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Soil sulfur speciation in semi-arid, subtropical Australia after 40 years of land use management

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ABSTRACT

Organic sulfur (S) accounts for >95 % of S in soils, making the soil S cycle particularly susceptible to changes that influence soil organic matter, such as land use change from native landscapes to agriculture. Using the Brigalow Catchment Study (BCS), a longitudinal land use change trial from semi-arid, subtropical Australia, we examined the effect of land use change on soil S composition to assess potential S availability over time. Bulk soil (0–10 cm depth) from three land uses, undisturbed (native Brigalow), cropping, and pasture, were analysed using X-ray absorption near-edge structure (XANES) spectroscopy for *in situ* analyses of S speciation. The concentration of total S in the bulk soil ranged 178–286 mg kg^{-1} with organic S accounting for 95–99 % (176–271 mg kg^{-1}). Over 40 years of land use change, there was a decrease in total soil S concentrations, being associated with a decrease in total organic carbon (TOC) and total soil nitrogen (TSN). In the pasture catchment total S decreased by 17 %, TOC by 14 %, and TSN by 29 %, whilst in the cropping catchment total S decreased by 34 %, TOC by 50 %, and TSN by 53 %. Changes in S composition resulted in a decreased average oxidation state of soil S in both the pasture and cropping catchments and an increased C-S:ester sulfate-S in the pasture catchment. This study has highlighted the need for better S management to avoid decreased S fertility and productivity through loss of total S and changes in S forms which may influence potential S availability.

1. Introduction

Sulfur (S) is the fourth major essential macronutrient for plant growth and is present in soil in both inorganic (SO_4^{2-}) and organic forms. Of the total S pool, >95 % is organically bound in most aerobic soils, which must be mineralised to become plant-available [1,2]. Historically, substantial inputs of S into soils occurred due to both atmospheric deposition of SO_X through industrial emissions, and the inadvertent application of S within fertilisers (for example, single superphosphate is 11 % S). However, the use of high-analysis (low S) fertilisers and increased regulation of atmospheric emissions coupled with increased crop S removal under intensive agriculture has resulted in changes in S forms in soils and an increasing frequency of S deficiency [3–5]. Therefore, the supply of S from organic forms in the soil becomes critical for sustaining crop growth. Since all forms of organic S in soil are not readily mineralised, it is important to identify and quantify the organic S species and their changes during long-term cropping and other productive agriculture.

Sulfur chemistry and dynamics in soil are complex, having six possible oxidation states (−2 to +6) [6]. Sulfate (SO_4^{2-}) is mobile and directly available to plants and is controlled by adsorption/desorption reactions. Organic forms of S are largely immobile and occur in two broad forms, carbon bonded S (C-S) and sulfate easters (C-O-S). Where inorganic S is limiting, organic forms of S become significant in meeting plant demand for S. Soil organic S correlates strongly with soil organic C (SOC) and total N (TSN) [2], making S an important part of soil organic matter (SOM). The soil C:N and C:S ratios are known to determine the net mineralisation of organic S or net immobilisation of inorganic S, including SO_4^{2-}, with both biological and biochemical mineralisation being important [7,8].

Total S concentrations in soils average 0.04 %, however, it is known that conversion of native landscapes to long-term agricultural production reduces total S and alters S speciation [9–11]. For example, in subtropical Australian soils, long-term cropping reduced total S by

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35–51 % [12]. This loss of S with land use change is because >95 % of S in most aerobic soils is organic and the conversion of land to agricultural production results in the loss of SOM by both decreasing inputs to soil (including accelerating rates of SOM mineralisation), and by increasing outputs in crop produce and residue, and leaching. This loss of SOM from cropping systems therefore not only has impacts on S cycling and potential plant availability but given the importance of SOM in the global C cycle and climate regulation, it is possible that changes in speciation and concentrations of S alters SOM behaviour. There is evidence that the C:N:P:S ratios in SOM are relatively constant globally, which has implications for ongoing C sequestration in soil [13]. Indeed, C sequestration and conversely, soil organic matter mineralisation is driven by nutrient stoichiometry [14,15], hence, mineralisation of organic C from SOM leads to the mineralisation of organic S in soil. Whilst the contribution of C and N to SOM stabilisation and persistence are understood and generally well quantified, the significance of S is comparatively less understood and much less characterised.

The complexity of S chemistry in soil makes it challenging to characterise S speciation because traditional wet-chemistry extractions modify oxidation states of inorganic S forms, react too broadly, and degrade organic S forms, resulting in experimental artefacts. In this regard, the use of S K-edge X-ray absorption near edge structure (XANES) spectroscopy as an *in-situ* technique to characterise S species in soil has been established and overcomes the difficulties associated with traditional wet-chemical methods [16,17].

In the present study, we investigated S dynamics using a long-term, paired-catchment, land use change study from the Brigalow Belt Bioregion, known as the Brigalow Catchment Study (BCS) in Queensland, Australia. Soil samples were collected between 1981 and 2022 from three adjacent catchments: native brigalow (control), pasture, and cropping. We utilised S K-edge XANES to compare S speciation in the 0–10 cm soil depth across the three land-uses over 40 years. We hypothesised that long-term cropping and pasture would result in the conversion of S to more oxidised forms compared to the native undisturbed brigalow forest due to a decrease in SOM which has been reported previously due to land use change [10,18,19]. The objectives of this study were to: 1) compare the changes in total S in soil over 40 years after land use change from native vegetation to cropping and pasture; 2) quantify changes in S species *in-situ* using S K-edge X-ray absorption near edge structure (XANES) spectroscopy; and 3) assess the impact of changes in the concentration of S species over time for soil fertility and productivity. This study will provide valuable information on S dynamics in a subtropical environment under different land use management strategies, potential S availability to plants over time, and increases our understanding of S contribution to SOM stabilisation.

2. Materials and methods

2.1. Site history, description, and experimental design

The Brigalow Catchment Study is a long-term, paired, calibrated catchment study located in the Fitzroy Basin, central Queensland, Australia (Figs. 1 and 2). In the mid-1960s, 4.5 Mha of the Fitzroy Basin was cleared and developed for agriculture as a result of the Land Development Fitzroy Basin Scheme [20]. To quantify the effects of this clearing on hydrology, productivity and resource condition, the Brigalow Catchment Study commenced in 1965. The study is located at 24.81°S, 149.80°E, and has a semi-arid, subtropical climate, with an average hydrological year (October 1965 to September 2018) rainfall of 648 mm [21]. Soils at the study site are predominantly Black and Grey Vertosols, with an average slope of 2.5 % [20] (Fig. S1). The native vegetation of the site in its pre-European state was dominated by brigalow (*Acacia harpophylla*), either in a monoculture or in association with other species, such as belah (*Casuarina cristata*) and Dawson River blackbutt (*Eucalyptus cambageana*) [22]. This vegetation association is colloquially known as brigalow scrub [20]. The extant uncleared

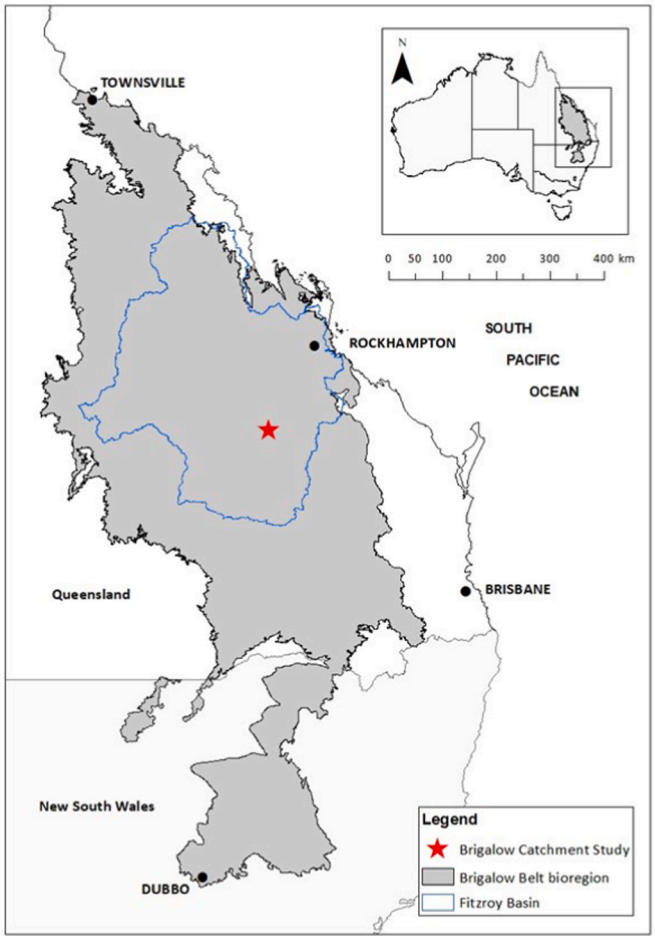

Fig. 1. Location of the Brigalow Catchment Study within the Brigalow Belt bioregion [44].

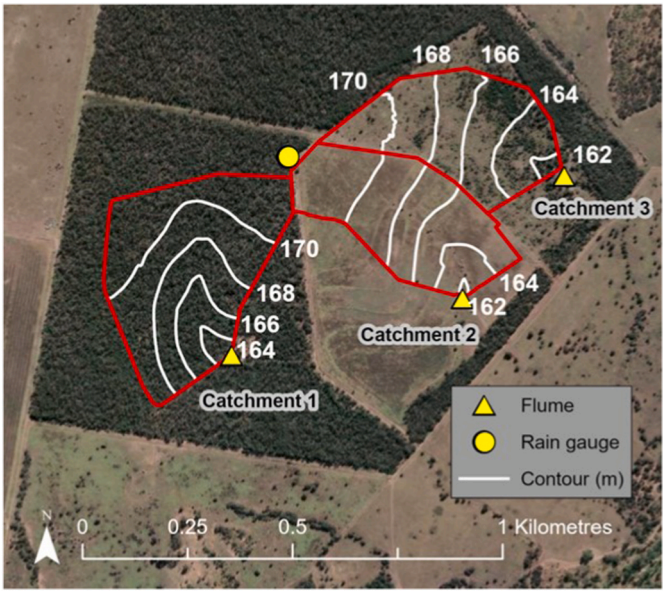

Fig. 2. An aerial view of the Brigalow Catchment Study showing Catchments 1 to 3
Catchment 1 is virgin, uncleared brigalow scrub. Catchment 2 was developed for cropping and Catchment 3 was developed for grazing on improved pastures [44].

vegetation of the study is classified as regional ecosystems 11.4.8, *Eucalyptus cambageana* woodland to open forest with *Acacia harpophylla or Acacia argyrodendron* on Cainozoic clay plains, and 11.4.9, *Acacia harpophylla* shrubby woodland with *Terminalia oblongata* on Cainozoic clay plains [23,24].

The study consists of three contiguous catchments of 11.7–16.8 ha and can be separated into four experimental stages: Stage I, hydrological calibration of the three catchments in an uncleared state from 1965 to 1982; Stage II, development of two catchments for agriculture from 1982 to 1983; Stage III, comparison of cropping or grazing land uses to virgin brigalow scrub from 1984 to 2010; and Stage IV, a comparison of leguminous and non-leguminous pastures to virgin brigalow scrub from 2010 to 2024 [24]. Throughout the stages Catchment 1 was retained in a virgin, uncleared state to provide a control treatment representative of the Brigalow Belt bioregion in its pre-European condition. Catchments 2 and 3 remained uncleared during Stage I. During Stage II they were cleared by bulldozer and chain in March 1982 and the fallen timber burnt in October 1982. Catchment 2 was then developed for cropping and Catchment 3 was developed for grazing of beef cattle on improved pasture with buffel grass (*Cenchrus ciliaris* cv. Biloela) sown in 1982. During Stage III, unfertilised dryland cropping was undertaken in Catchment 2, with the first crop, sorghum (*Sorghum bicolor*), sown in 1984. This was followed by annual wheat (*Triticum aestivum*) for 9 years. Fallows were initially managed using mechanical tillage (disc and chisel ploughs), which resulted in a significant soil disturbance and low soil cover. In 1992, a minimum-tillage philosophy was introduced and in 1995 opportunity cropping commenced with summer (sorghum) or winter [wheat, barley (*Hordeum vulgare*) and chickpea (*Cicer arietinum*)] crops sown when soil water content was adequate [21,25]. This continued until Stage IV, when a legume ley pasture of butterfly pea (*Clitoria ternatea*) was established. In 2018, the butterfly pea ley pasture was replaced with a Desmanthus (cv.Progardes) and buffel grass (*Cenchrus ciliaris* cv. Biloela) ley pasture. Stage III commenced in Catchment 3 with the commencement of grazing in 1983. Cattle breeds were *Bos indicus* and *Bos indicus*-cross [25]. The catchment was stocked at industry-recommended stocking rates, with utilisation to result in no less than 1000 kg/ha of pasture available at any time [21]. This land use continued throughout Stage IV. There has been no feed supplementation and no fertiliser application at any stage.

2.2. Soil fertility monitoring at the Brigalow Catchment Study

In each catchment, three permanent monitoring sites (20 m × 20 m) (forming three replicates) were established to monitor changes in soil fertility. Sites were initially stratified on soil type and slope position with a monitoring site allocated to both an upper- and lower slope position on Vertosols, and the third on a Sodosol irrespective of slope position. Secondary stratification was by way of 10 subunits, each 4 m × 10 m, within each monitoring site [20]. Baseline measurements of soil fertility were taken in 1981. Soil sampling for soil fertility assessment was typically conducted during the dry season (winter and spring). Surface (0–0.1 m) soil sampling was conducted annually from 1981 to 1987, with soil profile sampling (to 2 m or bedrock) occurring every second year commencing in 1981. Soil surface and profile samplings were then conducted in 1990, 1994, 1997, 2000, 2003, 2008, 2014, 2018, and 2023 [20,26]. Additional profile sampling was undertaken in 2022 and 2024. Surface soil samples were collected at each monitoring site using manual coring tubes of 0.05 m diameter; samples were typically a composite of eight 0.05 m cores. The eight cores were comprised of two cores sampled adjacent to each of four fixed locations within each subunit. More intensive sampling was undertaken pre-clearing in 1981, and in 2008, 2014, 2018 and 2023. In these years, samples were a composite of up to 20 cores, with four or five cores sampled adjacent to each of the four fixed locations. Soil profile samples were collected by taking five cores, typically using coring tubes of 0.05 m diameter. The five samples were divided into 0.1 m increments and bulked to form a composite sample for each depth and site, yielding three replicate samples per catchment per depth, with each individual replicate being a composite of five samples. Soil samples were dried at 40 °C, ground to pass <2 mm sieve, and stored at room temperature until analysis.

To examine changes in soil S, archived surface (0–10 cm) samples (three replicates) from 1981, 1997, and 0–0.1 m profile samples from 2022 from each of the three catchments were selected and analysed for S (see below). In addition, surface samples from 1983 were selected from the cropping and pasture catchments to examine the effect of burning. Furthermore, surface samples from 2000 were selected from the pasture catchment to examine the effect of pasture spelling. Hence a total of 12 treatments were analysed for S (resulting in 36 samples). Examination of changes in TSN and total organic carbon (TOC) concentrations utilised all 12 sampling time points in the three catchments (resulting in 108 samples).

2.3. Soil analysis for S, C and N

Air-dried soil was finely ground (≤53 μm) using a ball mill (Retsch MM 200) with total organic C and total N analysed by dry combustion using a LECO analyser (LECO Corporations, Michigan, USA, CN928 series). Total S was measured using hydrofluoric acid (HF) digestion followed by inductively-coupled plasma optical emission spectrometry (ICP-OES), given that Dumas (dry) combustion can potentially have poor precision for soil samples [27]. Certified reference material (National Institute of Standards and Technology) and blanks were included in the analysis for quality control. Extractable S was analysed according to Zhao and McGrath [28]. Using a 1:5 soil to solution ratio and an extraction solution of 0.016 M KH_2PO_4, soil suspensions were shaken for 1 h, followed by centrifugation at 2500*g*. The extractant was filtered using a 0.22 μm syringed filter. Total extractable S (SO_4-S and soluble organic S) was determined by ICP-OES, and inorganic SO_4-S was determined by ion chromatography (IC). Soluble organic S was calculated as the difference between total extractable S (ICP-OES) and inorganic S (IC).

2.4. S speciation using synchrotron-based X-ray absorption near edge structure (XANES)

Sulfur K-edge XANES spectra were collected at MEX 2 beamline of the Australian Synchrotron in Melbourne, Australia. The incident X-ray energy was selected using an Si (111) double-crystal monochromator, with a beam size of 5 × 2.7 mm and a photon flux of 1×10^{11} photons s^{-1}. Spectra were recorded in fluorescence mode using a four-element silicon drift detector (Vortex ME4) under vacuum. The sample compartment was continuously purged with N_2 gas to minimise X-ray absorption by air within the sample chamber. The X-ray energy was calibrated using the absorption edge (2472.02 eV) of $Na_2S_2O_3$ powder with an uncertainty of ±0.03 eV [29]. Spectra of the samples and standards were recorded with 2 s dwell across the energy range of 2420–2600 eV (2420–2460 eV in 5 eV steps, 2460–2466 eV in 0.5 eV steps, 2466–2486 eV in 0.05 eV steps, 2486 to 2520 in 0.020 K steps, and 2520 to 2600 in 0.050 K steps).

Air-dried soil was finely ground (≤53 μm) using a ball mill (Retsch MM 200) and thinly spread on double-sided carbon tape affixed to stainless steel sample holders. Samples were analysed by XANES, with each of the three replicates scanned, and with each of these replicates scanned twice (giving a total of six scans per treatment). These six scans were subsequently merged, with each individual scan taking approximately 20 min. In addition, spectra were collected on 11 standards, that represented a range of S oxidation states from −2 to +6, with AR grade standards diluted to 1 % S with boron nitride. Dilution of standards to 1 % S concentration has been reported to minimise self-absorption [16]. The standards analysed were: 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 [$SO3^{2-}$], taurine

[RS(=O)2OH], L-cysteic acid monohydrate [$RS(=O)_2O^-$], sodium sulfate [SO_4^{2-}], and sodium dodecyl sulfate [$ROSO_3$] (Fig. S3).

The S K-edge XANES spectra were analysed using Athena v0.9.26 [30]. Spectra were baseline corrected (from −52 to −15 eV) and edge normalised (+40 to + 100 eV). Spectra were deconvoluted using Gaussian peak fitting to quantify the relative proportions of five major S species according to Prietzel et al. [31] and Prietzel et al. [16] using the peak fit function in Athena v0.9.26 (Fig. S2). Peak assignments for each of the five major S species were validated against our S standards (Fig. S3). Suitable peak widths between 0 and 2 were initially manually determined and subsequently 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 the sample spectra, thus peaks were not fitted at ca. 2471 eV for FeS, 2472 eV for FeS_2 or ca. 2478 eV for inorganic sulfite S. Two arctangent functions were fitted, one at 2477 eV for the edge step of reduced S and one at 2483 eV for the edge step of oxidised S (both with a fixed width of 0.3 eV). 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 Table 1, from Prietzel et al. [31] to account for the S oxidation state dependency of absorption cross section.

2.5. Statistical analysis

Data were analysed using IBM SPSS Statistics v29. For total S, organic S, and extractable S, data were analysed using a two-way analysis of variance (ANOVA) with Fisher's least significant difference (LSD) post-hoc test.

3. Results

3.1. Temporal changes in soil S, organic C, and N

At the commencement of the experiment in 1981, the total S concentration was 278 mg kg^{-1} averaged across the three treatments, with no significant differences in total S concentrations between the three land uses at this initial timepoint ($P > 0.05$). When considering the total S concentrations in the soil, organic S accounted for >95 % of total S across all samples in the entire experiment regardless of time or treatment (Table 2).

Following land use change, the soil from the undisturbed brigalow catchment had higher total S concentrations compared to the other two catchments, with total S concentrations in 2022 significantly lower in both cropping and pasture than in the undisturbed brigalow ($P < 0.05$) (Fig. 3). At a depth of 0–10 cm, total S concentration was 280 mg S kg^{-1}in the soil from the brigalow catchment, but in the cropping catchment this decreased by 38 % over time, from 286 mg S kg^{-1}in 1981 to 178 mg S kg^{-1}in 2022. There was also a corresponding decrease in the pasture treatment, although the magnitude of the decrease was smaller (17 % decrease, from 269 to 223 mg S kg^{-1}). This significant decrease in total S in the cropping and pasture catchments was primarily the result of a decrease in organic S concentrations (Fig. 3). Although there were not initially any significant differences in organic S concentrations between the three land uses in 1981 ($P > 0.05$, average value of 270 mg S kg^{-1}), organic S concentrations were significantly lower in 2022 following land use change ($P < 0.05$), being 221 mg S $kg^{-1}$for pasture and 176 mg S $kg^{-1}$for cropping.

Extractable S concentrations ranged from 4 to 19 mg S kg^{-1}, being approximately 50 % inorganic and 50 % organic (Table 2). Concentrations of total extractable S decreased over time regardless of land use ($P < 0.05$), although the magnitude of the decrease was larger for cropping (18–4 mg kg^{-1}, being a 78 % decreased) than for the undisturbed Brigalow (18–8 mg kg^{-1}, being a 56 % decrease). This decrease in total extractable S occurred due to decreases in both extractable inorganic S and extractable organic S.

Although there were pronounced decreases in total extractable S, this accounted for only a small proportion of the decrease in total S loss in these soils. For example, in the cropping catchment, total S decreased by 108 mg kg^{-1}, from 286 to 178 mg kg^{-1}, with 94 % of this loss being from organic S (which decreased by 102 mg kg^{-1} from 278 to 176 mg kg^{-1}) whilst only 6 % of this loss was from inorganic S (which decreased 6 mg kg^{-1} from 8 to 2 mg kg^{-1}, Table 2). It is also noteworthy that although concentrations of inorganic S decreased over time in the cropping and pasture catchments, there was a noticeable (albeit non-significant, $P > 0.05$) increase in inorganic S in these two catchments after 1.7 y (1983), with this corresponding to the sampling conducted immediately after burning in these treatments.

Similar to S, there were no differences in SOC or TSN between any of the three land uses at the commencement of the experiment ($P > 0.05$). The undisturbed brigalow catchment showed no significant differences ($P > 0.05$) in SOC or TSN over the 40 year experimental period. In contrast, both SOC and TSN decreased over time in the cropping and pasture catchments, being significantly ($P < 0.05$) lower than the undisturbed brigalow (Fig. 4). Indeed, at the 2022 sampling, SOC concentration was an average of 22.6 g/kg in undisturbed brigalow soil, but 18.5 g/kg in pasture and 12.7 g/kg in the cropping soil (Fig. 4).

3.2. Synchrotron-based XANES analysis of the effect of land-use on S speciation

We utilised *in situ* synchrotron-based XANES analyses to examine the changes in S speciation over time with different land-uses. First, we examined the spectra of the 11 standards compounds, with substantial differences between the various compounds. For example, the energy corresponding to the white-line peaks increased with increasing oxidation state of S, ranging from 2471.0 eV for inorganic sulfide (FeS, oxidation state −2) to 2482.7 eV for inorganic sulfate (sodium sulfate, oxidation state +6) (Table S1 and Fig. S3). L-glutathione oxidised [RSSR] has two bonding environments for S [1s → σ*(S-S) and 1s → σ*(S-C)], hence the spectra contained two peaks corresponding to each type of S bond which were offset by 1.5 eV (Fig. S3).

Next, we examined the soil samples, first considering the undisturbed brigalow catchment samples. Peaks corresponding to reduced organic S (G2), intermediate S (G4) and the most oxidised form of S (G5) were prominent in the undisturbed samples (Fig. 5). Peak fitting analysis confirmed these observations (Fig. 6, Table S2), ester sulfate S and

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	0.76	+0.2	Disulfide S	RSSR	0.9
G2	2474.2	0.88	+0.5	Thiol	RSH	0.9
				Thio-ether	RSR	
G3	2476.3	0.62	+2	Sulfinic acid	RSO(OH)	0.6
				Sulfoxide S	RS(=O)R	
G4	2481.0	0.74	+4 to 5	Sulfonate S	$RS(=O)_2O^-$	0.4
				Sulfonic acid	$RS(=O)_2OH$	
G5	2482.7	0.87	+6	Sulfate S	SO_4^{2-}	0.35
				Ester sulfate	$ROSO_3$	

Table 2
Average values for total S and extractable S in soil under each land use at each sampling period.

Year	Land use	Total S (mg kg^{-1})	Total extractable S (mg kg^{-1})	Extractable inorganic S [SO_4^{2-}] (mg kg^{-1})	Extractable organic S[a] (mg kg^{-1})	Organic S[b] (mg kg^{-1})	Organic S[b] (%)
1981	**Brigalow**	280	18	9	9	271	97
	Cropping	286	18	8	10	278	97
	Pasture	269	17	8	9	261	97
1983	**Cropping**	267	18	10	7	257	96
	Pasture	221	19	12	7	209	95
1997	**Brigalow**	306	16	8	8	298	98
	Cropping	184	11	6	5	178	97
	Pasture	211	11	6	5	205	97
2000	**Pasture**	209	11	6	5	203	97
2022	**Brigalow**	269	8	4	4	265	98
	Cropping	178	4	2	3	176	99
	Pasture	223	7	2	4	221	99

[a] Extractable organic S is calculated as the difference between total extractable S and extractable inorganic SO_4^{2-}.
[b] Organic S is calculated as total S minus inorganic SO_4^{2-}.

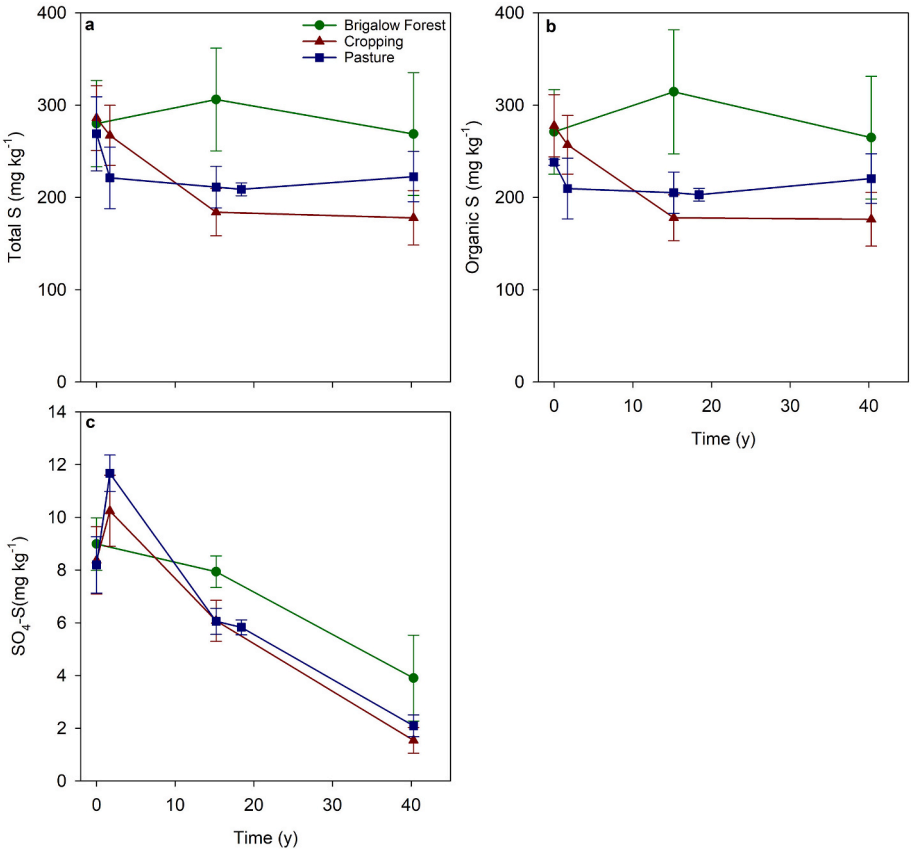

Fig. 3. Effect of land-use on concentrations of total S (a), organic S (b), and SO_4^{2-}-S (c) at a depth of 0–10 cm over a period of 40 y. Error bars denote standard error (n = 3).

inorganic sulfate (G5) contributed an average of 33 %, followed by thiol and thiol ether (G2) at an average of 26 % and sulfonate and sulfonic acid (G4) at an average of 20 %. The relative contribution from each of the prominent S forms remained relatively constant over time in these samples from the brigalow catchment, except a slight downward trend in inorganic sulfate (G5 – SO_4^{2-}) and a concurrent slight increase in ester sulfate-S (G5 – $ROSO_3$) (Figs. 5 and 6). The C-S:ester sulfate-S also remained constant over time in this catchment (Table 3).

We then examined the impact of different land-use management strategies on S speciation with time. At the initial sampling time (i.e. 1981), the speciation of S within the soils from both the cropping and the pasture catchments was similar to that of the undisturbed brigalow catchment (Fig. 5), with the relative contribution from each of the three dominant S forms increasing in the order of G4 (sulfonate, 20 %) < G2 (thiol and thiol-ether, 26 %) < G5 (ester sulfate-S and inorganic sulfate, 33-24 %) in both catchments (Fig. 6). However, changes were observed at the second sampling period in 1983, with this corresponding to the sampling after the native vegetation was burned in these catchments. For samples from the agricultural catchments post-clearing in 1983, the average contribution of reduced organic S (G1) and sulfonate (G4) decreased whilst there was an increase in sulfoxide (G3) and inorganic sulfate (G5) (Figs. 5 and 6). With further time following land use change, there was an increased contribution of reduced organic sulfur species (G1 and G2) in both the cropping and pasture catchments, and there was an increase in contribution of sulfoxide in the pasture system (G3) (Figs. 5 and 6). Similar to the brigalow catchment, there was a

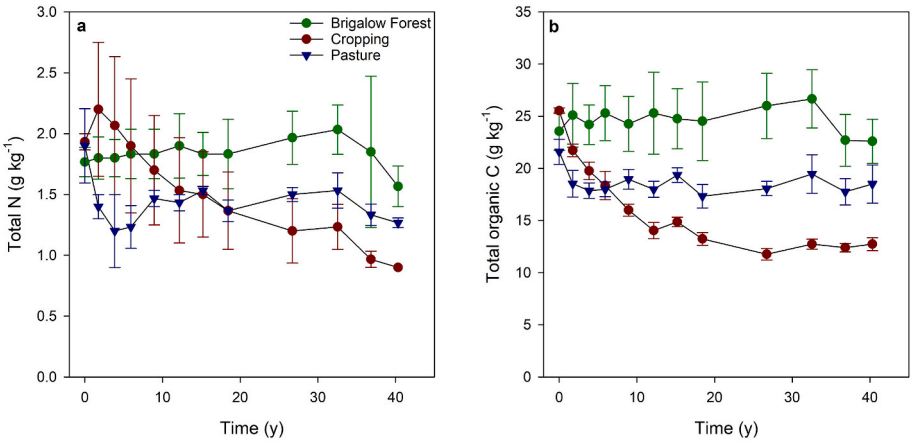

Fig. 4. Effect of land-use on concentrations of total N (a), and total organic C (b) at a depth of 0–10 cm over a period of 40 y. Error bars denote standard error (n = 3).

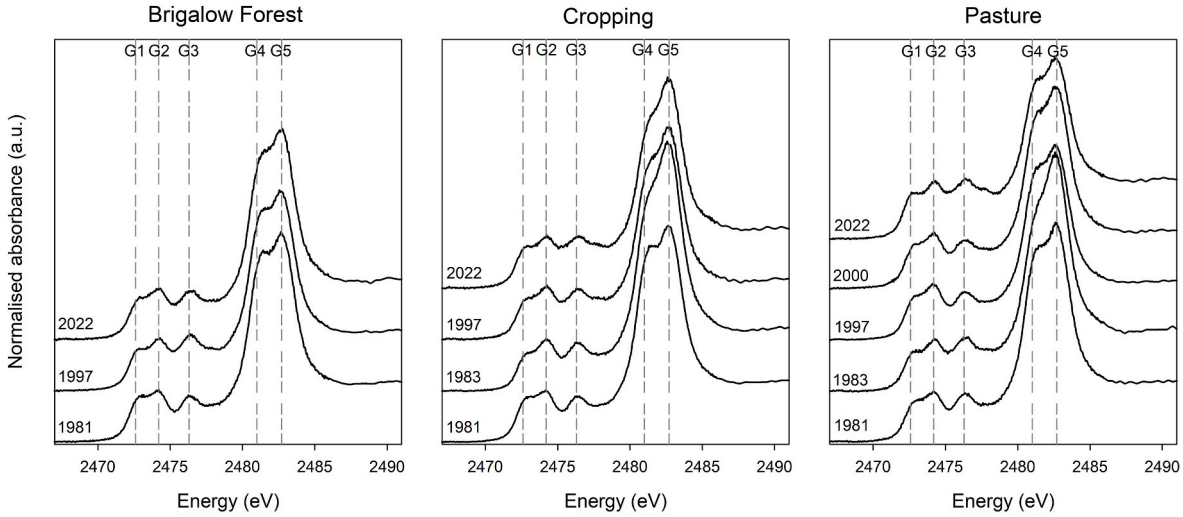

Fig. 5. Stacked XANES spectra for each land-use catchment over time. The dotted vertical reference lines correspond to the Gaussian peaks, G1 (2472.6 eV), G2 (2474.2eV), G3 (2476.3eV), G4 (2481.0eV), and G5 (2482.7eV).

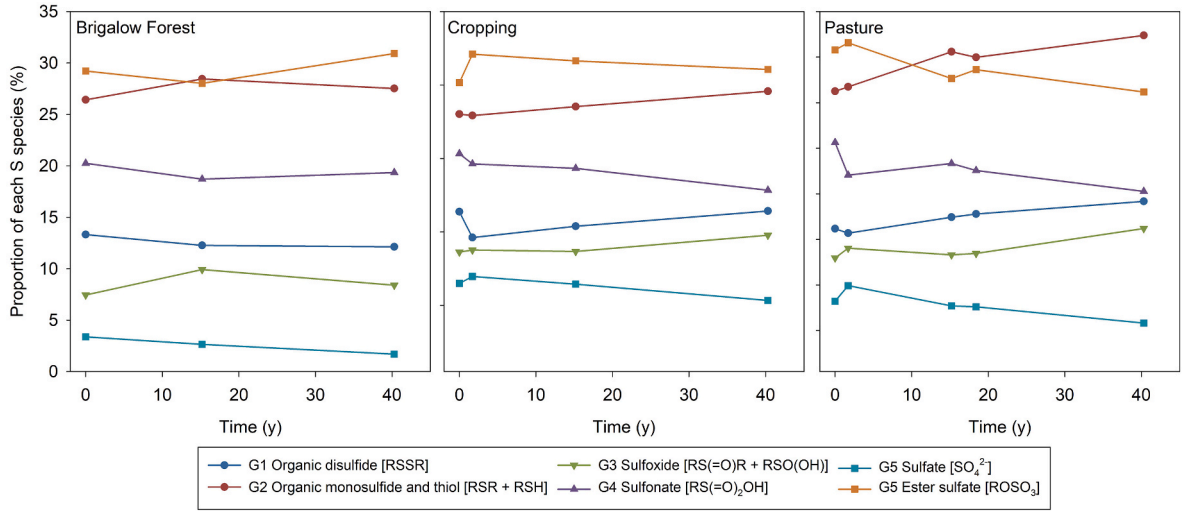

Fig. 6. The proportion of each S species over time in soil from each land use catchment.

Table 3
Temporal changes in estimated proportion of total S present as sulfate-S or ester sulfate-S and calculated C-S:ester sulfate-S for each land use catchment.

Year	Land use	Total sulfate and ester sulfate [SO_4^{2-} & $ROSO_3$][a] (%)	Sulfate [SO_4^{2-}][b] (%)	Ester sulfate [$ROSO_3$][c] (%)	C-bonded S: ester sulfate-S
1981	**Brigalow**	32.6	3.4	29.2	2.3
	Cropping	33.3	3.0	30.3	2.2
	Pasture	34.0	3.2	30.8	2.1
1983	**Cropping**	38.1	3.9	34.2	1.8
	Pasture	36.5	4.9	31.6	2.0
1997	**Brigalow**	30.7	2.6	28.0	2.5
	Cropping	36.2	2.9	33.3	1.9
	Pasture	30.4	2.7	27.6	2.5
2000	**Pasture**	31.2	2.6	28.6	2.4
2022	**Brigalow**	32.6	1.7	30.9	2.2
	Cropping	32.8	0.7	32.1	2.1
	Pasture	27.0	0.8	26.2	2.8

[a] Determined by XANES.
[b] Determined by IC.
[c] Determined as the difference.

downward trend in sulfonate (G4) and ester sulfate-S and inorganic sulfate (G5) with time. In the pasture catchment, C-S:ester sulfate-S increased with time (Table 3).

We then examined the average change in S oxidation state, finding that there was an initial increase in the proportion of oxidised S in soil from the cropping and pasture catchments at the second sampling period (i.e. 1983) followed by a decrease to more reduced forms of S with time (Fig. 7). In contrast, the average oxidation state of S in soil from the undisturbed brigalow catchment remained constant over the entire experimental duration (Fig. 7).

4. Discussion

4.1. Sulfur in the undisturbed brigalow catchment soil

As expected, in the undisturbed brigalow catchment, total S concentrations remained relatively constant over time, as did both TOC and TSN. Even though total S concentrations remained relatively constant, concentrations of extractable S (both extractable inorganic and extractable organic) decreased over time in this catchment. The observed decrease in extractable S could potentially be explained by decreased global atmospheric S deposition over the last 50 years [32,33]. Specifically, in Australia atmospheric S deposition have decreased ca. 2.5 % over the period of 1990 to 2015 [34]. Differences in soil conditions (time of year, moisture content) at each sampling time point could also influence the distribution of soil extractable S given the dynamic nature of soil S. Furthermore, from 2015 to 2021 hydrological years, the BCS site experienced consecutive below average rainfall, including the direst recorded year since the commencement of the study in 1965, thus any deposition of atmospheric nutrients would have declined during this period.

Speciation of soil S in the undisturbed brigalow catchment remained unchanged over time, with both C-S:ester sulfate-S and the average oxidation state remaining relatively constant over the 40 year period. We found ester sulfate S and inorganic sulfate (G5) contributed an average of 33 %, followed by thiol and thiol ether (G2) contributing 26 %, and sulfonate and sulfonic acid (G4) contributed 20 %. Typically, higher TOC and greater organic matter input has been shown to increase the proportion of C bonded S [9,17,35], however as a native, medium open forest in a semi-arid environment with an average annual temperature of 13.3–29.2 °C, and average annual rainfall of 697 mm (and where average monthly evaporation exceeds average monthly rainfall), organic matter input and turnover would be modest as evidenced by the stability of TOC and TSN in this catchment.

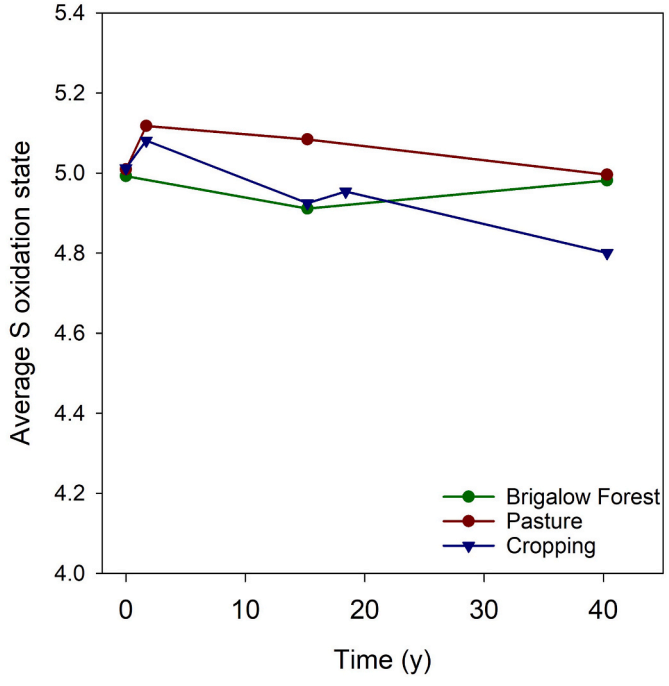

Fig. 7. The average oxidation state of S with time in soil from each land use catchment.

4.2. Impacts of long-term land use change on sulfur

Overall, land use change resulted in a decrease in total soil S, with a 38 % decrease in the cropping catchment (from 286 mg kg^{-1} to 178 mg kg^{-1}) and a 17 % decrease in the pasture catchment (from 269 mg kg^{-1} to 223 mg kg^{-1}) after 40 years, with this decrease largely driven by a loss of organic S. In our experimental system, Thorton and Shrestha (2020) reported crop removal of S accounted for 63 % of total soil S loss in the cropping catchment whereas S content of beef and liveweight gain data accounted for 5 % of total soil S loss in the pasture catchment, indicating removal of S in agricultural products was a major pathway under cropping but negligible under grazing. Loss of soil S with land use change has been previously attributed to accelerating rates of organic matter mineralisation, increased outputs in agricultural products, and increased leaching. For example, Bettany et al. [36] reported a 38 % decrease in organic S in Canadian prairie soils after cultivation for 65 years, Wang et al. [11] reported a 30 % decrease in organic S in cultivated North American soils, and Kopittke et al. [12] demonstrated a loss of 35–51 % of total S from subtropical Australian soils under long-term cropping (up to 70 years). We found that the decrease in total S corresponded with a decrease in SOC and TSN in the soils examined (Figs. 3 and 4) which was expected given the close association of soil S with soil organic matter [2]. In this study, the magnitude of soil S loss was less than that for C and N (for example, in the cropping catchment SOC decreased by 50 % and TSN decreased by 53 % *viz.* 35 % for S) which suggests soil S is more resistant to mineralisation and/or other losses compared to SOC and TSN [11,36].

Both long-term cropping and pasture resulted in a shift in the relative proportion of the major organic S species. In both catchments there was a relative increase in reduced and intermediate organic S species (G1, G2, and G3), and a decrease in oxidised organic S species (G4 and G5). Thus, for the duration of land use management practices there was a modest decrease in average S oxidation state (Fig. 7).

The increased proportion of reduced forms of S with long-term land use change was unexpected given that long-term cropping has been shown previously to increase the proportion of more oxidised forms of S, with this being attributed to increased soil disturbance, and ongoing

microbial decomposition of organic matter [10,18,19]. Indeed, as expected, both TOC and TSN decreased in the cropping and pasture catchments over 40 years. The loss of TOC and TSN in the agricultural catchments are interconnected to the decreased productivity (cropping productivity declined 20 % over 20 years, and pasture availability halved only 3 years after clearing) in these catchments after land-use change [37]. Thus, whilst it has been reported previously that land use change increased the proportion of oxidised S due to the loss of organic matter, our contrasting observation that land use change decreased the average oxidation state is likely due to the vastly different systems being examined. In our study, the site is in a subtropical, semi-arid region and the soils are highly weathered and infertile, with low atmospheric inputs – a highly S-limiting system. In contrast, Siebers and Kruse [19] examined a temperate soil from Germany, whilst Solomon et al. [18] examined soils from Oregon (USA) where these temperate soils are likely substantially more fertile. Thus, in our low input, fertility run-down experiment, where S is highly limiting, because of the demand for S, biochemical mineralisation presumably exceeded net biological mineralisation thereby decreasing the relative proportion ester sulfate-S and sulfate (Fig. 6, especially after burning), increasing the relative proportion of the more reduced forms of S, and decreasing the average oxidation state of the S species (Fig. 7). Whilst this differs from the findings of Siebers and Kruse [19] and Solomon et al. [18] in cropping systems, these findings are similar to those reported by Wang et al. [11] after the conversion of native grassland to cropping, where a greater proportion of ester sulfate-S was lost compared to C-S, likely due to continuous C inputs from pasture. In a similar manner Schmidt et al. [38] also showed, via chemical extraction methods, that residual S forms (intermediate G3 and G4) were dominant in a pasture soil. Regardless, the susceptibility of different S forms to loss upon land use change is variable, with others demonstrating an increase in ester sulfate-S relative to C-S [18,39,40].

Although contributing only a small proportion of total soil S, there was a distinct increase in SO_4^{2-} in both the cropping and pasture catchments after 1.7 years as a result of the burning of the remnant brigalow vegetation in 1982 in both these catchments. Fire releases nutrients, including S from soil organic matter, and this is reflected in the XANES analysis which showed an increase in both sulfate and ester sulfate-S (G5) and sulfoxide (G3) and a concomitant decrease in organic S species (G1 and G4) after 1.7 years (Figs. 5 and 6). However, as SO_4^{2-} is readily plant-available and is mobile within the soil profile, we observed that the increase in SO_4^{2-} as a result of burning was subsequently lost from the 0–10 cm soil with time (Fig. 6 and Table 3) due to either leaching or uptake by plants [41]. Sulfate S also decreased in the undisturbed brigalow catchment over 40 years, however the magnitude of loss was smaller than that for the cropping and pasture catchments (Fig. 6 and Table 3). The results indicate that the contribution of inorganic SO_4^{2-} in the ongoing supply of S to plants in the cropping and pasture catchments may be comparatively less important than the mineralisation of organic S forms.

In 1997, the pasture catchment underwent a change in management, and pasture spelling was introduced [37]. However, this change did not influence S speciation, suggesting minor changes in land management strategies are insignificant in comparison to the impact of the loss of SOM.

4.3. Estimating sulfur inputs and outputs in the brigalow catchments

Given the changes in S described above, it is useful to consider inputs and outputs of S in this system. Overall, S inputs into the three catchments examined are considered low. The Brigalow catchment study was designed as a fertility run-down experiment, with no fertilisers or supplement inputs applied to any catchment at any time. Furthermore, atmospheric S deposition is considered low, with the study site located approximately 200 km from the coastline – accordingly, marine-derived aerosol sulfate is minimal. Additionally, with an average annual rainfall of 648 mm y^{-1}, wet deposition is also low. In this regard, total atmospheric S deposition in this area is estimated as 0.5–1 kg S ha y^{-1} [33,42] noting also that atmospheric S deposition in Australia has decreased by on average 2.5 % over the period of 1990–2015 [34] (as discussed above).

Sulfur outputs via S removal in products are also considered low. Grain S removal in the cropping catchment was 3 kg ha y^{-1} over a 30 year period (1982–2014) (estimated as grain N removal multiplied by 10 %) with an average wheat yield of 0.6–2.9 t ha y^{-1} [25]. These low values for S removal are similar to those reported for another low-input low-rainfall system of Australia where crop removal of S was 1–4 kg S ha y^{-1} with wheat yields of 0.6–2.4 t ha y^{-1} [12]. Sulfur export in beef in the pasture catchment was 0.09 kg ha y^{-1} over a 30 year period (1982–2014) (estimated as liveweight gain multiplied by 0.16 %) [26].

Thus, considering S inputs and outputs, S removal in grain in the cropping catchment (3 kg ha y^{-1}) was likely greater than atmospheric S deposition (0.5–1 kg S ha y^{-1}), with this being in agreement with the decrease in total soil S and organic S observed when comparing cropping with the undisturbed native brigalow catchment (Table 2). In contrast, S export via beef in the pasture catchment (0.09 kg ha y^{-1}) was estimated to be lower than atmospheric S deposition, which may describe our observation of smaller losses of total soil S in the pasture catchment being 17 % compared to a 34 % decrease in the cropping catchment.

Given that the removal of S from crop products was expected to be larger than the S inputs from atmospheric deposition, it is also useful to consider changes in soil S over time and the supply of S from mineralisation of organic matter. In this regards, in the cropping catchment between 1983 and 1997 (i.e. the first 14 years after burning), organic S concentrations decreased by 79 mg kg^{-1} (Table 2) equating to 5.6 mg S kg y^{-1} in the cropping catchment when using a bulk density of 1.2 g cm^{-3} [26], equating to a loss of 6.8 kg S ha y^{-1} from the soil organic pool during this early stage of cropping. However, for the later time period, from 1997 to 2022 (25 y), organic S concentrations decreased by 2 mg kg^{-1} (Table 2), equating to 0.08 mg S kg y^{-1}, a loss of 0.10 kg S ha y^{-1}. Thus, in this low input, low-rainfall system, mineralisation of S from soil organic matter coupled with modest atmospheric S deposition was likely sufficient to replace S losses via crop removal in the early years after burning. However, in the later time periods of the study, rates of mineralisation decreased and were no longer adequate to replace S losses, even when coupled with the modest atmospheric S deposition. Thus, given that S outputs likely exceeded inputs, coupled with the greatly reduced mineralisation of organic S during the later periods of the study, this decrease in soil S fertility corresponds to the progressive decrease in yields as observed for this study as reported by Radford et al. (2007) and Thornton & Shrestha (2020).

5. Conclusions

Conversion of native brigalow forest to long-term agricultural production in a semi-arid, subtropical environment altered the composition of soil S. Overall, compared to the undisturbed native brigalow catchment, there was a decrease in total soil S in the cropping and pasture catchments over the 40 year period owing to a decrease in both inorganic SO_4^{2-} and organic S. The loss of S was associated with a decline in TOC and TSN. In the pasture catchment, total S decreased by 17 %, TOC by 14 %, and TSN by 29 %. In the cropping catchment total S decreased by 34 %, TOC by 50 %, and TSN by 53 %. The changes in S composition resulted in a decreased average oxidation state of soil S in both the pasture and cropping catchments and an increased C-S:ester sulfate-S in the pasture catchment. These results demonstrate the inherent link of S with SOM, and that the loss of SOM as a result of land use change will result in not only in the loss of C and N but also S. Of the S forms present in the bulk soil, more ester sulfate-S was lost in the conversion of native vegetation to cropping and pasture than C-S. Changes in land-use management practice in this low-input, semi-arid, subtropical environment resulted in an overall decrease in soil S and a shift in soil S

speciation. In conclusion, our study demonstrated that sustainable land management practices are essential for maintaining soil S in agricultural systems – the marked decrease in organic S following land use change highlights the need to maintain SOM through improved management practices. Furthermore, our study highlights the need for additional data on S dynamics to inform management strategies – in our study, not only did total S concentrations change but the speciation of S also changed, and hence sustainable land use decisions should not only consider total S but also the speciation of S for ensuring adequate nutrient supply.

CRediT authorship contribution statement

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

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jafr.2025.102337.

Data availability

Data will be made available on request.

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