences of the two pools in responses to climate change would lead to inaccurate predictions
296 and poor management strategies. Our findings suggest that in those warmer, drier regions (Dai,
297 2013), sulfate release from MAOS increases, heightening the risk of S leaching into aquatic
298 ecosystems, which can trigger severe environmental cascades such as mercury methylation,
299 eutrophication, and sulfide toxicity to native flora and fauna (Lamers et al., 2002; Regnell & Watras,
300 2019; Smolders & Roelofs, 1993; Wang & Chapman, 1999). In contrast, wetter terrestrial
301 ecosystems (O’Gorman, 2015) sequester more S in MAOS. In these areas, native plant
302 communities may face limited S availability, relying heavily on seasonal wet–dry cycles or climate-
303 driven hydrological shifts to sustain sulfate availability (Liu et al., 2021).

304 While derived from natural ecosystems, our findings offer a framework for targeted fertility
305 management in agricultural systems that leverages both POS and MAOS pools through practices
306 tailored to soil texture. In coarse, sandy soils, organic inputs (e.g., crop residues, cover crops, and
307 compost) build a labile POS pool for timely sulfate release (Barnard et al., 2025; Cardelli, Saviozzi,
308 Cipolli, & Riffaldi, 2008; Hansen, Eriksen, Jensen, Thorup-Kristensen, & Magid, 2021; Piutti et
309 al., 2015), while Fe- and Al-rich amendments or biochar expand MAOS, and retain sulfate and
310 limit its leaching (Ding et al., 2016; Lei et al., 2024; Penn, Bryant, Callahan, & McGrath, 2011).
311 Conversely, fine-textured (clay-rich) soils require moderate aeration and controlled MAOS
312 turnover (via brief drainage or shallow fertilizer banding) to release sulfate without depleting long-
313 term S reserves (Tariq et al., 2018; Zheng et al., 2024). Notably, any S management strategy must
314 be balanced with carbon sequestration goals. Because the mineral surfaces that stabilize MAOS
315 also protect SOC, aggressively mobilizing sulfate can oxidize stored carbon, whereas maximizing
316 SOC storage (e.g., via clay addition or no-till) can immobilize S and induce deficiencies (Janzen,
317 2006; Wright & Hons, 2005). Thus, an optimal strategy is to maintain a predominantly MAOC–

318 MAOS matrix while creating localized, temporal hotspots of S mineralization (through banded
319 fertilizer, rhizosphere redox shifts, or strip tillage) (Battisti, Zavattaro, Capo, & Blandino, 2022;
320 Bölscher et al., 2025; Brainard, Peachey, Haramoto, Luna, & Rangarajan, 2013; Tauchnitz,
321 Bischoff, Schrödter, Ebert, & Meissner, 2018) so that roots capture released sulfate and prevent S
322 deficiencies from undermining carbon sequestration efforts.

323 **Author Contributions**

324 Z.Z. conceptualized the study, performed experiments and data collection and analysis. M.F.C.
325 provided MAOM samples. H.-R.M. conducted structural equation modeling analysis. M.S.
326 collected S XANES data. M.Z. initiated and conceptualized the study, secured funding, and
327 supervised the project. Z.Z. and M.Z. co-wrote the manuscript, and all authors contributed to
328 editing and revision.

329 **Acknowledgments**

330 This work was partially supported by the U.S. National Science Foundation under DEB
331 2027284 and EAR-1752903. We thank Rebecca Even (Colorado State University) for her
332 assistance in MAOM separation. The National Ecological Observatory Network (NEON) is a
333 program sponsored by the U.S. National Science Foundation and operated under cooperative
334 agreement by Battelle. Sulfur K-edge XANES measurements were performed at the SXRMB
335 beamline at the Canadian Light Source (CLS), a national research facility of the University of
336 Saskatchewan, which is supported by the Canada Foundation for Innovation (CFI), the Natural
337 Sciences and Engineering Research Council (NSERC), the National Research Council (NRC), the
338 Canadian Institutes of Health Research (CIHR), the Government of Saskatchewan, and the
339 University of Saskatchewan.

340 **Competing Interest Statement**

341 The authors declare that they have no conflict of interest.

342 References

- 343 Averill, C., & Waring, B. 2018. "Nitrogen limitation of decomposition and decay: How can it
344 occur?". *Global Change Biology*, 24(4), 1417-1427.
- 345 Barnard, M., McKenna, B. A., Dalal, R. C., et al. 2025. "Sulfur's long game: 145 years of soil
346 sulfur speciation in the world's oldest agricultural experiments". *Global Change Biology*,
347 31(3), e70136.
- 348 Battisti, M., Zavattaro, L., Capo, L., et al. 2022. "Maize response to localized mineral or organic
349 NP starter fertilization under different soil tillage methods". *European Journal of*
350 *Agronomy*, 138, 126534.
- 351 Bölscher, T., Cardon, Z. G., Garcia Arredondo, M., et al. 2025. "Vulnerability of mineral-organic
352 associations in the rhizosphere". *Nature Communications*, 16(1), 5527.
- 353 Brainard, D. C., Peachey, R. E., Haramoto, E. R., et al. 2013. "Weed ecology and nonchemical
354 management under strip-tillage: implications for northern U.S. vegetable cropping
355 systems". *Weed Technology*, 27(1), 218-230.
- 356 Cardelli, R., Saviozzi, A., Cipolli, S., et al. 2008. "Compost and cattle manure as sources of
357 inorganic sulphur to soil". *Archives of Agronomy and Soil Science*, 54(2), 139-147.
- 358 Chakrawal, A., Lindahl, B. D., Qafoku, O., et al. 2024. "Comparing plant litter molecular
359 diversity assessed from proximate analysis and ¹³C NMR spectroscopy". *Soil Biology*
360 *and Biochemistry*, 197, 109517.
- 361 Christ, M. J., & David, M. B. 1996. "Temperature and moisture effects on the production of
362 dissolved organic carbon in a Spodosol". *Soil Biology and Biochemistry*, 28(9), 1191-
363 1199.
- 364 Churka Blum, S., Lehmann, J., Solomon, D., et al. 2013. "Sulfur forms in organic substrates
365 affecting S mineralization in soil". *Geoderma*, 200-201, 156-164.
- 366 Cotrufo, M. F., & Lavalley, J. M. 2022. Chapter One - Soil organic matter formation, persistence,
367 and functioning: A synthesis of current understanding to inform its conservation and
368 regeneration. In D. L. Sparks (Ed.), *Advances in agronomy* (Vol. 172, pp. 1-66):
369 Academic Press.
- 370 Cotrufo, M. F., Ranalli, M. G., Haddix, M. L., et al. 2019. "Soil carbon storage informed by
371 particulate and mineral-associated organic matter". *Nature Geoscience*, 12(12), 989-994.
- 372 Dai, A. 2013. "Increasing drought under global warming in observations and models". *Nature*
373 *Climate Change*, 3(1), 52-58.
- 374 Ding, Y., Liu, Y., Liu, S., et al. 2016. "Biochar to improve soil fertility. A review". *Agronomy for*
375 *Sustainable Development*, 36(2), 36.
- 376 Edwards, P. J. 1998. "Sulfur cycling, retention, and mobility in soils: a review".
- 377 Eriksen, J. 2009. Chapter 2 Soil sulfur cycling in temperate agricultural systems. In *Advances in*
378 *agronomy* (Vol. 102, pp. 55-89): Academic Press.
- 379 Eriksen, J., & Askegaard, M. 2000. "Sulphate leaching in an organic crop rotation on sandy soil
380 in Denmark". *Agriculture, Ecosystems & Environment*, 78(2), 107-114.
- 381 Eriksen, J., Murphy, M. D., & Schnug, E. 1998. The soil sulphur cycle. In E. Schnug (Ed.),
382 *Sulphur in Agroecosystems* (pp. 39-73). Dordrecht: Springer Netherlands.
- 383 Fakhraee, M., Li, J., & Katsev, S. 2017. "Significant role of organic sulfur in supporting
384 sedimentary sulfate reduction in low-sulfate environments". *Geochimica et*
385 *Cosmochimica Acta*, 213, 502-516.

386 Favaro, A., Carrillo, Y., Singh, B., et al. 2025. "Nutrient-rich mineral-associated organic matter
387 limits carbon storage under elevated carbon dioxide in a low phosphorus Eucalyptus
388 woodland soil". *Global Change Biology*, 31(11), e70585.

389 Feinberg, A., Stenke, A., Peter, T., et al. 2021. "Reductions in the deposition of sulfur and
390 selenium to agricultural soils pose risk of future nutrient deficiencies". *Communications
391 Earth & Environment*, 2(1), 101.

392 Gerson, J. R., & Hinckley, E.-L. S. 2023. "It Is time to develop sustainable management of
393 agricultural sulfur". *Earth's Future*, 11(11), e2023EF003723.

394 Haneklaus, S., Bloem, E., & Schnug, E. 2003. The global sulphur cycle and its links to plant
395 environment. In Y. P. Abrol & A. Ahmad (Eds.), *Sulphur in Plants* (pp. 1-28). Dordrecht:
396 Springer Netherlands.

397 Haneklaus, S., Bloem, E., & Schnug, E. 2008. History of sulfur deficiency in crops. In *Sulfur: A
398 Missing Link between Soils, Crops, and Nutrition* (pp. 45-58).

399 Hansen, V., Eriksen, J., Jensen, L. S., et al. 2021. "Towards integrated cover crop management:
400 N, P and S release from aboveground and belowground residues". *Agriculture,
401 Ecosystems & Environment*, 313, 107392.

402 Heckman, K., Hicks Pries, C. E., Lawrence, C. R., et al. "Beyond bulk: Density fractions explain
403 heterogeneity in global soil carbon abundance and persistence". *Global Change Biology*,
404 28(3), 1178-1196.

405 Heinze, S., Hemkemeyer, M., Schwalb, S. A., et al. 2021. "Microbial Biomass Sulphur—An
406 Important Yet Understudied Pool in Soil". *Agronomy*, 11(8), 1606.

407 Hinckley, E.-L. S., Crawford, J. T., Fakhraei, H., et al. 2020. "A shift in sulfur-cycle manipulation
408 from atmospheric emissions to agricultural additions". *Nature Geoscience*, 13(9), 597-
409 604.

410 Huffman, G. P., Mitra, S., Huggins, F. E., et al. 1991. "Quantitative analysis of all major forms of
411 sulfur in coal by x-ray absorption fine structure spectroscopy". *Energy & Fuels*, 5(4),
412 574-581.

413 Janzen, H. H. 2006. "The soil carbon dilemma: Shall we hoard it or use it?". *Soil Biology and
414 Biochemistry*, 38(3), 419-424.

415 Jia, J., Cao, Z., Liu, C., et al. 2019. "Climate warming alters subsoil but not topsoil carbon
416 dynamics in alpine grassland". *Global Change Biology*, 25(12), 4383-4393.

417 Jilling, A., Grandy, A. S., Daly, A. B., et al. 2025. "Evidence for the existence and ecological
418 relevance of fast-cycling mineral-associated organic matter". *Communications Earth &
419 Environment*, 6(1), 690.

420 Jilling, A., Keiluweit, M., Contosta, A. R., et al. 2018. "Minerals in the rhizosphere: overlooked
421 mediators of soil nitrogen availability to plants and microbes". *Biogeochemistry*, 139(2),
422 103-122.

423 Keiluweit, M., Wanzek, T., Kleber, M., et al. 2017. "Anaerobic microsites have an unaccounted
424 role in soil carbon stabilization". *Nature Communications*, 8(1), 1771.

425 Kirkby, C. A., Richardson, A. E., Wade, L. J., et al. 2013. "Carbon-nutrient stoichiometry to
426 increase soil carbon sequestration". *Soil Biology and Biochemistry*, 60, 77-86.

427 Kovar, J. L., & Grant, C. A. 2011. Nutrient Cycling in Soils: Sulfur. In *Soil Management:
428 Building a Stable Base for Agriculture* (pp. 103-115).

429 Lamers, L. P. M., Falla, S.-J., Samborska, E. M., et al. 2002. "Factors controlling the extent of
430 eutrophication and toxicity in sulfate-polluted freshwater wetlands". *Limnology and
431 Oceanography*, 47(2), 585-593.

432 Lavalley, J. M., Soong, J. L., & Cotrufo, M. F. 2020. "Conceptualizing soil organic matter into
433 particulate and mineral-associated forms to address global change in the 21st century".
434 *Global Change Biology*, 26(1), 261-273.

435 Lei, K., Dai, W., Wang, J., et al. 2024. "Biochar and straw amendments over a decade divergently
436 alter soil organic carbon accumulation pathways". *Agronomy*, 14(9), 2176.

437 Leuthold, S., Lavallee, J. M., Haddix, M. L., et al. 2024. "Contrasting properties of soil organic
438 matter fractions isolated by different physical separation methodologies". *Geoderma*,
439 445, 116870.

440 Lieberman, H. P., von Sperber, C., & Kallenbach, C. M. 2025. "Soil phosphorus dynamics are an
441 overlooked but dominant control on mineral-associated organic matter". *Global Change
442 Biology*, 31(7), e70307.

443 Liu, Q., Romani, M., Wang, J., et al. 2021. "Alternating wet–dry cycles rather than sulfate
444 fertilization control pathways of methanogenesis and methane turnover in rice straw-
445 amended paddy soil". *Environmental Science & Technology*, 55(17), 12075-12083.

446 Lugato, E., Lavallee, J. M., Haddix, M. L., et al. 2021. "Different climate sensitivity of particulate
447 and mineral-associated soil organic matter". *Nature Geoscience*.

448 Luo, W., Dijkstra, F. A., Bai, E., et al. 2016. "A threshold reveals decoupled relationship of sulfur
449 with carbon and nitrogen in soils across arid and semi-arid grasslands in northern China".
450 *Biogeochemistry*, 127(1), 141-153.

451 Manceau, A., & Nagy, K. L. 2012. "Quantitative analysis of sulfur functional groups in natural
452 organic matter by XANES spectroscopy". *Geochimica et Cosmochimica Acta*, 99, 206-
453 223.

454 Messick, D., Fan, M., & De Brey, C. 2005. "Global sulfur requirement and sulfur fertilizers".
455 *FAL—Agric Res*, 283, 97-104.

456 Niknahad-Gharmakher, H., Piutti, S., Machet, J. M., et al. 2012. "Mineralization-immobilization
457 of sulphur in a soil during decomposition of plant residues of varied chemical
458 composition and S content". *Plant and soil*, 360(1), 391-404.

459 O’Gorman, P. A. 2015. "Precipitation extremes under climate change". *Current Climate Change
460 Reports*, 1(2), 49-59.

461 Ofiti, N. O. E., Zosso, C. U., Soong, J. L., et al. 2021. "Warming promotes loss of subsoil carbon
462 through accelerated degradation of plant-derived organic matter". *Soil Biology and
463 Biochemistry*, 156, 108185.

464 Penn, C. J., Bryant, R. B., Callahan, M. P., et al. 2011. "Use of industrial by-products to sorb and
465 retain phosphorus". *Communications in Soil Science and Plant Analysis*, 42(6), 633-644.

466 Piutti, S., Slezack-Deschaumes, S., Niknahad-Gharmakher, H., et al. 2015. "Relationships
467 between the density and activity of microbial communities possessing arylsulfatase
468 activity and soil sulfate dynamics during the decomposition of plant residues in soil".
469 *European Journal of Soil Biology*, 70, 88-96.

470 Prietzel, J., Botzaki, A., Tyufekchieva, N., et al. 2011. "Sulfur speciation in soil by S K-edge
471 XANES spectroscopy: comparison of spectral deconvolution and linear combination
472 fitting". *Environmental Science & Technology*, 45(7), 2878-2886.

473 Prietzel, J., Thieme, J., Salomé, M., et al. 2007. "Sulfur K-edge XANES spectroscopy reveals
474 differences in sulfur speciation of bulk soils, humic acid, fulvic acid, and particle size
475 separates". *Soil Biology and Biochemistry*, 39(4), 877-890.

476 Regnell, O., & Watras, C. J. 2019. "Microbial mercury methylation in aquatic environments: A
477 critical review of published field and laboratory studies". *Environmental Science &
478 Technology*, 53(1), 4-19.

479 Ritchie, H., & Roser, M. 2021. "Air Pollution". *Published Online at OurWorldInData.org*.
480 Available online: <https://ourworldindata.org/explorers/air-pollution>.

481 Singh, B., Rengel, Z., & Bowden, J. W. 2006. "Carbon, nitrogen and sulphur cycling following
482 incorporation of canola residue of different sizes into a nutrient-poor sandy soil". *Soil
483 Biology and Biochemistry*, 38(1), 32-42.

484 Smolders, A., & Roelofs, J. G. M. 1993. "Sulphate-mediated iron limitation and eutrophication in
485 aquatic ecosystems". *Aquatic Botany*, 46(3), 247-253.

486 Solomon, D., Lehmann, J., & Martínez, C. E. 2003. "Sulfur K-edge XANES spectroscopy as a
487 tool for understanding sulfur dynamics in soil organic matter". *Soil Science Society of
488 America Journal*, 67(6), 1721-1731.

489 Soong, J. L., & Cotrufo, M. F. 2015. "Annual burning of a tallgrass prairie inhibits C and N
490 cycling in soil, increasing recalcitrant pyrogenic organic matter storage while reducing N
491 availability". *Global Change Biology*, 21(6), 2321-2333.

492 Spohn, M. 2020. "Phosphorus and carbon in soil particle size fractions: A synthesis".
493 *Biogeochemistry*, 147(3), 225-242.

494 Spohn, M. 2024. "Preferential adsorption of nitrogen- and phosphorus-containing organic
495 compounds to minerals in soils: A review". *Soil Biology and Biochemistry*, 194, 109428.

496 Tanikawa, T., Hashimoto, Y., Yamaguchi, N., et al. 2014. "Sulfur accumulation in Melanodermis
497 during development by upbuilding pedogenesis since 14–15cal.ka". *Geoderma*, 232-234,
498 609-618.

499 Tanikawa, T., Noguchi, K., Nakanishi, K., et al. 2014. "Sequential transformation rates of soil
500 organic sulfur fractions in two-step mineralization process". *Biology and Fertility of
501 Soils*, 50(2), 225-237.

502 Tanikawa, T., Sase, H., Fukushima, S., et al. 2022. "Sulfur accumulation in soil in a forested
503 watershed historically exposed to air pollution in central Japan". *Geoderma*, 407, 115544.

504 Tariq, A., Jensen, L. S., Sander, B. O., et al. 2018. "Paddy soil drainage influences residue carbon
505 contribution to methane emissions". *Journal of Environmental Management*, 225, 168-
506 176.

507 Tauchnitz, N., Bischoff, J., Schrödter, M., et al. 2018. "Nitrogen efficiency of strip-till combined
508 with slurry band injection below the maize seeds". *Soil and Tillage Research*, 181, 11-18.

509 Tolu, J., Bouchet, S., Helfenstein, J., et al. 2022. "Understanding soil selenium accumulation and
510 bioavailability through size resolved and elemental characterization of soil extracts".
511 *Nature Communications*, 13(1), 6974.

512 Wang, F., & Chapman, P. M. 1999. "Biological implications of sulfide in sediment—a review
513 focusing on sediment toxicity". *Environmental Toxicology and Chemistry*, 18(11), 2526-
514 2532.

515 Wojdyr, M. 2010. "Fityk: a general-purpose peak fitting program". *Journal of Applied
516 Crystallography*, 43(5 Part 1), 1126-1128.

517 Wright, A. L., & Hons, F. M. 2005. "Carbon and nitrogen sequestration and soil aggregation
518 under sorghum cropping sequences". *Biology and Fertility of Soils*, 41(2), 95-100.

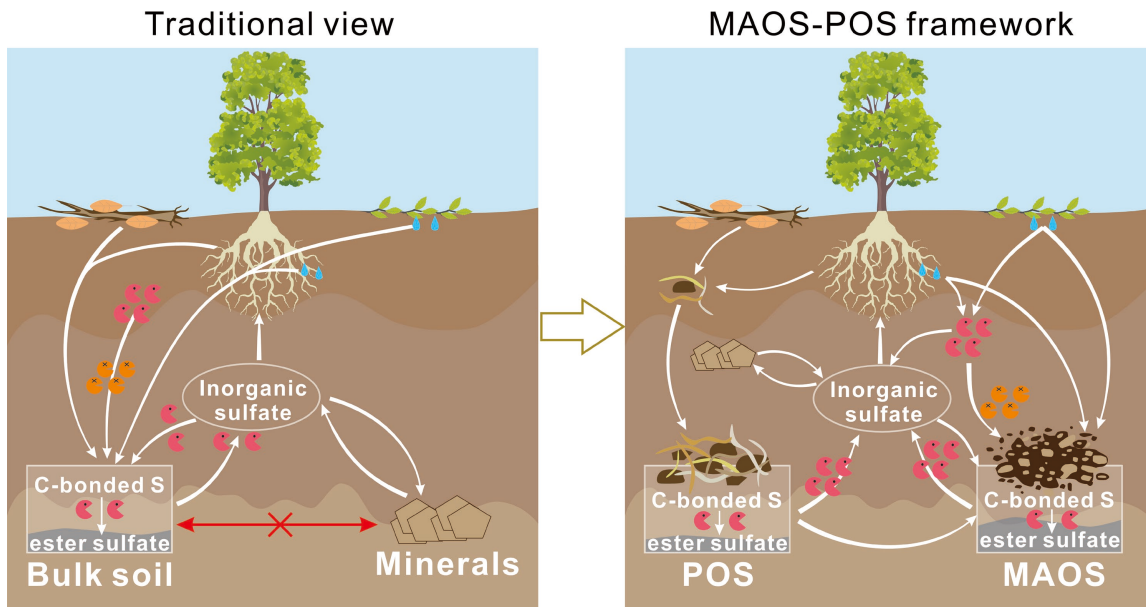
519 Yang, C., Lu, G., Chen, M., et al. 2016. "Spatial and temporal distributions of sulfur species in
520 paddy soils affected by acid mine drainage in Dabaoshan sulfide mining area, South
521 China". *Geoderma*, 281, 21-29.

522 Zeng, T., Arnold, W. A., & Toner, B. M. 2013. "Microscale characterization of sulfur speciation
523 in lake sediments". *Environmental Science & Technology*, 47(3), 1287-1296.

524 Zheng, Y., Jin, J., Wang, X., et al. 2024. "Disentangling the effect of nitrogen supply on the
525 priming of soil organic matter: A critical review". *Critical Reviews in Environmental
526 Science and Technology*, 54(8), 676-697.

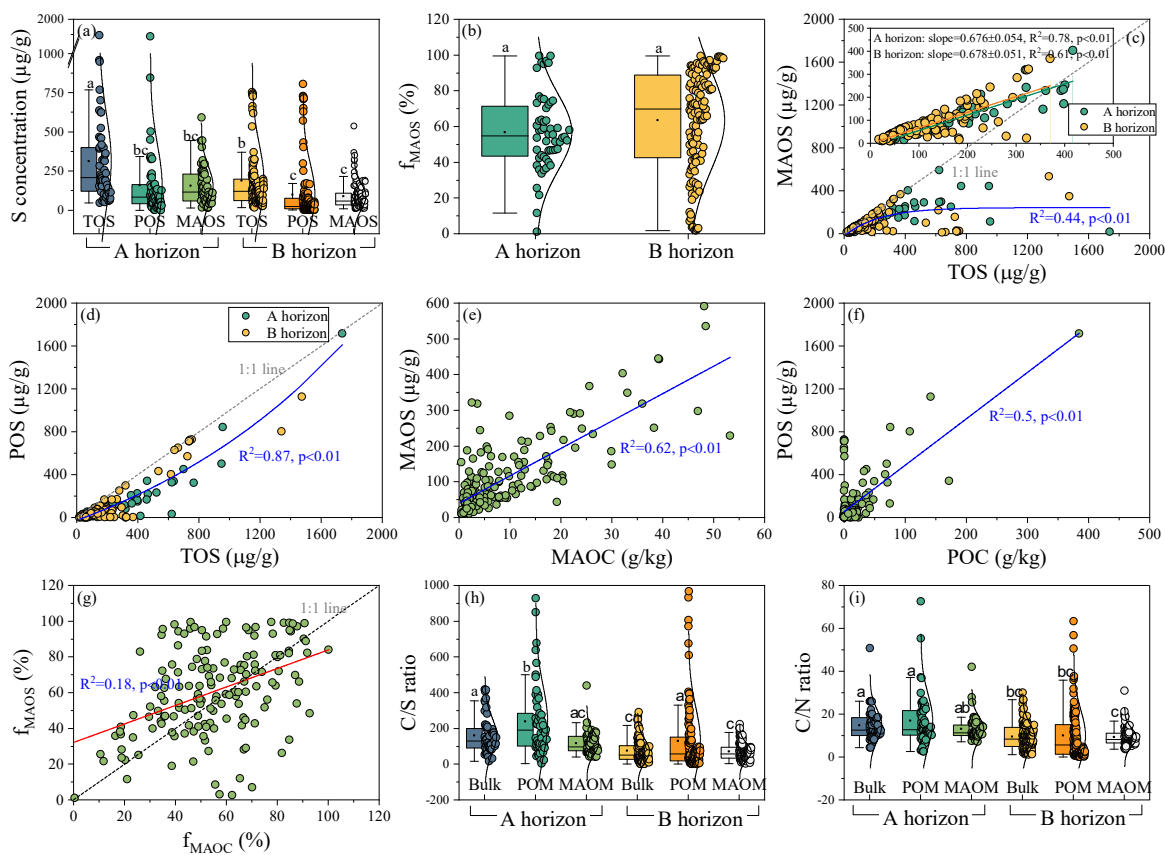
527 Zhu, M., Dam, T. T. N., Chadwick, O., et al. 2026. "Precipitation-driven shifts in organic sulfur
528 decomposition and oxidation state along rainfall gradients". *Environmental Science &
529 Technology*.

530



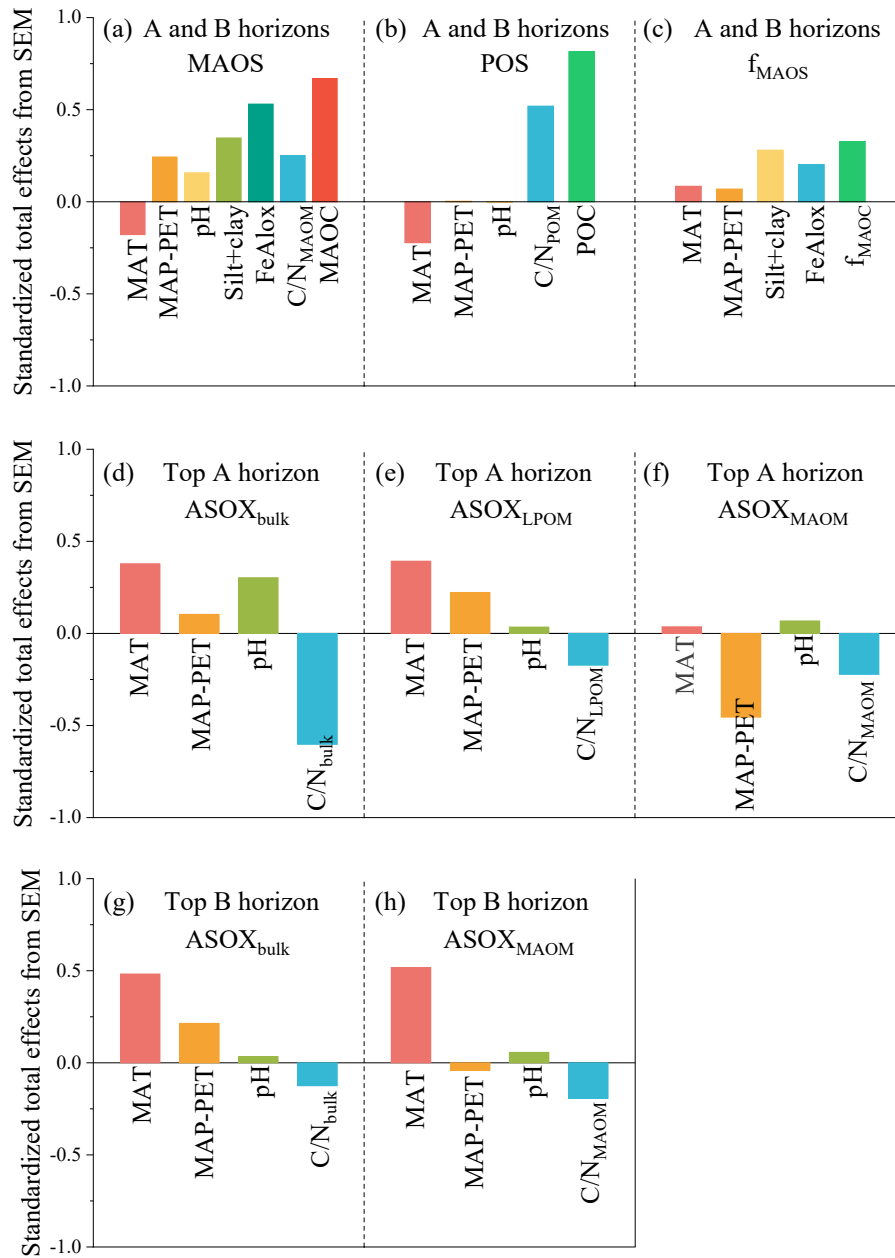
531
 532
 533
 534
 535
 536
 537
 538
 539

Figure 1. A two-pool conceptual framework for cycling of soil organic sulfur. Traditional research has treated organic-S mineralization at the bulk-soil scale, overlooking the stabilizing role of minerals. Here we separate organic S into particulate organic S (POS), largely derived from fragmented and translocated plant residues, and mineral-associated organic S (MAOS), formed through sorption of soluble compounds or by microbial transformation and subsequent deposition of microbial residues. Relative to POS, MAOS is typically more decomposed, chemically diverse, and sensitive to environmental change, yet its association with mineral surfaces constrains further conversion to plant-available sulfate. Ancillary pathways that influence inorganic sulfate are omitted for clarity.



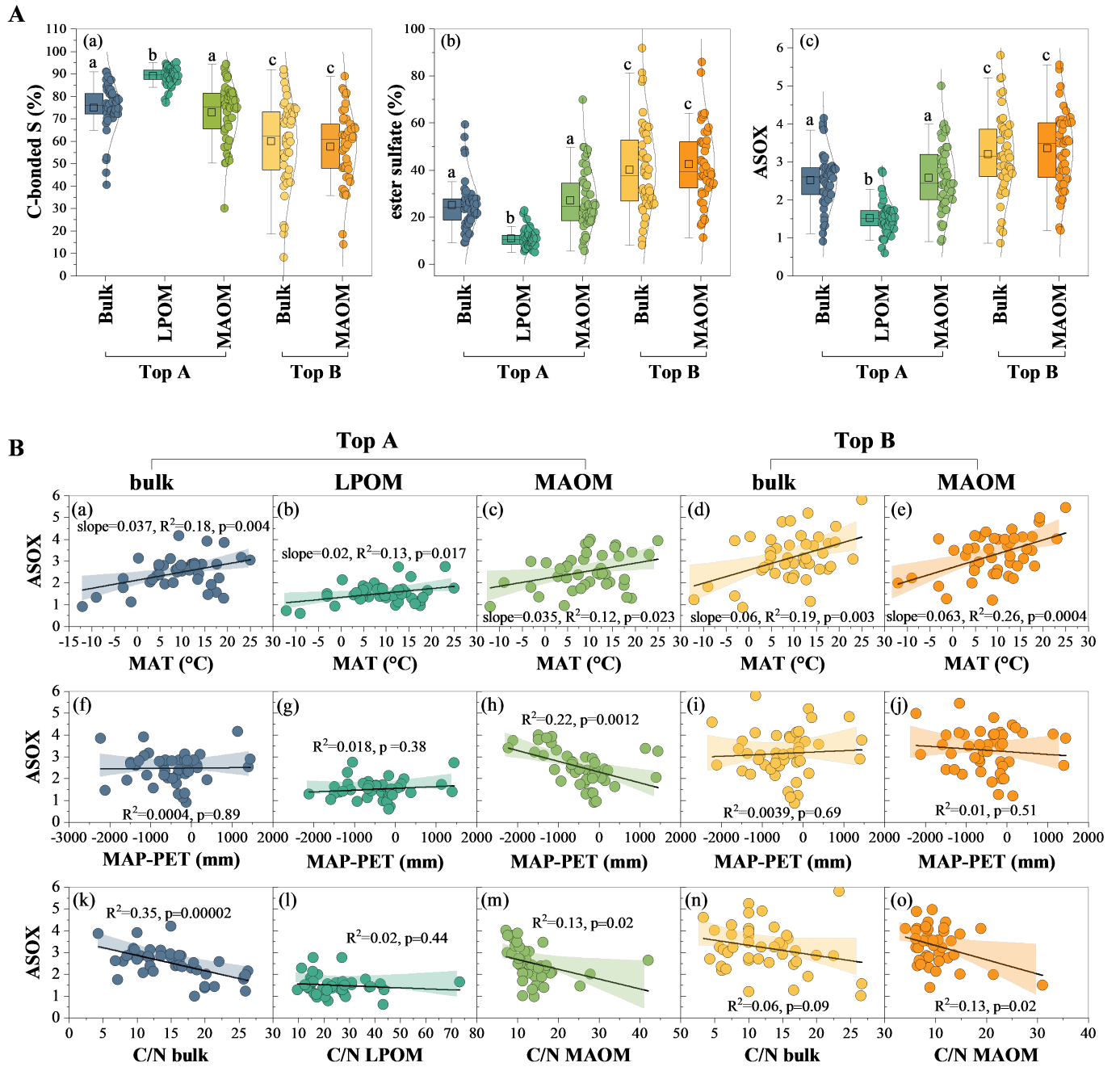
540
541
542
543
544
545
546

Figure 2. Distributions of MAOS and POS. (a) Distribution of organic S in bulk soil (TOS), POS and MAOS fractions in the A and B horizons. (b) Fractions of MAOS (f_{MAOS}) in the A and B horizons. (c, d) Correlations between TOS and MAOS or POS in concentrations in the A and B horizons. (e, f, g) Correlations between MAOS and MAOC, POS and POC, and f_{MAOS} and f_{MAOC} . (h, i) The C/S and C/N ratios in bulk soil, POM and MAOM fractions in the A and B horizons. POM is the sum of light POM and heavy POM. All concentrations are expressed as $\mu\text{g S/g}$ bulk soils.



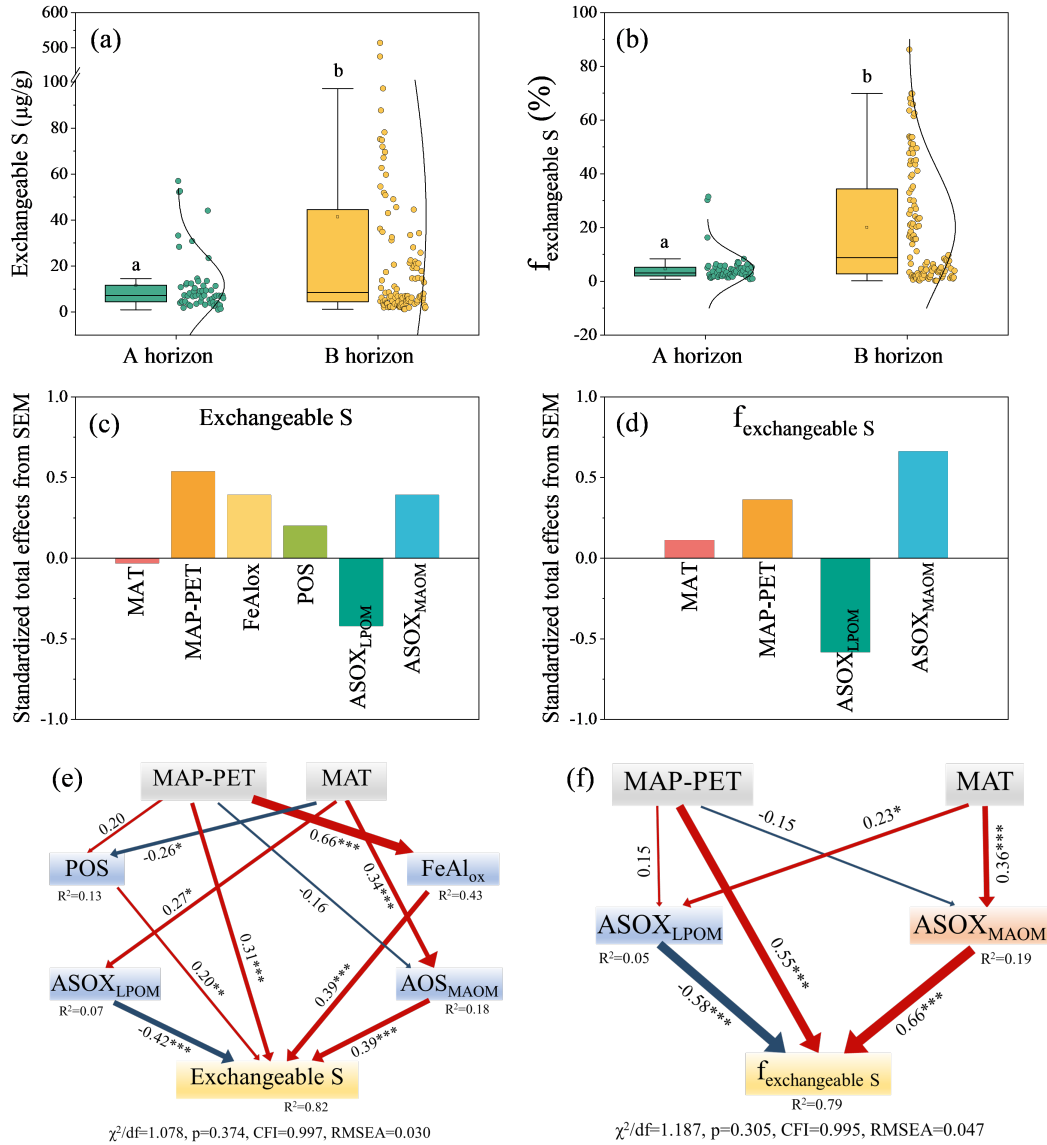
547

548 **Figure 3.** Standardized total effects (direct plus indirect effects) derived from the structural equation modelling. These effects show
 549 the controls on: (a-c) MAOS concentrations, POS concentrations, and f_{MAOS} in the A and B horizons; (d-f) average S oxidation
 550 states (ASOX) in bulk soil, LOPM and MAOM in the top A horizons; and (g, h) ASOX in bulk soil and MAOM in the top B
 551 horizons. The amount of LPOM material in B horizons was not sufficient for characterization.



552
553
554
555
556

Figure 4. Chemical composition and oxidation states of MAOS and LPOS. (A) The chemical composition and average sulfur oxidation states (ASOX) in bulk soil, light particulate organic matter (LPOM) and mineral-associated organic matter (MAOM) in the top A and B horizons, and (B) their correlations with mean annual temperature (MAT), effective soil moisture (mean annual precipitation minus potential evapotranspiration, i.e., MAP-PET), and the C/N ratio.



557

558 **Figure 5.** Sulfate availability and effects. (a, b) Concentration and proportion of exchangeable S in the A and
 559 B horizons. (c, d) Standardized total effects (direct plus indirect effects) derived from (e, f) the structural
 560 equation modelling (SEM) identifying the controls on exchangeable S concentration and percentage in the A
 561 and B horizons.

Supporting Information for

Mineral stabilization of soil organic sulfur at the continental scale

Zhuojun Zhang^{1,2}, M. Francesca Cotrufo³, Benjamin L. Turner⁴, Hai-Ruo Mao¹, Chao Liang⁵, Mohsen Shakouri⁶, and Mengqiang Zhu^{1,7*}

¹ Department of Ecosystem Science and Management, University of Wyoming, Laramie, Wyoming 82071, United States

² State Key Laboratory of Lake and Watershed Science for Water Security, Nanjing Institute of Geography and Limnology, Chinese Academy of Sciences, Nanjing, Jiangsu 211135, China

³ Department of Soil and Crop Science and Natural Resource Ecology Laboratory, Colorado State University, Fort Collins, Colorado 80523, United States

⁴ Institute of Agriculture and Life Sciences, Gyeongsang National University, 501 Jinju-Daero, Jinju 52828, South Korea

⁵ Institute of Applied Ecology, Chinese Academy of Sciences, Shenyang, Liaoning 110016, China

⁶ Canadian Light Source Inc., University of Saskatchewan, Saskatoon, Saskatchewan S7N 2V3, Canada

⁷ Department of geological, Environmental, and Planetary Sciences, University of Maryland, College Park, Maryland 20740, United States

* Corresponding author: Mengqiang Zhu

Email: mqzhu@umd.edu

This PDF file includes:

Figures S1 to S9
Tables S2

Other supporting materials for this manuscript include the following:

Table S1

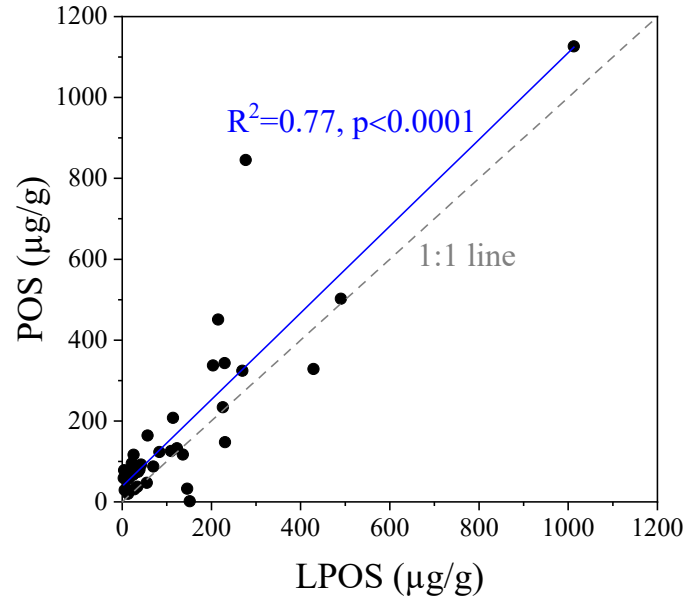


Fig. S1. Correlation between LPOS and POS in the topsoil.

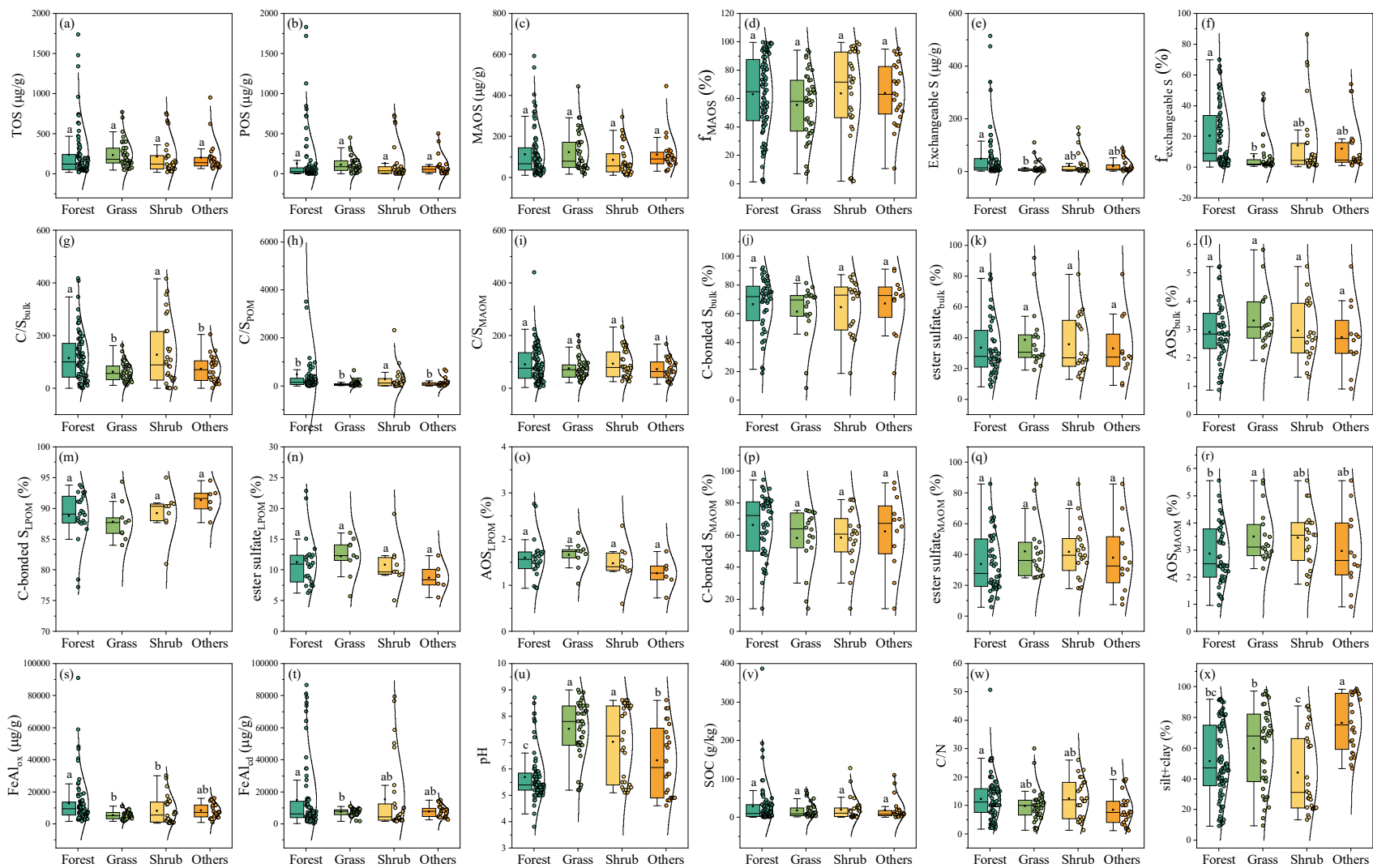


Fig. S2. A comparative analysis of key organic S and soil characteristics across different ecosystems.

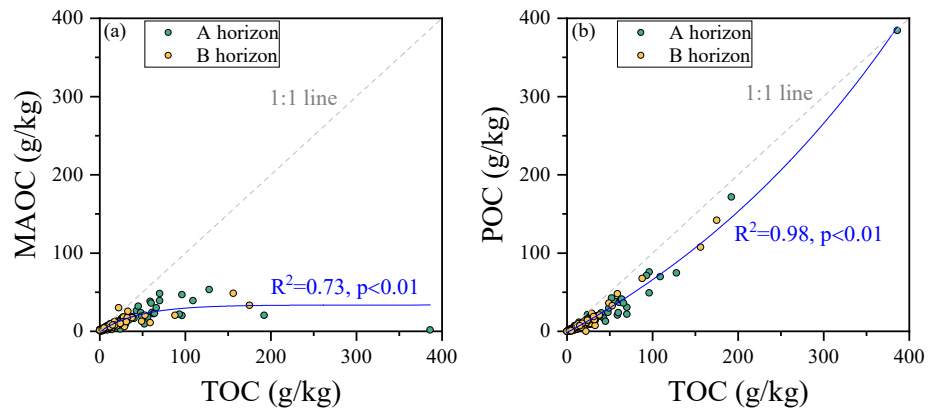


Fig. S3. Correlations between TOC (g/kg soil) and concentrations of MAOC and POC (g/kg soil) in the A and B horizons.

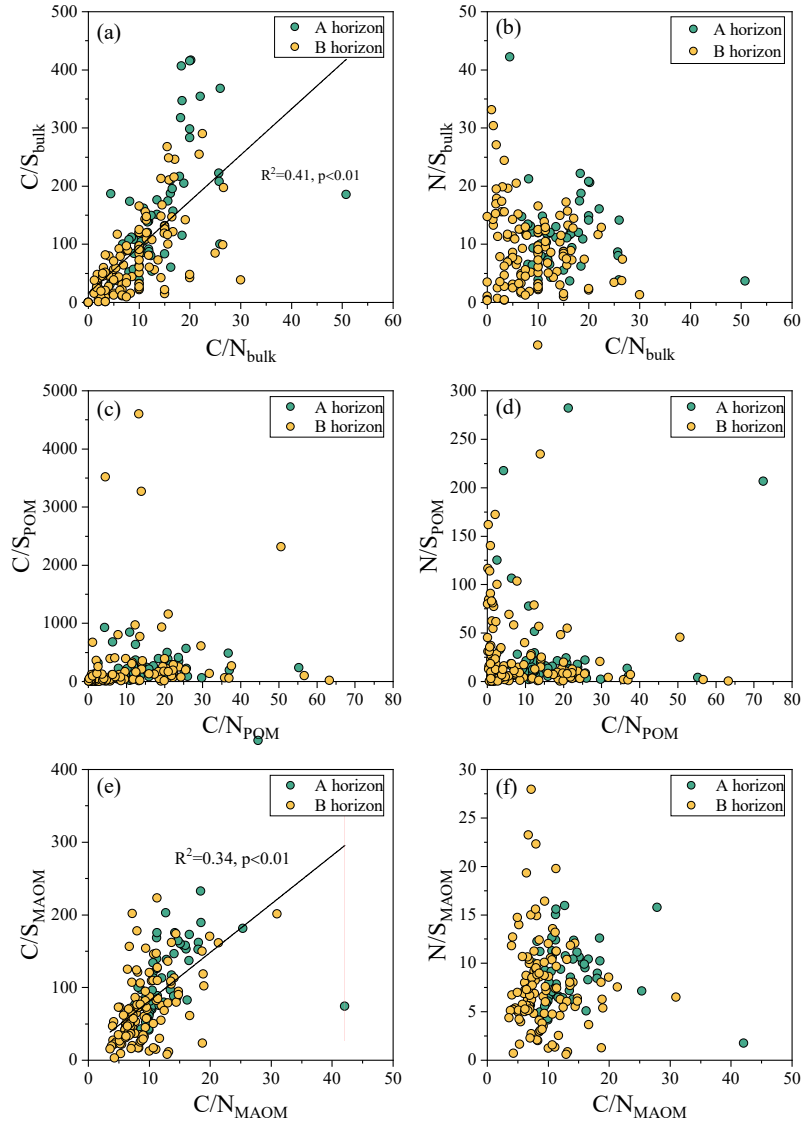


Fig. S4. Correlations between C/S and C/N ratios, as well as N/S and C/N ratios, in bulk soil, POM, and MAOM fractions.

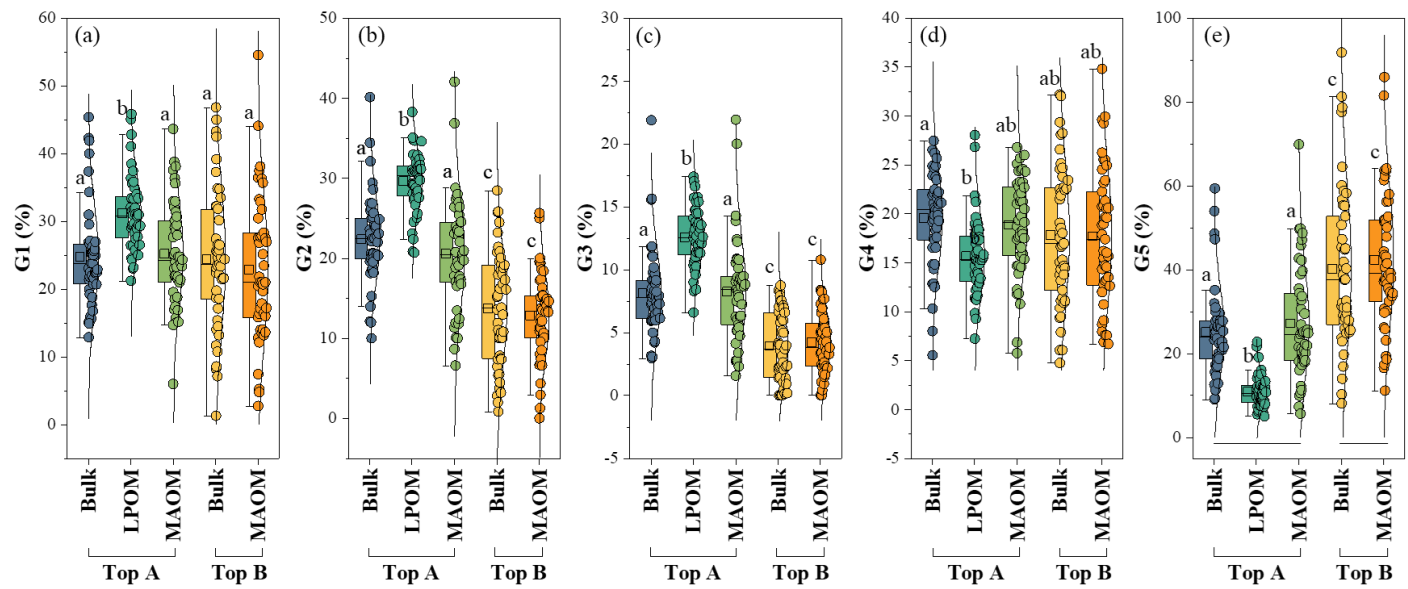


Fig. S5. The chemical composition of organic S groups in bulk soil, LOPM and MAOM in the top A and B horizons.

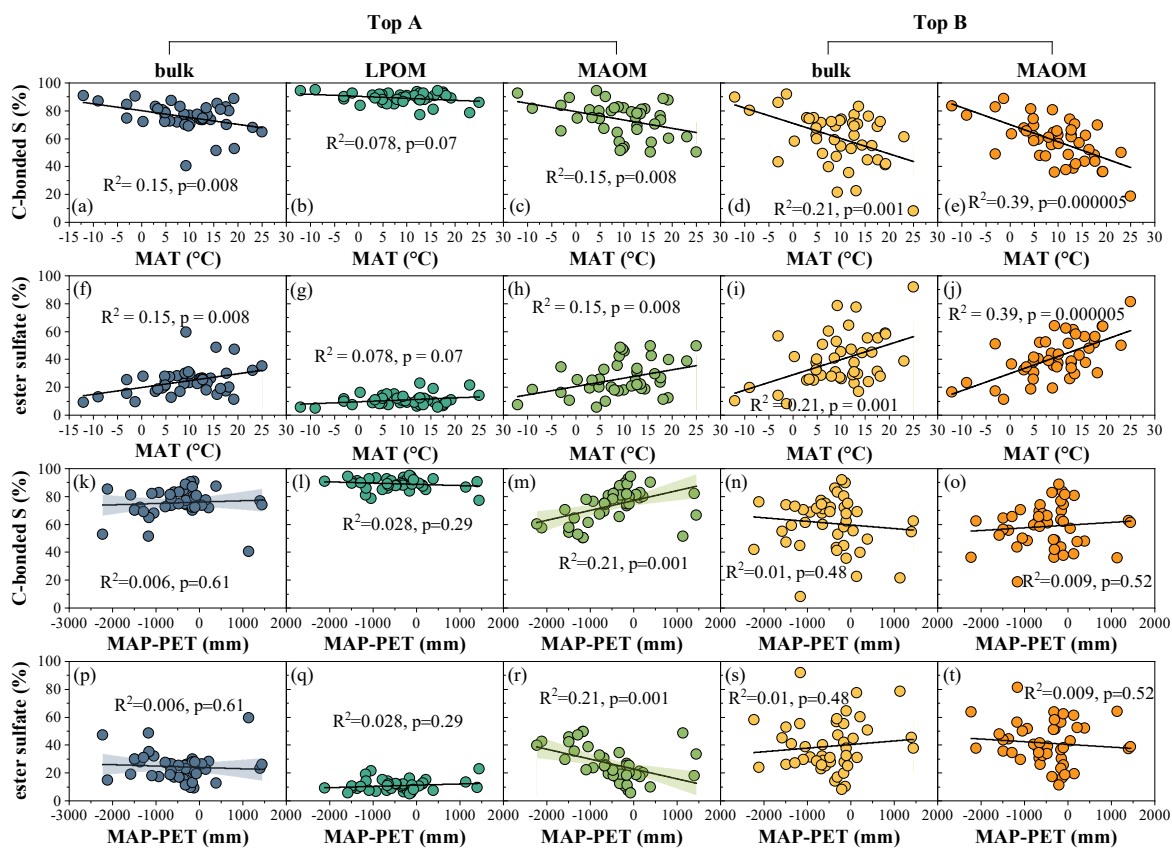


Fig. S6. Correlations of the proportions of C-bonded S and ester sulfate with MAT and MAP-PET in bulk soil, LOPM, and MAOM across the top A and B horizons.

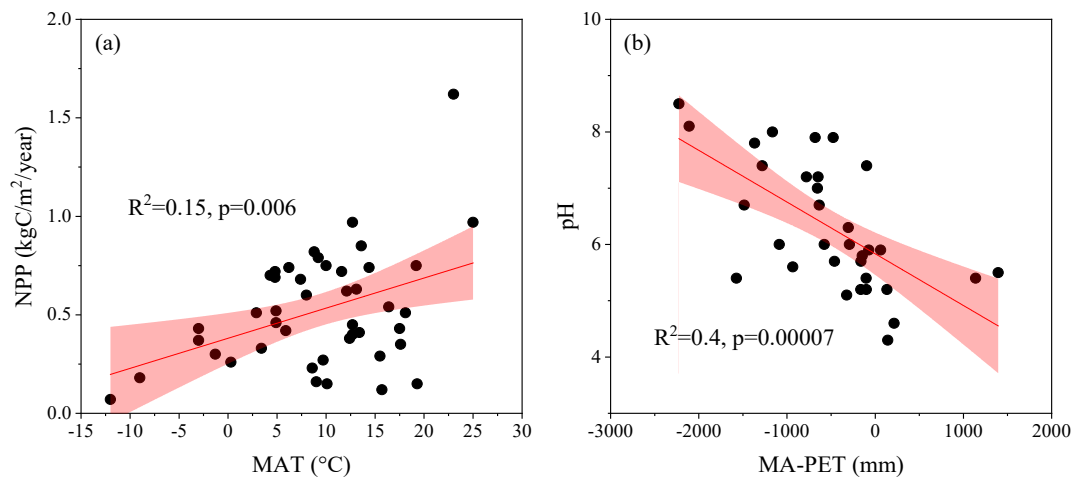


Fig. S7. (a) Correlation between NPP and MAT, and (b) correlation between soil pH and MAP-PET (b).

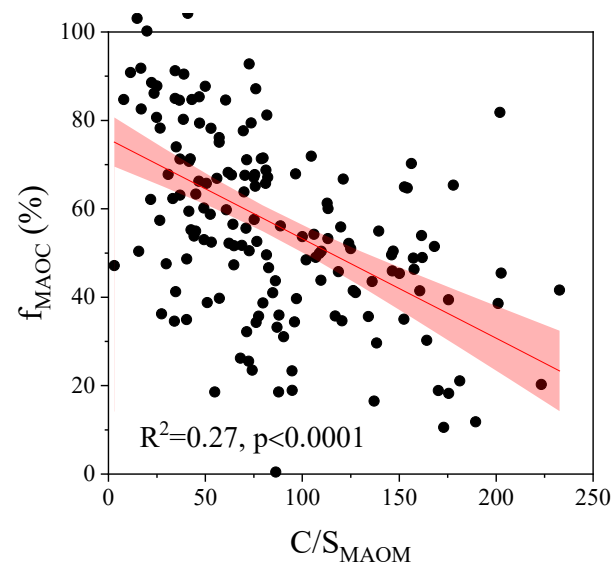


Fig. S8. Correlation between f_{MAOC} and C/S_{MAOM} .

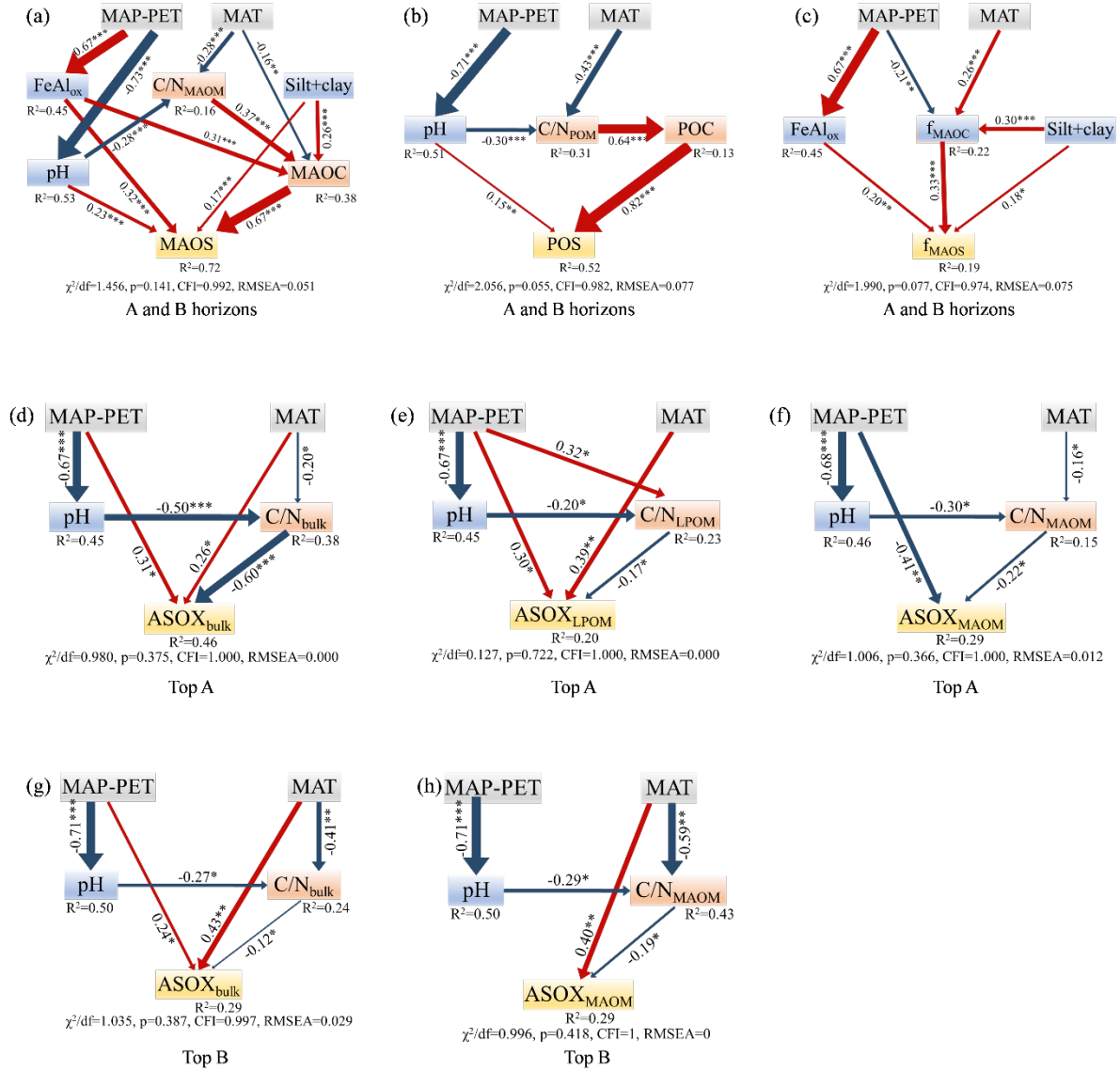


Fig. S9. A schematic representation of the structural equation modelling used to identify the controls on MAOS concentrations, POS concentrations, f_{MAOS} in the A and B horizons (a-c), ASOX in bulk soil, LOPM and MAOM in the top A horizons (d-f), and ASOX in bulk soil and MAOM in the top B horizons (g, h).

Table S2 The relative proportions of S species obtained from the Gaussian curve fitting results.

Sample name	G1 (%)	G2 (%)	G3 (%)	G4 (%)	G5 (%)	Average oxidation state
ABBY_A_bulk	23.0	23.6	8.2	21.9	23.3	2.5
BARR_Cgjj_bulk	45.4	26.8	8.5	10.3	9.0	0.9
BART_A_bulk	15.1	40.1	15.6	16.6	12.7	1.9
BLAN_Ap1_bulk	19.9	23.1	6.0	24.9	26.2	2.8
BONA_Bg Oajj_bulk	37.4	20.6	7.3	19.2	15.6	1.8
CLBJ_A_bulk	42.3	19.6	6.0	14.9	17.3	1.6
CPER_A_bulk	21.4	26.0	7.4	17.4	27.8	2.6
DCFS_A1_bulk	21.8	22.1	7.8	24.2	24.0	2.7
DEJU_A_bulk	31.0	20.3	9.2	14.3	25.2	2.2
DELA_A1_bulk	22.5	20.4	6.2	21.0	29.9	2.8
GRSM_A1_bulk	23.8	20.6	8.0	23.9	23.7	2.6
GUAN_A_bulk	19.3	18.1	6.0	24.7	32.0	3.2
HARV_A_bulk	15.9	22.5	6.9	26.5	28.2	3.1
HEAL_A Cjj_bulk	41.9	26.2	9.8	12.8	9.4	1.1
JERC_A_bulk	26.9	34.4	21.9	5.5	11.3	1.3
JORN_A_bulk	29.6	32.1	15.7	8.0	14.6	1.5
OAES_Klemme_A_bulk	15.6	12.1	3.1	20.6	48.5	3.9
KONA_AP_bulk	26.7	19.9	5.0	22.1	26.3	2.6
KONZ_A_bulk	21.9	20.6	6.0	24.9	26.6	2.8
LAJA_Ap_bulk	24.9	15.3	4.2	20.4	35.2	3.0
LENO_A_bulk	27.2	24.1	9.2	19.4	20.1	2.2
Mameyes_A_bulk	12.9	14.0	4.3	14.8	54.0	4.0
MLBS_A_bulk	23.8	25.0	6.3	22.5	22.5	2.5
MOAB_A_bulk	25.4	18.6	6.5	19.9	29.7	2.7
NIWO_A1_bulk	17.6	18.7	8.3	27.5	27.8	3.1
NOGP_A1_bulk	20.8	22.5	7.8	21.6	27.3	2.8
ONAQ_A1_bulk	25.3	19.9	7.4	17.3	30.0	2.7
ORNL_A_bulk	18.8	23.8	7.2	23.8	26.4	2.8
PUUM_Bw1_bulk	21.6	19.5	6.6	26.2	26.0	2.9
RMNP_A_bulk	26.2	26.8	11.8	18.3	16.8	2.0
SCBI_A_bulk	22.4	23.8	7.9	23.5	22.4	2.6
SERC_A_bulk	24.9	24.1	7.9	20.3	22.7	2.4
SJER_A1_bulk	34.3	20.5	9.7	16.6	18.9	1.9
SOAP_A1_bulk	22.3	29.4	11.9	18.6	17.8	2.2
SRER_A_bulk	16.7	12.0	3.0	21.0	47.2	3.8
STEI_A_bulk	25.5	22.8	8.9	22.0	20.8	2.4
STER_Ap1_bulk	25.0	18.2	6.0	19.9	30.9	2.8
TEAK_A_bulk	25.6	28.6	11.1	17.6	17.1	2.0
TOOL_Bg_bulk	40.0	25.1	9.2	12.9	12.9	1.3
TREE_A E_bulk	20.7	22.0	7.3	22.2	27.8	2.8
UKFS_A1_bulk	22.5	20.3	6.1	25.7	25.4	2.8

UNDE_A_bulk	22.9	25.7	11.0	21.2	19.2	2.3
WOOD_AO_bulk	25.9	23.1	8.2	21.1	21.6	2.4
WREF_Ac_bulk	15.0	10.0	3.1	12.5	59.4	4.2
YELL_A_bulk	27.0	24.9	10.2	19.3	18.7	2.1
ABBY_Bw1_bulk	37.2	6.5	1.4	9.4	45.5	2.9
BARR_CgjjF2_bulk	39.2	28.4	8.3	13.8	10.3	1.2
BART_Bs1_bulk	18.7	13.6	6.7	10.4	50.7	3.6
BLAN_Bt1_bulk	32.2	7.4	2.1	11.1	47.2	3.1
BONA_Cg_bulk	43.2	20.8	7.1	15.0	13.9	1.4
CLBJ_Bt1_bulk	32.2	15.2	2.2	19.1	31.3	2.6
CPER_Bt1_bulk	27.4	11.9	2.3	17.5	40.8	3.2
DCFS_Bw_bulk	22.5	15.3	3.6	26.6	32.1	3.2
DEJU_Bw_bulk	23.1	2.8	4.2	13.2	56.7	3.9
DELA_Bt_bulk	19.8	11.1	2.4	11.4	55.3	3.8
GRSM_Bw_bulk	8.2	2.0	0.0	12.2	77.6	5.2
GUAN_Bk1_bulk	23.5	18.0	3.2	16.6	38.8	3.1
HARV_Bw1_bulk	8.5	5.4	1.5	24.6	60.1	4.8
HEAL_Cfjj_bulk	46.8	25.7	8.4	10.9	8.1	0.9
JERC_Bt1_bulk	24.6	5.5	0.0	11.1	58.8	3.9
JORN_Bw_bulk	22.2	23.2	8.2	22.6	23.8	2.6
OAES_Klemme_Bw_bulk	15.4	10.0	2.6	16.7	55.2	4.1
KONA_Bt1_bulk	34.9	19.6	4.1	18.6	22.9	2.1
KONZ_Bt1_bulk	25.6	16.2	4.0	25.2	29.0	2.9
LAJA_Bssyz1_bulk	1.3	0.8	0.0	6.1	91.8	5.8
LENO_Bw_bulk	25.6	18.6	5.8	22.2	27.9	2.7
Mameyes_Bkk1_bulk	7.1	3.7	0.0	7.9	81.3	5.2
MLBS_Bg1_bulk	42.5	10.2	2.0	14.4	30.9	2.2
MOAB_Bw_bulk	31.8	19.2	5.0	18.0	26.0	2.3
NIWO_Bw1_bulk	11.6	10.7	3.7	32.2	41.8	4.1
NOGP_Bt1_bulk	30.2	18.0	7.9	15.3	28.6	2.4
ONAQ_Bw_bulk	23.7	7.8	1.0	14.7	52.8	3.7
ORNL_Bt1_bulk	23.4	7.5	0.5	23.8	44.9	3.7
PUUM_2Bw2_bulk	14.0	13.9	5.2	29.4	37.6	3.8
RMNP_AB_bulk	24.7	21.4	7.5	21.5	24.9	2.6
SCBI_Bt1_bulk	21.4	4.5	0.2	9.5	64.5	4.2
SERC_Bt1_bulk	45.0	24.5	7.5	6.1	16.9	1.1
SJER_Bw_bulk	26.6	10.0	1.4	17.0	45.0	3.4
SOAP_Bt1_bulk	21.6	20.8	6.1	21.9	29.5	2.9
SRER_Bw_bulk	10.8	7.3	0.9	22.7	58.3	4.6
STEI_Bs1_bulk	17.1	16.8	6.0	22.4	37.7	3.4
STER_Bt_bulk	34.8	18.8	5.0	14.5	27.0	2.2
TEAK_2C3_bulk	21.6	19.2	8.7	22.6	27.9	2.9
TOOL_Cg_bulk	33.5	25.8	7.2	13.8	19.7	1.8
TREE_Bs_bulk	18.5	17.3	7.0	24.7	32.5	3.2

UKFS_Bt1_bulk	25.8	12.9	2.3	28.1	30.9	3.1
UNDE_BS1_bulk	26.5	16.1	4.0	28.3	25.1	2.8
WOOD_2Bw_bulk	14.5	10.9	2.4	32.0	40.3	4.0
WREF_Bw_bulk	13.2	3.2	0.2	4.7	78.6	4.8
YELL_Bt1_bulk	24.4	20.0	6.6	23.4	25.6	2.7
ABBY_A_maom	27.7	26.4	9.1	18.7	18.1	2.1
BARR_Cgjj_maom	43.6	28.8	8.4	11.8	7.4	0.9
BART_A_maom	19.5	42.0	13.9	14.7	9.9	1.6
BLAN_Ap1_maom	25.0	23.1	9.4	21.0	21.6	2.4
BONA_Bg_Oajj_maom	37.5	20.8	6.2	19.3	16.1	1.8
CLBJ_A_maom	38.8	17.8	7.5	12.2	23.7	1.9
CPER_A_maom	17.0	24.0	6.1	17.4	35.6	3.1
DCFS_A1_maom	23.0	18.9	8.3	25.1	24.6	2.8
DEJU_A_maom	21.9	17.1	9.0	17.6	34.4	3.0
DELA_A1_maom	33.0	23.5	2.7	13.9	26.9	2.2
GRSM_A1_maom	24.1	23.6	9.3	21.8	21.2	2.4
GUAN_A_maom	18.5	16.6	8.0	18.1	38.9	3.3
HARV_A_maom	22.0	27.4	9.2	21.3	20.2	2.4
HEAL_A_Cjj_maom	36.4	27.8	10.5	14.7	10.6	1.4
JERC_A_maom	32.0	28.0	21.9	5.8	12.3	1.3
JORN_A_maom	17.5	11.3	4.1	24.4	42.7	3.7
Klemme_A_maom	23.3	8.6	2.7	15.7	49.7	3.6
KONA_AP_maom	30.2	19.5	5.2	14.6	30.6	2.5
KONZ_A_maom	25.1	19.1	7.8	23.1	25.0	2.7
LAJA_Ap_maom	15.7	11.9	2.8	19.8	49.8	3.9
LENO_A_maom	35.6	27.0	14.3	11.9	11.2	1.3
Mameyes_A_maom	6.0	6.6	1.6	15.9	69.9	5.0
MLBS_A_maom	32.9	22.8	8.6	18.3	17.3	1.9
MOAB_A_maom	15.1	10.1	3.4	25.7	45.8	4.0
NIWO_A1_maom	21.5	17.4	9.1	26.8	25.2	2.9
NOGP_A1_maom	21.8	17.8	6.3	21.4	32.6	3.0
ONAQ_A1_maom	14.7	13.5	5.1	24.5	42.2	3.8
ORNL_A_maom	29.1	25.4	9.2	17.7	18.5	2.0
PUUM_Bw1_maom	18.8	17.4	5.6	24.6	33.6	3.3
RMNP_A_maom	25.4	23.3	10.9	21.2	19.2	2.3
SCBI_A_maom	24.8	22.1	9.5	22.8	20.9	2.4
SERC_A_maom	31.4	24.5	8.7	16.6	18.9	1.9
SJER_A1_maom	16.9	16.8	10.8	26.0	29.5	3.2
SOAP_A1_maom	21.0	26.4	12.4	17.9	22.3	2.4
SRER_A_maom	24.8	10.0	2.3	23.3	39.6	3.4
STEI_A_maom	28.6	20.0	12.2	19.1	20.2	2.2
STER_Ap1_maom	15.1	11.8	5.4	20.5	47.1	3.9
TEAK_A_maom	38.1	19.8	8.8	15.3	17.8	1.7
TOOL_Bg_maom	29.4	24.5	10.1	17.5	18.4	2.0

TREE_A E_maom	21.4	20.5	10.8	22.1	25.2	2.7
UKFS_A1_maom	27.9	20.6	6.3	23.2	21.9	2.4
UNDE_A_maom	30.7	36.9	20.0	6.9	5.6	1.0
WOOD_AO_maom	23.8	19.8	6.3	24.3	25.8	2.7
WREF_Ac_maom	23.3	12.5	4.8	10.8	48.7	3.4
YELL_A_maom	24.3	20.9	7.2	22.7	24.9	2.6
ABBY_Bw1_maom	36.5	11.0	3.3	12.0	37.2	2.6
BARR_CgjjF2_maom	30.4	25.0	7.3	20.8	16.5	2.0
BART_Bs1_maom	12.8	11.3	5.0	18.8	52.0	4.1
BLAN_Bt1_maom	20.4	11.3	2.4	14.4	51.4	3.7
BONA_Cg_maom	37.5	19.5	6.7	19.0	17.4	1.8
CLBJ_Bt1_maom	21.8	12.5	5.1	8.7	51.8	3.5
CPER_Bt1_maom	27.6	12.0	3.4	12.7	44.3	3.1
DCFS_Bw_maom	26.8	17.3	4.5	20.8	30.7	2.8
DEJU_Bw_maom	12.1	13.8	5.0	17.9	51.2	4.0
DELA_Bt_maom	13.9	12.2	2.3	15.5	56.2	4.1
GRSM_Bw_maom	7.5	13.5	3.0	14.7	61.3	4.5
GUAN_Bk1_maom	15.8	10.3	2.4	21.3	50.1	4.0
HARV_Bw1_maom	13.5	6.7	2.6	24.5	52.6	4.3
HEAL_Cfjj_maom	44.1	19.4	10.8	14.6	11.2	1.3
JERC_Bt1_maom	14.0	0.0	0.0	22.3	63.7	4.8
JORN_Bw_maom	27.8	10.6	4.3	19.6	37.7	3.1
Klemme_Bw_maom	16.4	10.0	1.1	16.2	56.3	4.1
KONA_Bt1_maom	27.9	15.2	3.9	15.7	37.5	2.9
KONZ_Bt1_maom	33.3	17.4	5.7	17.4	26.2	2.3
LAJA_Bssyz1_maom	5.2	1.3	0.0	12.0	81.5	5.4
LENO_Bw_maom	25.2	18.6	6.5	19.6	30.2	2.8
Mameyes_Bkk1_maom	2.7	2.9	0.4	8.0	85.9	5.6
MLBS_Bg1_maom	54.6	14.6	2.4	9.1	19.4	1.2
MOAB_Bw_maom	17.1	8.0	1.8	29.6	43.5	4.0
NIWO_Bw1_maom	17.9	14.4	5.5	25.5	36.6	3.5
NOGP_Bt1_maom	28.3	14.4	3.6	13.1	40.5	2.9
ONAQ_Bw_maom	32.9	16.3	8.4	6.9	35.6	2.4
ORNL_Bt1_maom	31.8	15.4	2.2	7.6	43.1	2.8
PUUM_2Bw2_maom	13.2	13.3	5.4	29.2	38.9	3.8
RMNP_AB_maom	19.7	15.3	6.9	25.5	32.5	3.2
SCBI_Bt1_maom	21.0	6.9	2.2	7.6	62.3	4.0
SERC_Bt1_maom	21.0	4.3	3.3	13.3	58.1	4.0
SJER_Bw_maom	20.7	9.6	8.3	13.5	47.9	3.6
SOAP_Bt1_maom	38.1	14.8	4.7	12.6	29.7	2.2
SRER_Bw_maom	4.8	7.4	0.9	23.1	63.7	5.0
STEI_Bs1_maom	27.5	18.4	7.7	20.5	25.9	2.5
STER_Bt_maom	36.3	14.1	4.2	10.7	34.7	2.4
TEAK_2C3_maom	16.4	14.9	6.1	23.4	39.2	3.6

TOOL_Cg_maom	27.0	25.6	8.2	16.0	23.2	2.2
TREE_Bs_maom	16.0	13.4	7.7	25.0	38.0	3.6
UKFS_Bt1_maom	23.5	13.3	3.3	26.2	33.7	3.2
UNDE_BS1_maom	35.7	20.0	5.0	20.6	18.6	2.0
WOOD_2Bw_maom	13.6	8.5	1.5	34.8	41.5	4.2
WREF_Bw_maom	21.0	6.6	1.6	6.7	64.1	4.0
YELL_Bt1_maom	17.2	14.6	3.8	30.0	34.4	3.5
<hr/>						
ABBY_A LPOM	32.0	31.1	12.6	14.7	9.6	1.4
BARR_Cgjj/Oajj_LPOM	45.1	29.3	10.3	9.9	5.5	0.7
BART_A LPOM	26.4	38.3	14.1	13.8	7.4	1.3
BLAN_Ap1_LPOM	36.4	30.8	17.4	9.3	6.2	1.0
BONA_Bg Oajj_LPOM	38.5	23.1	9.0	17.8	11.6	1.5
CLBJ_A_LPOM	41.0	28.1	12.9	11.4	6.6	1.0
CPER_A_LPOM	33.4	29.2	13.2	15.3	8.9	1.4
DCFS_A1_LPOM	29.0	27.3	10.6	19.0	14.0	1.8
DEJU_A_LPOM	29.4	33.0	15.7	12.2	9.7	1.4
DELA_A1_LPOM	31.5	34.7	14.8	11.3	7.7	1.2
GRSM_A1_LPOM	31.0	29.1	10.8	17.0	12.1	1.6
GUAN_A LPOM	21.2	20.8	8.3	28.0	21.6	2.8
HARV_A_LPOM	24.5	30.9	9.8	19.7	15.0	2.0
HEAL_A/Cjj_LPOM	42.8	27.5	11.1	11.2	7.4	0.9
JERC_A_LPOM	24.3	34.7	14.7	15.3	10.9	1.6
JORN_A LPOM	35.6	26.6	15.4	13.2	9.1	1.3
Klemme_A_LPOM	26.5	22.4	10.2	21.8	19.1	2.3
KONA_AP_LPOM	37.4	28.8	13.8	12.5	7.5	1.1
KONZ_A_LPOM	29.4	30.8	12.2	16.0	11.5	1.6
LAJA_Ap_LPOM	33.4	24.5	9.6	18.5	14.0	1.7
LENO_A_LPOM	31.8	32.4	12.7	14.1	9.0	1.3
Mameyes_A_LPOM	29.7	28.2	11.4	18.4	12.3	1.7
MLBS_A_LPOM	28.2	31.9	8.4	19.0	12.5	1.7
MOAB_A_LPOM	34.9	28.3	13.6	13.9	9.3	1.3
NIWO_A1_LPOM	25.7	25.0	12.0	21.2	16.0	2.1
NOGP_A1_LPOM	27.4	30.8	11.6	15.1	15.1	1.8
ONAQ_A1_LPOM	31.9	25.6	13.7	18.4	10.4	1.6
ORNL_A_LPOM	29.1	31.2	13.0	16.0	10.7	1.6
PUUM_Bw1_LPOM	23.1	20.7	6.6	26.8	22.8	2.7
RMNP_A_LPOM	28.9	32.9	14.5	14.9	8.9	1.4
SCBI_A_LPOM	31.1	31.4	13.3	15.3	9.0	1.4
SERC_A_LPOM	27.7	30.9	11.9	17.4	12.1	1.7
SJER_A1_LPOM	35.8	31.1	15.8	11.6	5.7	1.0
SOAP_A1_LPOM	25.0	35.0	17.0	15.6	7.3	1.5
SRER						
STEI_A_LPOM	29.5	32.3	16.6	12.9	8.6	1.4
STER_Ap1_LPOM	34.0	28.4	12.2	15.3	10.1	1.4

TEAK_A_LPOM	26.5	31.7	13.6	16.3	12.0	1.7
TOOL_Bg_LPOM	45.8	29.9	12.1	7.2	5.0	0.6
TREE_A/E_LPOM	30.8	31.1	11.4	15.6	11.1	1.5
UKFS_A1_LPOM	31.1	27.5	11.4	17.6	12.4	1.7
UNDE_A_LPOM	33.4	31.2	14.5	12.9	8.0	1.2
WOOD_AO_LPOM	29.3	30.0	11.3	17.4	12.0	1.7
WREF_Ac_LPOM	23.1	34.6	15.4	13.4	13.4	1.7
YELL A_LPOM	31.0	29.7	12.6	15.8	10.8	1.5
