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Rapid remediation of sandy sulfuric subsoils using straw-derived dissolved organic matter

Angelika Kölbl [a,*], Klaus Kaiser [a], Aaron Thompson [b], Luke Mosley [c], Rob Fitzpatrick [c], Petra Marschner [d], Leopold Sauheitl [e], Robert Mikutta [a]

[a] Soil Science and Soil Protection, Martin Luther University Halle-Wittenberg, 06120 Halle (Saale), Germany
[b] Dept. of Crop and Soil Sciences, The University of Georgia, Athens, GA, USA
[c] Acid Sulfate Soils Centre, The University of Adelaide, South Australia 5064, Australia
[d] School of Agriculture, Food and Wine, The University of Adelaide, South Australia 5005, Australia
[e] Institute of Soil Science, Leibniz University Hannover, 30419 Hannover, Germany

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ABSTRACT

When acid sulfate soils dry, oxidation of pyrite can cause acidification and formation of iron (Fe) oxyhydroxy sulfate phases such as jarosite. Remediation via re-establishment of reducing conditions requires submergence and addition of biodegradable organic carbon (OC) to stimulate activity of reducing bacteria. Addition of fresh plant litter has been shown to activate reducing bacteria, likely due to the release of readily available soluble organic matter. However, the effectiveness of soluble organic matter from plant residues has not been tested yet. Here, we tested the potential of wheat straw-derived dissolved OC (DOC) for remediation of a sandy sulfuric (pH < 4) soil. In a second set of experiments, we used combinations of wheat straw-derived DOC with lactate, which is a preferred substrate of sulfate reducing bacteria. All incubation experiments were conducted in the dark at 20 °C. The results showed that addition of DOC from wheat straw induces reduction reactions and rapidly increases the pH by 2–3 units after 3 weeks of incubation under submerged conditions. Mössbauer spectroscopy and X-ray diffraction revealed that jarosite was lost after 200 days of anoxic incubation. Short range-ordered Fe^{III} oxyhydroxides were formed, most likely by Fe^{II}-catalysed transformation of jarosite. A second addition of DOC, as well as the addition of lactate, resulted in the almost complete loss of jarosite with increased proportions of Fe^{III} oxyhydroxides in the remaining solids, but not in the formation of Fe^{II} sulfides. The formation of Fe^{III} oxyhydroxides reduces the risk of both Fe leaching and renewed acidification in the event of future oxidation. The results suggest that deep injection of wheat straw-derived DOC is a promising approach for rapid and sustainable remediation of sandy sulfuric subsoils.

1. Introduction

Acid sulfate soils are characterized by past, actual, or potential generation of sulfuric acid in quantities likely to cause lasting effects on soil characteristics (Pons, 1973). They are wide-spread throughout the world in coastal and inland areas (Fanning et al., 2017), and are an important environmental issue in some areas in southern Australia (Fitzpatrick et al., 2011). Acid sulfate soils are either already strongly acidic, or have the potential to become strongly acidic when exposed to oxygen due to the presence of Fe^{II} sulfide minerals. When acid sulfate soils become aerated (e.g. due to natural or artificial drainage), oxidation of Fe^{II} sulfides (mainly pyrite) causes the formation of sulfuric acid and thus strong acidification (pH < 4). Oxidation and acidification are often accompanied by the formation of jarosite [$KFe_3(SO_4)_2(OH)_6$], which is a characteristic mineral in sulfuric soils and acidic, sulfate-rich environments (e.g. Baron and Palmer, 1996). Jarosite is only stable between pH 3 and 4 (Zahrai et al., 2013; Trueman et al. 2020) under sufficiently oxic conditions (Eh > 400 mV; Keene et al., 2010).

A common approach to remediate sulfuric (pH < 4) soils is re-submergence (e.g. Fanning et al., 2017) to re-establish reducing conditions and induce an increase in pH. Many reducing microorganisms are heterotrophic and require organic carbon (OC) for growth and metabolism (Berner, 1984; Plugge et al., 2011). Several previous studies have shown that addition of plant residues can activate a sequence of

* Corresponding author.
E-mail address: angelika.koelbl@landw.uni-halle.de (A. Kölbl).

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reducing bacteria, resulting in a pH increase up to circumneutral levels during submerged periods (Yuan et al., 2015a, 2015b; Jayalath et al., 2016a, 2016b; Kölbl et al., 2018, Kölbl et al., 2021). The decrease in redox potential (Eh) and the concomitant pH increase causes dissolution of jarosite, with Fe^{III} being reduced at higher Eh values than sulfate. Thus, reductive and pH-induced dissolution of jarosite results in increased solution concentrations of aqueous Fe^{II} (Fe^{II}_{aq}) and sulfate under inundated conditions (Chu et al., 2006). The formation of Fe^{II}_{aq} under anoxic conditions is known to promote the Fe^{II}-catalysed transformation of Fe^{III} oxyhydroxysulfate to Fe^{III} oxyhydroxides such as goethite and lepidocrocite (e.g. Burton et al., 2007; Jones et al., 2009; Vithana et al., 2015; Kölbl et al., 2021). However, Fe^{II} sulfides can also form after dissolution of jarosite, but formation of these phases requires low Eh values and a high activity of microbial reducers, which allows for the reduction of both Fe^{III} and SO_4^{2-} and formation of high concentrations of elemental S or H_2S in soil solution (Ivarson et al., 1982; Herzsprung et al., 2002).

The formation of Fe^{III} oxyhydroxides instead of Fe^{II} sulfides has several implications and potential advantages for remediation of sulfuric soils and materials (Kölbl et al., 2021). Fe^{III} oxyhydroxides, unlike Fe^{II} sulfides, are stable under oxic conditions and do not carry the risk of renewed acidification in the case of future aeration. Therefore, transformation of jarosite to more stable Fe^{III} oxyhydroxides while avoiding sulfide formation is desirable. This could be achieved by moderate addition of OC, which favours Eh values near the Fe^{II}–Fe^{III} redox couple, while avoiding lower Eh conditions necessary for sulfate-reduction (Kölbl et al., 2021).

Under field conditions, the addition of OC as particulate plant residues (e.g., straw) for remediation purposes is mostly limited to the topsoil. However, many sulfuric soils are characterized by severe subsoil acidification (e.g. Mosley et al., 2017). Dissolved organic compounds have the advantage that, in addition to their immediate microbial availability, they can be transported more easily with the pore water to deeper soil layers, especially in sandy soils with low reactive mineral surface areas. However, low molecular weight OC sources, such as glucose, sodium acetate, or sodium lactate, do not induce microbially-mediated reducing conditions with increased pH in sulfuric soils (Jayalath et al., 2016a; Högfors-Rönnholm et al., 2020), probably due to the lack of adequate nitrogen sources (Jayalath et al., 2016a). Lactate addition was only successful in creating reducing conditions if added in combination with wheat straw (Kölbl et al., 2019). Further, dissolved OC (DOC) derived from highly decomposed, low molecular weight organic compounds (Schwertmann and Fischer, 1973) or high concentrations of fulvic acid (Jones et al., 2009) may retard the Fe^{II}-catalysed transformation of Fe^{III} oxyhydroxides such as schwertmannite and ferrihydrite, to more stable Fe^{III} oxyhydroxides such as goethite. Adsorption of highly decomposed organic compounds onto the Fe^{III} mineral surfaces is assumed to reduce the direct adsorption of Fe^{II} to these surfaces, thus inhibiting the transformation process of the respective mineral phases (Jones et al., 2009).

However, the effects of less decomposed, plant litter-derived DOC sources on the transformation of jarosite have not been thoroughly evaluated so far. Therefore, the present study aims to elucidate the effectiveness of water-extractable, wheat straw-derived DOC for remediation of a sandy sulfuric soil. In addition, combinations of DOC with lactate were used to test if this specifically promotes sulfate reducing bacteria (Kölbl et al., 2019). We assumed that (i) addition of straw-derived DOC alone is sufficient to induce dissolution of jarosite due to reductive dissolution and pH increase, whereby (ii) the amount of DOC controls the generation of Eh/pH values that allow the formation of Fe^{III} oxyhydroxides while avoiding Fe^{II} sulfide formation. Further, we assumed that (iii) an additional supply of lactate is necessary to promote the formation of Fe^{II} sulfides.

2. Materials and methods

2.1. Sampling area

As described in Kölbl et al. (2021), samples of a sandy acid sulfate soil with sulfuric material were collected in November 2017 from the Gillman site in the Barker Inlet estuary (sandy marine deposits) close to Adelaide (South Australia). The Gillman site is a former tidal wetland, which was covered with mangrove woodland (Fitzpatrick et al., 2012). The area was reclaimed from intertidal and supratidal areas in 1935 when a series of bund walls were constructed. The loss of tidal inundation lowered the water table and aerated the hypersulfidic material, which induced pyrite oxidation, resulting in pH values $\leq$ 4 and the formation of sulfuric material (Poch et al., 2009; Fitzpatrick et al., 2012; Michael et al., 2015). Pale yellow jarosite mottles formed along relict mangrove roots and pneumatophore channels (Pohl et al., 2021). The soil is classified as sulfuric soil in accordance with the Australian acid sulfate soil classification (Fitzpatrick, 2013). According to the Australian Soil Classification (Isbell and National Committee on Soils and Terrain, 2016), the soil is classified as Peaty, Sulfuric, Hypersalic Hydrosol; as Salic Fluvisol (Hyperthionic, Drainic) according to WRB identification keys (IUSS Working Group WRB, 2015), and as Hydraquentic Sulfaquept according to US Soil Taxonomy (Soil Survey Staff 2003; see Poch et al., 2009). A detailed description of the soil profile is given in Poch et al. (2009).

Soil samples were collected from a sandy soil horizon ($pH_{H2O} = 3.0$) at 80 – 100 cm depth in a pit. We selected the deep subsoil layer to minimise the influence of fresh organic matter (OM) supplied from vegetation at the soil surface and to exclude inputs from living roots (see Poch et al., 2009), thus, allowing us to study of the impact of added DOC sources. After collection, the soil was immediately dried in a fan-forced oven at 60 °C to suppress microbial activity, sieved to $<$ 2 mm, and then shipped to Germany for analysis and experimentation. Basic soil properties are provided in Table 1.

2.2. Incubation experiments

2.2.1. Preparation of incubation set 1

Sub-samples (25 g) of the dry sandy sulfuric soil were placed in 250 ml incubation bottles. In total, 60 replicates were prepared. All samples were adjusted to field water holding capacity (determined by preliminary experiments) by adding 5 ml of distilled water (H_2O_{dest}) and pre-incubated in the dark for two weeks at 20 °C under oxic conditions to re-establish field conditions. After pre-incubation, all samples were further processed under Ar atmosphere in an airtight glovebox ($pO_2 \leq$ 2%). 30 soil samples were submerged by adding 50 ml of degassed H_2O_{dest}; the remaining 30 samples were submerged with 50 ml wheat straw-derived DOC-solution. The DOC-solution was prepared by mixing 5.4 g of ground wheat straw ($\leq$ 5 mm) with 835 ml H_2O_{dest}. This straw-to-solution ratio was chosen in accordance with a previous study (Kölbl et al., 2019). The suspension was shaken for 1 h in a reciprocating shaker, pressure-filtered using 0.45-µm polyethersulfone membranes (Pall Corporation, USA), and then added to the soil samples in 50 ml portions. The initial DOC concentration of the solution was 161 mg l^{-1}. The anoxic incubations were conducted in the dark at 20 °C for 10 weeks.

To assess the microbial activity, CO_2 concentrations were measured in the headspace of the incubation bottles. At day 1, 3, 5, 10, and once a week thereafter, headspace samples were collected into pre-evacuated gas vials while recording the pressure within the incubation flasks and the sample vials before and after sampling. After headspace sampling, the incubation bottles were opened in the glovebox under Ar atmosphere and flushed with Ar to remove remaining CO_2. Then, samples were shaken and suspensions analysed for pH and Eh (combined pH and redox electrode, type sensION™ + MM150, Hach Lange GmbH, Germany).

Table 1
Basic properties of the sulfuric soil (SD. standard deviation); data from Kölbl et al. (2021).

pH_{water}	OC		N		total Fe		total S		sand	silt	clay
	mg g^{-1}		mg g^{-1}		mg g^{-1}		mg g^{-1}		%	%	%
	mean	SD	mean	SD	mean	SD	mean	SD			
3.0	3.57	0.19	0.22	0.04	*8.31	0.16	*3.05	0.02	92	6	2

* Analysed by digestion with $HF/HClO_4$ and subsequent Fe and S analysis with ICP-OES.

Every week, three subsamples of each treatment (with and without DOC addition) were removed from incubation. The suspensions were then transferred into airtight centrifugation bottles and centrifuged for 10 min at 3000*g*. The supernatants were filtered in the glovebox through 0.45-µm polyethersulfone membranes, and stored at −20 °C. The settled soil material was freeze-dried.

The concentrations of CO_2 in gas samples were analysed with a 7890B gas chromatograph (Agilent Technologies, USA) modified for gas analysis by Chromtech GmbH (Bad Camberg, Germany) using a He ionization detector (for details, see Surey et al., 2020). The measured CO_2 concentration was recalculated to the total amount of CO_2 in the headspace of the incubation flasks following the general gas law. The total quantity of CO_2-C (in mg g^{-1} soil) produced between two sampling time points was calculated for the entire 10-week incubation period.

2.2.2. Preparation of incubation set 2

This incubation set tested the effect of higher and repeated DOC additions. Beside a control without DOC addition and treatments with wheat straw-derived DOC as substrate for reducing bacteria, this experiment also included lactate treatments. The preparation of the incubation bottles and the setup of the incubation experiment was similar to that described above for incubation set 1. Here, 30 g of dry sandy sulfuric soil was used, samples were adjusted to field water holding capacity by adding 6 ml of H_2O_{dest}. In total, 40 replicates were prepared.

The samples were pre-incubated for 15 days under oxic conditions to re-establish conditions similar to those in the field. The pH and redox values were measured at day 1, 8, and 15. At day 16, the anoxic incubation was started by submerging the samples under Ar atmosphere in a glovebox as described above. Sixteen soil samples were submerged by adding 60 ml of degassed H_2O_{dest} and 24 samples were submerged with 60 ml wheat straw-derived DOC-solution. Here, 8.3 g of milled wheat straw was mixed with 700 ml H_2O_{dest}, shaken for 1 h and pressure-filtered as described above, resulting in an initial DOC concentration of 304 mg l^{-1}. Four subsamples without DOC addition were removed from incubation immediately after submergence. The soil material was separated from the solution as described above and sieved into a sand-sized fraction > 63 µm (quartz-dominated) and a fine fraction < 63 µm enriched in Fe oxyhydroxides, Fe oxyhydroxy sulfates, or Fe sulfides, but low in the amount of quartz. All soil samples were freeze-dried (thereby minimizing contact with oxygen) and stored in airtight vessels under Ar atmosphere prior to analysis.

The remaining incubation bottles were shaken and suspensions analysed for pH and Eh once a week under Ar atmosphere as described above. At day 42 and 120, four subsamples of each treatment (with and without DOC addition) were removed from incubation. The soil was separated from the solution as described above.

At day 120, 12 samples with DOC addition received further DOC additions (Table 2 and supporting information SI 1.1): four samples obtained 6 ml of a high-concentrated wheat straw-derived DOC-solution (DOC: 1440 mg l^{-1}); four samples obtained 6 ml of a lactate solution adjusted to a DOC concentration of 1620 mg l^{-1} (sodium DL-lactate solution, 50% (w/w) in H_2O, Sigma-Aldrich, Steinheim, Germany), and four samples received 6 ml of a combination of both (1:1 straw: lactate mixture; DOC: 1530 mg l^{-1}). Until the end of experiment at day 200, pH and redox values were monitored weekly. After termination of the experiment, bulk soil material and soil solution were separated under Ar atmosphere in the glovebox as described above.

2.3. Elemental analysis of soil solution

Dissolved OC was measured with a TOC-analyser (Multi N/C3100, Analytik Jena AG, Germany) after acidification to pH < 2 with 0.1 M HCl. Total concentrations of Fe, K, and S in the supernatants were measured by inductively coupled plasma optical emission spectroscopy (ICP-OES) (Ultima 2, Horiba Ltd., Japan). Prior to the measurements, the samples were acidified to pH < 2 using 0.1 M HCl. For incubation set 1, dissolved Fe^{II}_{aq} was determined by reaction with ferrozine (modified after Stookey, 1970) in the glovebox and subsequent photometric detection at 562 nm (Specord 210 plus, Analytik Jena AG, Germany). Saturation indices for Fe oxyhydroxides, Fe oxyhydroxy sulfates, and Fe sulfides were estimated from element concentrations and pH/Eh properties of the soil solution using Visual MINTEQ3.1 (https://vminteq.lwr.kth.se).

Table 2
Incubation set 1. Concentrations of soil organic carbon (OC), dissolved OC (DOC), and cumulated CO_2-C release before and after incubation with and without straw-DOC (mean values and standard deviation (SD) of three replicates).

	soil OC		DOC		DOC	Σ CO_2-C	
	mg g^{-1}		mg l^{-1}		mg g^{-1} soil	mg g^{-1} soil	
	mean	SD	mean	SD		mean	SD
before incubation							
no straw-DOC	3.57	0.19	0.0	0.0	0.00	0.00	0.00
+ straw-DOC	3.57	0.19	161.2	1.0	0.32	0.00	0.00
after incubation							
no straw-DOC	3.09	0.41	16.1	0.2	0.04	0.04	0.00
+ straw-DOC	3.34	0.31	74.7	1.9	0.16	0.45	0.05

2.4. Characterization of sulfuric soils before and after incubation

All bulk soil samples (incubation set 1) and soil fractions at < 63 μm and > 63 μm (incubation set 2) were analysed for OC by dry combustion at 950 °C using a Vario MAX cube elemental analyser (Elementar Analysensysteme GmbH, Germany).

The mineral composition of one fine fraction (<63 μm, incubation set 2) of each treatment was analysed by X-ray diffraction (XRD) and ^{57}Fe Mössbauer spectroscopy. For XRD, random powder samples were scanned by an X-ray device (D5005, Siemens AG, Germany) with Cu Kα-radiation (λ = 1.541 nm) from 2 to 80 °2θ in stepscan mode with 0.02 °2θ-step size, fixed slits, and 10 s counting time. Transmission ^{57}Fe Mössbauer spectroscopy was performed with a variable temperature He-cooled system with a 1024 channel detector. A ^{57}Co source (~ 50 mCi or less) embedded in a Rh matrix was used at room temperature. Freeze-dried powder samples were mounted between two pieces of 0.127 mm thickness Kapton tape. Samples were prepared in a glovebox under Ar atmosphere to minimize contact of the samples with oxygen and transferred to the spectrometer cryostat. Velocity (i.e., gamma-ray energy) was calibrated using α-Fe foil at 295 K and all center shifts (CSs) and peak positions are reported with respect to this standard. The transducer was operated in constant acceleration mode and folding was performed to achieve a flat background. Details of the spectral analyses, fitting approach and statistical evaluation of the fits are described in the supporting information (SI 2.2).

3. Results

3.1. Incubation set 1

3.1.1. Development of pH, redox potentials and CO_2 release

After submergence with degassed H_2O_{dest}, treatments without DOC addition had pH values between 3.4 and 3.6 throughout the entire incubation (Fig. 1). The Eh values increased slightly from 540 to 650 mV within the first 3 weeks of incubation and remained constant thereafter. The CO_2-C release was low and did not exceed 0.01 mg g^{-1} soil. The pH values of the treatments with DOC addition increased from 4.0 to 5.4 within the first 10 days of anoxic incubation, and reached pH 6.1 at the end of the incubation. The Eh values decreased from 470 to 170 mV within 10 days, and approached ~ 100 mV at the end of the incubation. The CO_2-C release was highest after 10 days (0.11 mg g^{-1} soil), decreased strongly to 0.03 mg g^{-1} soil at day 30, and decreased further until the end of the incubation (< 0.01 mg g^{-1} soil).

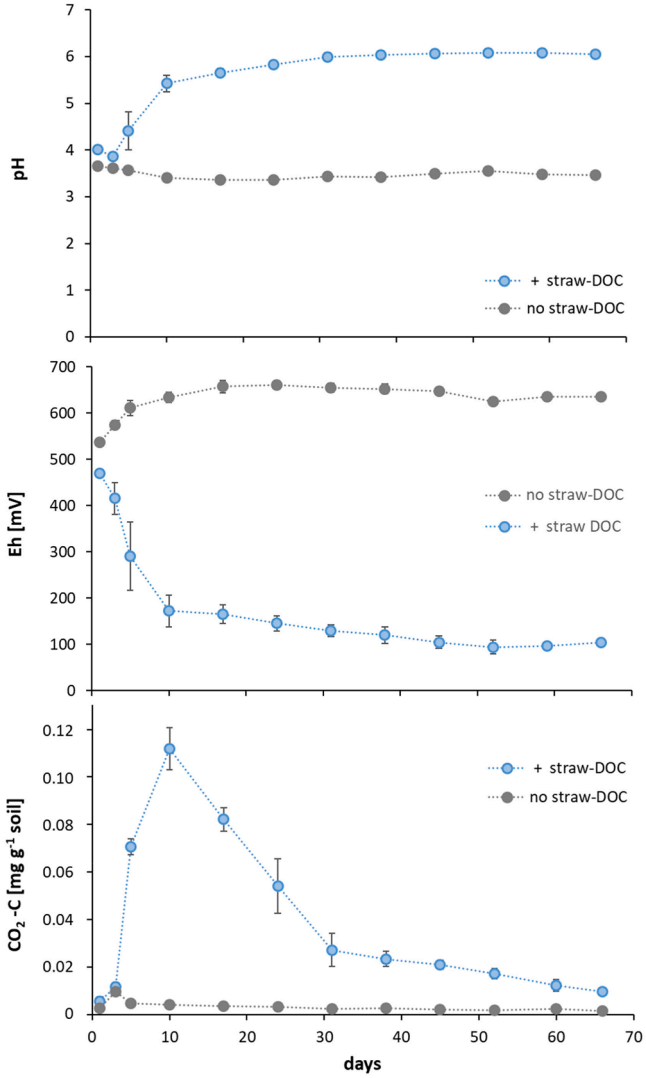

Fig. 1. Time course of pH, Eh values and CO_2 release during the incubation experiment of set 1. Data points show mean values ± standard deviations (n = 3).

Table 3
Incubation set 1. Concentrations of Fe, K, S, and DOC in the soil solutions during incubation (mean values and standard deviation (SD) of three replicates).

day	Fe		K		S		DOC		molar ratio
	mg l^{-1}		mg l^{-1}		mg l^{-1}		mg l^{-1}		Fe:S
	mean	SD	mean	SD	mean	SD	mean	SD	
no straw-DOC									
5	**1.7**	0.1	**53.8**	1.7	**175**	6	**16.1**	1.0	**0.0**
10	**1.6**	0.0	**52.6**	0.5	**175**	6	**16.9**	0.3	**0.0**
17	**1.6**	0.0	**53.7**	1.4	**176**	4	**17.2**	0.1	**0.0**
24	**1.8**	0.2	**56.2**	1.2	**198**	4	**18.5**	0.2	**0.0**
31	**1.5**	0.0	**53.8**	1.2	**183**	8	**17.8**	0.2	**0.0**
38	**1.6**	0.2	**53.4**	0.7	**183**	6	**17.6**	0.3	**0.0**
45	**1.5**	0.0	**52.9**	1.1	**186**	12	**17.3**	0.4	**0.0**
52	**1.5**	0.0	**52.9**	3.8	**182**	13	**17.3**	0.1	**0.0**
59	**1.5**	0.0	**50.7**	3.8	**169**	23	**15.0**	0.2	**0.0**
66	**1.6**	0.0	**50.8**	4.1	**187**	19	**16.1**	0.2	**0.0**
mean	**1.6**	0.1	**56.0**	6.8	**182**	8	**17.0**	1.0	**0.0**
+ straw-DOC									
5	**12**	2	**126**	3	**192**	21	**89.9**	1.7	*__0.7__
10	**168**	50	160	10	**297**	29	**95.2**	5.0	*__0.8__
17	**290**	41	**196**	12	**382**	32	**82.5**	0.9	*__0.8__
24	**264**	41	**187**	10	**357**	28	**79.9**	2.1	*__0.9__
31	**256**	10	**184**	5	**354**	15	**83.7**	1.8	*__0.9__
38	**330**	74	**213**	32	**419**	55	**72.5**	3.8	*__0.8__
45	**337**	35	**212**	8	**426**	26	**79.2**	1.5	*__0.8__
52	**359**	53	**215**	20	**440**	44	**70.9**	0.6	*__0.8__
59	**341**	62	**210**	21	**429**	45	**75.0**	5.0	*__0.8__
66	**376**	37	**224**	15	**454**	34	**74.7**	1.9	*__0.8__
straw DOC	**0.1**	0.0	**95.4**	0.1	**0.0**	0.0	**161.2**	1.0	

* Calculated after subtracting the background concentration for S (mean value of S in no straw-DOC treatment).

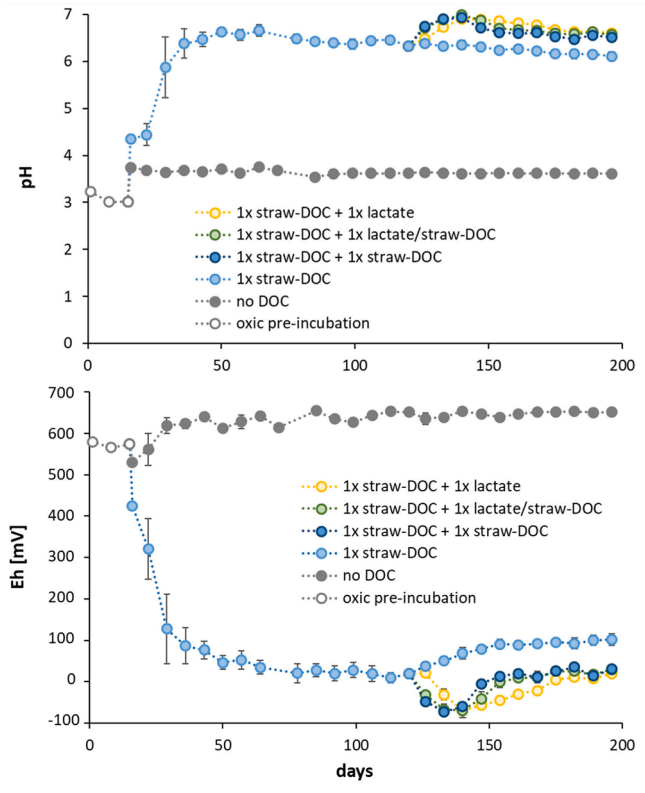

Fig. 2. Time course of pH and Eh values during the incubation experiment of set 2. Data points show mean values ± standard deviations (n = 4).

3.1.2. Organic carbon before and after incubation

Soil OC concentrations were ~ 0.2 – 0.4 mg g^{-1} lower after incubation. In treatments without DOC addition, small amounts of OC were released as DOC or CO_2-C (each ~ 0.04 mg g^{-1}, Table 2). In treatments with DOC addition, the DOC concentration has halved by the end of the incubation (from 161 to 75 mg l^{-1}). This corresponds to a decrease of 0.16 mg g^{-1} soil. Cumulative CO_2-C release was 0.45 mg g^{-1} and is consistent with the decrease of soil OC + DOC.

3.1.3. Soil solution composition

Treatments without DOC addition had constant solution concentrations of Fe, S, K, and DOC throughout the entire incubation (Table 3). Iron concentrations were low (< 2 mg l^{-1}), average K and S concentrations were 56 and 182 mg l^{-1}, and concentrations of DOC ranged between 15 and 19 mg l^{-1}.

Treatments with DOC addition showed a strong increase in Fe concentrations from 12 to 376 mg l^{-1}, with > 90% being Fe^{II}_{aq} throughout the incubation period (supporting information SI 1.3). Potassium concentrations increased from 126 to 224 mg l^{-1} (95 mg l^{-1} being straw-derived), and S concentrations increased from 192 to 454 mg l^{-1}. Addition of straw DOC added no Fe and S to the soil solution; increasing Fe and S concentrations can therefore be attributed to the dissolution of jarosite. The molar Fe:S ratio in the DOC treatment remained ~ 0.8 throughout the entire incubation (Table 3), which is lower than the ratio of 1.5 expected for congruent dissolution of jarosite. The initial DOC concentration was 161 mg l^{-1} and decreased to 90 mg l^{-1} at day 5 and to 75 mg l^{-1} at the end of the incubation.

Aluminium concentrations were generally low (~ 0.5 and ~ 0.1 mg l^{-1}) in treatments without or with DOC addition; Ca concentrations ranged between 77 and 102 mg l^{-1}, and Mg concentrations were between 151 and 169 mg l^{-1} and did not show any changes over time and with respect to treatments (supporting information SI 1.2 and SI 1.3).

Table 4
Incubation set 2. Concentrations of soil organic carbon (OC) and dissolved OC (DOC) before and after incubation (mean values and standard deviation (SD) of four replicates).

	soil OC < 63 µm mg g^{-1} mean	SD	soil OC > 63 µm mg g^{-1} mean	SD	DOC mg l^{-1} mean	SD	DOC mg g^{-1} soil
after oxic pre-incubation	1.89	0.19	1.45	0.26	15	1.6	0.03
DOC addition							
1x straw-DOC					304	2.7	0.61
+ 1x straw-DOC					+92	0.9	+0.29
+ 1x lactate					+104	2.0	+0.32
+ 1x lactate/straw-DOC					+98	1.4	+0.31
after anoxic incubation							
no DOC	1.83	0.07	1.45	0.31	20	1.1	0.05
1x straw-DOC	2.07	0.15	1.23	0.15	68	3.9	0.21
1x straw-DOC + 1x straw-DOC	2.06	0.07	1.32	0.21	72	5.3	0.23
1x straw-DOC + 1x lactate	2.03	0.03	1.32	0.30	59	2.9	0.19
1x straw-DOC + 1x lactate/straw-DOC	2.03	0.06	1.21	0.18	62	2.4	0.21

Table 5
Incubation set 2. Concentrations of Fe, K, S, and DOC in the soil solutions during incubation (mean values and standard deviation (SD) of four replicates).

	day	**Fe**		**K**		**S**		**DOC**		**molar ratio**
		mg l^{-1} mean	SD	mg l^{-1} mean	SD	mg l^{-1} mean	SD	mg l^{-1} mean	SD	Fe:S
after oxic pre-incubation		**1.2**	0.11	**43**	1.6	**152**	3.7	**15**	1.6	**0.0**
no straw DOC										
	42	**0.3**	0.34	**51**	4.6	**178**	12.1	**21**	2.8	**0.0**
	120	**0.2**	0.22	**46**	0.7	**156**	6.8	**22**	0.4	**0.0**
	200	**0.0**	0.02	**43**	4.4	**138**	2.6	**20**	1.1	**0.0**
1x straw-DOC*		**0**	0	**173**	1	**10**	0	**304**	2.7	
	42	**338**	36	**281**	20	**475**	68.1	**100**	6.8	**0.4**
	120	**492**	48	**301**	24	**549**	39.5	**72**	3.8	**0.5**
	200	**426**	36	**296**	20	**497**	42.4	**68**	3.9	**0.5**
1x straw-DOC + 1x straw-DOC*		**0**	0	**225**	1	**13**	0	**163**	0.9	
	200	**474**	29	**346**	13	**556**	38.0	**72**	5.3	**0.5**
1x straw-DOC + 1x lactate*		**0**	0	**173**	1	**11**	0	**176**	2.0	
	200	**454**	40	**341**	31	**580**	29.1	**59**	2.9	**0.5**
1x straw-DOC + 1x lactate/straw-DOC*		**0**	0	**199**	1	**12**	0	**170**	1.4	
	200	**413**	39	**334**	14	**524**	46.7	**62**	2.4	**0.4**

* DOC-derived elemental concentrations; ** Calculated after subtracting the background concentration for S (mean value of S in no straw-DOC treatment).

3.2. Incubation set 2

3.2.1. Development of pH and redox potentials

During oxic pre-incubation, pH values decreased slightly from 3.2 to 3.0, and Eh values varied between 570 and 580 mV (Fig. 2). After submergence without DOC addition, pH values ranged between 3.6 and 3.7, and Eh values between 620 and 650 mV throughout the entire incubation period.

Addition of DOC induced a pH increase to 6.6 after 50 days of incubation. The pH varied between 6.4 and 6.5 until day 120, and then decreased to pH 6.1 until the end of the incubation. The Eh values decreased to 55 mV at day 50 and to 10 mV until day 120, and then increased to 100 mV at the end of incubation. In treatments that received additional DOC at day 120, the pH increased to ~ 6.9 and the Eh decreased to −70 mV until day 140. Thereafter, pH decreased again to ~ 6.5, and Eh increased to ~ 30 mV at the end of the incubation. Differences between treatments that received additional DOC were minimal.

3.2.2. Organic carbon before and after incubation

Soil OC tended to decrease in the > 63 µm fractions after incubation with DOC solutions (from ~ 1.4 to ~ 1.2 mg g^{-1}), while soil OC tended to increase in the < 63 µm fractions (from ~ 1.8 to ~ 2.0 mg g^{-1}; Table 4). There were no differences between treatments with one or two DOC additions, and the type of added DOC did also not change soil OC concentrations in the fine fractions. After incubation, DOC concentration was lowest in the treatment without DOC addition (20 mg l^{-1}). In incubations with added DOC, the final DOC concentrations ranged between 59 and 72 mg l^{-1}, without clear differences between treatments with one or two additions, or the type of added DOC.

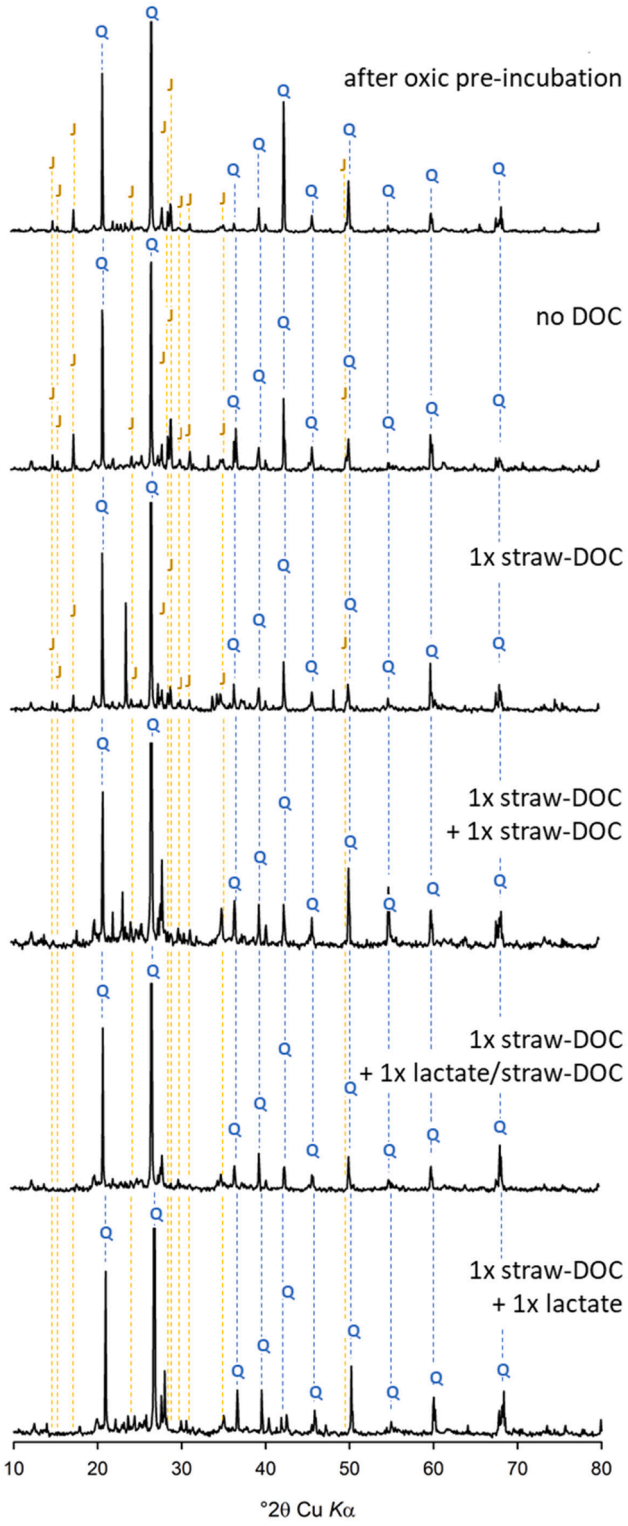

Fig. 3. Powder XRD patterns (fine fractions) after oxic pre-incubation and at the end of anoxic incubation. J = jarosite; Q = quartz.

3.2.3. Soil solution composition

After oxic pre-incubation, Fe concentrations were low (1.2 mg l^{-1}), K and S had concentrations of 43 and 152 mg l^{-1}, respectively (Table 5); DOC concentration was 15 mg l^{-1}. In treatments without DOC addition, the elemental concentrations showed no marked change during anoxic incubation. Elemental concentrations strongly increased in treatments with DOC addition, but there were no clear differences or trends between different DOC treatments. Iron concentrations were > 400 mg l^{-1} and S concentrations > 500 mg l^{-1} at the end of the incubation, and K concentrations were between 120 and 168 mg l^{-1} after subtracting the straw-derived K contribution. The molar solution Fe:S ratio in treatments with DOC addition ranged between 0.4 and 0.5, irrespective the amount and type of added DOC.

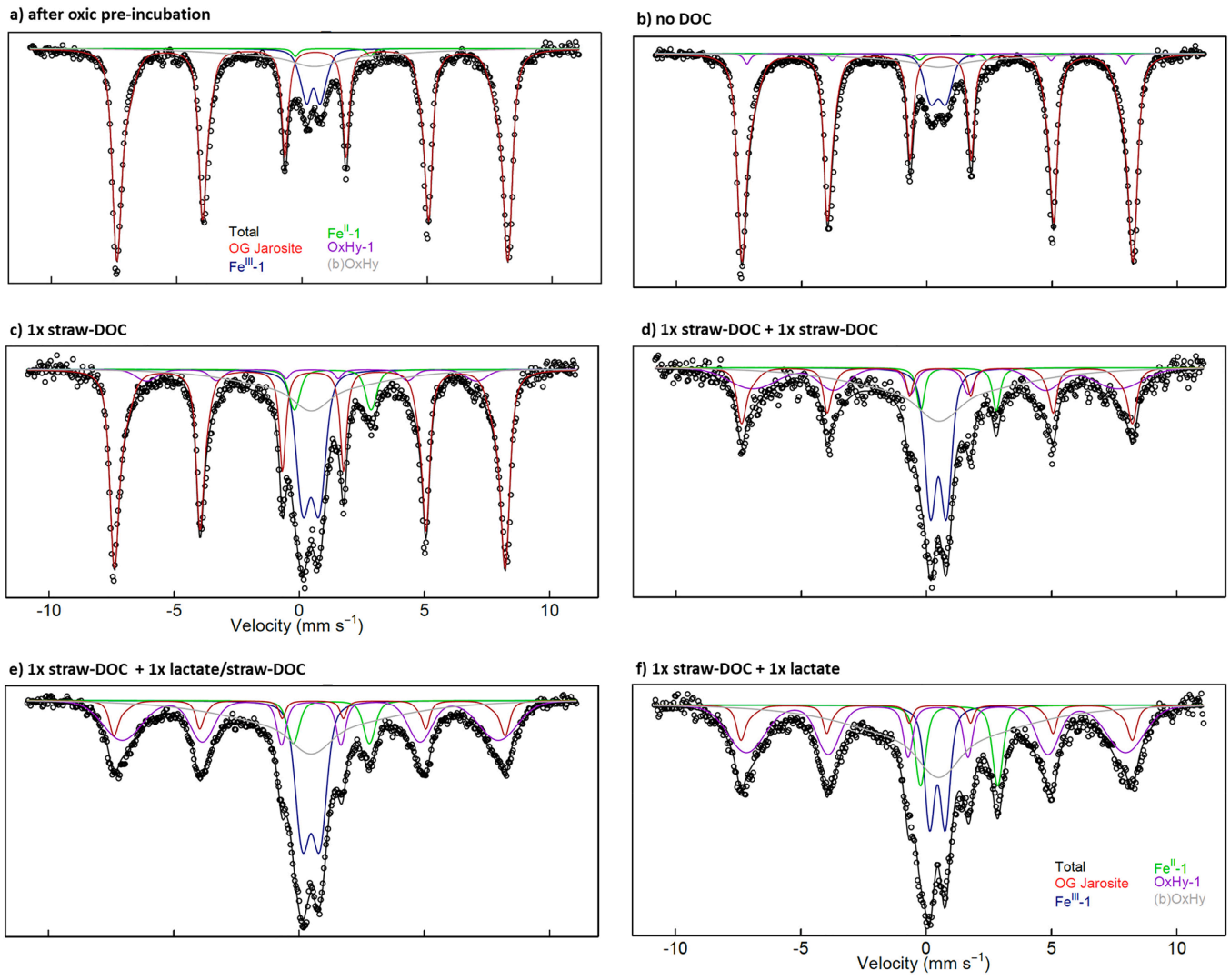

Fig. 4. Mössbauer spectra (recorded at 5 K) and proportions of identified Fe phases of selected samples after incubation with and without DOC addition.

Table 6
Incubation set 2. Proportions Fe phases obtained from Mössbauer spectra recorded at 5 K taking into account the dissolved portion of Fe. OxHy and (b) OxHy represent very small and/or short range-ordered Fe^{III} oxyhydroxides like nano-goethite and ferrihydrite. Full tables of Mössbauer spectral parameters are given in the supporting information (Tables SI 2.1–2.6).

	Jarosite	OxHy	(b) OxHy	Fe^{III}	Fe^{II}	Fe in solution
			%			
After oxic pre-incubation	78.1	0	12.0	9.0	0.9	0
no straw DOC	78.0	2.4	9.5	9.2	0.9	0
1x straw-DOC	44.4	4.3	14.4	16.5	4.4	16
1x straw-DOC + 1x straw-DOC	14.8	19.4	25.7	18.0	4.1	18
1x straw-DOC + 1x lactate/ straw-DOC	8.5	26.8	23.2	19.3	5.2	17
1x straw-DOC + 1x lactate	7.5	27.6	28.0	11.1	7.8	18

3.2.4. *Fe species before and after incubation*

X-ray diffraction patterns clearly revealed the occurrence of jarosite after oxic pre-incubation (Fig. 3). Incubation without DOC addition did not affect the presence of jarosite and even after incubation with 1x straw-derived DOC, jarosite was still detectable. In all soils that received a second DOC addition, however, jarosite was no longer detectable by XRD. Mössbauer spectroscopy allows a more detailed insight into the changes of Fe populations in the incubated soils. Since no Fe was removed or added to the incubation flasks, changes in the Fe distribution during incubation could be assessed quantitatively. After oxic pre-incubation and in treatments without DOC addition, the ferric sextets at 5 K representing jarosite comprised 78% of total Fe (Fig. 4a, b; Table 6). Twelve percent of total Fe was associated with very small and/or short range-ordered (SRO) Fe oxyhydroxides, such as nano-goethite and ferrihydrite (OxHy + (b)OxHy; Table 6). Nine percent of total Fe formed a ferric doublet at 5 K, representing Fe^{III} in phyllosilicates and/or Fe – organic associations; while only 1% of total Fe was identified as Fe^{II} (likely present in layer silicate clay minerals, or adsorbed, or in organic associations). This agrees with the low amount of clay-sized minerals (2%, Table 1), and the low proportion of illite and kaolinite (supporting

information SI 1.7) in this soil. Already after incubation with 1x straw-derived DOC, the portion of Fe in the original jarosite decreased strongly to 44% of total Fe with corresponding increases in SRO Fe^{III} oxyhydroxides (OxHy + (b)OxHy ~ 19%) and an increase in the ferric doublet at 5 K to 17% of total Fe (Fig. 4c; Table 6). After the second addition of straw-derived DOC, < 15% of total Fe was recovered as the original jarosite, whereas there was a strong increase in the proportion of Fe with SRO Fe^{III} oxyhydroxides (~ 45%). In treatments that received lactate with the second DOC addition, the proportion of Fe with jarosite was reduced even more (to ~ 8%) with a corresponding increase in SRO Fe^{III} oxyhydroxides (≥ 50%; Fig. 4d, e, f; Table 6). In all treatments incubated with DOC, the proportions of Fe^{II} and Fe^{III} likely bound to mineral surfaces and/or in Fe–organic associations (or potentially in clay minerals) increased slightly (4–8% and 11–19% of total Fe). Based on the mass balance, the proportion of Fe in solution was 16–18% of total Fe.

4. Discussion

4.1. Dissolved organic matter induced reduction processes and pH increases in submerged sulfuric soils

The results of the anoxic incubation set 1 showed that the addition of wheat straw-derived DOC to a sandy sulfuric soil is able to induce reductive processes and increase the pH by ~ 2 units after only 10 days of incubation at 20 °C. This indicates little stored acidity in the sandy sulfuric soil (Kölbl et al., 2021). With final pH of ~ 6, the soil is no longer classified as sulfuric at the end of the experiment. The reductive processes went along with strong CO_2-C release (and corresponding decrease of soil OC and DOC, Table 2), indicating high microbial activity during the first 10 days. Thereafter, the CO_2-C release decreased sharply, indicating decreasing microbial activity until day 31, and low activity until the end of the incubation (Fig. 1). This is in strong agreement with the minor changes in redox potentials and pH values from day 10 up to the end of the incubation.

Incubation set 2 was designed to monitor longer-term processes after DOC addition, and to investigate effects of a second DOC addition. Similar to incubation set 1, sharply decreasing Eh values in conjunction with strongly increasing pH values within the first 21 days of the anoxic incubation indicated that the highest activity of reducing microbes occurred during this period (Fig. 2). DOC additions that were almost twice as high as in incubation set 1 likely caused the longer duration of the first phase in incubation set 2, resulting in lower Eh and higher pH values. The development of higher pH and lower Eh values over time is in agreement with our previous study where ground wheat straw was added to the same sulfuric soil (Kölbl et al., 2021). The present study shows that addition of water-extractable DOC of straw alone can cause similar redox processes. In other studies, only low molecular weight DOC sources (glucose, sodium acetate, sodium lactate) have been tested in similar or even higher OC-to-soil ratios than in the present study, but these compounds did not induce reducing conditions and pH increases in sulfuric soils (Jayalath et al., 2016a; Högfors-Rönnholm et al., 2020). More complex, plant litter-derived DOC appears to be needed to effectively fuel anoxic soil microbial processes, suggesting that the type of DOC source is a major factor of remediation efficiency. In the long term (> 100 days anoxic conditions), however, the Eh values rose again slightly, combined with slightly decreasing pH values, implying that a single and/or low DOC addition is not sufficient to sustain permanent reducing conditions. Instead, we assume that ongoing slow dissolution of jarosite (Trueman et al., 2020) consumed OH^- ions, resulting in the observed pH decrease (Mosley et al., 2017). A second addition of DOC led to lower Eh and higher pH values, indicating that it is possible to control Eh and pH values of re-submerged sulfuric soils by adjusting amounts and intervals of DOC addition.

4.2. Redox processes and pH increase induced dissolution and transformation of jarosite

The decreasing CO_2-C release indicated decreasing microbial activity after 10 days of anoxic incubation (incubation set 1, Fig. 1). The concentrations of Fe, S, and K, however, continued to increase throughout the incubation period, indicating combined reductive- and pH-induced dissolution of jarosite (Table 3), which is consistent with findings of Trueman et al. (2020) on these soils. A comparison of both incubation sets after a similar incubation period (set 1, day 31 and set 2, day 42 (including 2 weeks oxic pre-incubation)) indicated greater release rates of Fe and S following additions of higher DOC concentrations. Thus, the dissolution rate of jarosite seems to be influenced by DOC concentration. Higher DOC concentrations may not only fuel microbially-mediated reductive dissolution, but may also increase the proportion of organic anions that can be adsorbed to the mineral surface, thereby weakening the Fe^{III}–O bonds and increasing reductive dissolution (Schwertmann, 1991). As a consequence, the Fe, S, and K concentrations further increased as the anoxic incubation progressed, reaching a maximum on day ~ 120 (Table 5) and then did not increase further, regardless of the amount and type of DOC added. This suggests jarosite dissolution may have stopped, or that an equilibrium was achieved between jarosite dissolution and sorption/precipitation/transformation processes that control the element concentrations in the soil solution.

Soil solution data was used to calculate saturation indices (supporting information SI 1.4 and SI 1.6) in order to assess possible dissolution-precipitation of Fe oxyhydroxy sulfates, Fe oxyhydroxides, and Fe sulfides. The saturation indices showed that jarosite tends to be stable in the short-term in treatments without DOC addition (incubation set 1). In contrast, thermodynamically favourable conditions for jarosite dissolution existed during incubation in all treatments with DOC addition, even at the early incubation stages (day 5, incubation set 1). At the same time, the saturation indices indicate a possible precipitation of Fe oxyhydroxides. Similar to experiments where ground wheat straw was added (Kölbl et al., 2021), circumneutral pH and Eh values between ~ 0 and ~ 100 mV promote reductive dissolution of jarosite and the release of Fe^{II}_{aq} (e.g. Johnston et al., 2011). This likely also then promotes the subsequent Fe^{II}-catalyzed transformation of jarosite and precipitation of Fe^{III} oxyhydroxides (Jones et al., 2009). The saturation indices showed that formation of Fe^{II} sulfides is unlikely (supporting information SI 1.4 and SI 1.6). Instead, Eh values of ≥ 0 mV suggest that redox conditions were mainly poised by the Fe^{II}–Fe^{III} redox couple at the DOC concentrations used here.

4.3. Transformation products of jarosite dissolution with respect to type and amount of DOC addition

Instead of the expected molar Fe:S ratio of 1.5, we observed much lower ratios in solution (~ 0.8 in set 1 and ~ 0.5 in set 2; Tables 3 and 5), supporting the idea that Fe^{III} oxyhydroxides instead of Fe^{II} sulfides have formed in treatments with DOC addition. This is in agreement with studies showing that incongruent dissolution of jarosite at circumneutral pH is accompanied by the precipitation of Fe^{III} oxyhydroxide phases such as goethite (Smith et al., 2006; Trueman et al., 2020) that would tend to be nanocrystalline (Welch et al., 2008). The lower molar ratios in incubation set 2 suggest formation of larger amounts of Fe oxyhydroxides, probably due to faster and more intense reduction and subsequent Fe^{II}-catalyzed transformation of jarosite due to the higher DOC addition.

In the treatment with a single DOC addition, jarosite was still detectable by XRD, and Mössbauer data confirmed that jarosite represented 44% of total Fe (Table 6). In contrast, jarosite was no longer detectable by XRD after 200 days of anoxic incubation in treatments receiving a second DOC addition, indicating strongly decreased particle size and/or almost complete loss of jarosite. This was supported by the Mössbauer data, showing that < 15% of total Fe was in the original

jarosite. Instead, SRO Fe^{III} oxyhydroxides had formed (comprising ≥ 45% of total Fe) that cannot be detected by XRD. Lactate treatments resulted in even more complete jarosite dissolution. However, Mössbauer data did not reveal obvious formation of Fe^{II} sulfides—although low amounts cannot be completely excluded (see supporting information SI 2.3)—suggesting that lactate addition does not necessarily promote sulfate-reducing bacteria as long as redox conditions are mainly poised by the Fe^{II}–Fe^{III} redox couple.

Interestingly, the proportions of Fe^{II} and Fe^{III} that cannot be ascribed to Fe^{III} oxyhydroxides and Fe in solution vary within a narrow range, regardless the amount and type of added DOC. Fe^{III} and Fe^{II} may partly occur in Fe–organic associations, but may also be adsorbed to mineral surfaces. Fe^{II} can catalyze the transformation of jarosite to Fe^{III} oxyhydroxides (e.g. Jones et al., 2009; Vithana et al., 2015; Bao et al., 2018), which likely contributed to the almost complete dissolution of jarosite in the high DOC treatments. Potential passivation of jarosite due to formation of Fe oxyhydroxide coatings, which may inhibit further jarosite dissolution (Elwood Madden et al., 2012; Welch et al., 2008), was not relevant in this context.

Progressing jarosite dissolution and transformation to Fe^{III} oxyhydroxides instead of Fe^{II} sulfides should have caused increasing S concentrations and consequently decreasing molar Fe:S ratios in the soil solution over time. However, molar Fe:S ratios remained fairly constant, irrespective of amount and type of added DOC. The released sulfate may have been sorbed by the newly formed Fe^{III} oxyhydroxides, but less sulfate can be sorbed by Fe^{III} oxyhydroxides per unit Fe than is bound in jarosite. In addition, the slightly lower Eh values of the treatments receiving a second DOC addition may have caused H_2S formation, and thus, gaseous S losses which were not analysed in the present study. Another explanation could be that Ca sulfate minerals formed. Indeed, saturation indices indicate concentrations of Ca and sulfate were close to equilibrium with gypsum and anhydrite, which suggests that the sulfate concentration was at least partly controlled by precipitation with Ca (supporting information SI 1.6). The amount of gypsum formed during incubation was probably too low to be detected by XRD, but Trueman et al. (2020) previously identified gypsum in this saline soil.

4.4. *Implication for remediation of sulfuric soils*

The present laboratory incubation study shows that almost complete loss of jarosite in a sandy sulfuric (pH < 4) soil can be achieved by controlled addition of wheat straw-derived DOC, particularly in combination with lactate. The resulting pH and Eh values induced the formation of SRO Fe^{III} oxyhydroxides while preventing the formation of Fe^{II} sulfides. Several studies (e.g. Jones et al., 2009; Vithana et al., 2015; Kölbl et al., 2021) have shown pH- and redox-mediated transformation of jarosite to goethite and lepidocrocite, with no (re-)formation of sulfides. This reduces the risk of re-acidification during future aeration. The rapid formation of Fe^{III} oxyhydroxides has another advantageous effect with regard to sulfuric soil remediation: strong release of Fe^{II}_{aq} following reductive dissolution of jarosite would be a serious environmental concern once transported off-site to neighbouring estuaries due to the acidification and deoxygenation when Fe^{II} is oxidized to Fe^{III} (Jones et al., 2009). However, the Fe^{II}-catalyzed formation of Fe^{III} oxyhydroxides instead of continuous Fe^{II} release counteracts this risk. Therefore, the adjustment of pH and Eh to values that promote the formation of Fe^{III} oxyhydroxides is desirable for the remediation of sulfuric soils. This can be achieved by repeated addition of DOC in combination with continuous monitoring of pH and Eh values. Beside application on topsoils, deep injection of wheat straw-derived DOC might be a promising approach for rapid and sustainable remediation of sandy sulfuric subsoils. In the future this potential acid sulfate soil remediation strategy could be tested in field experiments, and also in different soil types and textures (e.g. clayey soils).

5. Conclusions

The addition of water-extractable DOC from wheat straw rapidly induced redox processes and pH increase in a sandy sulfuric soil. Controlled and repeated addition of DOC enabled adjustment of Eh and pH values to ranges that promoted jarosite dissolution and Fe^{II}-catalyzed transformation into Fe^{III} oxyhydroxides while circumventing Fe^{II} sulfide formation. The combination of straw DOC with lactate resulted in almost complete jarosite removal without formation of Fe^{II} sulfides. The observed formation of Fe^{III} oxyhydroxides is advantageous with regard to the remediation of sulfuric soils containing jarosite as it reduces the risk of leaching Fe^{II} to neighbouring environments and minimizes renewed acidification in the case of future aeration. Due to its potential to migrate deep into soil, application of DOC from crop residues, such as wheat straw, is a promising approach to remediate sulfuric subsoils.

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 material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.geoderma.2022.115875.

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