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Oxidation and incorporation of hydrogen sulfide by dissolved organic matter

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Abstract

Redox reactions of sulfide with dissolved organic matter (DOM) are potentially important for sulfur cycling in anoxic environments. We investigated the chemical oxidation of H_2S with a peat humic acid in batch experiments at pH 6, quantified the electron accepting capacity (EAC), and applied a first order kinetic model to estimate reaction constants. Dissolved ferric iron was used to quantify electron donating capacities (EDC). Hydrogen sulfide was oxidized to thiosulfate and also incorporated into DOM. Fourier-transformed infrared (FTIR) spectroscopy suggested formation of aryl polysulfide. Electron transfer was significantly correlated to DOM concentration and amounted to 0.60 (EAC) and 0.63 (EDC) meq g^{-1} C. DOM concentrations > 60 mg l^{-1} lead to decreased capacities per unit mass carbon. The overall reaction of sulfide with DOM could be adequately described by a kinetic model comprising a redox-active and an S-incorporating DOM pool. The overall reaction was fast, with H_2S half-lives on the order of several hours. The results suggest that DOM may chemically reoxidize H_2S in organic rich soils and sediments at significant rates.

Keywords: Sulfide oxidation; DOM; Humic acids; Thiosulfate

1. Introduction

Natural dissolved organic matter (DOM) serves as a terminal electron acceptor in the microbial oxidation of organic substrates (Lovley et al., 1996) and affects pollutant degradation and metal mobility due to its involvement in complexation, sorption, and redox processes (e.g. Schwarzenbach et al., 1990; Redman et al., 2002; Chen et al., 2003). The redox properties of DOM have been mainly attributed to quinones, which are ubiquitous moieties in humic substances and can both accept or donate electrons depending on their redox state (Scott et al., 1998). Relevant for the redox properties of DOM are also other phenolic structures, contents of complexed ferric iron, and conformational changes of the DOM structure, which depend on pH and DOM concentration (Coates et al., 2000; Struyk and Sposito, 2001; Chen et al., 2003).

As a consequence of DOM bound electron transfer, the rates and pathways of microbial respiration in anoxic environments can be altered. Methanogenesis, for example, can be inhibited by competition between quinone reducing bacteria and methanogens for substrates and by toxic effects of quinones on methanogens (Cervantes et al., 2000, 2001). Iron reduction is potentially facilitated because DOM can function as an electron shuttle between metal hydroxides and microorganisms, as was shown in studies using model compounds such as anthraquinone-

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2,6-disulfonate (AQDS) and humic acids (Lovley et al., 1998; Kappler et al., 2004).

Another process of relevance for elemental cycling is the chemical oxidation of H_2S by DOM. In anoxic environments, H_2S is produced by bacterial reduction of sulfate or thiosulfate (Jorgensen, 1990; Elsgaard and Jorgensen, 1992) and may subsequently be chemically or microbially reoxidized by electron transfer to inorganic electron acceptors (e.g. Böttcher and Thamdrup, 2001; Poulton et al., 2004). A reoxidation of H_2S has also been documented for anoxic environments poor in inorganic electron acceptors, though. The anoxic and organic-rich soils of ombrotrophic peat bogs provide an example, where reoxidation of sulfide supports high rates of bacterial sulfate reduction (Wieder and Lang, 1988; Vile et al., 2003). As a consequence of sulfate reduction, the production and emission of methane from the globally relevant peatland source may be reduced (Segers, 1998). Chemical reoxidation of H_2S by DOM represents a possible key process in this phenomenon and requires investigation.

The formation of organic sulfur compounds (e.g. Casagrande et al., 1980; van Dongen et al., 2003) has to be considered as well because this process may prevent H_2S from reoxidation. The presence of organic sulfur has been widely taken as an indicator for its *in situ* formation in marine and freshwater sediments (Casagrande et al., 1980; Wieder and Lang, 1988; Henneke et al., 1997; Urban et al., 1999). One possible pathway of incorporation is the addition of H_2S by Michael and radical addition to quinone structures (Perlinger et al., 2002).

In this contribution, our specific objectives were (I) to characterize the products and kinetics of chemical H_2S oxidation with a peat humic acid, (II) to quantify the dependency of the reaction on DOM concentration, and (III) to determine to what degree sulfide oxidation and sulfide incorporation compete for sulfide in DOM solutions.

2. Materials and methods

2.1. Experiments

Pahokee Peat Reference Humic Acid (1R103H, PPHA) from the International Humic Substances Society (IHSS) was dissolved (see supporting information for detail) and used after filtration (0.2 μm nylon) to provide sterile conditions. In addition to data provided by the IHSS, metal content was determined by atomic emission spectroscopy (ICP-AES, Table 1). To prevent photoreactions (e.g. Fukushima and Tatsumi, 1999), all vessels employed for reactions and reagent storage were wrapped in aluminium foil. Blank experiments were conducted analogously to kinetic and batch assays in the absence of HA. Anoxic conditions and reagent stability were tested in preliminary experiments (see supporting information).

2.2. Kinetics of H_2S oxidation by DOM

A reaction flask was equipped with electrodes for pH (Inlab 411, Mettler) and H_2S (pH_2S, Watertest), the latter connected to a data logger. 300 ml of oxygen-free HA solution (50 mg C l^{-1}, pH ~6) was transferred to the flask in a glove box containing nitrogen, about 2% H_2, and a Pd catalyst (McCoy). The buffer was added as 1250 mg $NaHCO_3$, yielding a final concentration of 50 mM; pH was adjusted to 6.00 with 9.83 ml of 1 M deoxygenated HCl and the vessel was crimped with a thick butyl rubber stopper. The solution was stirred with a Teflon-coated stirring bar at constant rate, H_2S gas was added by syringe to a final concentration of 420 μM, and the electrode potential recorded every 10 s. Subsamples (6 ml) were withdrawn by syringes after injection of an equal volume of argon gas. Sulfide was determined on a 2 ml aliquot as described below. The remainder was transferred to oxygen-free crimped vials, purged with nitrogen (>99.999% N_2) for at least 30 min to remove excess H_2S and carbonate buffer and was stored at 4 °C in the dark until analysis. During the experiment,

Table 1
Element composition (% w/w) of Pahokee Peat Reference HA along with its carboxyl content and acidity, and free radical content (electron spin resonance data), as provided by the IHSS (www.ihss.gatech.edu)

	IHSS	This study[a]
H_2O[b]	10.4	
Ash	1.72	
C	56.84	
H	3.6	
O	36.62	
N	3.74	
S	0.7	
P	0.03	
Fe		0.01
K		0.03
Na		1.81
Si		0.09
COOH (mol_c kg^{-1})	8.87	
Log K_A^c	4.26	
Free radicals (spins g^{-1})	2.82×10^{17}	

Additionally, concentrations of Fe, K, Na, and Si were determined in solution by ICP-AES.
[a]Determined on a 50 mg C l^{-1} solution (0.2 μm filtered), referring to a dry weight basis.
[b]As reported by the IHSS, subject to air water content.
[c]Acidic constant of carboxyl moieties.

temperature was 21±1 °C and pH was within 6.00± 0.05 except at 5 and 23 h, when 0.2 and 0.4 ml of 1 M HCl were required for pH readjustment.

2.3. Dependency on DOM concentration

Experiments were carried out in batch assays with five DOM concentrations. 18 ml HA solution was transferred to 20 ml headspace vials in an anoxic glove box, 50 mM bicarbonate buffer was added, and the vials were sealed with butyl rubber stoppers. Gaseous H_2S was injected to a final concentration of about 250 μM, with vials held overhead to avoid gas loss upon needle removal. After 24±0.5 h on a horizontal shaker (f=100 min^{-1}), a 1 ml aliquot for sulfide determination was sampled in the glovebox and the remainder processed as described above.

2.4. DOM oxidation with ferric iron

Electron donor capacities of untreated ('actual EDC') and reduced humic acid ('potential EDC') were determined using a modified approach of Lovley et al. (1996). Fe(III)-ferrozine reagent (2 mM ferrozine, 0.5 mM $FeCl_3$ in 100 mM acetate buffer, pH 6.00) and a control reagent (without $FeCl_3$) were prepared and deoxygenated with nitrogen for 1 h. To a volume of 1.5 ml of DOM solution we added 1.5 ml of either ferrozine or control reagent in disposable cuvettes. The cuvettes were sealed with plastic stoppers, shaken, and after 24±1 h in the dark, absorption was determined. After the reaction was completed, pH in selected samples was 7.2±0.2 (S.D., n=5).

2.5. Analyses and calculations

Total sulfide was determined by the methylene blue method (Cline, 1969). The ZnOAc buffer (0.1 M) used was deoxygenated with nitrogen and overlaid by argon. Sulfite, sulfate, and thiosulfate were determined on filtered samples (0.2 μm, nylon) by ion chromatography (Metrohm IC-System, Metrosep Anion Dual 3 column, 0.8 ml min^{-1} with chemical suppression). For sulfite and elemental sulfur measurements see supporting information. The Fe–ferrozine complex was determined at 562 nm on a Varian Cary 1E spectrophotometer (Stookey, 1970).

After acidification to pH 5 with HCl and removal of residual buffer by purging with nitrogen for 1 h, Fourier-transformed infrared (FTIR) spectra of non-reduced and reduced HA preparations were determined on freeze-dried samples on a Bruker Vector 22 instrument using KBr pellets (200 mg KBr+2 mg sample, 32 scans from 4000 to 500 cm^{-1} at 1 cm^{-1}, automatic background correction). Spectra were baseline corrected. Relative changes in peak intensity ratios, as proposed by Niemeyer et al. (1992), were determined to identify structural changes between reduced and non-reduced HA.

Electron accepting capacities per unit mass carbon were calculated as the charge equivalents resulting from net concentrations of oxidized sulfur species after subtraction of a reagent blank. Electron donating capacities (EDC) were calculated analogously from formed Fe^{2+}. A schematic overview of the determined and calculated electron transfer capacities is given in Fig. 1.

2.6. Kinetic modeling

Thiosulfate was the major reaction product in our experiments (see results). The oxidation of H_2S to thiosulfate by a model quinone Q, which is reduced to QH_2 can be represented by

$$4Q + 2H_2S + 3H_2O \rightarrow 4QH_2 + S_2O_3^{2-} + 2H^+ \qquad (1)$$

Incorporation of sulfur into the organic structure at reactive site X was accounted for as an additional, sulfide-

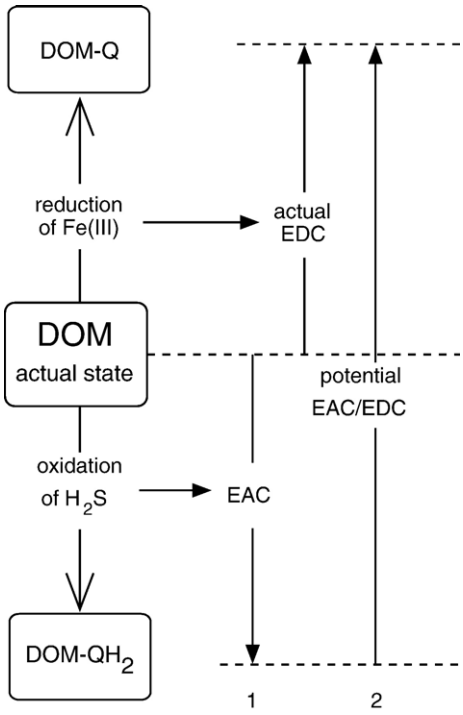


Fig. 1. Schematic for the determination of electron donating and accepting capacities (EDC, EAC). –Q and –QH symbolize oxidized and reduced quinone moieties. Capacities were determined in the numbered order.

consuming process. Assuming rates being pseudo-first order with respect to Q and X, the overall rate equation for the consumption of hydrogen sulfide comprising both oxidation by quinones and incorporation into organic matter can be described as

$$\mathrm{d}[H_2S]/\mathrm{d}t = -k^1_{obs} \cdot 4[Q] - k^2_{obs} \cdot [X] \quad (2)$$

where k^1_{obs} and k^2_{obs} are the pseudo-first order rate constants and $[Q]$ and $[X]$ the pool concentrations of quinones and sulfur-incorporating moieties, respectively.

For a given DOC concentration, the pool concentration $[Q]$ was estimated from the concentration of products after completion of the reaction. The pool concentration $[X]$ was then calculated as the difference between consumed sulfide and formed reaction products.

When $[Q]$ and $[X]$ are expressed as relative fractions q and x of the total sulfur pool, including the appropriate stoichiometric factors given by Eq. (1), we can denote Eq. (2) as

$$\mathrm{d}[H_2S] / \mathrm{d}t = -k^1_{obs} \cdot q - k^2_{obs} \cdot x \quad (3)$$

with the time-dependent solution

$$[H_2S](t) = [S_{tot}] \cdot \left(q \cdot e^{-k^1_{obs} \cdot t} + x \cdot e^{-k^2_{obs} \cdot t} + (1 - q - x) \right) \quad (4)$$

Fraction q and rate constant k^1_{obs} were derived by nonlinear regression of thiosulfate concentration over time of the form

$$[S_2O_3](t) = q/2 \cdot [S_{tot}] \cdot \left(1 - e^{(-k^1_{obs}/2 \cdot t)}\right) \quad (5)$$

in which $[S_{tot}]$ is the total initial sulfur concentration and the division by two accounts for the stoichiometry in Eq. (1). Eq (4) was then applied to fit the rate constant k^2_{obs} by nonlinear regression. Half-life for reaction i was calculated as

$$t_{1/2}(i) = \frac{\ln(2)}{k^i_{obs}} \quad (6)$$

3. Results

3.1. Inorganic reaction products and kinetics

Oxidized sulfur in solution was detected as thiosulfate at concentrations of up to 8 μM (Figs. 2 and 3). Its concentration was linearly correlated to the employed concentration of DOM, which suggests that reaction of H_2S with DOM was responsible for the production. Thiosulfate also occurred at background concentrations of 2.7±0.3 μM in experiments conducted without DOM. We attribute this background, that did not obscure the experimental results, to traces of oxygen in nitrogen gas used for purging of solutions. A significant contribution of inorganic electron acceptors, in particular ferric iron, to the determined EAC can also be excluded. Total iron content in the HA was 0.01% (Table 1) and nitrate and manganese could not be detected. For further details consult the supporting information.

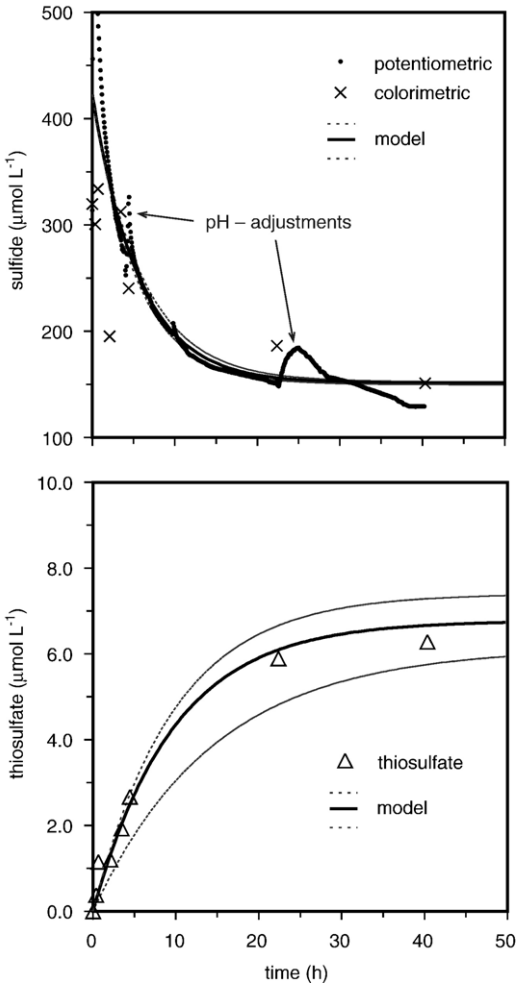
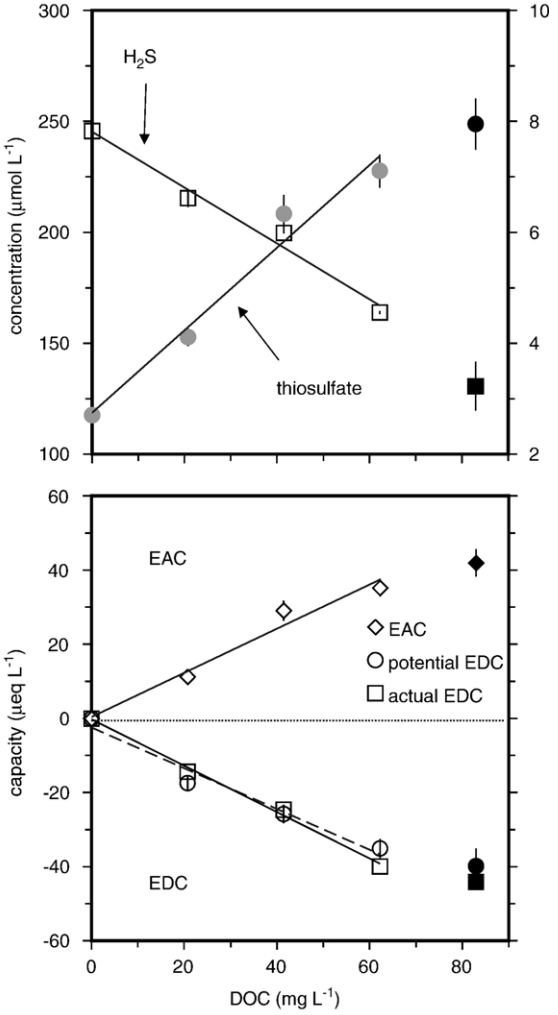


Fig. 2. Measured and fitted (Eq. (4)) time series of hydrogen sulfide and thiosulfate concentration. Dashed lines represent the 95% confidence interval.

Sulfate was not considered a major reaction product, as concentrations were typically below 5 μM and did neither increase in the kinetic experiment with time, nor with DOM concentration. Elemental sulfur and sulfite were not detected. The sum of thiosulfate and sulfide only accounted for half of the initial sulfur after 24 h, indicating sulfide incorporation into the DOM.

In the kinetic experiment, H_2S was rapidly consumed for about five hours and more slowly afterwards (Fig. 2). Thiosulfate reached a final concentration of 6.7 μM. The



Linear regression results		R^2	F
H_2S (µM)	= -1.26 DOC + 245.30	0.98	101
thiosulfate (µM)	= 0.07 DOC + 2.75	0.97	67
EAC (µeq L^{-1})	= 0.60 DOC + 0.36	0.97	67
actual EDC (µeq L^{-1})	= 0.63 DOC + 0.24	0.99	397
potential EDC (µeq L^{-1})	= 0.55 DOC + 2.52	0.97	61

Fig. 3. Hydrogen sulfide and thiosulfate (upper panel) and electron accepting and donating capacities (EAC, EDC; lower panel) as a function of DOC concentration in mg l^{-1}. Thiosulfate blanks were not subtracted and constitute the *y*-intercept. Linear regressions were significant at $p=0.05$ (*F*-test). Data represented by filled symbols were excluded from regressions. Mean values ($n=3$) and standard deviations are shown.

overall consumption of sulfide could be described by a reaction with two DOM pools, or reaction pathways, as

$$[H_2S](t) = 421 \cdot (0.032 \cdot e^{-0.206 \cdot t} + 0.611 \cdot e^{-0.176 \cdot t} + 0.357) \quad (7)$$

$R^2=0.95$; with $[H_2S]$ in µM and time *t* in hours. This means that only 3.2% of the initial sulfide was oxidized to thiosulfate at a rate of 0.206 h^{-1}, 61.1% was incorporated at 0.176 h^{-1}, and 35.7% did not react. The oxidizing and the incorporating pool thus only slightly varied in reactivity but differed by an order of magnitude in size. Half-lives according to Eq. (6) were 3.4 h for DOM reduction and 3.9 h for sulfur incorporation. Based on an analogously conducted blank experiment without humic acid, potentiometric sulfide readings in the period of 0.9–40 h were taken for calculations.

3.2. Concentration dependencies

Hydrogen sulfide consumption and thiosulfate production in the assays significantly and linearly increased with the employed DOC concentration ($p=0.05$) up to a DOC concentration of 60 mg l^{-1}. Hydrogen sulfide was consumed at 1.26 meq g^{-1} C and thiosulfate produced at 0.07 meq g^{-1} C (Fig. 3). With eight moles of charge transferred per mole of thiosulfate formed, the EAC amounted to 0.60±0.07 meq g^{-1} C (standard error).

Both potential EDC, using pre-reduced PP-HA, and actual EDC, using freshly prepared PP-HA, followed the same pattern with respect to increases in DOC concentration (Fig. 3). The potential EDC reached 0.55± 0.07 meq g^{-1} C. Curiously, the actual EDC was slightly higher (0.63 meq g^{-1} C). This result could not be reproduced in experiments with filtered DOM from a peat bog. In those experiments, the potential EDC always exceeded the actual EDC by an average factor of 1.64, which is closer to expectation (Fig. S1, supporting information; Heitmann et al., submitted for publication). The carbon normalized capacity of DOM to transfer electrons decreased above a DOC concentration of 60 mg C l^{-1} (filled symbols in Fig. 3).

3.3. Incorporation of sulfur

Infrared absorbance of reduced and non-reduced DOM (Fig. 4) was similar at larger wavenumbers and differed in carbonyl bands and in the fingerprint range (<1000 cm^{-1}). Peaks of antisymmetric and symmetric C–H stretching vibrations of methylene groups at 2930 and 2860 cm^{-1} and a peak at 1401 cm^{-1} did not vary among one another and were chosen as reference for the calculation of standardized absorption intensities (Table 2).

The strongest change in IR absorption occurred around 460 cm^{-1} indicating a formation of aryl disulfide bonds (Table 2, Fig. 4). Reduction further decreased relative absorption at 1720 cm^{-1} by 15% (ketone/quinone or carboxylic C═O) and at 1630 cm^{-1} by 6% (C═O and conjugated C═C stretch), and intensified it at 1209 cm^{-1} by 15% (C═S or alkyl ethers). Carbon bonded sulfur

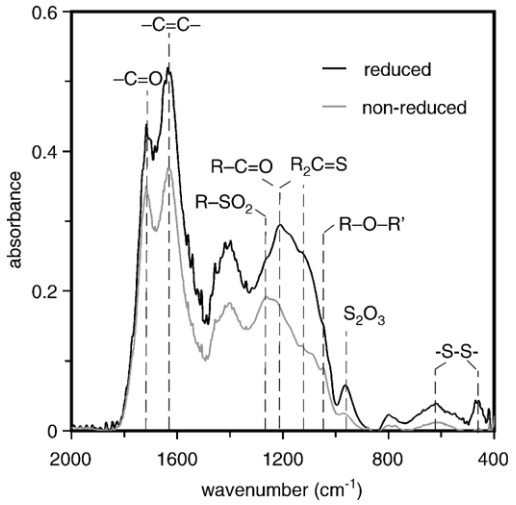


Fig. 4. Fourier-transformed infrared (FTIR) spectra of Pahokee Peat reference humic acid before and after reaction with hydrogen sulfide (baseline corrected, without scaling). For clarity, only wavenumbers <2000 cm^{-1} are shown. Differences between treatments at wavenumbers >2000 cm^{-1}, and shifts in peak intensity ratios at characteristic wavelengths are summarized in Table 2.

probably also increased absorption at 1125 cm^{-1}. An influence of sulfate seems unlikely due to its low dissolved concentration of ~5 μM. Absorbance at 1262 cm^{-1} and around 2565 cm^{-1} (thiols or overtone/combination) decreased by 12% after reduction, possibly influenced by the formation of disulfide bonds.

3.4. Discussion

Thiosulfate was the only inorganic reaction product whose production could be detected. The chemical oxidation of H_2S with DOM would differ in this respect from the oxidation of H_2S with ferric iron hydroxides, which mainly produces elemental sulfur and polysulfides (Peiffer et al., 1992; Poulton et al., 2004). This finding is important because it is generally believed that thiosulfate formation under anoxic conditions requires the presence of bacteria (Elsgaard and Jorgensen, 1992).

About the reaction mechanisms we can presently only speculate. Thiosulfate is also formed from the oxidation of H_2S with oxygen. In this reaction, elemental sulfur and sulfite are initially formed by a polar or free radical chain mechanism (e.g. Chen and Morris, 1972; Zhang and Millero, 1994). Produced sulfur and sulfite may then either react with additional sulfide and oxygen to thiosulfate, or directly with oxygen to sulfate. Quinone reduction has been described as two single-electron reactions to hydroquinone via the partially stabilized semiquinone radical (Scott et al., 1998; Struyk and Sposito, 2001; Nurmi and Tratnyek, 2002). In analogy, it may be that a radical reaction with DOM initially also produced sulfite, which further reacted with H_2S, and whose rapid turnover prevented it from detection.

The sulfur mass balance further suggested that sulfur was incorporated into the organic matter, with some uncertainty regarding inorganic species that we did not attempt to analyze, such as tetrathionate. This is not surprising as incorporation has been amply documented (Casagrande et al., 1980; Henneke et al., 1997; Urban et al., 1999). The FTIR spectra tentatively hinted at a formation of organic (poly-) sulfide groups in DOM during reaction with H_2S. This would be in agreement with Michael and radical addition reactions of H_2S to quinones and the formation of aryl thio-compounds, as described by Perlinger et al. (2002). The authors pointed out that mercaptojuglone may further react with thiyl radicals to disulfides. The formation of aryl disulfides thus seems mechanistically reasonable.

The kinetic model that was based on these considerations adequately described sulfide consumption, although the assumption of one redox-active pool grossly simplifies the range of putative redox couples within DOM (e.g. Nurmi and Tratnyek, 2002). Some confidence in the model can be drawn from the fact that different methods of estimating the pool sizes delivered similar results. Estimated from the kinetic experiments, the redox-active pool was 3.2% of total S. This pool was only slightly different (2.9%) when calculated from the concentration dependency experiment. More uncertain

Table 2
Difference between FTIR peak intensities of non-reduced and reduced humic acid preparations, standardized to three reference peaks

Peak center (cm^{-1})	Difference ± sd (%)	Assignment	Alternative
3421	−2.8±0.2	–OH	
3407	−1.9±0.2	–OH	
2565	−11.8±0.2	R–SH	$R–SO_2$
1712	−14.5±0.2	ketone C═O	COOH
1630	−6.1±1.1	aryl C═C	COO^-, C═O
1262	−11.8±1.0	$R–SO_2$	R_2–SO, Φ–OH
1209	−15.0±1.3	R–C–O	$R_2C═S$
1125	−45.0±1.7	$R_2C=S$, R–O–R′	SO_4^{2-}
1062	−30.5±0.3	R–O–R′	
972	−69.8±2.0	$S_2O_3^{2-}$	
623	+122.4±0.5	C–S stretch in S–S	
459	+2207.9±5.5	S–S stretch in Φ–S_{2-}	

Mean values ± standard deviations. Reference peaks used were 2930, 2860 and 1401 cm^{-1} (peak assignment after Niemeyer, 1992 and Coates, 2000a).

Table 3
Rates and reaction conditions of sulfide consuming processes at room temperature (294–299 K) and similar ionic strength (0.1 M, this study: 0.05 M), calculated for an initial sulfide concentration of 1 mM

Acceptor	Surface area (m^{-2} g^{-1})	$-\lg R_S^a$	$-\lg R_S^b$	pH	Reference
Lepidocrocite	57.3	0.7	0.2	7.5	(Peiffer et al., 1992)
	57.3	3.4	2.8	6.0	
	61.5	5.5	5.0	7.5	(Poulton et al., 2004)
Ferrihydrite	300–600	4.8–5.4	5.3–5.5	7.5	
Goethite	36.5	6.5	6.8	7.5	
Magnetite	2.8	6.7	5.8	7.5	
Hematite	2.5	6.8	5.9	7.5	
O_2		6.5[c]		6.0	(Zhang and Millero, 1994)
DOM		5.5[d]		6.0	This study
		5.5[e]		6.0	

[a]Rate (mol min^{-1} mg^{-1}) in terms of mineral weight for 50 mg l^{-1}.
[b]Rate (mol min^{-1} mg^{-2}) in terms of mineral surface area for 10 m^2 l^{-1}.
[c]Calculated for 1 mM oxygen.
[d]For 48 mg C L^{-1}.
[e]Estimated rate for organosulfur formation.
See text for further explanations.

seems the pool size of sulfur-incorporating moieties. Determined by mass balance, this pool accounted for about 60% of total sulfur, determined from the concentration dependency this figure was 20%. The analysis further suggested that both processes compete for H_2S, as rate constants were similar with 0.206 and 0.176 h^{-1}.

In comparison to other possible sinks for H_2S, which we collated from the literature and recalculated for comparable pool sizes (Table 3), oxidation and incorporation by DOM were fairly rapid. Our results suggest that in the pH range used, the reactivity of sulfide towards DOM is well above that towards molecular oxygen and crystalline Fe (oxyhydr)oxides and below the reactivity towards poorly crystalline forms of Fe(III). DOM should thus be capable of chemically oxidizing H_2S at similar rates as iron minerals in many organic rich soils and sediments and could provide a significant H_2S sink based on the determined reaction rates.

Thiosulfate production, H_2S consumption, and ferrous iron production increased linearly up to a DOC concentration of 60 mg l^{-1} in the assays, similarly as reported earlier for the oxidation of DOM by ferric iron (Chen et al., 2003). The increase lessened between 60 and 80 mg l^{-1}, particularly when DOM treated with H_2S was used for reaction with ferric iron (Fig. 3, 'potential EDC'). The small difference in EDC between DOM treated and untreated with H_2S may have been caused by sulfurization and subsequent coagulation of DOM. Coagulation decreases the surface area and accessibility of reactive groups and has been observed after exposure of polysaccharides to low sulfide concentrations in seawater (e.g. Ciglenecki et al., 2000). Although no precipitates were visible and thus direct evidence is lacking, this process seems plausible and in agreement with the detection of disulfide bridges by FTIR (Fig. 4). Alternatively, sulfide addition may have depleted carbonyl units which are both redox active and targets for sulfurization (van Dongen et al., 2003).

Electron transfer capacities amounted to 0.60 (EAC) and 0.63 meq g^{-1} C (actual EDC), which is similar to an earlier EDC value reported for PP-HA (0.41 meq g^{-1} C) using iron-citrate as oxidant at pH 6.9 (Scott et al., 1998). Comparable capacities of 0.46–1.3 meq g^{-1} C were also reported for other humic acids using citrate-complexed iron and potassium hexacyanoferrate(III) as electron acceptors (Lovley et al., 1996; Kappler et al., 2004). It can thus be speculated that similar quantities of electrons could be shuttled from H_2S to DOM and from DOM to dissolved ferric iron. Electron transfer capacities of DOM are, however, highly dependent on pH, iron speciation, and the redox potential of oxidants and reductants (Chen et al., 2003; Bauer et al., submitted for publication). We did not investigate effects of pH on H_2S oxidation by DOM and caution is thus appropriate regarding the generality of the determined EAC and EDC values.

Hydrogen sulfide oxidation by organic moieties may have important implications. A recycling of sulfide to thiosulfate could support anaerobic sulfur respiration in absence of sulfate, as many sulfate reducing bacteria utilize thiosulfate as an electron acceptor (Jorgensen, 1990; Elsgaard and Jorgensen, 1992). If thiosulfate was microbially disproportionated into sulfate and H_2S (Elsgaard and Jorgensen, 1992), bacterial sulfate reduction could be supported in sulfate poor and organic rich peat soils, where sulfate pools would rapidly deplete if H_2S was not reoxidized (Wieder and Lang, 1988; Vile

et al., 2003). It has to be considered that the determined EAC per unit mass of carbon was fairly small. The significance of the process would be amplified if humified organic matter in the solid phase of soils and sediments oxidized H_2S as well. Nothing is known about this possibility yet. Electron shuttling from H_2S to inorganic electron acceptors of little reactivity, and advective transport of oxidized DOM, would add to the biogeochemical significance of the process.

4. Conclusions

The experiments demonstrated that humic acids, an abundant class of DOM in organic rich soils and sediments, oxidize H_2S to thiosulfate at pH 6, and moreover incorporate substantial quantities of hydrogen sulfide, likely as aryl polysulfide. The kinetics of both reactions was faster than reported from the reaction of H_2S with molecular oxygen and crystalline iron oxides. Based on these findings, the process could be a relevant pathway of sulfur oxidation in organic rich environments, such as ombrotrophic peatland soils, lake sediments, and organic rich aquifers, and support the respiratory activity of sulfate reducing bacteria under sulfate limited conditions. As the electron accepting capacity of DOM was fairly small, we suggest that further investigations should focus on humic-like solid phase materials, which are much more abundant than DOM, and on electron shuttling processes involving inorganic electron acceptors, DOM, and H_2S.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.chemgeo.2006.05.011.

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