Agriculture, Ecosystems and Environment 393 (2025) 109833

Contents lists available at ScienceDirect

Agriculture, Ecosystems and Environment

journal homepage: www.elsevier.com/locate/agee

Bringing soil sulfur to the forefront: How long-term cropping impacts sulfur speciation in soil organic matter fractions

Meghan Barnard [a], Ram C. Dalal [a], Brigid A. McKenna [a], Jeremy L. Wykes [b], Bruce C.C. Cowie [b], Peter M. Kopittke [a,*]

[a] The University of Queensland, School of Agriculture and Food Sustainability, St Lucia, Queensland 4072, Australia
[b] ANSTO, The Australian Synchrotron, Clayton, Victoria 3168, Australia

ARTICLE INFO

Keywords:
Sulfur
Soil fertility
Vertisol
Soil fractions
Cropping
Soil organic matter

ABSTRACT

Soil sulfur (S) cycling is of increasing interest for crop S supply, given that S inputs to soils have declined due to the application of high-analysis (low-S) fertilisers and decreased atmospheric SO_2 emissions. This study uses three paired sites [undisturbed (native) and cropped (up to 82 y)] from subtropical Australia to examine the impact of land use change on soil S composition. Soil organic matter (SOM) was separated into three fractions: free particulate organic matter (fPOM), occluded POM (oPOM), and fine mineral-associated organic matter (fine-MAOM), before using X-ray absorption near-edge structure (XANES) spectroscopy for analyses of S speciation. In the native soils, S speciation across the SOM fractions was distinct. Both POM fractions were dominated by reduced thiol and thio-ether groups (~33 %), with an average S oxidation state of +2.4. In contrast, the S in the fine-MAOM was mostly oxidised sulfate ester and sulfate (44 %), with an average oxidation state of +3.9. The loss of SOM during long-term cropping caused a concomitant loss in S – up to 99 % of S was lost from the less protected fPOM fraction, while only 44 % of S was lost from the fine-MAOM. Under cropping, the bulk soil shifted to higher proportions of oxidised S. However, this was not caused by a change in S speciation within any SOM fraction but was due to the decreased contributions of POM fractions to the bulk soil. This study develops our understanding of the influence of cropping on S speciation and the role of SOM fractions in S dynamics.

1. Introduction

Sulfur (S) is an essential macronutrient for plants and plays a role in the synthesis of chlorophyll and amino acids (Eriksen, 2009; Narayan et al., 2023). Although S can occur in both inorganic and organic forms, 95–98 % of soil S is organic in most well-drained aerobic soils (Solomon et al., 2011). To become plant-available, this organic S must be converted to inorganic SO_4^{2-} via mineralisation (Kertesz and Mirleau, 2004). In the past, considerable inorganic S was inadvertently added to soil through both atmospheric deposition and through fertilisers that also contained S (such as superphosphate). However, the increased regulation of atmospheric emissions combined with the transition to the application of low-S fertilisers (such as monoammonium phosphate, MAP) has decreased S inputs to soil (Eriksen, 2009). As such, the incidence of S deficiency has increased substantially within the last 20 years and is expected to worsen (Feinberg et al., 2021; Sharma et al., 2024). Therefore, there is an increasing interest in S behaviour and cycling in soils, including identification of changes in organic forms over time in managed systems.

Sulfur can take a range of oxidation states ranging from −2 to +6. The organic chemistry of S is, therefore, highly diverse (Solomon et al., 2011), although two broad categories of organic S exist. The first is C-bonded S (S directly bonded to C) with the second being sulfate ester (S indirectly bonded to C) (Scherer, 2009). The mineralisation pathways of these two different categories of S are generally considered to be distinct – whilst C-bonded S is converted to SO_4^{2-} via *in vivo* biological mineralisation and is governed by the microbial demand for energy, sulfate ester S is converted to SO_4^{2-} via *ex vivo* biochemical mineralisation during hydrolysis with sulfatase enzymes and is governed by the demand for S (McGill and Cole, 1981). However, it is acknowledged that this framework originally proposed by McGill and Cole (1981) may be an oversimplification, with it being possible to argue these two mineralisation pathways are not entirely discrete (Ghani et al., 1992). Regardless, this model still serves a useful foundation for understanding

* Corresponding author.
E-mail addresses: m.barnard@uq.edu.au (M. Barnard), r.dalal@uq.edu.au (R.C. Dalal), b.mckenna1@uq.edu.au (B.A. McKenna), jeremyw@ansto.gov.au (J.L. Wykes), brucec@ansto.gov.au (B.C.C. Cowie), p.kopittke@uq.edu.au (P.M. Kopittke).

https://doi.org/10.1016/j.agee.2025.109833
Received 14 September 2024; Received in revised form 22 June 2025; Accepted 24 June 2025
Available online 1 July 2025

S dynamics in soil (Eriksen, 2009).

Previously, analytical techniques have generally been limited to the isolation of these two broad groups of organic S. However, synchrotron-based X-ray absorption near-edge structure (XANES) spectroscopy can distinguish between several S functional groups based on the oxidation state of S (Prietzel et al., 2007; Solomon et al., 2003). An additional benefit of XANES is that it allows for non-destructive analyses rather than relying on chemical extractions, minimising the risk of experimental artefacts.

As most S in soil occurs in the organic form, S availability is often linked with SOC stocks (Chapman, 1997; Prietzel et al., 2007; Wang et al., 2006). However, it is well established that land use change, particularly the conversion of native land to cropping, reduces SOC stocks (Guo and Gifford, 2002; Lal, 2004; Sanderman et al., 2018), which also alters organic S in agricultural soils. However, it is not well understood how these losses of total soil organic matter (SOM) and S influence the organic chemistry of S. Addressing this knowledge gap will enable improved land management practices to maintain SOM and, most importantly, maintain the availability of organic S to crops in agricultural soils.

Our understanding of SOM dynamics and persistence has been transformed within the last few decades. Traditionally, emphasis had been placed on the inherent chemical resistance of SOM to degradation (Kleber and Lehmann, 2019; MacCarthy, 2001; Schmidt et al., 2011). However, there is a growing body of evidence demonstrating that the physical protection and reduced accessibility of SOM via aggregation to the decomposer community (i.e. soil microbes) is critically important to SOM persistence (Lehmann and Kleber, 2015). As such, current SOM research often employs fractionation schemes to separate SOM into several fractions representing different stabilisation mechanisms so that SOM in each fraction can be studied separately (Chenu et al., 2015; Poeplau et al., 2018). These fractions are the degrading plant materials referred to as particulate organic matter (POM), which either exist as free and unprotected POM within the soil matrix (fPOM) or as POM that has become entrapped within aggregates forming occluded POM (oPOM). In addition, the SOM, which has undergone continued microbial decomposition, can also become soluble. SOM in this form can then interact with reactive mineral surfaces of soil particles, forming mineral-associated organic matter (MAOM) (Basile-Doelsch et al., 2020; Lehmann and Kleber, 2015). Recently, many studies have improved our understanding of C and N dynamics by studying SOM fractions (Almeida et al., 2021; Cotrufo et al., 2019; Witzgall et al., 2021). However, to our knowledge, no previous studies have expanded this method to organic S.

We investigate the organic S chemistry within a series of high clay content soils from an area of agricultural significance in subtropical south-east Queensland, Australia. This soil series comprises samples that have been cropped up to 82 y which had caused a loss of up to 72 % of total SOC (Table 2). The first objective of this study was to characterise organic S functional group chemistry within the bulk soil and the different SOM fractions of native (undisturbed) soil using synchrotron-based XANES spectroscopy. Secondly, paired samples from cropped land were investigated to assess changes to organic S exerted by cropping, with a specific interest in how long-term cropping changes the concentrations and forms of S in the various SOM fractions. We hypothesise that (a) the fine-MAOM fraction would have a higher proportion of oxidised S due to increased microbial processing compared to both the POM fractions, and (b) S speciation within cropped soils would have a higher proportion of oxidised S compared to native soils as a result of the change in vegetation, crop S removal, and loss of SOC and total S in soil.

2. Materials and methods

2.1. Sampling location

Soil samples were collected from an area of agricultural significance in south-east Queensland, Australia (26.5°S and 28°S and 148°E to 152°E). Mean annual rainfall within the study region ranges from 571 to 664 mm, with more than 60 % received during summer (December – February). Mean annual temperatures range from 18.9 to 19.6 °C. The highest monthly temperature occurs in January, and the lowest in July. Three soil series were selected: Billa Billa, Cecilvale, and Langlands-Logie. All three soils are classified as Vertisols, Typic Chromusterts (Soil Survey Staff.. 2003), classified as Vertosols in the Australian Soil Classification (Isbell, 2021).

A native (undisturbed) and adjacent cropped sample pair were selected for each soil type (yielding a total of six bulk soil samples). The sample pairs were collected from within 50–100 m of each other. Cropping durations for the cropped samples varied from 25 y for Billa Billa to 82 y for Langlands-Logie (Table 2). Representative soil samples were collected at each location by sampling a 0.1 ha area on a grid (5 m by 8 m) to a depth of 0–0.1 m using a 46 mm internal diameter core. A total of 25 sub-samples were collected from within the grid, with five of these subsamples being combined to yield a total of five replicate samples for each location. These five replicates were then combined to produce a single composite for each sampling location (each "composite" is referred to as a sample hereafter). The soil samples were sealed in plastic bags in the field, transported to the laboratory and kept at 4 °C until further processing for analysis. The samples were dried at 25 °C, sieved to < 2 mm and stored in sealed plastic containers.

A detailed description of the region, soils, native vegetation (in the case of undisturbed sites) and crop management practices (in the case of cropped sites) is given by Dalal and Mayer (1986). Billa Billa had *Casuarina cristata* (forest); Cecilvale had *Eucalyptus populnea* and *Dicanthium sericeum* (woodland, savannah); and Langlands-Logie had *Acacia harpophylla* (forest). The adjacent cropped soils were used for cereal cropping, primarily wheat (*Triticum aestivum*) and barley (*Hordeum vulgare*) grown in the winter season whilst summer crops were generally sorghum (*Sorghum bicolor*). Stubble was retained rather than being burnt. On average, Billa Billa received 2 kg ha^{-1} year^{-1} phosphorus (P) and zero nitrogen (N), Cecilvale received 7.7 kg ha^{-1} year^{-1} P and 18 kg ha^{-1} year^{-1} N, and Langlands-Logie received zero P and 7.5 kg ha^{-1} year^{-1} N. Fertiliser was given in the form of MAP, urea and anhydrous ammonia. The average number of cultivations per year varied from 4 to 5 depending upon the soil series.

2.2. Physical and density fractionation

Soil samples were separated into four fractions using a density and size fractionation protocol based upon the method of Kölbl and Kögel-Knabner (2004) and Schweizer et al. (2021). Briefly, 20 g of air-dried and sieved (<2 mm) soil was introduced to 200 mL of sodium polytungstate (SPT) (1.8 g cm $^{-3}$) and left overnight to isolate the fPOM, which was collected using a vacuum pump system. The remaining sample was then sonicated using a 13 mm diameter probe (inserted approximately 15 mm deep). A cumulative energy value of 400 J mL^{-1} was applied to disrupt aggregate structures and release the oPOM. The sample temperature was maintained below 40 °C by applying the sonication treatment in two waves (200 J mL^{-1} each) and using a jacketed beaker with room-temperature (22 °C) water flowing internally. This energy intensity was determined to be the least energy required to maximise oPOM recovery. After sonication, samples were centrifuged at 1932*g* for 30 min to separate the mineral fraction from the oPOM. The floating oPOM was aspirated in the same manner as the fPOM fraction. The two POM fractions were then filtered with deionised water until the electrical conductivity (EC) was < 5 μS.cm^{-1}, while the remaining mineral component was filtered until EC was < 50 μS.cm^{-1} using a pressure filtration system (Sartorius Stedim Biotech GmbH, Germany) operated at 5 bar with a 0.22 μm polyvinylidene difluoride filter membrane. Wet sieving was then undertaken on the mineral component to separate the fine-MAOM (< 53 μm) from the coarse-MAOM (53–2000 μm). The POM fractions were freeze dried while the mineral fractions

were dried in a dehydrating oven (40°C). As the coarse-MAOM fractions contributed minimal SOC across all soils (< 3 % of total SOC), this fraction was omitted from further analyses.

2.3. Total organic carbon and sulfur

Total organic C and total S for the fine-MAOM and the bulk soil were determined by dry combustion using a LECO CNS analyser following homogenisation with a ball mill. Acid pre-treatment was unnecessary after testing revealed negligible carbonates in these surface soils. For the fine-MAOM fraction, it was determined that filtering during the fractionation procedure may have resulted in a loss of soluble S due to leaching, given that recovery of total S following fractionation was 75 % and 100 % for Billa Billa native and cropped, 75 % and 76 % for Cecilvale native and cropped, 92 % and 97 % for Langlands-Logie native and cropped soils (Table 2).

Due to low sample mass of POM fractions (< 1 g), total organic C and total S concentrations were determined by isotopic ratio mass spectrometry (IRMS, Stable Isotope Facility at UC Davis, USA). Samples were prepared for IRMS by grinding with an agate pestle and mortar and pelletised into tin capsules (2 mg for OC and 20 mg for S).

2.4. Extractable sulfur

Extractable S concentrations in the bulk soils were determined according to Zhao and McGrath (1994) using a ratio of 1:5 soil to solution extraction with 0.016 M KH_2PO_4 and shaking for one hour. Total extractable S (SO_4-S and soluble organic S) was determined by inductively-coupled plasma optical emission spectrometry (ICP-OES), while ion chromatography (IC) was used to determine inorganic SO_4-S. Soluble organic S was determined as the difference between the total and inorganic S.

2.5. XANES spectroscopy

The S K-edge XANES spectroscopy was performed at the MEX-2 beamline at the Australian Synchrotron in Victoria, Australia. The incident X-ray energy was selected using a Si(111) double crystal monochromator, with a photon flux of 1×10^{11} photons.sec^{-1}. The S K-edge spectra were acquired with a four-element Si drift detector (Vortex ME4) operating in fluorescence mode under vacuum of 2.5×10^{-6} mbar. The beam was calibrated with $Na_2S_2O_3$ at 2472.02 eV and was set to an area 5 mm × 3 mm. The dwell time was 2 s per energy across the entire energy range of 2420 and 2600 eV. Step sizes were 5 eV from 2420 to 2460 eV, 0.5 eV from 2460 to 2466 eV, 0.05 eV from 2466 to 2486 eV, 20 eV from 2486 to 2520 eV, and finally from 2520 to 2600 eV in steps of 0.05 K.

Samples were ball milled and spread evenly onto adhesive carbon tape mounted to a stainless-steel sample holder. Two replicate spectra were collected for each sample. To assist with peak fitting (see below), spectra were also collected for 11 standards, namely: iron sulfide [S^{2-}], iron disulfide [S^{1-}], L-glutathione-oxidised [RSSR], L-methionine [RSR], L-cysteine [RSH], DL methionine sulfoxide [RS(=O)R], sodium sulfite [SO_3^{2-}], taurine [$RS(=O)_2OH$], L-cysteic acid monohydrate [$RS(=O)_2O^-$], sodium dodecyl sulfate [$ROSO_3$] and sodium sulfate [SO_4^{2-}] (Supplementary Table S1). These compounds encompass a range of S oxidation states from −2 to +6. Standards were diluted to 1.5 % S with boron nitride.

2.6. XANES peak fitting

Deconvolution of the S K-edge XANES spectra was undertaken to quantify the relative proportions of five S species in accordance with Prietzel et al. (2019) and (2003) (Supplementary Fig. S2). Spectra were first baseline corrected (from −52.25 to −15 eV) and edge normalized (normalization range +40 to +100 eV). Replicate spectra were then merged to yield one spectrum per sample. Gaussian peak fitting was then undertaken using the peak fit function in Athena v. 0.9.26 (Ravel and Newville, 2005). This peak-fitting method was determined to better capture trends observed in sample spectra. Using the standards establish the appropriate peak position, five gaussian curves were then fitted for the major S species (Table 1). Suitable peak widths between 0 and 2 were first manually determined and then fixed for each peak (Table 1). No reduced inorganic S forms (e.g. FeS or FeS_2) or inorganic sulfite (SO_3^{2-}) were detected in sample spectra, thus peaks were not fitted for either reduced inorganic S at ca. 2470 eV or inorganic sulfite-S at ca. 2478 eV. Two additional arctangent functions were fitted (2477 eV and 2483 eV, with a fixed width of 0.3), representing the edge steps of reduced and oxidised S, respectively. The proportion of each S species was calculated as the area under the curve for each peak over the sum of the area under the curve for all S peaks. Peak areas were multiplied by correction factors shown in Table 1 [from Prietzel et al. (2019)] to account for the S oxidation state dependency of absorption cross section.

2.7. Statistical analysis

A principal component analysis (PCA) was conducted on the deconvolution results using the factoextra and PCAtest package in R (Camargo, 2024; Kassambara and Fabian, 2020; R Core Team, 2023) to evaluate the composition of S species across the fractions of all soil series and cropping periods.

3. Results

3.1. Soil organic carbon and sulfur properties in native soils

We first assessed the total SOC and S in the native soils (Table 2 and Supplementary Fig. S3). Bulk soil SOC contents varied between 18 g C kg^{-1} in Cecilvale to 29 g C kg^{-1} in Langlands-Logie. Total S in the bulk soil was proportional to SOC, with the lowest concentration recorded for Cecilvale (0.28 g S kg^{-1}) and highest in Langlands-Logie (0.43 g S kg^{-1}). Bulk soil C:S ratios were variable, ranging from 65 for Cecilvale to 75 for Billa Billa (Table 2). We also assessed extractable S from the bulk soil. Total extractable S was proportional to SOC, with Cecilvale having the lowest (16 mg S kg^{-1}) while Langlands-Logie had the most (25 mg S kg^{-1}). The extractable S was comprised of almost half inorganic (52 %)

Table 1
XANES spectra peak fitting parameters.

Peak	Peak Assignment (eV)	Peak width	Oxidation state of S	Species	Structure	Peak area correction factor
G1	2472.6	0.59	+0.2	Disulfide S	RSSR	0.9
G2	2474.2	0.72	+0.5	Thiol	RSH	0.9
				Thio-ether	RSR	
G3	2476.3	0.64	+2	Sulfinic acid	RSO(OH)	0.6
				Sulfoxide S	RS(=O)R	
G4	2481.0	0.77	+4–5	Sulfonate S	$RS(=O)_2O^-$	0.4
				Sulfonic acid	$RS(=O)_2OH$	
G5	2482.7	0.81	+6	Sulfate S	SO_4^{2-}	0.35
				Sulfate ester	$ROSO_3$	

Table 2
Values for organic carbon (OC), total sulfur (TS), C:S ratios, total extractable sulfur (TES), extractable inorganic sulfate (EIS) and extractable organic sulfur (EOS) for the native-cropped sample pairs for different fractions of each soil type. All concentrations are on a 'per unit bulk soil' basis and not on a 'per unit fraction' basis.

	Native						Cropped					
	OC	TS	C:S	TES	EIS	EOS	OC	TS	C:S	TES	EIS	EOS
	— g kg bulk soil^{-1} —			— mg S kg bulk soil^{-1} —			— g kg bulk soil^{-1} —			— mg S kg bulk soil^{-1} —		
Billa Billa							*25 years*					
fPOM	3.7	0.027	136	-	-	-	0.59	0.0032	187	-	-	-
oPOM	6.6	0.042	155	-	-	-	1.8	0.011	158	-	-	-
Fine-MAOM	11	0.17	65	-	-	-	7.9	0.19	42	-	-	-
Bulk	23	0.30	75	25	13	12	10	0.20	52	7.8	3.9	3.9
Cecilvale							*35 years*					
fPOM	2.1	0.0089	239	-	-	-	0.29	0.00092	315	-	-	-
oPOM	5.0	0.031	158	-	-	-	0.81	0.0040	205	-	-	-
Fine-MAOM	11	0.18	59	-	-	-	7.76	0.17	45	-	-	-
Bulk	18	0.28	65	16	7.5	8.6	8.7	0.23	38	15	9.0	6.1
Langlands-Logie							*82 years*					
fPOM	8.9	0.071	125	-	-	-	0.28	0.00059	470	-	-	-
oPOM	7.0	0.065	106	-	-	-	0.94	0.0056	167	-	-	-
Fine-MAOM	16	0.27	58	-	-	-	5.7	0.15	38	-	-	-
Bulk	29	0.43	68	25	15	11	6.4	0.16	40	5.1	2.7	2.5

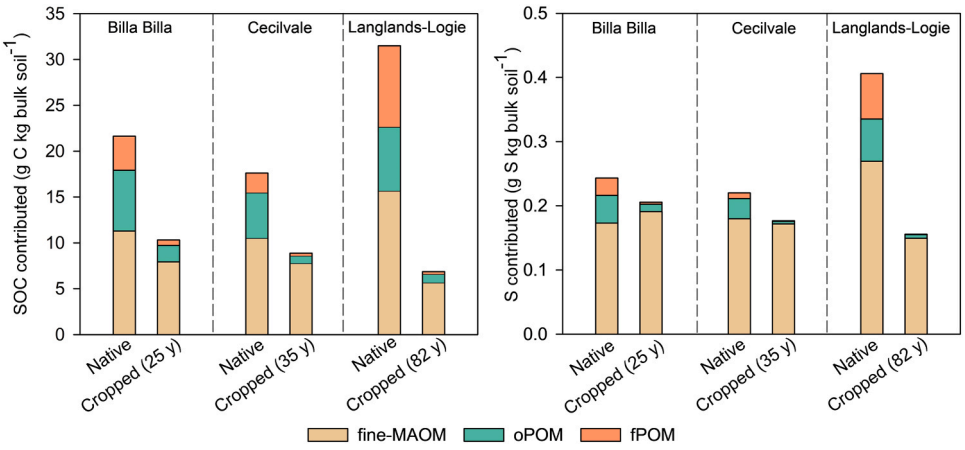

Fig. 1. Total SOC and S contributed from each fraction for the native and cropped paired sites of each Vertisol.

and half organic S (48 %, Table 2).

When expressed according to unit mass of fraction in the bulk soil, the fine-MAOM fraction contributed the most SOC and S to bulk soil (Fig. 1). Indeed, SOC derived from fine-MAOM ranged from 11 to 16 g C kg bulk soil^{-1} (by mass making up 60–82 % of the bulk soil) while S ranged from 0.17 to 0.27 g S kg bulk soil^{-1} (Table 2). The oPOM fraction was generally the second largest contributor of SOC and S while fPOM generally contributed the least. The C:S ratios were distinct between fractions in all soils. The fine-MAOM fraction had the lowest C:S ratios, ranging between 58 in Langlands-Logie to 65 in Billa Billa. The C:S ratios in POM fractions were more than 2-fold higher than fine-MAOM, ranging between 125 and 239 for fPOM, and between 106 and 158 for oPOM (Table 2).

3.2. Impact of cropping on soil organic carbon and sulfur properties

Cropping caused a substantial decrease in bulk soil SOC and S concentrations across all three soils, although the magnitude of loss differed between soils due to different cropping durations (Table 2 and Fig. 1). For example, Cecilvale (cropped for 35 y), lost 54 % of its SOC, while Langlands-Logie (cropped for 82 y) lost 78 % (Supplementary Fig. S4). Changes in total S concentrations in the bulk soil generally reflected those for SOC. For example, Langlands-Logie had the lowest bulk soil SOC (6.4 g C kg^{-1}) and lowest total S (0.16 mg S kg^{-1}). However, it was noted that whilst Billa Billa had the highest bulk soil SOC (12 g C kg^{-1}) the highest total S was found in Cecilvale (0.23 mg S kg^{-1}).

Extractable S concentrations in the cropped soils ranged between 5.1 mg S kg^{-1} in Langlands-Logie and 15 mg S kg^{-1} in Cecilvale (Table 2). As observed for the native soils, the extractable S in the cropped soils was approximately half inorganic (54 %) and half organic S (46 %) (Table 2). It was also noted that the C-bonded S:sulfate ester S ratio for the bulk soil decreased by 0.4 – 1.4 units relative to the native soils (Table 3).

For the cropped soils, the fine-MAOM fraction contributed the most to total SOC (5.6–7.9 g C kg bulk soil^{-1}) and S (0.15–0.19 g S kg bulk soil^{-1}) in the bulk soil and lost the least SOC (26–64 %) and S (0–45 %) compared to both POM fractions (Table 2, Fig. 1 and Supplementary Fig. S4). In all cropped soils, oPOM was the second biggest contributor of SOC (0.81–1.8 g C kg bulk soil^{-1}) and S (0.0040–0.011 g S kg bulk soil^{-1}), while fPOM consistently had markedly lower SOC (0.28–0.59 g C kg bulk soil^{-1}) and S (0.00059–0.0032 g S kg^{-1}) concentrations (Table 2). The C:S ratios in cropped soils were distinct between fractions following the trend fine-MAOM (38−45) < oPOM (158−205) < fPOM (187−470) (Table 2). In the cropped sample pairs, C:S ratios in the bulk soil and fine-MAOM generally decreased while C:S ratios in both POM fractions increased (Supplementary Fig. S4).

Table 3
Proportion (%) of total S that is sulfate-S or sulfate ester-S estimated for the bulk soil and soil pH.

Soil	Landuse	Total sulfate and sulfate ester [SO_4^{2-} & $ROSO_3$]^1	Sulfate [SO_4^{2-}]^2	Sulfate ester [$ROSO_3$]^3	C-bonded S:sulfate ester S	Soil pH (H_2O)
Billa-Billa	Native	42	4.4	37	1.6	6.9
	Cropped	47	1.9	45	1.2	8
Cecilvale	Native	41	2.7	39	1.5	7.3
	Cropped	49	3.9	45	1.1	7.7
Langlands-	Native	32	3.4	29	2.4	7.1
Logie	Cropped	50	1.7	49	1.0	8.2

1 – determined from XANES, 2 – determined from IC, 3 – determined by difference.

3.3. Synchrotron-based XANES analyses of S speciation

The spectra for each of the 11 standards were first used for peak identification. White-line peaks were found to increase in energy with increasing oxidation state of S (Supplementary Fig. S2, Supplementary Table S1). For the soil samples, we first investigated native soils to gain an insight into the composition of S across different soil fractions, with the XANES spectra revealing distinct differences between the various fractions (Fig. 2). For the two POM fractions, peaks corresponding to reduced organic S (G1 and G2) and intermediate S (G3 and G4) were prominent, especially for G2 (RSH and RSR, +0.5) and G4 (sulfonate S and sulfonic acid, +4/5). The bulk soil and fine-MAOM fraction had dominant peaks for the most oxidised form of S (G5: organic and inorganic sulfate S, +6); however, this was most prominent in the fine-MAOM fraction. The deconvolution results from peak fitting confirmed these observations (Fig. 3, Supplementary Table S2). For fPOM, G2 (RSH and RSR, +0.5) had the greatest contribution with an average of 32 % across all soils, followed by G4 (sulfonate S and sulfonic acid, +4/5) at 22 %. Oxidised organic and inorganic sulfate S (G5, +6) had the lowest contribution at 16 %. Overall, C-bonded S comprised 84 % of the fPOM fraction. The oPOM fraction had a similar composition of S, with G2 (RSH and RSR, +0.5) being most dominant (33 %), followed by G4 (sulfonate S and sulfonic acid, +4/5) at 23 %. Total C-bonded S in the oPOM fraction was 86 %. Oxidised organic and

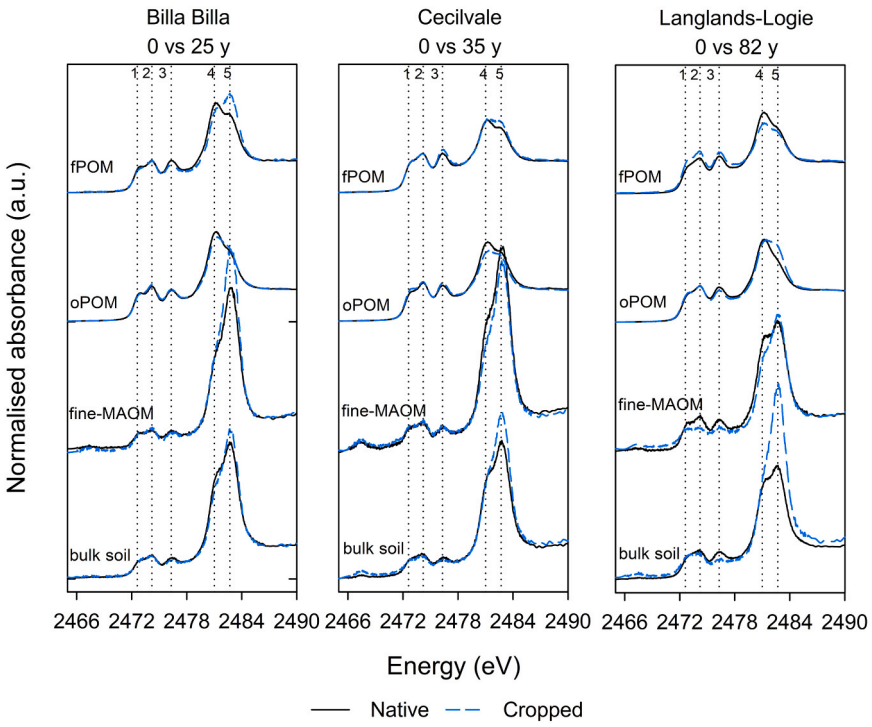

Fig. 2. XANES spectra for native and cropped paired sites of each Vertisol. The dotted vertical reference lines correspond to: 1 = G1 (2472.6 eV), 2 = G2 (2474.2 eV), 3 = G3 (2476.3 eV), 4 = G4 (2481.0 eV), and 5 = G5 (2482.7 eV).

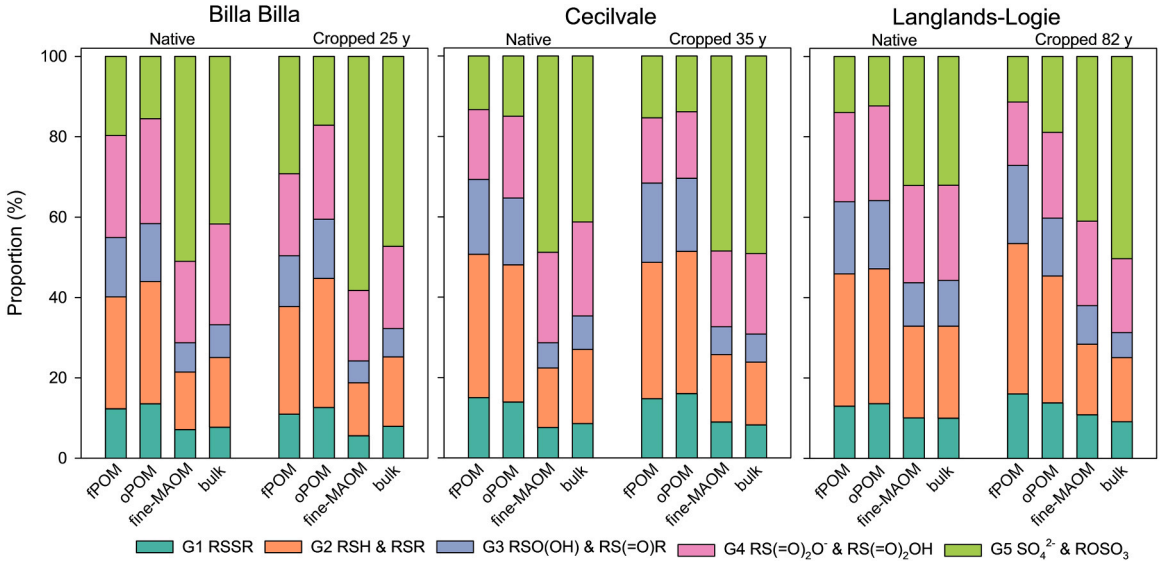

Fig. 3. The proportions of each S species for the native and cropped paired sites for each Vertisol.

inorganic sulfate (G5, +6) made up 44 % of S in the fine-MAOM fraction with C-bonded S, therefore, making up 56 % of S. The main S species within the C-bonded S of the fine-MAOM fraction was G4 (sulfonate S and sulfonic acid, +4/5) at 22 % and G2 (RSH and RSR, +0.5) at 17 %. Finally, S composition within the bulk soil reflected an average S composition of the fractions, with G5 (oxidised organic and inorganic sulfate, +6) comprising 38 % of S followed by G4 at 24 % (sulfonate S and sulfonic acid, +4/5) and 20 % as G2 (RSH and RSR, +0.5). The average oxidation state of S (Supplementary Fig. S5) reflects the distinct S compositions across each of the fractions following the trend of fPOM (2.4) = oPOM (2.4) < bulk soil (3.7) < fine-MAOM (3.9).

Next, we assessed how cropping impacted the composition of S in each fraction. The sample spectra for cropped soils (Fig. 2) had similar characteristics to those from the native soils. Although for the bulk soil, spectra showed a slight shift towards more oxidised S. Indeed, deconvolution results (Fig. 4 and Supplementary Table S2) showed no consistent changes across each fraction, with the most variability being observed for the fPOM and oPOM fractions. The bulk soil consistently had a greater proportion of oxidised S (oxidised organic and inorganic sulfate, +6) in the cropped counterpart of each soil type. For example, in the bulk soil of all three Vertisols, the proportion of G5 (oxidised organic and inorganic sulfate, +6) had an increase of 13–57 %, with this increasing according to cropping duration. The average oxidation state of S (Supplementary Fig. S5) of the cropped soils shows a notable

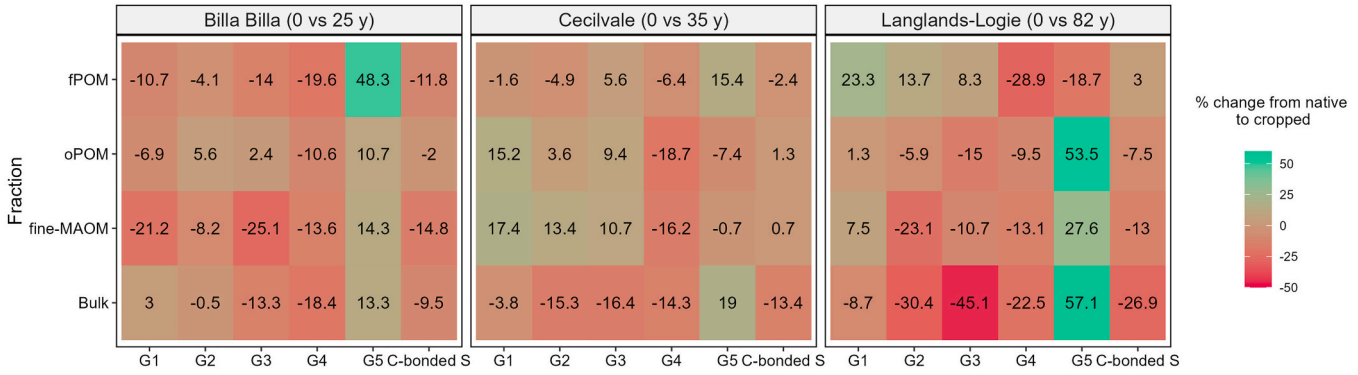

Fig. 4. Percentage change of all S species across the bulk soil and all fractions between the native and cropped paired sites of each Vertisol.

increase for the bulk soil only, following the trend fPOM (2.4) = oPOM (2.4) < bulk soil (4.1) = fine-MAOM (4.1).

By combining deconvolution data (Supplementary Table S2) with extractable S contents (Table 2), it was possible to distinguish between inorganic sulfate S (SO_4^{2-}) and organic sulfate ester-S ($ROSO_3$) in the bulk soil (Table 3). Accordingly, it was found that 91 % of oxidised S (G5) in the native soils was comprised of sulfate ester-S. The proportion of sulfate ester-S in cropped soils was comparable, being 95 %.

Finally, PCA (Fig. 5) aided the characterisation of S composition across each fraction and land use. The first component (PC1) relates to the inverse relationship between more reduced S (G1-G3) and oxidised S (G5). The second component (PC2) relates to the weakly inverse relationship between intermediate S (G4) and the remaining S species. When all fractions of native and cropped soils were examined together, the PCA biplot showed POM fractions had the most variable composition dominated by reduced forms of S (G1–3). In contrast, the fine-MAOM and bulk soil had a more confined distribution and was characterised as being dominant in oxidised S forms (G5).

4. Discussion

4.1. Differences in sulfur composition of soil fractions

Native soils showed that there is clear differences in S composition across the SOM fractions, which likely reflect the constituents of each fraction and the degree of microbial processing. It was found that more reduced C-bonded S dominated the S composition of fPOM (84 %) and oPOM (86 %, Fig. 3). As a result, these fractions had markedly lower average oxidation states compared to the fine-MAOM (Supplementary Fig. S5). Although, to our knowledge, no studies have yet characterised S in isolated fPOM and oPOM fractions using XANES spectroscopy, we suggest this is because POM fractions primarily consist of organic materials at early stages of decomposition, thus, their S composition resembles that of fresh crop residues which have been reported to contain more than 75 % of S as C-bonded and sulfate ester-S (Churka Blum et al., 2013).

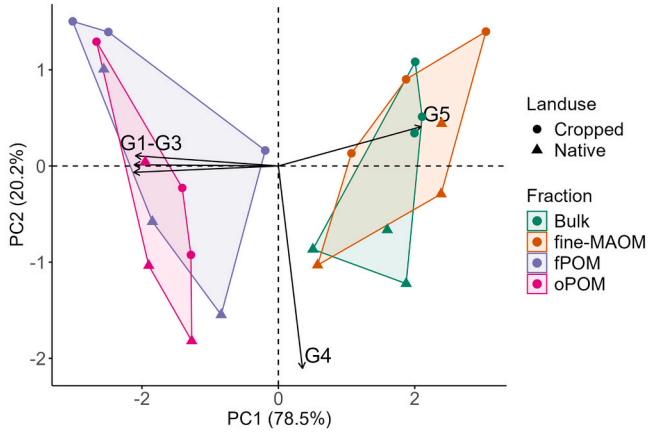

Fig. 5. Principal component analysis biplot visualising the variation in the composition of S species within the bulk soil and each fraction for all soil types and land uses. Arrows indicate the loadings of each variable. Concentration ellipses have been added to visualise distribution of data points. A matrix of principal components is presented in Supplementary Table S3.

Conversely, the fine-MAOM was dominated by oxidised S (Fig. 3), resulting in a higher average S oxidation state (Supplementary Fig. S5). This finding can be attributed to the capacity for these weathered soils to adsorb sulfate in conjunction with the supply of oxidised S resulting from ongoing microbial processing of SOM. During the decomposition of organic materials, the reduced C-bonded S is the most easily mineralisable (Ghani et al., 1991; Möller et al., 2002) through *in vivo* biological processes which convert reduced forms of organic S to sulfate or sulfate ester-S (McGill and Cole, 1981). While most of this oxidised S may be leached or consumed by plants or soil microbes, a portion of the resulting oxidised S maybe retained through specific adsorption to variable charge mineral surfaces (Edwards, 1998; Harrison et al., 1989; Tabatabai, 1987).

Previously, Prietzel et al. (2007) raised the concern that the isolation of particle size separates using water-based separation methods (such as wet-sieving) results in the accumulation of oxidised S and water-soluble SO_4^{2-} in the finest-sized fraction. Whilst leaching of oxidised sulfate-S has most likely occurred in the current study, we do not consider that this has resulted in an artificial redistribution of S that is sufficiently large to impede the interpretation of these results because the fractionation procedure used involved the filtering and removal of filtrate from the mineral fraction prior to the final wet-sieving step. In addition, as the fine-MAOM fraction makes up most of the bulk soil (60–82 %), the bulk soil indicates how much oxidised-S can be expected within the fine-MAOM. Indeed, S composition within the bulk soil and the fine-MAOM were similar (Fig. 5), with organic and inorganic sulfate S composition in the fine-MAOM being within 9 % of the bulk soil (Supplementary Table S2).

Finally, when all samples were pooled together, S composition was found to be more distinct across the fractions rather than land use (Fig. 5). Across the fractions, S composition was mainly defined by the proportion of more reduced organic S (G1: disulfide-S, G2: thiol and thio-ether, and G3:sulfinic acid and sulfoxide S) in conjunction with the proportion of oxidised S (G5: sulfate and sulfate ester-S). The composition of S shifted from reduced to oxidised S transitioning from the two POM fractions to the fine-MAOM, highlighting the differences in S composition of POM and fine-MAOM discussed earlier. The proportions of intermediate forms of S (G4: sulfonate S and sulfonic acid), on the other hand, were most similar between different fractions with G4, therefore, sitting near perpendicular to the PC1 axis. This may indicate

the less labile nature of intermediate forms of S, as postulated by Solomon et al. (2003) and Schroth et al. (2007).

4.2. The impact of long-term cropping on sulfur composition

Within the bulk soil, long-term cropping influenced the composition of S, with a consistent shift to more oxidised S with cropping and the magnitude of this change being proportional to cropping duration (Fig. 4). Since the bulk soil is made up of both POM and fine-MAOM, which have distinct S compositions (Fig. 5), S within the bulk soil reflects the balance between these fractions. Since POM fractions are most sensitive to land use change (Poeplau and Don, 2013), proportionately more POM is lost as a result of cropping compared to fine-MAOM (Fig. 1 and Supplementary Fig. S4). Moreover, the loss of total SOC and S in POM fractions also increased with cropping duration (Fig. 1 and Supplementary Fig. S4). As such, this change in the bulk soil reflects the decreasing influence of POM on the overall composition of soil S in cropped soils. However, within the fine-MAOM fraction, which makes up most of the bulk soil (Fig. 1), there was only a shift to more oxidised forms of S in two of the three soils investigated (Fig. 4). This shift may reflect the increased microbial processing of SOM bound to mineral surfaces as a result of the increased physical disturbance and subsequent aeration of soil (Schlesinger et al., 2000). However, overall, these changes in the fine-MAOM fraction are not distinct. The observed changes in S composition of the bulk soil following the conversion to cropping have also been documented by other studies, such as Solomon et al. (2003) and Solomon et al. (2011). However, in the present study, we extend this by showing that the shift to more oxidised S is primarily due to a proportionately greater loss of POM within the bulk soil rather than any particular change in S composition within each SOM fraction (Figs. 2–4).

Combining XANES data and extractable S enables the ability to discern the impact of cropping on C-bonded S and indirectly C-bonded S (sulfate ester-S) within the bulk soil. The decreasing C-bonded S:sulfate ester S ratio revealed proportionately more C-bonded S was mineralised compared to sulfate ester S, indicating the biological mineralisation of S (McGill and Cole, 1981) was dominant (Table 3). Unlike Wang et al. (2006) who observed the opposite effect in bulk soils of the Great Plains of North America, our findings support conclusions made by Solomon et al. (2011), Churka Blum et al. (2013) and Möller et al. (2002) and demonstrate the importance of reduced C-bonded S for the continued supply of S for plant uptake. Wang et al. (2006) did, however, acknowledge this discrepancy in the changes to C-bonded S:sulfate ester S ratios following cropping, suggesting this indicates that S dynamics and mineralisation likely have an ecosystem dependence. Thus, perhaps a combination of climate factors (mean annual temperature and precipitation) and soil characteristics (pH and mineralogy) introduce additional complexity to S mineralisation, which requires more detailed investigation.

Although both SOC and S were lost from each fraction across all three soils, differences were observed in the rate of loss of either SOC or S across the different fractions. Relative to SOC, there was a comparatively smaller loss of total S after cropping within the bulk soil, as shown by the decrease in C:S ratios (Supplementary Fig. S4). This change to bulk soil C:S ratios following cropping can be related to the depletion of POM fractions with high C:S ratios (Table 2). However, this may have also been compounded by the substantial decrease in C:S ratios within the fine-MAOM fraction (Supplementary Fig. S4). Although only a small dataset, this suggests proportionately more mineral-associated C was lost due to cropping than S, as was also reported by Wang et al. (2006). This observation possibly indicates the preferential stabilisation of S-containing organic compounds compared to C-only functional groups, as found for N-containing compounds (Kopittke et al., 2018). In both the POM fractions, however, C:S ratios increased substantially after land use changed to cropping. This possibly reflects the increased mineralisation of S from POM fractions resulting from increased disturbance or may also be a result of the incorporation of crop residues with higher C:S ratios relative to biomass inputs derived from native vegetation as has been observed for C:N ratios (Barnard et al., 2024). However, overall, it is interesting that despite the decrease of S relative to SOC within the POM fractions, S seems to be preferentially stabilised within fine-MAOM, demonstrating the importance of organo-mineral associations for the nutrient retention of S.

The impact of cropping on the composition of S within POM fractions was not distinguishable, with the different soils displaying different trends. For example, the average oxidation state of fPOM increased in the cropped soil of Cecilvale while values declined for the oPOM fraction. However, the reverse was found for the POM fractions of Langlands-Logie (Supplementary Fig. S5). The SOC within POM fractions is regarded as being at an earlier stage of decomposition and is generally more transient than SOC stored as fine-MAOM. Indeed, mean residence times of fPOM and oPOM are up to an order of magnitude shorter than that of mineral-associated SOC due to increased accessibility to decomposer organisms (Lavallee et al., 2020; Liao et al., 2006). Therefore, we propose that as the more reduced forms of organic S in these POM fractions undergo microbial processing, the resulting more oxidised S would either be incorporated as minerally bound S (thus forming part of the fine-MAOM), be consumed by plant or microbial life as a nutrient, or be leached from the soil matrix and would not accumulate or be retained as oxidised forms of S.

5. Conclusions

Unlike previous studies that have focused on humic extracts or bulk soil, in the present study, we have demonstrated distinct differences in S composition and trends across different physically separated soil fractions. We also show that the loss of SOC and S caused by land use change was only associated with a change in the composition of S in the bulk soil, which was attributed to the proportionately greater loss of POM fractions, which comprise mostly reduced C-bonded S, during cropping. The biological mineralisation of reduced forms of C-bonded S for the supply of plant-available S is also demonstrated, with organo-mineral associations potentially supporting the retention of the resulting mineralised S. Overall, this study supports our understanding of long-term S dynamics by extending our understanding of the S composition changes across different soil fractions in cropping systems.

CRediT authorship contribution statement

Brigid A. McKenna: Writing – review & editing, Methodology, Data curation. **Meghan Barnard:** Writing – original draft, Investigation, Formal analysis, Data curation, Conceptualization. **Ram C. Dalal:** Writing – review & editing, Resources, Data curation. **Peter M. Kopittke:** Writing – review & editing, Supervision, Methodology, Funding acquisition, Conceptualization. **Jeremy L. Wykes:** Methodology, Investigation, Data curation. **Bruce C.C. Cowie:** Methodology, Investigation, Data curation.

Declaration of Competing Interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Peter Kopittke reports financial support was provided by Grains Research and Development Corporation. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper

Acknowledgments

The authors acknowledge funding from the Grains Research and Development Corporation (GRDC) (UOQ1910-003RTX). Part of this

research was undertaken on the Medium X-ray spectroscopy beamline (MEX-2) at the Australian Synchrotron, part of ANSTO. Tony King and Dr. Andrew Biggs from the Queensland Department of Resources are also gratefully acknowledged for their custodianship of the Vertisol soil series.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.agee.2025.109833.

Data availability

Data will be made accessible on UQ eSpace http://doi.org/10.48610/3b46392.

References

Almeida, L.F.J., Souza, I.F., Hurtarte, L.C.C., Teixeira, P.P.C., Inagaki, T.M., Silva, I.R., Mueller, C.W., 2021. Forest litter constraints on the pathways controlling soil organic matter formation. Soil Biol. Biochem. 163. https://doi.org/10.1016/j.soilbio.2021.108447.

Barnard, M., Dalal, R.C., Weng, Z.H., Schweizer, S.A., Kopittke, P.M., 2024. Physicochemical protection is more important than chemical functional composition in controlling soil organic carbon retention following long-term land-use change. Geoderma 452, 117098. https://doi.org/10.1016/j.geoderma.2024.117098.

Basile-Doelsch, I., Balesdent, J., Pellerin, S., 2020. Reviews and syntheses: The mechanisms underlying carbon storage in soil. Biogeosciences 17 (21), 5223–5242. https://doi.org/10.5194/bg-17-5223-2020.

Camargo, A., 2024. Statistical significance of PCA. ⟨https://arleyc.github.io/PCAtest/⟩.

Chapman, S.J., 1997. Carbon substrate mineralization and sulphur limitation. Soil Biol. Biochem. 29 (2), 115–122. https://doi.org/10.1016/S0038-0717(96)00302-1.

Chenu, C., Rumpel, C., Lehmann, J., 2015. Methods for studying soil organic matter. Soil Microbiol. Ecol. Biochem. 383–419. https://doi.org/10.1016/b978-0-12-415955-6.00013-x.

Churka Blum, S., Lehmann, J., Solomon, D., Caires, E.F., Alleoni, L.R.F., 2013. Sulfur forms in organic substrates affecting S mineralization in soil. Geoderma 200-201, 156–164. https://doi.org/10.1016/j.geoderma.2013.02.003.

Cotrufo, M.F., Ranalli, M.G., Haddix, M.L., Six, J., Lugato, E., 2019. Soil carbon storage informed by particulate and mineral-associated organic matter. Nat. Geosci. 12 (12), 989–994. https://doi.org/10.1038/s41561-019-0484-6.

Dalal, R.C., Mayer, R.J., 1986. Long term trends in fertility of soils under continuous cultivation and cereal cropping in southern Queensland. I. Overall changes in soil properties and trends in winter cereal yields. Aust. J. Soil Res. 24 (2), 265–279. https://doi.org/10.1071/SR9860265.

Edwards, P.J., 1998. Sulfur cycling, retention, and mobility in soils: a review / Pamela J. Edwards. https://doi.org/10.2737/NE-GTR-250.

Eriksen, J., 2009. Chapter 2 soil sulfur cycling in temperate agricultural systems. In: Advances in Agronomy. Academic Press, pp. 55–89. https://doi.org/10.1016/s0065-2113(09)01002-5.

Feinberg, A., Stenke, A., Peter, T., Hinckley, E.L.S., Driscoll, C.T., Winkel, L.H.E., 2021. Reductions in the deposition of sulfur and selenium to agricultural soils pose risk of future nutrient deficiencies. Commun. Earth Environ. 2 (1). https://doi.org/10.1038/s43247-021-00172-0.

Ghani, A., McLaren, R.G., Swift, R.S., 1991. Sulfur Mineralization in Some New-Zealand Soils. Biol. Fertil. Soils 11 (1), 68–74. https://doi.org/10.1007/BF00335838.

Ghani, A., McLaren, R.G., Swift, R.S., 1992. Sulphur mineralisation and transformations in soils as influenced by additions of carbon, nitrogen and sulphur. Soil Biol. Biochem. 24 (4), 331–341. https://doi.org/10.1016/0038-0717(92)90193-2.

Guo, L.B., Gifford, R.M., 2002. Soil carbon stocks and land use change: a meta analysis. Glob. Change Biol. 8 (4), 345–360. https://doi.org/10.1046/j.1354-1013.2002.00486.x.

Harrison, R.B., Johnson, D.W., Todd, D.E., 1989. Sulfate adsorption and desorption reversibility in a variety of forest soils. J. Environ. Qual. 18 (4), 419–426. https://doi.org/10.2134/jeq1989.00472425001800040004x.

Isbell, R.F., 2021. Australian Soil Classification, 3rd ed. CSIRO Publishing.

Kassambara, A.M., Fabian, 2020. factoextra: Extract and Visualize the Results of Multivariate Data Analyses. ⟨https://CRAN.R-project.org/package=factoextra⟩.

Kertesz, M.A., Mirleau, P., 2004. The role of soil microbes in plant sulphur nutrition. J. Exp. Bot. 55 (404), 1939–1945. https://doi.org/10.1093/jxb/erh176.

Kleber, M., Lehmann, J., 2019. Humic substances extracted by alkali are invalid proxies for the dynamics and functions of organic matter in terrestrial and aquatic ecosystems. J. Environ. Qual. 48 (2), 207–216. https://doi.org/10.2134/jeq2019.01.0036.

Kölbl, A., Kögel-Knabner, I., 2004. Content and composition of free and occluded particulate organic matter in a differently textured arable Cambisol as revealed by solid-state ^{13}C NMR spectroscopy. Z. Pflanz. ähr. Bodenk 167 (1), 45–53. https://doi.org/10.1002/jpln.200321185.

Kopittke, P.M., Hernandez-Soriano, M.C., Dalal, R.C., Finn, D., Hoeschen, C., Mueller, C.W., 2018. Nitrogen-rich microbial products provide new organo-mineral associations for the stabilization of soil organic matter. Glob. Change Biol. 24 (4), 1762–1770. https://doi.org/10.1111/gcb.14009.

Lal, R., 2004. Soil Carbon Sequestration Impacts on global climate change and food security. Science 304 (5677), 1623–1627. https://doi.org/10.1126/science.1097396.

Lavallee, J.M., Soong, J.L., Cotrufo, M.F., 2020. Conceptualizing soil organic matter into particulate and mineral-associated forms to address global change in the 21st century. Glob. Change Biol. 26 (1), 261–273. https://doi.org/10.1111/gcb.14859.

Lehmann, J., Kleber, M., 2015. The contentious nature of soil organic matter. Nature 528 (7580), 60–68. https://doi.org/10.1038/nature16069.

Liao, J.D., Boutton, T.W., Jastrow, J.D., 2006. Organic matter turnover in soil physical fractions following woody plant invasion of grassland: Evidence from natural 13C and 15N. Soil Biol. Biochem. 38 (11), 3197–3210. https://doi.org/10.1016/j.soilbio.2006.04.004.

MacCarthy, P., 2001. The principles of humic substances. Soil Sci. 166 (11), 738–751. https://doi.org/10.1097/00010694-200111000-00003.

McGill, W.B., Cole, C.V., 1981. Comparative aspects of cycling of organic C, N, S and P through soil organic matter. Geoderma 26 (4), 267–286. https://doi.org/10.1016/0016-7061(81)90024-0.

Möller, A., Kaiser, K., Kanchanakool, N., Anecksamphant, C., Jirasuktaveekul, W., Maglinao, A., Niamskul, C., Zech, W., 2002. Sulfur forms in bulk soils and alkaline soil extracts of tropical mountain ecosystems in northern Thailand. Aust. J. Soil Res. 40 (1), 161–175. https://doi.org/10.1071/SR01001.

Narayan, O.P., Kumar, P., Yadav, B., Dua, M., Johri, A.K., 2023. Sulfur nutrition and its role in plant growth and development. Plant Signal. Behav. 18 (1). https://doi.org/10.1080/15592324.2022.2030082, 2030082-2030082.

Poeplau, C., Don, A., 2013. Sensitivity of soil organic carbon stocks and fractions to different land-use changes across Europe. Geoderma 192 (1), 189–201. https://doi.org/10.1016/j.geoderma.2012.08.003.

Poeplau, C., Don, A., Six, J., Kaiser, M., Benbi, D., Chenu, C., Cotrufo, M.F., Derrien, D., Gioacchini, P., Grand, S., Gregorich, E., Griepentrog, M., Gunina, A., Haddix, M., Kuzyakov, Y., Kühnel, A., Macdonald, L.M., Soong, J., Trigalet, S., Vermeire, M.-L., Rovira, P., van Wesemael, B., Wiesmeier, M., Yeasmin, S., Yevdokimov, I., Nieder, R., 2018. Isolating organic carbon fractions with varying turnover rates in temperate agricultural soils – a comprehensive method comparison. Soil Biol. Biochem. 125, 10–26. https://doi.org/10.1016/j.soilbio.2018.06.025.

Prietzel, J., Prater, I., Colocho Hurtarte, L.C., Hrbacek, F., Klysubun, W., Mueller, C.W., 2019. Site conditions and vegetation determine phosphorus and sulfur speciation in soils of Antarctica. Geochim. Et. Cosmochim. Acta 246, 339–362. https://doi.org/10.1016/j.gca.2018.12.001.

Prietzel, J., Thieme, J., Neuhäusler, U., Susini, J., Kögel-Knabner, I., 2003. Speciation of sulphur in soils and soil particles by X-ray spectromicroscopy. Eur. J. Soil Sci. 54 (2), 423–433. https://doi.org/10.1046/j.1365-2389.2003.00543.x.

Prietzel, J., Thieme, J., Salome, M., Knicker, H., 2007. Sulfur K-edge XANES spectroscopy reveals differences in sulfur speciation of bulk soils, humic acid, fulvic acid, and particle size separates. Soil Biol. Biochem. 39 (4), 877–890. https://doi.org/10.1016/j.soilbio.2006.10.007.

R Core Team, 2023. R: a language and environment for statistical computing. R. Found. Stat. Comput. ⟨https://www.R-project.org/⟩.

Ravel, B., Newville, M., 2005. ATHENA, ARTEMIS, HEPHAESTUS: data analysis for X-ray absorption spectroscopy using IFEFFIT. J. Synchrotron Radiat. 12 (4), 537–541. https://doi.org/10.1107/S0909049505012719.

Sanderman, J., Hengl, T., Fiske, G.J., 2018. Correction for Sanderman et al., Soil carbon debt of 12,000 years of human land use. Proc. Natl. Acad. Sci. USA 115 (7), E1700. https://doi.org/10.1073/pnas.1800925115.

Scherer, H.W., 2009. Sulfur in soils. J. Plant Nutr. Soil Sci. 172 (3), 326–335. https://doi.org/10.1002/jpln.200900037.

Schlesinger, W.H., Andrews, J.A., Rustad, L.E., Huntington, T.G., Boone, R.D., 2000. Soil respiration and the global carbon cycle. Biogeochemistry 48 (1), 7–20. https://doi.org/10.1023/A:1006247623877.

Schmidt, M.W., Torn, M.S., Abiven, S., Dittmar, T., Guggenberger, G., Janssens, I.A., Kleber, M., Kogel-Knabner, I., Lehmann, J., Manning, D.A., Nannipieri, P., Rasse, D. P., Weiner, S., Trumbore, S.E., 2011. Persistence of soil organic matter as an ecosystem property. Nature 478 (7367), 49–56. https://doi.org/10.1038/nature10386.

Schroth, A.W., Bostick, B.C., Graham, M., Kaste, J.M., Mitchell, M.J., Friedland, A.J., 2007. Sulfur species behavior in soil organic matter during decomposition. J. Geophys. Res. 112 (G4). https://doi.org/10.1029/2007JG000538. G04011-n/a.

Schweizer, S.A., Mueller, C.W., Höschen, C., Ivanov, P., Kögel-Knabner, I., 2021. The role of clay content and mineral surface area for soil organic carbon storage in an arable toposequence. Biogeochemistry 156 (3), 401–420. https://doi.org/10.1007/s10533-021-00850-3.

Sharma, R.K., Cox, M.S., Oglesby, C., Dhillon, J.S., 2024. Revisiting the role of sulfur in crop production: a narrative review. J. Agric. Food Res. 15, 101013. https://doi.org/10.1016/j.jafr.2024.101013.

Soil Survey Staff, 2003. Keys to Soil Taxonomy, 9th ed. U.S. Dept. of Agriculture, Natural Resources Conservation Service.

Solomon, D., Lehmann, J., Martínez, C.E., 2003. Sulfur K-edge XANES spectroscopy as a tool for understanding sulfur dynamics in soil organic matter. Soil Sci. Soc. Am. J. 67 (6), 1721–1731. https://doi.org/10.2136/sssaj2003.1721.

Solomon, D., Lehmann, J., de, Zarruk, K.K., Dathe, J., Kinyangi, J., Liang, B., Machado, S., 2011. Speciation and long- and short-term molecular-level dynamics of soil organic sulfur studied by X-ray absorption near-edge structure spectroscopy. J. Environ. Qual. 40 (3), 704–718. https://doi.org/10.2134/jeq2010.0061.

Tabatabai, M.A., 1987. Physicochemical Fate of Sulfate in Soils. Japca 37 (3), 34–38. https://doi.org/10.1080/08940630.1987.10466197.

Wang, J., Solomon, D., Lehmann, J., Zhang, X., Amelung, W., 2006. Soil organic sulfur forms and dynamics in the Great Plains of North America as influenced by long-term cultivation and climate. Geoderma 133 (3-4), 160–172. https://doi.org/10.1016/j.geoderma.2005.07.003.

Witzgall, K., Vidal, A., Schubert, D.I., Hoschen, C., Schweizer, S.A., Buegger, F., Pouteau, V., Chenu, C., Mueller, C.W., 2021. Particulate organic matter as a functional soil component for persistent soil organic carbon. Nat. Commun. 12 (1), 4115. https://doi.org/10.1038/s41467-021-24192-8.

Zhao, F., McGrath, S.P., 1994. Extractable sulphate and organic sulphur in soils and their availability to plants. Plant Soil 164 (2), 243–250. https://doi.org/10.1007/BF00010076.