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Influence of dissolved organic matter on carbonyl sulfide and carbon disulfide formation from cysteine during sunlight photolysis†

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Carbonyl sulfide (COS) and carbon disulfide (CS₂) are important atmospheric gases that are formed from organic sulfur precursors present in natural waters when exposed to sunlight. However, it remains unclear how specific water constituents, such as dissolved organic matter (DOM), affect COS and CS₂ formation. To better understand the role of DOM, irradiation experiments were conducted in O₂-free synthetic waters containing four different DOM isolates, acquired from freshwater to open ocean sources, and the sulfur-based amino acid, cysteine (CYS). CYS is a known natural precursor of COS and CS₂. Results indicated that COS formation did not vary strongly with DOM type, although small impacts were observed on the kinetic patterns. COS formation also increased with increasing CYS concentration but decreased with increasing DOM concentration. Quenching experiments indicated that [•]OH was not involved in the rate-limiting step of COS formation, whereas excited triplet states of DOM (³CDOM*) were plausibly involved, although the quenching agents used to remove ³CDOM* may have reacted with the CYS-derived intermediates as well. CS₂ was not formed under any of the experimental conditions. Overall, DOM-containing synthetic waters had a limited to no effect towards forming COS and CS₂, especially when compared to the higher concentrations formed in sunlit natural waters, as examined previously. The reasons behind this limited effect need to be explored further but may be due to the additional water quality constituents present in these natural waters. The findings of this study imply that multiple variables beyond DOM govern COS and CS₂ photoproduction when moving from freshwaters to open ocean waters.

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Environmental significance

Carbonyl sulfide (COS) and carbon disulfide (CS₂) are two atmospheric gases that play an important role in the global sulfur cycle and climate change. By examining their sunlight-driven photoproduction from cysteine (CYS) in the presence of dissolved organic matter (DOM), DOM type was found to have a limited effect, whereas DOM concentration had an inverse effect, on COS formation. CS₂ was not formed under any tested conditions. These results raise questions about which specific natural water constituents actually drive COS and CS₂ formation and why increased COS formation is observed when moving from open ocean waters to coastal waters. These drivers are likely not DOM-dependent but rather due to differences in other water constituents or dissolved organic sulfur (DOS) content.

Introduction

Carbonyl sulfide (COS) and carbon disulfide (CS₂) are low molecular weight sulfur gases that are produced in natural

waters at low pM to nM concentrations.^{1–7} They can volatilize into the atmosphere,^{5,8} where COS can reach the stratosphere due to its >1 year atmospheric lifetime^{5,9} and CS₂ can react with hydroxyl radicals ([•]OH) to form COS.^{10,11} COS is a greenhouse gas,⁹ but it can also form sulfate aerosols in the stratosphere, which counteract global warming.¹² While the ocean is one major source of COS and CS₂,^{2,4,10,13–22} these gases are also known to form in freshwaters^{3,6} and coastal waters.^{4,7}

One major route by which COS and CS₂ are generated in these waters occurs when naturally present organic sulfur compounds are photochemically transformed by sunlight.^{7,22–25} In fact, the COS concentration in ocean waters follows a diurnal cycle and decreases with depth from the ocean surface.^{4,26} The addition of various types of organic sulfur precursors (e.g.

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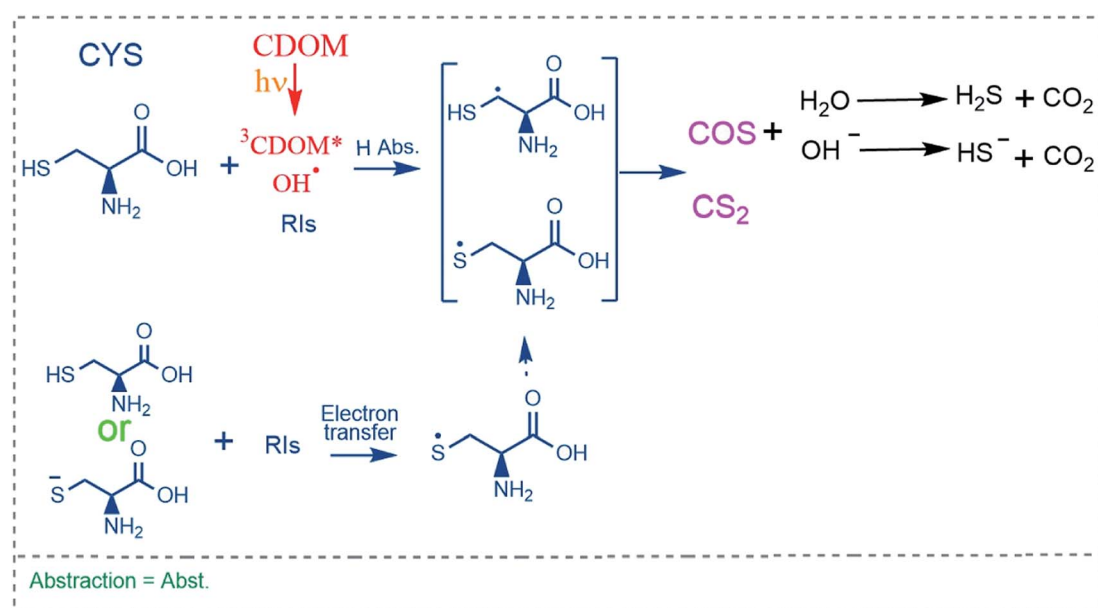
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thiols, disulfides, and thioethers) to such waters has been shown to further elevate COS and CS₂ levels to varying degrees.^{11,23,24} The thiol, cysteine (CYS) (Scheme 1), is one organic sulfur precursor of particular interest since it is present in natural waters⁵ and forms relatively higher levels of COS and CS₂ than other precursors.^{23,24} CYS does not form COS and CS₂ by direct photolysis, since CYS incurs negligible absorption to sunlight, but more likely through transformations occurring *via* indirect photolysis.

Our recent study proposed an indirect photochemical mechanism pertaining to how COS and CS₂ could be formed from CYS.²⁴ A condensed version of this mechanism is provided in Scheme 1. Overall, this mechanism proposes that CYS can form COS and CS₂ *via* two major steps. First, CYS reacts with one or a range of reactive intermediates (RIs) to form a sulfur- or carbon-centered radical (*i.e.* cysteine-derived intermediate) (Scheme 1). CYS is known to react with a wide range of RIs (*e.g.*, [•]OH,²⁷ H₂O₂,²⁷ ¹O₂,²⁷ and ³CDOM*^{27,28}), although it is currently unclear what specific RIs are involved. Several prior studies have suggested that ³CDOM* and [•]OH are involved in forming COS²³ and CS₂ (ref. 11), but that ¹O₂ is not involved in forming COS specifically.^{7,25} Both the thiol (–SH) and thiolate (R–S[–]) forms of CYS (Scheme 1) may also be involved, as they are both present given CYS's pK_a of 8.4,²⁷ which falls in line with the typical range of pH values of natural waters.²⁹ However, the CYS thiolate (R–S[–]) form is known to be more reactive than its thiol (–SH) form.²⁸ After this first step, these radicals ultimately form COS and CS₂ through a sequence of additional steps that remain unknown (Scheme 1), although several possibilities have been hypothesized.²⁴ COS formation is also complicated by the fact that it simultaneously undergoes hydrolysis and base-catalyzed hydrolysis (Scheme 1);³⁰ note, a description of the hydrolysis kinetics and rate constants is provided in Text S1 of the ESI.†

One water quality constituent that potentially serves as a key source of the RIs responsible for forming COS and CS₂ is dissolved organic matter (DOM). Previous studies have indicated that COS formation increases when different sources of DOM (*e.g.* Suwannee River natural organic matter (SRNOM)²⁵ or Suwannee River fulvic acid (SRFA)²⁴ or humic acid²³ are amended to sunlit waters containing CYS. Moreover, in our previous study where nine CYS-spiked natural waters were irradiated with sunlight, COS formation increased when the DOM concentration for each water increased.²⁴ DOM is hypothesized to play a role since one fraction of its content, chromophoric dissolved organic matter (CDOM), serves as the main photosensitizer in natural waters after nitrate.^{31–33} Absorption of light by CDOM leads to formation of various RIs, including ³CDOM*, ¹O₂, [•]OH, and H₂O₂.^{32,34–37} The concentration and distribution of RIs can vary based on the DOM source, since different DOM types can incur different levels of photo-reactivity.^{35,36,38–43} At present, it remains unclear which of these DOM-derived RIs (excluding ¹O₂ for COS, as noted above) contribute to the reaction pathway leading CYS to form COS and CS₂ (Scheme 1).

The aim of this study was to specifically isolate how different DOM types affected the ability for CYS to form COS and CS₂ during sunlight exposure and to then identify which DOM-derived RIs were involved in the reaction pathways. With only DOM present in solution, it was hypothesized that these DOM-derived RIs controlled COS and CS₂ formation (Scheme 1). To then test this hypothesis, a series of photochemical experiments were conducted wherein synthetic waters containing CYS and one of four different DOM isolates, ranging from freshwater to open ocean DOM, were exposed to simulated sunlight over 4 h. Conditions including DOM concentration and CYS concentration were also varied from 0.5–20 mg-C L^{–1} and 1–100 μM,



Scheme 1 A condensed schematic of the proposed indirect photochemical pathways involved in forming COS and CS₂ from CYS during sunlight photolysis (adopted from a schematic described in Gharehveran *et al.* 2018 (ref. 24)).

respectively. All of the synthetic solutions were deoxygenated prior to sunlight exposure for two key reasons. The first reason was to extend the $^3\text{CDOM}^*$ lifetime, since O_2 serves as the main quencher of excited triplet states,³³ and to extend CYS-derived radical lifetimes, since O_2 can also quench sulfur-based radicals.⁴⁴ This protocol mitigated analytical constraints in measuring COS and CS_2 , as their formation levels were maximized without O_2 , as similarly observed by our previous study.²⁴ The second reason was to ensure that CYS was stable in solution, since CYS can react with O_2 over time in the presence of trace metals.²⁷ Quenching experiments were also conducted using isopropanol, phenol, trimethylphenol (TMP), or sorbic acid to quench $^{\bullet}\text{OH}$ ^{40,45–48} or $^3\text{CDOM}^*$,⁴⁹ respectively. Overall, this study was intended to build upon our mechanistic understanding of the global photochemical processing of organic sulfur in sunlit natural waters.

Materials and methods

Standards and reagents

CS_2 , CYS, 2-nitrobenzaldehyde (2-NBA), phenol, TMP, and sorbic acid were purchased from Sigma Aldrich. COS was purchased as a calibration gas standard at 1 ppm (mol mol^{-1}) in N_2 from Gasco. SRFA (Suwannee River, GA, US) was purchased from the International Humic Substances Society (IHSS). Isopropanol and tris base were purchased from Alfa Aesar and Roche Diagnostics, respectively. These and other chemicals, such as methanol (MeOH), acetonitrile (ACN), and NaOH, were purchased at reagent grade or higher. Reagent grade water ($\geq 18.2 \text{ M}\Omega \text{ cm}$) was obtained from a Nanopure (Thermo Scientific) water purification system. All glassware was acid washed to prevent trace metal contamination.

Stock preparation

Stock solutions containing CYS were prepared at a $500 \mu\text{M}$ concentration in N_2 -purged reagent-grade water to prevent CYS from reacting with O_2 over time, for reasons described above. SRFA stock solutions were prepared at $\sim 368 \text{ mg-C L}^{-1}$ in reagent-grade water. The final concentration of the SRFA stock solution was calculated based on the elemental percentage of

carbon within SRFA reported by IHSS. Phenol, TMP, and sorbic acid stock solutions were prepared at 1.0 M in 20/80% ACN/water, 20/80% ACN/water, and 100% ACN, respectively. Since these stock solutions were prepared at such a high concentration, the final percentage of ACN in the photolyzed solutions remained very low at 0.02%, 0.003%, and 0.1% (v/v) for the reaction solutions containing phenol, TMP, and sorbic acid, respectively. These levels of ACN were unlikely to quench $^3\text{CDOM}^*$, given that a number of studies have evaluated the ability for $^3\text{CDOM}^*$ to react with O_2 when ACN was used as a solvent.^{50,51} These levels of ACN were also confirmed to not quench $^{\bullet}\text{OH}$ since the reaction of ACN with $^{\bullet}\text{OH}$ is relatively slow ($k_{\text{ACN}}^{\text{OH}} = 2.5 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ (ref. 52)). Therefore, the pseudo-first order reaction rate constant of $^{\bullet}\text{OH}$ with ACN, over the range of concentrations added, fell orders of magnitude lower ($= k_{\text{ACN}}^{\text{OH}} \times [\text{ACN}]_0 = \sim 10^2 \text{ to } 10^3 \text{ (s}^{-1}\text{)}$) than its comparable value with CYS ($= k_{\text{CYS}}^{\text{OH}} \times [\text{CYS}]_0 = 2.5 \times 10^5 \text{ (s}^{-1}\text{)}^{\text{27}}$).

Collection and spectral characterization of the DOM isolates

The three DOM isolates used in this study beyond SRFA were collected in 2013 by Dr Michael Perdue (Ball State University) from the Altamaha River (GA, US) and the Gulf Stream off the eastern coast of the US. The specific sampling sites of these waters are shown and listed in Fig. S1† and Table 1, respectively. Once collected, the sampled waters were treated by reverse osmosis to reduce the water volume and by electrodialysis to remove salts.⁵³ Samples were then stored in the dark at -20°C before use. The total organic carbon (TOC) content of these isolates was measured by a TOC-V Shimadzu Total Organic Carbon Analyzer. These isolates represented a freshwater to ocean water DOM gradient, where: (i) the Altamaha river sample represented freshwater to brackish water DOM (henceforth labeled as “Altamaha DOM”), and (ii) the Gulf Stream samples represented open ocean DOM (henceforth labeled as “Ocean DOM-I” and “Ocean DOM-II”). Absorbance-derived metrics, namely E_2/E_3 (the ratio of absorbance at 250 nm to 365 nm), specific ultraviolet (UV) absorbance at 254 nm (SUVA_{254} , calculated as UV absorbance at 254 nm divided by the DOC concentration), and the spectral slope from 275 to 295 nm ($S_{275-295}$, calculated as the slope of the log transformed absorbance

Table 1 Locations and key spectral metrics of the tested DOM isolates

DOM type	Location	$\text{SUVA}_{254} (\text{L m}^{-1} (\text{mg C})^{-1})$	$E_2 : E_3$	$S_{275-295}$	BIX	FI	HIX
SRFA	Originating from the Okefenokee swamp in south GA, US	3.26 (4.3 (ref. 82), 3.04 (ref. 83)) ^a	5.24 (4.04 (ref. 84), 4.58 (ref. 35), 4 (ref. 85)) ^a	0.020	0.67	1.38 (1.15–1.40 (ref. 58)) ^a	3.10
Altamaha DOM	Altamaha River, GA, US	7.06	5.12	0.017	0.55	1.48	3.83
Ocean DOM-I	Gulf Stream Latitude: $31^\circ 28.2'$ Longitude: $79^\circ 21.4'$	0.98	5.41	0.027	2.20	1.80	0.22
Ocean DOM-II	Gulf Stream Latitude: $31^\circ 29.5'$ Longitude: $79^\circ 19.2'$	0.60	9.80	0.036	0.76	1.65	0.42

^a Previously-reported values.

from 275 to 295 nm), were recorded for each DOM source using previously described methods⁵⁴ (Table 1). The following fluorescence characteristics were also calculated for each DOM source using established methods with the corresponding fluorescence excitation–emission matrices (EEMs): biological index (BIX, calculated as the ratio of fluorescence at 380 nm to that at 630 nm for excitation at 310 nm); fluorescence index (FI, calculated as the ratio of fluorescence at 450 nm to that at 500 nm for excitation at 370 nm); and humification index (HIX, calculated as the ratio of the integrated fluorescence for 435–480 nm to that at 300–345 nm for excitation at 255 nm).^{55–58}

Photochemical reactor setup

A solar simulator (OAI Tri-Sol; AM 1.5G filter) was employed to create a collimated beam of artificial sunlight. The light intensity was measured to be $1.6\text{--}1.8\text{ mJ cm}^{-2}\text{ s}^{-1}$ from 300–400 nm by coupling data from an Optics 2000+ spectrophotometer with results obtained from chemical actinometry using 2-NBA. Photochemical reactors (11 mL total volume) were custom designed from quartz glass and had a flat top along with a threaded bottom opening with a septum-capped screw top allowing for gas-tight sampling. The solutions inside of the reactors were headspace-free and constantly stirred. The temperature was controlled at $20 \pm 1\text{ }^{\circ}\text{C}$ using a circulating water bath. The reactor path length was 3.97 cm, as determined by previously described methods.²⁴

Experimental procedure

Experiments were performed using synthetic solutions that each contained 14 μM CYS and a single DOM isolate (SRFA, Altamaha DOM, ocean DOM-I, or ocean DOM-II). The solutions were maintained at pH 8.3 (a relevant pH for natural waters) with 10 mM tris buffer and initially purged with N_2 for 30 min to remove dissolved O_2 . Solutions were then left in the dark or exposed to simulated sunlight for 240 min, and samples (5 mL) were periodically drawn from reaction vials over time to measure COS and CS_2 . It should be noted that the 10 mM tris buffer effectively quenched any $\cdot\text{OH}$ that were generated in solution, since tris effectively reacts with $\cdot\text{OH}$ (reaction rate constant = $1.1 \times 10^9\text{ M}^{-1}\text{ s}^{-1}$ (ref. 59)). However, additional experiments were conducted at a lower tris buffer concentration of 0.5 mM and pH 8.3 to evaluate its effect on COS and CS_2 formation. Moreover, specific water quality constituents and conditions within the reaction solutions were also adjusted, including: (i) the DOM concentration, which was varied from 0.5–20 mg-C L^{-1} ; a range typically found in most natural waters,^{29,60} and (ii) the CYS concentration, which was varied from 1–100 μM . For the quenching experiments, solutions were amended with (i) 10 mM isopropanol, (ii) 1.0 mM phenol, (iii) 0.125 mM TMP, or (iv) 0.5 mM sorbic acid. A summary of the initial conditions used for all of the experiments is provided in Table S1.†

Analytical methods

COS and CS_2 were measured using GC-MS (Agilent 6420) coupled with headspace injection, as previously described.²⁴

Briefly, the samples drawn from the reaction vials were transferred into pre-capped headspace vials that were previously purged with N_2 . The samples were then placed in an agitator at $35\text{ }^{\circ}\text{C}$ for 5 min to reach equilibrium. A portion of the headspace (1 mL) was injected into the GC injection port at $250\text{ }^{\circ}\text{C}$ at a split ratio of 1 : 10. Separation occurred using a GC GS-GasPro (30 m $\times$ 320 μm $\times$ 0 μm) column. The oven was programmed in gradient mode, which started at $60\text{ }^{\circ}\text{C}$ for 2 min, increased to $160\text{ }^{\circ}\text{C}$ (rate of $20\text{ }^{\circ}\text{C min}^{-1}$), was held at $160\text{ }^{\circ}\text{C}$ for 4 min, and then post-run at $60\text{ }^{\circ}\text{C}$ for 2 min. The carrier gas (He) was held at a velocity of 24 cm s^{-1} . The transfer line and MS source temperatures were held at 250 and $320\text{ }^{\circ}\text{C}$, respectively. The mass spectrometer (EI mode, 70 eV) was run in SIM mode at m/z values of 60 and 76 to detect COS and CS_2 , respectively. For this method, the detection limits (d.l.), defined as the minimum concentration found to be greater than zero with a p -value >0.01 ,⁶¹ for COS and CS_2 in the aqueous phase were 5 and 11 pM, respectively.

Results and discussion

Effect of DOM type

When synthetic solutions containing CYS (14 μM) and each DOM type (5.0 mg-C L^{-1}) were exposed to sunlight, COS formation increased from <d.l. values to reach low nM concentrations ($\sim 3\text{ nM}$) (Fig. 1). These concentrations represented up to $\sim 0.02\%$ conversion yields from CYS, which generally aligned with previously reported values, although these previous values were obtained within CYS-spiked natural waters instead²⁵ (Fig. 1). COS concentrations were considerably lower for the dark controls, where COS did not form above the d.l. without CYS and only changed slightly, if at all, with CYS for all of the DOM types (Fig. 1). Dark formation of COS from CYS has been previously observed.^{21,23,24} Little to no change in COS formation was also observed when these waters were exposed to sunlight without CYS (Fig. 1). Overall, such results without CYS indicated that low amounts of other precursors present in these reaction solutions transformed to form COS through both non-photochemical and/or photochemical processes, albeit to a lower degree. These other precursors likely stemmed from the inherent dissolved organic sulfur (DOS) pool within each DOM type.^{62,63} While the DOS content of these isolates was not measured, it is expected that they would lie in the range of previously reported values of 1.0 $\mu\text{g-S per mg-C}$ for SRFA⁶⁴ and 0.04–0.4 μM (1.3–13.4 $\mu\text{g-S L}^{-1}$) for open ocean waters.^{62,63}

When the waters were exposed to sunlight with CYS, differences in COS formation between DOM types were: (i) rather minimal ([COS] ranged $\sim 1\text{--}3\text{ nM}$) and (ii) statistically different ($p < 0.05$) from each other in only half of the cases (SRFA *vs.* ocean DOM-I, SRFA *vs.* ocean DOM-II, and ocean DOM-I *vs.* ocean DOM-II) (see Text S2† for details regarding the statistical procedure and results). In addition, the statistical significance in two of these cases (SRFA *vs.* ocean DOM-I; SRFA *vs.* ocean DOM-II) was only achieved at the latter stages of each reaction (Text S2†). This fact demonstrated that differences between certain DOM types were observed but more likely driven by the slight changes that occurred between their kinetic profiles

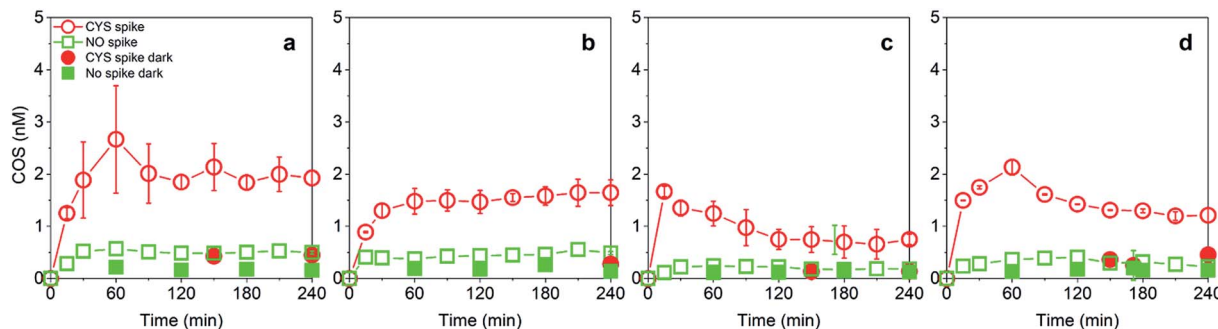


Fig. 1 Effect of (a) SRFA, (b) Altamaha DOM, (c) ocean DOM-I, and (d) ocean DOM-II on COS formation with and without sunlight exposure ($[CYS]_0 = 14 \mu M$, $[DOM]_0 = 5.0 \text{ mg-C L}^{-1}$, $pH = 8.3$, temperature = $21 \pm 1^\circ C$). Error bars show the standard deviation of ≥ 3 replicate measurements.

(Fig. 1). For example, the COS concentration with SRFA and Altamaha DOM increased and then plateaued over time, whereas with ocean DOM-I and -II, the COS concentration increased but then decayed over time (Fig. 1). These kinetic patterns were expected, given that they were hypothesized to be controlled by two co-existing effects: (i) COS growth (*i.e.* formation), which is controlled by some rate-limiting step involving CYS or plausibly the CYS intermediate with a RI (Scheme 1), where the RI is assumed to be at a steady-state concentration ($[RI]_{ss}$) (rate = $k_1 \times [CYS/CYS \text{ intermediate}] \times [RI]_{ss}$) and (ii) COS decay, which is controlled by the hydrolysis/base-catalyzed hydrolysis of COS (Scheme 1) (rate = $(k_{H_2O} + k_{OH^-} \times [OH^-]) \times [COS]$).³⁰ Both of these effects are involved in the overall expression describing the reaction kinetics of COS, as seen in eqn (1) below:

$$\frac{d[COS]}{dt} = k_1 \times [CYS \text{ or } CYS \text{ intermediate}] \times [RI]_{ss} - (k_{H_2O} + k_{OH^-} \times [OH^-]) \times [COS] \quad (1)$$

where k_1 = the formation rate constant ($M^{-1} s^{-1}$), k_{H_2O} = the hydrolysis rate constant (s^{-1}) (see Text S1† for value), and k_{OH^-} = the base-catalyzed rate constant ($M^{-1} s^{-1}$) (see Text S1† for value). Ideally, this equation could then be directly fit to the experimental data for each DOM type (Fig. 1), where the $[RI]_{ss}$ value would be experimentally determined for each experimental condition and k_1 would serve as the fitting parameter. It is hypothesized that different $[RI]_{ss}$ values would be acquired for the different DOM types, which would resultingly explain the different kinetic trends that are observed for COS (Fig. 1). This hypothesis could not be validated though, because measuring the $[RI]_{ss}$ values for such RIs (*e.g.*, $^3CDOM^*$) for each experimental condition fell outside the scope of this study.

Given this limitation, these kinetic differences were then evaluated more qualitatively, where the behavior of COS with time (eqn (1)) was predicted based on what was expected if the $[RI]_{ss}$ value were to change. These differences were then compared with the experimental data, where different kinetic profiles were observed for the different DOM types (Fig. 1). To do this, it was first acknowledged that the kinetic behavior of COS (eqn (1)), was expected to match the classic kinetic profile of an intermediate by-product (B) in a consecutive reaction.⁶⁵

Such a consecutive reaction includes three total chemical species, labeled A, B, and C, which undergo two sequential forward reactions and no back reactions, such that $A \rightarrow B \rightarrow C$. This reaction sequence matches what is expected to occur when CYS photochemically transforms to produce COS but where COS also decays, as seen in Scheme 1. In this case, A is equal to CYS or the CYS intermediate, B is equal to COS, and C is equal to the products generated from COS hydrolysis/base-catalyzed hydrolysis (Scheme 1). These labels (A, B, or C) could then be substituted into eqn (1) to generate eqn (2):

$$\frac{d[B]}{dt} = k_1 \times [A] \times [RI]_{ss} - (k_{H_2O} + k_{OH^-} \times [OH^-]) \times [B] \quad (2)$$

Overall, the kinetic behavior of a consecutive reaction dictates that if the growth term ($=k_1 \times [A] \times [RI]_{ss}$) is relatively similar to the decay term ($=(k_{H_2O} + k_{OH^-} \times [OH^-]) \times [B]$) (eqn (2)), a bell-shaped curve for the kinetics of B (*i.e.* COS) is achieved over time.⁶⁵ This profile is well matched to the similar bell-shaped kinetic profiles observed in the solutions containing ocean DOM-I and -II (Fig. 1c and d). However, as this growth term then begins to decrease, which is potentially driven in this case by a lower $[RI]_{ss}$ value, the kinetic behavior of B (*i.e.* COS) transforms into a curve that initially increases and then plateaus.⁶⁵ This pattern is similarly reflected by the COS kinetics observed in the solutions containing SRFA (albeit, accounting for the standard deviation from replicate samples) or Altamaha DOM (Fig. 1a and b). Consequently, this overall kinetic shift between DOM types is hypothesized to be controlled by the decreasing $[RI]_{ss}$ values generated by each DOM type when moving from the ocean-based DOMs to the SRFA/Altamaha DOMs.

This hypothesis is further supported by the information extracted from the spectral metrics, including the E_2/E_3 and FI values, obtained for each DOM type. These metrics have been previously linked to DOM photoreactivity.^{35,42,66,67} For example, formation quantum yields of $^3CDOM^*$ and 1OH and overall $[^3CDOM^*]_{ss}$ have been shown to increase with increasing E_2/E_3 values, which reflect smaller DOM molecules.^{35,41} Table 1 shows that the E_2/E_3 values for the DOM isolates decreased as follows: ocean DOM-II (lowest molecular weight) > ocean DOM-I > SRFA > Altamaha DOM (highest molecular weight). These results

suggested that the $[^3\text{CDOM}^*]_{\text{ss}}$ concentrations for each DOM type decreased in the same manner, a trend that matched the COS formation kinetics between DOM types and the decreasing $[\text{RI}]_{\text{ss}}$ concentrations (Fig. 1). These results suggest a correlation between the E_2/E_3 ratio and COS formation; however, the magnitude of E_2/E_3 was not linearly correlated to COS formation ($R^2 = 0.07$). Similar results were found for SUVA_{254} (positively related to COS formation, $R^2 = 0.40$) and $S_{275-295}$ (negatively related to COS formation, $R^2 = 0.37$).

The fluorescence parameters provided further insight into the DOM types. For example, a lower FI indicated a terrestrial source and a higher FI suggested a microbial source.^{55,58} As indicated in Table 1, the FI values of the DOM isolates fell within the global range of 1.2–1.8 and decreased in the following order: ocean DOM-I > ocean DOM-II > Altamaha DOM > SRFA. The corresponding FI values supported the similarity of the SRFA and Altamaha isolates as more terrestrial DOM, whereas the Ocean DOM-I and -II isolates were more microbial DOM (Table 1). The BIX and HIX values aligned with these conclusions. The Altamaha isolates had the lowest BIX, suggesting that this DOM was not of autochthonous origin. Similarly, the HIX was higher in the SRFA and Altamaha isolates, indicating more aromatic DOM.⁵⁷ The FI and COS formation were negatively correlated, suggesting that terrestrial DOM led to higher COS formation. In fact, every one-unit change in FI resulted in a 2.78 nM decrease in COS formation ($R^2 > 0.998$). Weak correlations were also observed for BIX (negatively related to COS formation, $R^2 = 0.72$) and HIX (positively related to COS formation, $R^2 = 0.76$). These findings emphasize the importance of FI values or DOM origin on COS formation.

Moreover, CS_2 did not form above its d.l. when irradiating this same set of synthetic solutions and any other solutions mentioned hereafter. These results conflicted with previous studies where CS_2 formation increased to 1.5 (ref. 24) and 2.5 nM (ref. 11) when natural waters were spiked with low μM levels of CYS and exposed to simulated sunlight over several hours.^{11,24} This comparison is especially important since one of these studies included our previous study,²⁴ where an identical experimental system and conditions was used, including irradiation conditions and the CYS purity (additional details provided in Text S3†). Therefore, the fact that CS_2 formation was

not observed here is likely attributed to the additional water constituents present in the previously tested natural waters, including Cl^- , Br^- , carbonates ($\text{HCO}_3^-/\text{CO}_3^{2-}$), and nitrate (NO_3^-). These specific water quality constituents are included for two important reasons. First, they are present in natural waters over a wide-range of concentrations (see Table S2† for values). Second, they are known to form a host of RIs (e.g. $\text{Br}^\cdot$, $\text{Cl}^\cdot$, $\text{CO}_3^{\cdot-}$ and $\text{NO}_2^\cdot$; see reaction mechanisms in Text S4†) that can further react with organic sulfur compounds such as CYS.^{5,27,68,69} It is hypothesized that such RIs likely: (i) reacted with CYS or cysteine-based intermediates to form CS_2 and/or (ii) quenched some reaction that competed with CS_2 formation over time. The experimental solutions tested here lacked these additional constituents, suggesting that the RIs generated from DOM alone (e.g. $^3\text{CDOM}^*$) did not form CS_2 but did form COS, as noted above.

Effect of DOM concentration

An increase in the DOM concentration from 0.5 to 20 mg-C L^{-1} led to a decrease in COS formation during sunlight exposure for most of the tested DOM types (one exception included the COS increase observed when transitioning from 5 to 20 mg-C L^{-1} SRFA) (Fig. 2). These trends were unexpected given that the $[\text{RI}]_{\text{ss}}$ for DOM-derived RIs, including $^3\text{CDOM}^*$ and $^\cdot\text{OH}$, are known to increase when DOM concentrations have increased up to 40 $\text{mg L}^{-1}\text{-C}$ for $[^3\text{CDOM}^*]_{\text{ss}}$ ⁷⁰ or up to 16 $\text{mg L}^{-1}\text{-C}$ for $[\text{OH}]_{\text{ss}}$.⁷¹ It should be noted that for $[^3\text{CDOM}^*]_{\text{ss}}$, this increase can be rather slight and begin to reach a plateau when various DOM types including SRNOM are $>20 \text{ mg L}^{-1}\text{-C}$.⁷⁰ Since these RIs are plausibly involved in the COS reaction pathway (Scheme 1), such increases, albeit possibly slight increases, were expected to cause the COS concentration to increase or remain unchanged rather than decrease with higher DOM concentrations (Fig. 2).

However, an opposite effect was observed (Fig. 2), which was hypothesized to be controlled by the counteracting ability of specific DOM moieties to react with cysteine-derived intermediate(s) formed during the reaction (Scheme 1). One of these intermediates includes the thiyl (*i.e.* sulfur-centered) radical (Scheme 1), which is likely quenched after accepting an electron from another DOM moiety to reform CYS. A similar

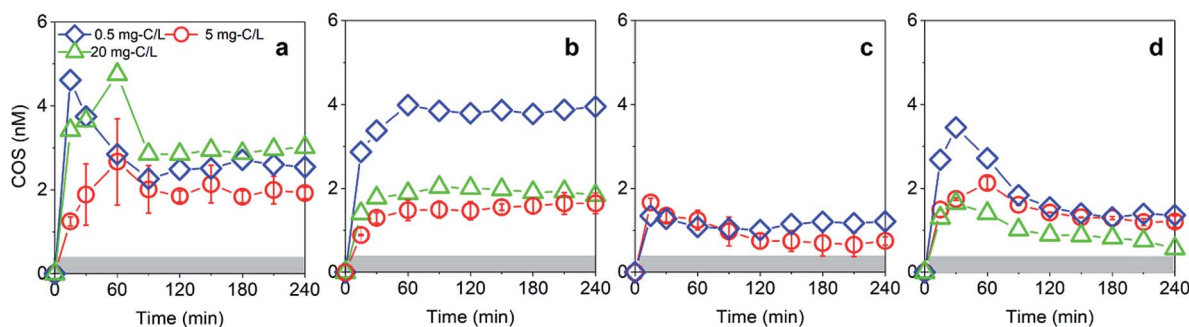
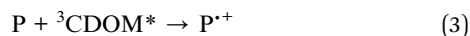


Fig. 2 Effect of DOM concentration with (a) SRFA, (b) Altamaha DOM, (c) ocean DOM-I, and (d) ocean DOM-II on COS formation ($[\text{CYS}]_0 = 14 \mu\text{M}$, $\text{pH} = 8.3$, temperature = $21 \pm 1^\circ\text{C}$). The grey box shows the general level of dark formation of COS, which was similar for all scenarios with and without CYS and with 0.5, 5, or 20 mg-C L^{-1} of each DOM type. Error bars show the standard deviation of ≥ 3 replicate measurements.

phenomenon has been previously observed, wherein DOM scavenged intermediates produced from an organic compound precursor.⁷² In this case, the precursor (P) first reacted with an oxidizing radical and/or an excited triplet state to form a radical cation (eqn (3)). This radical cation was then later reduced by DOM to reform the precursor, while generating an oxidized DOM radical, DOM^{•+} (eqn (4)).⁷²



A greater concentration of such DOM moieties in solution would increase this quenching capacity. Such a behavior has enabled increases in DOM concentration to inhibit probe compound (e.g., TMP) and organic contaminant loss.^{72,73} These effects could then translate into lower by-product formation when DOM concentrations increased, as observed here for COS.

Effect of CYS concentration

To confirm that CYS was not a limiting factor in forming COS, additional experiments were conducted over a wider range of CYS concentrations (1–100 μM), in which solutions were further amended with the ocean DOM-II isolate. Overall, the increasing CYS concentration slightly increased COS formation in the dark, while a greater increase occurred in the presence of light (Fig. 3). This increase with irradiation was limited though, as increasing the CYS concentration by a factor of 100 only increased COS formation by a factor of 3 (Fig. 3). These results demonstrated that CYS did not limit COS formation (*i.e.* serve as the limiting reactant) under the tested experimental conditions. Rather, COS formation was more limited by the presence of other species involved in the reaction pathway, most likely cysteine-based radicals or an RI (Scheme 1).

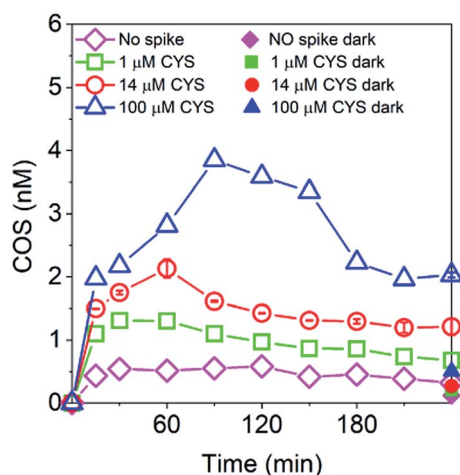


Fig. 3 COS formation when the CYS concentration was varied from 1–100 μM in synthetic waters containing ocean DOM-II under both dark and sunlit conditions ($[\text{DOM}]_0 = 5.0 \text{ mg-C L}^{-1}$, pH = 8.3, temperature = $21 \pm 1^\circ\text{C}$). Error bars show the standard deviation of ≥ 3 replicate measurements.

Role of quenching agents

Quenching of $\cdot\text{OH}$. To understand the role of $\cdot\text{OH}$ in forming COS and CS_2 , two techniques were used where: (i) the tris buffer concentration was lowered (Fig. S4†) or (ii) solutions were further amended with the quenching agent, isopropanol (Fig. 4). Both of these techniques were tested by irradiating solutions containing each DOM type (5.0 $\text{mg L}^{-1}\text{-C}$) but where the $[\cdot\text{OH}]_{\text{ss}}$ values generated from them were not directly measured. Notably, these solutions also did not contain O_2 , and while some studies have assessed the $[\cdot\text{OH}]_{\text{ss}}$ ($\sim 1 \times 10^{-16}$ to $5 \times 10^{-16} \text{ M}$) from DOM isolates (SRFA, SRNOM, and Pony Lake Fulvic Acid (PLFA); 5.0 $\text{mg L}^{-1}\text{-C}$) in O_2 -containing waters,^{71,74} no known studies have reported their concentrations without O_2 . There is strong evidence though that $\cdot\text{OH}$ is formed from CDOM by both O_2 -dependent (*i.e.* H_2O_2 -dependent) and O_2 -independent (*i.e.* H_2O_2 -independent) pathways,⁴⁷ although the H_2O_2 -dependent pathway possibly accounts for only up to $\sim 50\%$ of $\cdot\text{OH}$ production.^{74,75}

Given this, the role of $\cdot\text{OH}$ was first examined by lowering the tris buffer concentration to 0.5 mM in the reaction solutions. In all other scenarios, tris was added as a buffer at 10 mM, leading it to fully quench $\cdot\text{OH}$, as discussed above. This complete quenching with 10 mM tris was proven given that the pseudo-first order reaction rate between tris and $\cdot\text{OH}$ ($\text{tris}/\cdot\text{OH}$) ($= k_{\text{tris}}^{\cdot\text{OH}} \times [\text{tris}]_0 = 1.1 \times 10^7 \text{ (s}^{-1})$ ³⁹) was orders of magnitude greater than the rate between CYS and $\cdot\text{OH}$ ($\text{CYS}/\cdot\text{OH}$) ($= k_{\text{CYS}}^{\cdot\text{OH}} \times [\text{CYS}]_0 = 2.5 \times 10^5 \text{ (s}^{-1})$ ²⁷). These kinetics were then shifted with 0.5 mM tris, where the $\text{tris}/\cdot\text{OH}$ rate was now only slightly greater than the $\text{CYS}/\cdot\text{OH}$ rate by a factor of ~ 2 ($\text{tris}/\cdot\text{OH} = 5.5 \times 10^5 \text{ (s}^{-1}) > \text{CYS}/\cdot\text{OH} = 2.5 \times 10^5 \text{ (s}^{-1})$). Both CYS and tris were then able to react with $\cdot\text{OH}$, as confirmed through modeling results using Kintecus (see Text S5† for more details). The $[\cdot\text{OH}]_{\text{ss}}$ values applied in this model ranged from 1×10^{-16} to $5 \times 10^{-16} \text{ M}$, which were representative of values obtained after irradiating 5.0 mg-C L^{-1} SRNOM, SRFA, and PLFA^{74,76} (Text S5†). The modeling results indicated that CYS still decayed up to 12% and that the total moles of CYS consumed equaled up to $\sim 43\%$ of the total moles of tris consumed after 240 min (Text S5†). In the end, this lowered buffer concentration and $\cdot\text{OH}$ quenching capacity led the COS concentration to remain unaffected (Fig. S4†) and the CS_2 concentration to remain at $< \text{d.l.}$, when synthetic waters containing each DOM type were irradiated for 240 min. These findings suggested that $\cdot\text{OH}$ were not involved in the rate-determining step of COS or CS_2 formation. In addition, it further implied that the tris buffer did not quench or affect any other precursors that were involved in their formation, such as cysteine-derived intermediates (Scheme 1).

Moreover, solutions containing each DOM type and 10 mM tris buffer were further amended with 10 mM isopropanol, that would additionally quench $\cdot\text{OH}$ once it was formed ($\cdot\text{OH}$ (isopropanol)/ $\cdot\text{OH}$) ($k_{\text{isopropanol}}^{\cdot\text{OH}} \times [\text{isopropanol}]_0 = 4.3 \times 10^7 \text{ (s}^{-1})$ (see Table S3† for the $k_{\text{isopropanol}}^{\cdot\text{OH}}$ value)). As expected, isopropanol addition did not affect COS formation in the dark or with light for any of the DOM types (Fig. 4), except for the Altamaha DOM where COS formation increased in the presence

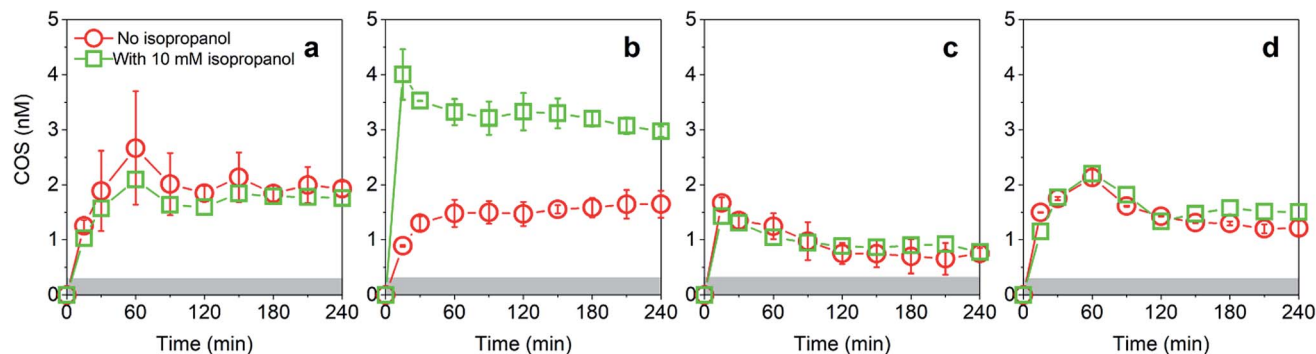


Fig. 4 Influence of isopropanol on COS formation when amended with either (a) SRFA, (b) Altamaha, (c) ocean DOM-I, or (d) ocean DOM-II ($[\text{DOM}]_0 = 5.0 \text{ mg-C L}^{-1}$, $[\text{CYS}]_0 = 14 \mu\text{M}$, $\text{pH} = 8.3$, temperature = $21 \pm 1^\circ\text{C}$). The grey box shows the general level of dark formation of COS with and without CYS when isopropanol was not added, which was similar for all scenarios. Error bars show the standard deviation of ≥ 3 replicate measurements.

of light (Fig. 4b). While it is currently unclear what phenomenon is driving this increased effect for the Altamaha DOM, it is hypothesized that isopropanol may be quenching other RIs. These other RIs can react with the cysteine-based intermediates (Scheme 1), or intermediates formed from the other sulfur-based precursors present in solution, that usually trigger other non-COS forming pathways. Isopropanol quenching of other unknown long-lived RIs, aside from $\cdot\text{OH}$, has been observed previously when photolyzing SRFA.⁷⁷

Quenching of $^3\text{CDOM}^*$. A second set of quenching agents including phenol,⁴⁹ TMP,⁴⁹ and sorbic acid³³ was used for quenching $^3\text{CDOM}^*$ at varying degrees and rates (Table S3†). All three of these quenching agents were added to solutions containing each DOM type (Fig. 5). These quenching agents did not affect COS formation in the dark but did decrease COS formation with light, although this decrease occurred to varying degrees depending on the type of quenching agent added (Fig. 5). In all cases, phenol did not influence COS formation, whereas TMP and sorbic acid decreased COS formation (Fig. 5).

These results were driven by two possible effects: first, that these quenching agents quenched $^3\text{CDOM}^*$ to different degrees, which resultingly affected COS formation since $^3\text{CDOM}^*$ is the RI involved in the rate-determining step of its reaction pathway (see Scheme 1), or second, the quenching

agents, instead reacted with cysteine-based intermediates that served as precursors for COS (see Scheme 1). It should be noted that when comparing the different quenching agents with each other, their differences fell in line well with their ability to compete with CYS in reacting with $^3\text{CDOM}^*$ ($k_{\text{CYS}}^{\text{Sen}^*} = 0.4 - 1.1 \times 10^9 \text{ (M}^{-1} \text{s}^{-1})$ at $\text{pH} = 8$;²⁷ Scheme 1), further supporting the notion that the first effect was valid to some degree. Therefore, in this case, the reactivity of each quenching agent as well as CYS with $^3\text{CDOM}^*$ was evaluated by comparing their pseudo-first order reaction rate values, which equaled $k_{\text{quenching agent or CYS}}^{\text{Sen}^*} \times [\text{quenching agent or CYS}]$. These values decreased according to the following order: sorbic acid = $2.2 \times 10^6 \text{ (s}^{-1})$ ⁷⁸ > TMP = $5.4 \times 10^5 \text{ (s}^{-1})$ ²⁷ > phenol = $4 \times 10^5 \text{ (s}^{-1})$ ⁴⁹ > CYS = $0.56 - 1.54 \times 10^4 \text{ (s}^{-1})$ (at $\text{pH} = 8$).²⁷ The higher reaction rate of TMP compared to phenol can be attributed to its higher oxidation potential of 1.22 V (ref. 33) than compared to phenol at 0.79 V.⁷⁹

Overall, this pattern indicated that the quenching agents should be able to outcompete CYS for reaction with $^3\text{CDOM}^*$ but to different extents, which would directly impact their ability to lower COS formation. In fact, COS formation decreased according to the following pattern where no quenching agent $\approx$ phenol > (TMP and sorbic acid), although the difference between TMP and sorbic acid changed in order or

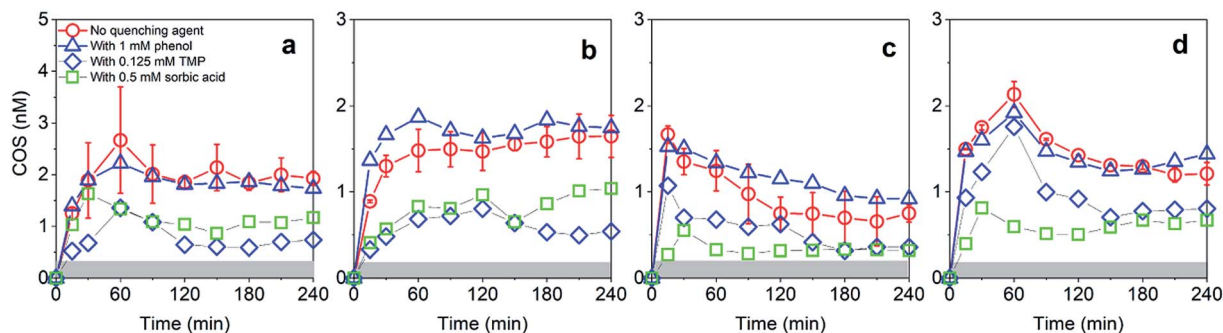


Fig. 5 Influence of phenol, TMP, and sorbic acid with (a) SRFA, (b) Altamaha, (c) ocean DOM-I, and (d) ocean DOM-II ($[\text{DOM}]_0 = 5.0 \text{ mg-C L}^{-1}$, $[\text{CYS}]_0 = 14 \mu\text{M}$, $\text{pH} = 8.3$, temperature = $21 \pm 1^\circ\text{C}$). The grey box shows the general level of dark formation of COS with and without CYS when no quenching agent was added, which was similar for all scenarios. Error bars show the standard deviation of ≥ 3 replicate measurements.

were roughly equivalent based on DOM type (Fig. 5). This pattern for the most part well matched the inverse strength of each quenching agent where their reaction rates with $^3\text{CDOM}^*$ followed the order of sorbic acid > THM > phenol. Alternatively, the second effect was related to the fact that these quenching agents could have also quenched CYS-derived intermediates (Scheme 1) instead of $^3\text{CDOM}^*$, which would have similarly lowered COS formation. This quenching could have also occurred following the same order of reactivity with CYS-derived intermediates as they do with $^3\text{CDOM}^*$. If this is the case, future research efforts are needed to specifically identify which of these two potential effects are causing the COS concentrations to be lowered.

Comparison of COS formation between DOM-spiked synthetic waters and natural waters

One of the additional motivations of this work was aimed at evaluating how COS formation differed between: (i) solutions containing DOM alone, taken from data collected in this study, and (ii) “whole” natural waters, taken from data collected from our prior study,²⁴ when CYS was used as a precursor. Additional details regarding how these natural waters were collected, stored, and characterized are provided previously²⁴ but briefly described in Text S6.†

Overall, COS formation was evaluated over 720 min (12 h) of sunlight exposure for both the CYS-spiked water types, where clear differences were observed regarding: (i) the formation kinetics of COS (Fig. 6a) and (ii) the final net COS concentrations formed after 240 min (4 h) (Fig. 6b) or 720 min (12 h) (Fig. 6c). In this latter case, net COS concentrations were obtained by subtracting the COS formed from the irradiated unspiked controls from the COS formed for the irradiated CYS-

spiked experiments. First, for the formation kinetics, COS concentrations either plateaued or exhibited a bell-shaped curve for the DOM-spiked synthetic waters, as discussed previously, or increased steadily and somewhat linearly for the three natural waters irradiated under this scenario (Fig. 6a). COS formation from the irradiated non-CYS spiked controls for both water types was not considered a contributing factor here since their concentrations essentially leveled off at <0.7 and 1.7 nM for the DOM-spiked synthetic waters and natural waters, respectively (Fig. 6a).

A specific sub-set of this data was then extracted to compare COS net formation at specific sunlight exposures of 240 (Fig. 6b) or 720 min (Fig. 6c), as a function of each water's DOM concentration. These results led to two important points. First, after 240 min, the net COS formation for the natural waters was negligible to significantly greater than the synthetic waters as the DOM concentration moved from lower to higher levels, respectively (Fig. 6b). Second, after 720 min, such differences were considerably more magnified (Fig. 6c). These differences suggested that COS formation in natural waters can become more elevated and be consistently formed over time in comparison to waters containing only DOM, possibly due to the presence of additional water quality constituents. These constituents would likely be similar to those specified for increasing CS_2 formation in the same natural waters (e.g. Cl^- , Br^- , carbonates ($\text{HCO}_3^-/\text{CO}_3^{2-}$), and nitrate (NO_3^-)), as noted above, and enact such changes by inducing similar mechanistic effects. Interestingly, results from one previous study⁸⁰ also seem to hint that these additional water quality constituents are important. Here, COS formation was linear when irradiating a CYS-spiked (10 μM) natural water (Biscayne Bay seawater) but also when irradiating the same water without its inherent DOM but spiked with SRFA ($[\text{SRFA}]_0 = 2.8 \text{ mg-C L}^{-1}$).⁸⁰ This latter

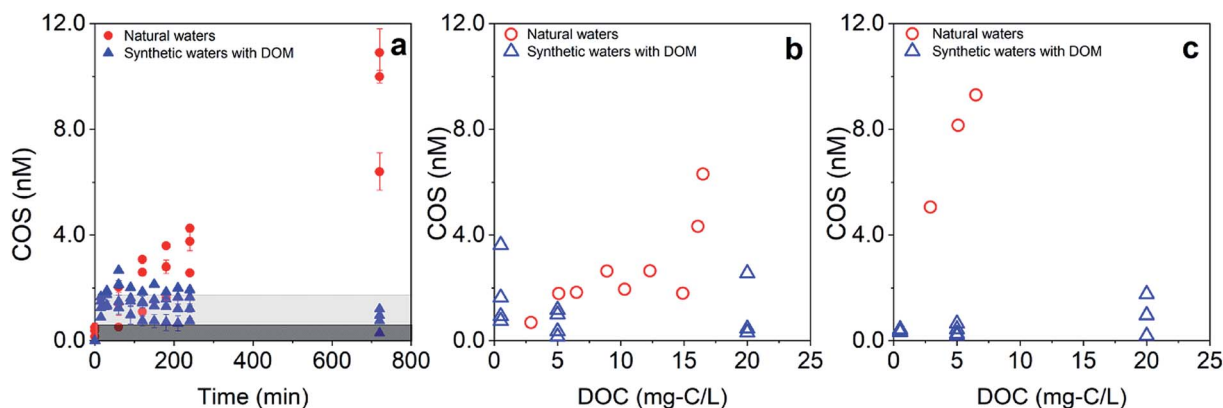


Fig. 6 Differences in (a) the kinetics of COS formation over 720 min (12 h) and the overall COS formation after (b) 240 min (4 h) and (c) 720 min (12 h), following the exposure of DOM-spiked synthetic waters or natural waters to sunlight. Other conditions for the DOM-spiked synthetic waters were: $[\text{CYS}]_0 = 14 \mu\text{M}$, $[\text{DOM}]_0 = 5.0 \text{ mg-C L}^{-1}$ for sub-figure (a) and $0.5\text{--}20 \text{ mg-C L}^{-1}$ for sub-figures (b) and (c), $\text{pH} = 8.3 \pm 0.4$, and temperature $= 21 \pm 1^\circ\text{C}$. Other conditions for the natural waters were: $[\text{CYS}]_0 = 14 \mu\text{M}$ and temperature $= 21 \pm 1^\circ\text{C}$, where the additional water quality concentrations and conditions for these waters are provided in Text S6.† For sub-figure (a), the dark and light grey boxes show the maximum COS formation for the non-spiked irradiated controls after 720 min (12 h) for DOM-spiked synthetic waters (dark grey box) and natural waters (light grey box). It should be noted that from the previous study,²⁴ all nine natural waters were exposed to sunlight over 240 min (4 h), as seen in sub-figure (b), whereas only three of these natural waters were exposed to sunlight over 720 min (12 h), as seen in sub-figure (c). Error bars show the standard deviation of ≥ 3 replicate measurements. Kinetic data for the natural waters, as seen in sub-figure (a), were reported previously²⁴ and are reproduced here with permission of the American Chemical Society (ACS).

water type was identical to our DOM-spiked synthetic solutions but where the other natural water quality constituents remained in solution.⁸⁰ Unfortunately, these data could not be more directly compared to our own data since their solutions were irradiated over a shorter length of sunlight exposure (60 min), but where the irradiation dose was either unreported or unknown.⁸⁰

Conclusions

This study evaluated how DOM can form COS and CS₂ from thiols, such as CYS, during sunlight photolysis. This study was conducted in clean synthetic waters rather than in natural waters, which subsequently offered a deeper insight into the specific role that different DOM types have on forming COS and CS₂. Several novel findings resulted from this work. First, both COS and CS₂ concentrations decreased for the most part when shifting from natural waters with CYS, as explored previously,²⁴ to synthetic waters with only DOM and CYS. This fact was particularly true for CS₂ over all lengths of sunlight exposure but more so true for COS over longer sunlight exposures. These results suggested that other water quality constituents present in natural waters may be elevating COS and CS₂ levels, although how this occurs from a photochemistry perspective remains unknown and should be explored in future research efforts. Second, COS formation, in particular, was also found to be relatively unchanged by DOM type. Both of these facts interestingly added to the early research in this area that directly attributed the higher COS concentrations in coastal waters compared to open ocean waters (by a factor of 40) to differences in DOM content.^{2,25,81} From this work, it seems more plausible that DOM type is likely less responsible for this effect, while differences attributed to the presence of additional water quality constituents and/or differences in DOS concentration/content are more likely responsible.

Regardless of DOM type, these results did indicate that DOM can make some contribution to overall COS formation. The DOM-generated RIs that are involved in the rate-limiting step of COS formation did not appear to include [•]OH, whereas it remained inconclusive whether ³CDOM* was involved, based on the results obtained with quenching agents. The quenching agents targeted to remove ³CDOM* could have plausibly removed CYS-derived radicals as well, further demonstrating that future experiments are needed to clearly distinguish if ³CDOM* is specifically involved in forming COS. Additional research efforts are also needed to quantify [³CDOM*]_{ss}, especially to assess how it impacts COS formation as a function of DOM concentration and to evaluate the role of other DOM-derived RIs (e.g. H₂O₂) so that a more quantitative kinetic model can be built. Such mechanistic information can then be integrated into better evaluating how COS is generated in more complex natural water matrices where: (i) the role of O₂ is further evaluated, given that it can quench both ³COM*³³ and plausibly CYS-derived radicals,²⁷ and (ii) more complex organic sulfur substrates are considered that are more reflective of the inherent composition of DOS. Ultimately, this work provides a strong initial framework towards understanding the effect of

different DOM types and what key indirect photochemical pathways are involved in forming COS and CS₂ from CYS during sunlight exposure.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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