Supplementary data for:

## Influence of Dissolved Organic Matter on Carbonyl Sulfide and Carbon Disulfide Formation from Cysteine During Sunlight Photolysis

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(15 Pages, 3 Tables, 4 Figures, and 6 Text Sections)

~	Experimental Type									
Constituent Type or Concentration in Reactor	Effect of DOM type	Effect of DOM concentration	Effect of CYS concentration	•OH quenching	<sup>3</sup> CDOM* quenching					
DOM type	SRFA, Altamaha DOM, ocean DOM-I, and -II	SRFA, Altamaha DOM, ocean DOM-I, and -II	Ocean DOM- II	SRFA, Altamaha DOM, ocean DOM-I, and -II	SRFA, Altamaha DOM, ocean DOM-I, and -II					
CYS (µM)	14	14	0, 1, 14, 100	14	14					
DOM (mg-C/L)	5	0, 0.5, 5, 20	5	5	5					
Tris buffer (mM)	10	10	10	0.5, 10	10					
Phenol (mM)					1					
TMP (mM)					0.125					
Sorbic acid (mM)					0.5					
Isopropanol (mM)				10						

**Table S1**. Description of the different constituents present for each experiment conducted in this study.

 Table S2. Concentrations of various water quality constituents in natural waters.

Water Quality Constituent	Freshwater	Seawater	
Cl <sup>-</sup> (mg/L)	11 <sup>14</sup> (mean)	19,20015	
Br (mg/L)	0.1 <sup>16</sup> (mean)	6717	\
Carbonates (mM)	0.1-518	2.318	
NO <sub>3</sub> -(mg/L as NO <sub>3</sub> -)	typically < 4 <sup>19</sup> (in US)	0.43 <sup>15</sup> (euphotic zone)	

Table S3.	The	reaction	rate	constants	of	various	quenching	agents	when	scavenging	•OH	or
<sup>3</sup> CDOM <sup>*</sup> .												

Quenching agent	•ОН	<sup>3</sup> CDOM <sup>*</sup> (M <sup>-1</sup> s <sup>-1</sup> ) <sup>a</sup>
Isopropanol	$(4.3 \pm 1.3 \times 10^9 \text{ M}^{-1} \text{ s}^{-1})^{-1}$	-
Phenol	$(0.841 \pm 0.042 \times 10^{-10} \text{ M}^{-1} \text{ s}^{-1})^{-2}$	4×10 <sup>8</sup> (pH 8) <sup>3</sup>
ТМР	$(9.75 \pm 0.98 \times 10^{-8} \text{ L molecule}^{-1} \text{ s}^{-1})^{-4}$ or $(1.61 \pm 0.16 \times 10^{-31} \text{ M}^{-1} \text{ s}^{-1})^{-4}$	43 ×10 <sup>8</sup> (pH 10) <sup>5</sup>
Sorbic acid	_	$(4.4 \pm 4.29 \times 10^9)^{6}$

<sup>a</sup> These reaction rate constants are between the quenching agents and either the general DOM isolates (precursors for both high- and low-energy-triplet-states of DOM) or the ketone sensitizers, which form low-energy-triplet-states of DOM.



**Figure S1.** The location of sampling sites for: (a) Altamaha and (b) Gulf Stream isolates (ocean DOM-I and ocean DOM-II). The right-side map is adopted from a picture provided in a previous study<sup>7</sup>.



Figure S2. The absorbance spectra of the DOM isolates at 5.0 mg-C/L using a 1.0 cm pathlength.



**Figure S3**. EEM fluorescence spectra for (a) SRFA, (b) Altamaha DOM, (c) ocean DOM-I, and (d) ocean DOM-II. Fluorescence intensity is normalized to the Raman shift in water and plotted on the same scale (0-3) for all samples for comparative purposes.



**Figure S4.** Effect of the tris buffer concentration on COS formation with different DOM isolates after 240 min irradiation ([CYS]<sub>0</sub> = 14  $\mu$ M, [DOM]<sub>0</sub> = 5.0 mg-C/L, pH = 8.3, temperature = 21±1°C). Error bars show the standard deviation of  $\geq$  3 replicate measurements.

Text S1. Rate constants for COS hydrolysis and base-catalyzed hydrolysis.

The combined effect of hydrolysis and base-catalyzed hydrolysis on COS is determined by the pseudo-first-order (i.e. observed) rate constant ( $k_{obs}$  (s<sup>-1</sup>)), as seen in eq. S1. This constant is equal to several constant variables, as seen in eq. S2.

$$\frac{d [COS]}{dt} = k_{obs} (s^{-1}) \times [COS] (M)$$
(S1)  
$$k_{obs} (s^{-1}) = k^{H2O} (s^{-1}) + k^{HO^{-1}} (M^{-1}s^{-1}) \times [OH^{-1}] (M)$$
(S2)

The value for  $k^{H2O}$  equals  $2.23 \times 10^{-5} \text{ s}^{-1}$ , and the value for  $k^{OH^-}$  equals  $12.9 \text{ M}^{-1} \text{s}^{-1}$  at  $20 \text{ °C.}^8$ Since the [OH<sup>-</sup>] is held constant over time and increases with increasing pH, the  $k_{obs}$  values increase as well, as shown by Table S4 below.

**Table S4.**  $k_{pseudo-first-order}$  values for COS hydrolysis/base-catalyzed hydrolysis as a function of pH.pH

pН	k <sub>psuedo-first-order</sub> (s <sup>-1</sup> )
7	$12.9 \times 10^{-7}$
8.3	25.8 × 10 <sup>-6</sup>
10	$12.9 \times 10^{-4}$

**Text S2.** Details regarding the statistical procedure used and results obtained when comparing the COS formation kinetics for each DOM type in the presence of sunlight.

A statistical analysis was conducted for a portion of the data provided in Fig. 1. This data included the COS formation kinetics when each DOM type was exposed to sunlight over time. This statistical analysis was used to assess if each kinetic trend obtained for each DOM type was statistically different from each other by conducting a t-test with a 95% confidence interval, where a p value was obtained. The software used to do this analysis was OriginPro 2020. Thus, a

p value was obtained when two individual sets of DOM types were compared at different time points over the course of each reaction (Table S5). These times included 15 min, 1 h, 2 h, 3 h, and 4 h (Table S5). One DOM type was considered statistically different from the other if the majority of time points (at least 3 out of 5 time points) obtained a p value of < 0.05.

**Table S5**. Statistics results for t-test with 95% confidence level (p value < 0.05) used for intergroup comparison of COS formation between different DOM types and reaction times.

р	15 min		15 min			1 h		2 h			3 h				4 h					
value	SRFA	Alt.	0-I	O-II	SRFA	Alt.	0-I	O-II	SRFA	Alt.	0-I	O-II	SRFA	Alt.	0-I	O-II	SRFA	Alt.	O-I	O-II
SRFA		0.041	0.069	0.158		0.162	0.121	0.377		0.086	0.004	0.022		0.167	0.009	0.015		0.314	0.010	0.041
Alt.			0.001	< 0.001			0.431	0.085			0.072	0.802			0.072	0.153			0.034	0.157
0-I				0.044				0.045				0.037				0.112				0.036
O-II																				

Altamaha DOM: Alt, ocean DOM-I: O-I, and ocean DOM-II: O-II.

Text S3. Comparison of the experimental setup in this study to our previous study<sup>9</sup>.

In this study and our previous study<sup>9</sup>, an identical experimental system was maintained. First, the light intensity from 300 to 400 nM was the same for both studies, which equaled 1.6-1.8 mJ/cm<sup>2</sup>/s for this study and 1.1-1.8 mJ/cm<sup>2</sup>/s for our previous study<sup>9</sup> when using the same solar simulator. Second, the CYS salt purity that was used between studies was identical. This result was verified by purchasing a new CYS salt for this study (purchased in Oct 2018). Both the old CYS salt (used in the previous study<sup>9</sup>) and new CYS salt (used in this study) were then amended to synthetic waters containing ocean DOM-II that were subsequently exposed to sunlight over 240 min. COS formation from both CYS salts was cross-compared and found to be same (Fig. S5).



**Figure S5.** COS formation when different sources of cysteine purchased at different times (old versus new) were spiked into synthetic water containing ocean DOM-II and subsequently irradiated over 240 min ([CYS]<sub>0</sub> = 14  $\mu$ M, [DOM]<sub>0</sub> = 5.0 mg-C/L, pH = 8.3, temperature = 21±1°C). Error bars show the standard deviation of  $\geq$  3 replicate measurements.

Text S4. Formation of RIs from different water quality constituents.

•OH + Br $\rightarrow$ Br •	$(1)^{20}$
$^{\bullet}\mathrm{OH} + \mathrm{Cl}^{-} \rightarrow \mathrm{Cl}^{*}$	$(2)^{21}$
$\bullet OH + CO_3^{2-} / HCO_3^{-} \rightarrow CO_3^{}$	$(3)^{22}$
$NO_3^- + hv \rightarrow NO_2^+ + O^{}$ where $O^{} + H^+ \rightarrow OH$	$(4)^{17}$

**Text S5.** Description of the kinetic model used to predict loss of CYS or tris when reacting with [•OH]<sub>ss</sub>

A kinetic model was derived using Kintecus (version 5.2)<sup>10</sup>, which predicted the loss of CYS and tris when reacting individually with [•OH]<sub>ss</sub>. A summary of the reactions and specific second order reaction rate constants (k; M<sup>-1</sup>s<sup>-1</sup>) that were inserted into the model are shown in Table S6.

	k (M <sup>-1</sup> s <sup>-1</sup> )	Reaction	Comments
	1.8E+10 <sup>a</sup>	$CYS + [\bullet OH]_{ss} ==>$	CYS reaction with •OH at 20°C
	1.1E+9 <sup>b</sup>	$tris + [\bullet OH]_{ss} ==>$	tris reaction with •OH at 20°C
-			

the reactions and reaction rates constants used in the Kintecus model.

<sup>a</sup> taken from Chu et *al*. 2016<sup>5</sup>

<sup>b</sup> taken from Hicks and Gebicki 1986<sup>11</sup>

In the model, the initial concentrations that were set for CYS ( $[CYS]_0$ ) and tris ( $[tris]_0$ ) were 14  $\mu$ M and 0.5 mM (500  $\mu$ M), respectively. In addition,  $[\cdot OH]_{ss}$  was assumed to be 1 ×10<sup>-16</sup> or 5 ×10<sup>-16</sup> M, which covered a range of  $[\cdot OH]_{ss}$  values obtained previously when 5.0 mg/L-C of SRNOM, SRFA, or PFLA was photolyzed at 365 nm<sup>12,13</sup>. The loss of tris and CYS were monitored over 240 min (Fig. S6).



**Figure S6**. Modeling results for CYS and tris following their reaction with •OH over 240 min, when (a)  $[•OH]_{ss} = 10^{-16}$  and (b)  $[•OH]_{ss} = 5 \times 10^{-16} ([CYS]_0 = 14 \ \mu\text{M}, [Tris]_0 = 500 \ \mu\text{M} (0.5 \text{ mM})$ , temperature = 20 °C).

When  $[\bullet OH]_{ss}$  equaled 1 ×10<sup>-16</sup> and 5 ×10<sup>-16</sup> M, the results indicated that CYS can compete with tris in its reaction with •OH, where CYS loss achieved between 40-43% of the tris loss after 240 min (Fig. S6 and Table S7).

**Table S7**: Summary of results when modeling the CYS and tris reactions with •OH by Kintecus.

	$[\bullet OH]_{ss} = 10^{-16}$									
Time (min)	CYS (µM)	Tris (µM)	% loss of CYS after 240 min	CYS loss (μM) Tris loss (μM)						
0	14	500								
240	13.6	499	2.9	0.4						

	$[\bullet OH]_{ss} = 5 \times 10^{-16}$									
Time (min)	ne CYS (μM) Tris (μM)		% loss of CYS after 240 min	CYS loss (μM) Tris loss (μM)						
0	14	500								
240	12.3	496	12.1	0.425						

**Text S6.** A brief description of the collection, storage, and characterization of the natural waters used in our previous study<sup>9</sup>.

In short, these waters were collected off the coast of Florida, Louisiana, and Maine in 2017 and ranged in salinity to represent five freshwaters, two brackish waters, and one open ocean water <sup>9</sup>. These waters were pre-filtered using a 0.7- $\mu$ m glass-fiber filter prior to shipping and were stored at 4 °C prior to use. These waters were also deoxygenated prior to sunlight exposure. Various water quality characteristics including [DOC], pH, [Cl<sup>-</sup>], and carbonate ([HCO<sub>3</sub><sup>-</sup>] + [CO<sub>3</sub><sup>-2</sup>]) were measured and ranged from 2.9-16.5 mg-C/L, 7.8-8.1, 0.09-0.42 M, 1256-2548  $\mu$ M/kg, respectively<sup>9</sup>. Similar to this study, the [DOS] in these waters was not measured, but to account for its contribution towards forming COS, these waters were also irradiated without spiking in CYS, which represented the no-spike control.

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