



# The influence of dissolved organic matter on the marine production of carbonyl sulfide (OCS) and carbon disulfide (CS<sub>2</sub>) in the Eastern Tropical South Pacific

5 <sup>1</sup> M <sup>2</sup> <sup>1</sup> <sup>1</sup> <sup>5</sup> <sup>6</sup> <sup>7,8</sup> <sup>8</sup> <sup>9</sup>

10 <sup>1</sup> M <sup>2</sup> <sup>3</sup> <sup>4</sup> <sup>5</sup> <sup>6</sup> <sup>7</sup> <sup>8</sup> <sup>9</sup> <sup>10</sup> <sup>11</sup> <sup>12</sup> <sup>13</sup> <sup>14</sup> <sup>15</sup> <sup>16</sup> <sup>17</sup> <sup>18</sup> <sup>19</sup> <sup>20</sup> <sup>21</sup> <sup>22</sup> <sup>23</sup> <sup>24</sup> <sup>25</sup>

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**Abstract.** <sup>1</sup> <sup>2</sup> <sup>3</sup> <sup>4</sup> <sup>5</sup> <sup>6</sup> <sup>7</sup> <sup>8</sup> <sup>9</sup> <sup>10</sup> <sup>11</sup> <sup>12</sup> <sup>13</sup> <sup>14</sup> <sup>15</sup> <sup>16</sup> <sup>17</sup> <sup>18</sup> <sup>19</sup> <sup>20</sup> <sup>21</sup> <sup>22</sup> <sup>23</sup> <sup>24</sup> <sup>25</sup>

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deuterated dimethyl sulfide (DMS-d<sub>6</sub>) was prepared by purging seawater with deuterated acetylene glycol. During purging, 500 μL gaseous deuterated DMS (d<sub>3</sub>-M<sub>0.2</sub>) was added to the seawater. The concentration of DMS-d<sub>6</sub> in the seawater was determined by gas chromatography-mass spectrometry (GC-MS). The concentration of DMS-d<sub>6</sub> in the seawater was determined by GC-MS. The concentration of DMS-d<sub>6</sub> in the seawater was determined by GC-MS. The concentration of DMS-d<sub>6</sub> in the seawater was determined by GC-MS.

2.3 Chromophoric dissolved organic matter (CDOM)

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CDOM was determined using a spectrophotometer. The concentration of CDOM was determined by measuring the absorbance at 350 nm and 440 nm. The concentration of CDOM was determined by measuring the absorbance at 350 nm and 440 nm. The concentration of CDOM was determined by measuring the absorbance at 350 nm and 440 nm.

2.4 Fluorescent dissolved organic matter (FDOM)

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FDOM was determined using a fluorescence spectrophotometer. The concentration of FDOM was determined by measuring the fluorescence intensity at 350 nm excitation and 450 nm emission. The concentration of FDOM was determined by measuring the fluorescence intensity at 350 nm excitation and 450 nm emission. The concentration of FDOM was determined by measuring the fluorescence intensity at 350 nm excitation and 450 nm emission.







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## 2.8 Determination of OCS dark production rates

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$$15 \quad P_D = L_H = [OCS] \cdot k_h \quad (2)$$

1989

$$k_h = e^{(24.3 - \frac{10450}{T})} + e^{(22.8 - \frac{6040}{T})} \cdot \frac{K_w}{a[H^+]}$$

$$-\log_{10} K_w = \frac{3046.7}{T} + 3.7685 + 0.0035486 \cdot \sqrt{S}$$

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$$\ln\left(\frac{P_D}{a_{350}}\right) = \frac{a}{T} + b \quad (5)$$

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## 2.9 Surface box models to estimate photoproduction rate constants

2017 and 2000. In-situ measurements were also taken during the 2001 and 2017 campaigns. The photoproduction rate constants were estimated using a surface box model. The model consists of a surface layer of depth  $z$  and a mixed layer of depth  $H$ . The surface layer is well-mixed, and the mixed layer is also well-mixed. The photoproduction rate constant is denoted by  $k_{photo}$ . The photoproduction rate constant is estimated using the following equation (6):

$$\frac{dc_{photo}}{dt} = \int_{MLD}^0 UV \cdot a_{350} \cdot p \quad (6)$$

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$$\frac{dc_{photo}}{dt} = \int_{MLD}^0 UV \cdot a_{350} \cdot p \quad (6)$$

2000 In-situ measurements were taken during the 2001 and 2017 campaigns. The photoproduction rate constants were estimated using a surface box model. The model consists of a surface layer of depth  $z$  and a mixed layer of depth  $H$ . The surface layer is well-mixed, and the mixed layer is also well-mixed. The photoproduction rate constant is denoted by  $k_{photo}$ . The photoproduction rate constant is estimated using the following equation (6):

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## 2.10 1D water column modules for OCS and CS<sub>2</sub>

2001 and 2017. The photoproduction rate constants were estimated using a surface box model. The model consists of a surface layer of depth  $z$  and a mixed layer of depth  $H$ . The surface layer is well-mixed, and the mixed layer is also well-mixed. The photoproduction rate constant is denoted by  $k_{photo}$ . The photoproduction rate constant is estimated using the following equation (6):

$$\frac{dc_{photo}}{dt} = \int_{MLD}^0 UV \cdot a_{350} \cdot p \quad (6)$$

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$$\frac{dc_{photo}}{dt} = \int_{MLD}^0 UV \cdot a_{350} \cdot p \quad (6)$$

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$$\frac{dc_{photo}}{dt} = \int_{MLD}^0 UV \cdot a_{350} \cdot p \quad (6)$$

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$$\frac{dc_{photo}}{dt} = \int_{MLD}^0 UV \cdot a_{350} \cdot p \quad (6)$$





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### 3.2 Carbonyl Sulfide (OCS)

#### 3.2.1 Horizontal and vertical distribution

... r ... r ... d ... r ... 6 ... 1 ...<sup>1</sup> ... r ... 0.5 ...<sup>1</sup> ...  
d ... r ... 2017 ... r ... r ... d ... r ...  
15 ... r ... 8 ... 12 ... d ... r ... d ... 16 ... 2 ...  
... d ... r ... d ... 2 ... 7 ... d ... 18 ... 10 ...<sup>1</sup> ...  
... r ... 7 ... d ... 18 ... r ... d ...  
... r ... d ... 5 ... d ... r ...  
... r ... d ... 75 ... d ... r ... r ...  
20 ... d ... 6 ...

#### 3.2.2 Dark production

... d ... r ... d ... r ... 0.86 ... d ... 1.81 ...<sup>1</sup> ...<sup>1</sup> ...  
... d ... 0.16 ... d ... 0.81 ...<sup>1</sup> ...<sup>1</sup> ... 50 ...  
... d ... r ... d ... r ... 5.66 ... 10<sup>-10</sup> ...  
25 ... r ... d ... r ... d ... r ... d ... r ...  
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$$P_b = a_{350} \cdot \exp\left(-\frac{15182}{T} + 53.1\right) \quad \square \quad \square \quad \square \quad \square$$

... r ... d ... M ... r ...<sub>2</sub> ... d ...  $a_{350}$  ... 5 ... d ...  
r ... d ... 50 ... d ... 6 ... r ... r ... d ... r ...  
... d ...  $a_{350}$  ...



$P_D = a_{350} \cdot \exp\left(-\frac{16692}{T} + 58.5\right)$

$$P_D = a_{350} \cdot \exp\left(-\frac{16692}{T} + 58.5\right)$$

### 5 3.2.3 Diapycnal fluxes

Diapycnal fluxes were calculated using the diapycnal velocity component ( $w$ ) and the density anomaly ( $\sigma_t$ ) from the ADCIRC model. The diapycnal flux ( $F_D$ ) is defined as the product of the diapycnal velocity and the density anomaly. The diapycnal flux was calculated for the period from 2001 to 2017. The diapycnal flux was calculated using the following equation:

$$F_D = \int_{\sigma_{t1}}^{\sigma_{t2}} w \cdot \sigma_t \cdot d\sigma_t$$

where  $w$  is the diapycnal velocity,  $\sigma_t$  is the density anomaly, and  $d\sigma_t$  is the differential density anomaly. The diapycnal flux was calculated for the period from 2001 to 2017. The diapycnal flux was calculated using the following equation:

$$F_D = \int_{\sigma_{t1}}^{\sigma_{t2}} w \cdot \sigma_t \cdot d\sigma_t$$

### 3.2.4 Photoproduction

Photoproduction was calculated using the following equation:

$$p = 85.8 \cdot [FDOM\ C2] + 828.76$$

where  $p$  is the photoproduction rate, and  $[FDOM\ C2]$  is the concentration of the fluorescent dissolved organic matter (FDOM C2). The photoproduction rate was calculated for the period from 2001 to 2017. The photoproduction rate was calculated using the following equation:

$$p = 85.8 \cdot [FDOM\ C2] + 828.76$$

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The photoproduction rate was calculated for the period from 2001 to 2017. The photoproduction rate was calculated using the following equation:

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The photoproduction rate was calculated for the period from 2001 to 2017. The photoproduction rate was calculated using the following equation:

$$p = 85.8 \cdot [FDOM\ C2] + 828.76$$



### 3.3 Carbon Disulfide (CS<sub>2</sub>)

#### 3.3.1 Horizontal and vertical distribution

CS<sub>2</sub> concentrations were measured in the M... 178, 89...  
... 7... 2015...  
5... CS<sub>2</sub>... 2... 2...  
... CS<sub>2</sub>... 2... 5... 18...  
... 200... 1... 1... 20...  
10... 15... 18... 10... 1... 20...  
... 2... 18... 10... 1... 20...

#### 3.3.2 Diapycnal fluxes

CS<sub>2</sub>... 18...  
15... CS<sub>2</sub>... *in-situ*... 2... 7... 18... *in-situ*...  
... 2... 18...  
... M... 7... 6... 10<sup>11</sup>... 10<sup>11</sup>... 19... 10<sup>11</sup>... 0.98...  
2... 5... 7... 18... 1... 1... 18...  
... M... 0.98... 1... 0... 1... 2...

#### 20 3.3.3 Photoproduction of CS<sub>2</sub>

CS<sub>2</sub>... 5... 70...  
... M... 0.05... 0.08... 0...  
25... 8... 5... M... 1... M...  
... 2... 2... 5... 7... 1998... 6... 98...  
... 98... 2... 5... 6...



1000 98d d 98 1000 r 1000 r d  
1000 r 1000 r d  
1000 r d  
1000 1998 d 2 1000 C<sub>2</sub> 1000 r d 2  
5 1000 r d 6 1000 d r d r  
1000 r d 1000 r 00 00 1000 98 2 d r r d  
1000 r d 1000 r d 1000 r d 1000 r d 6

#### 4 Discussion

##### 4.1 Carbonyl Sulfide

2 5 7 d 18 r r r d d  
1000 r d 1000 r d 1000 r d r d  
1000 r d d 1000 r 5 1000 r d  
1000 r d 2016  
15 1000 r d 55  
1000 r d 1 81 1 1000 r d r d r d r d r d r d r d r d  
1000 r 2001 1000 r 1995 1000 r 1996 d dr 1996  
1000 1999 M r 1000 1999 r r  
1000 r d 1000 r r d  
20 1000 a<sub>350</sub> d r d r 15 18 1000 r d d r r d  
1000 7 d 8 r r d 1000 2001 r M d r r  
1000 r d a<sub>350</sub> 1000 r r r 1000 r 1000 r 1000 r 2001  
25 r d r r d r r r d r r r  
r d r d r d r d r d r d r d r d r d r d r d r d r d  
1000 a<sub>150</sub> d d 1000 d 2 1000 r r 1000 r  
1000 r d d d r d r d r d r d r d r d  
00 1998 r r d d r d r d r d r d r d r d r d r d r d r d r d



16  $\sigma_{\theta}$  ( $\text{kg m}^{-3}$ ) and  $\sigma_{\theta}^*$  ( $\text{kg m}^{-3}$ ) are defined as  

$$\sigma_{\theta} = \rho(\theta, S, \text{ref}) - \rho(\theta_0, S_0, \text{ref})$$

$$\sigma_{\theta}^* = \sigma_{\theta} - \rho(\theta_0, S_0, \text{ref})$$
 where  $\rho(\theta, S, \text{ref})$  is the density of seawater with temperature  $\theta$  and salinity  $S$  at reference pressure  $p_{\text{ref}}$ .  
 200  $\sigma_{\theta}^*$  ( $\text{kg m}^{-3}$ ) is used as a reference density for the definition of the density anomaly  $\sigma_{\theta}^*$ .  
 25 7  $\text{m}^2 \text{s}^{-2}$  and 18  $\text{m}^2 \text{s}^{-2}$  are the reference values for the kinetic energy of the mean motion  $K$  and the kinetic energy of the eddy motion  $K'$ , respectively.  
 50  $\text{m}^2 \text{s}^{-2}$  is used as a reference value for the kinetic energy of the eddy motion  $K'$ .  
 The density anomaly  $\sigma_{\theta}^*$  is defined as the difference between the density  $\rho$  and the reference density  $\rho_0$ .  
 The density anomaly  $\sigma_{\theta}^*$  is defined as the difference between the density  $\rho$  and the reference density  $\rho_0$ .  
 The density anomaly  $\sigma_{\theta}^*$  is defined as the difference between the density  $\rho$  and the reference density  $\rho_0$ .  
 100  $\rho$  is defined as the density of seawater at reference pressure  $p_{\text{ref}}$ .  
 The density anomaly  $\sigma_{\theta}^*$  is defined as the difference between the density  $\rho$  and the reference density  $\rho_0$ .  
 The density anomaly  $\sigma_{\theta}^*$  is defined as the difference between the density  $\rho$  and the reference density  $\rho_0$ .  
 2015 and 2011 are the years of the observations.  
 2012 and 2011 are the years of the observations.  
 15  $\rho$  is defined as the density of seawater at reference pressure  $p_{\text{ref}}$ .  
 The density anomaly  $\sigma_{\theta}^*$  is defined as the difference between the density  $\rho$  and the reference density  $\rho_0$ .  
 The density anomaly  $\sigma_{\theta}^*$  is defined as the difference between the density  $\rho$  and the reference density  $\rho_0$ .  
 20  $\rho$  is defined as the density of seawater at reference pressure  $p_{\text{ref}}$ .  
 The density anomaly  $\sigma_{\theta}^*$  is defined as the difference between the density  $\rho$  and the reference density  $\rho_0$ .  
 The density anomaly  $\sigma_{\theta}^*$  is defined as the difference between the density  $\rho$  and the reference density  $\rho_0$ .  
 25  $\rho$  is defined as the density of seawater at reference pressure  $p_{\text{ref}}$ .  
 The density anomaly  $\sigma_{\theta}^*$  is defined as the difference between the density  $\rho$  and the reference density  $\rho_0$ .  
 The density anomaly  $\sigma_{\theta}^*$  is defined as the difference between the density  $\rho$  and the reference density  $\rho_0$ .  
 00  $\rho$  is defined as the density of seawater at reference pressure  $p_{\text{ref}}$ .  
 The density anomaly  $\sigma_{\theta}^*$  is defined as the difference between the density  $\rho$  and the reference density  $\rho_0$ .  
 The density anomaly  $\sigma_{\theta}^*$  is defined as the difference between the density  $\rho$  and the reference density  $\rho_0$ .



...  $75.8 \pm 1.8$  ...  $85.8 \pm 1.8$  ...  $7$  ...

50 ...  $0$  ...  $1$  ...  $95$  ...  $2017$  ...  $17$  ...  $p$  ...  $M$  ...  $2$  ...  $19$  ...  $5$  ...  $18$  ...  $50$  ...  $1$  ...  $200$  ...

150 ...

#### 4.2 Carbon Disulfide

...  $2001$  ...  $10.9$  ...  $1$  ...  $7$  ...  $1$  ...  $16$  ...  $1$  ...

250 ...  $1999$  ...  $2017$  ...  $1999$  ...  $09$  ...  $7/2$  ...  $8$  ...  $12$  ...

300 ...  $2$  ...







...6d... $\text{CO}_2$ ...  
...00...  
...1999...  
... $\text{CO}_2$ ...  
... $\text{CO}_2$ ...200...5 10...<sup>1</sup>...20...<sup>1</sup>...  
...200...*in-situ*...  
... $\text{CO}_2$ ...  
... $\text{CO}_2$ ...  
... $\text{CO}_2$ ...

20 **5 Summary and conclusion**

... $\text{CO}_2$ ...  
...M...  
...  
...M...  
... $\text{CO}_2$ ...  
... $\text{CO}_2$ ...  
... $\text{CO}_2$ ...



50  
100  
150  
200

2001  
2017  
2020  
2022  
2025  
2030  
2037  
2048

100  
600  
800  
1000

2017

### Author contributions

250







- 10 1126 1126 6 1178 11961
- 5 1177 1150 2008
- 10 1029 2000 d9006 0 2001
- 15 1002 2015 r000511 2016
- 20 10 1126 7796 2016
- 25 20 1102 1102 10 1002 2015 d02 09 2015
- 0 15 2295 12 10 519 15 2295 2015 2015
- 5 56 6 57 6 66 2017
- 0 17 85 02 10 519 17 85 2017 2017
- 5 M 22 1 01 10 10 1016 0278 02 00009 2 2002
- 5 M 12 10 1029 2006 d007665 2007





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- [https://doi.org/10.1029/2018JG002601](#) (2018)
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- [https://doi.org/10.1029/2018JG002601](#) (2018)
- 25  [https://doi.org/10.1029/2018JG002601](#) (2018)
- [https://doi.org/10.1029/2018JG002601](#) (2018)
- 30  [https://doi.org/10.1029/2018JG002601](#) (2018)
- [https://doi.org/10.1029/2018JG002601](#) (2018)
- 35  [https://doi.org/10.1029/2018JG002601](#) (2018)
- [https://doi.org/10.1029/2018JG002601](#) (2018)
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- 45  [https://doi.org/10.1029/2018JG002601](#) (2018)
- [https://doi.org/10.1029/2018JG002601](#) (2018)
- 50  [https://doi.org/10.1029/2018JG002601](#) (2018)





## Figures

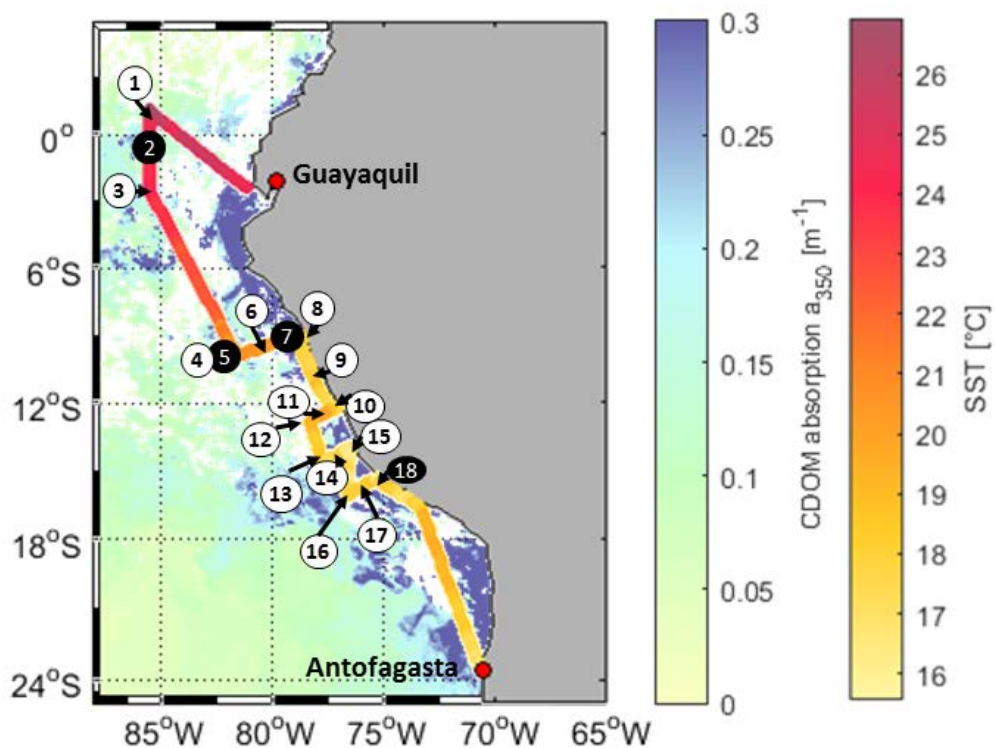


Figure 1: Cruise track of ASTRA-OMZ with stations 1-18 (in black circles: stations where OCS profiles were taken). The cruise track shows sea surface temperature (SST) measured onboard. For visualization only, the background is Aqua MODIS satellite data for the absorption of CDOM and detritus corrected from 443 nm to 350 nm with the mean slope of our *in-situ* measurements (0.0179, 300-450 nm, Aqua MODIS composite for October 2015). Note: As a monthly composite does not necessarily reflect the exact conditions during the cruise, *in-situ* measurements are illustrated in Fig. 2e. White areas: not satellite data available.

□

□

□

□

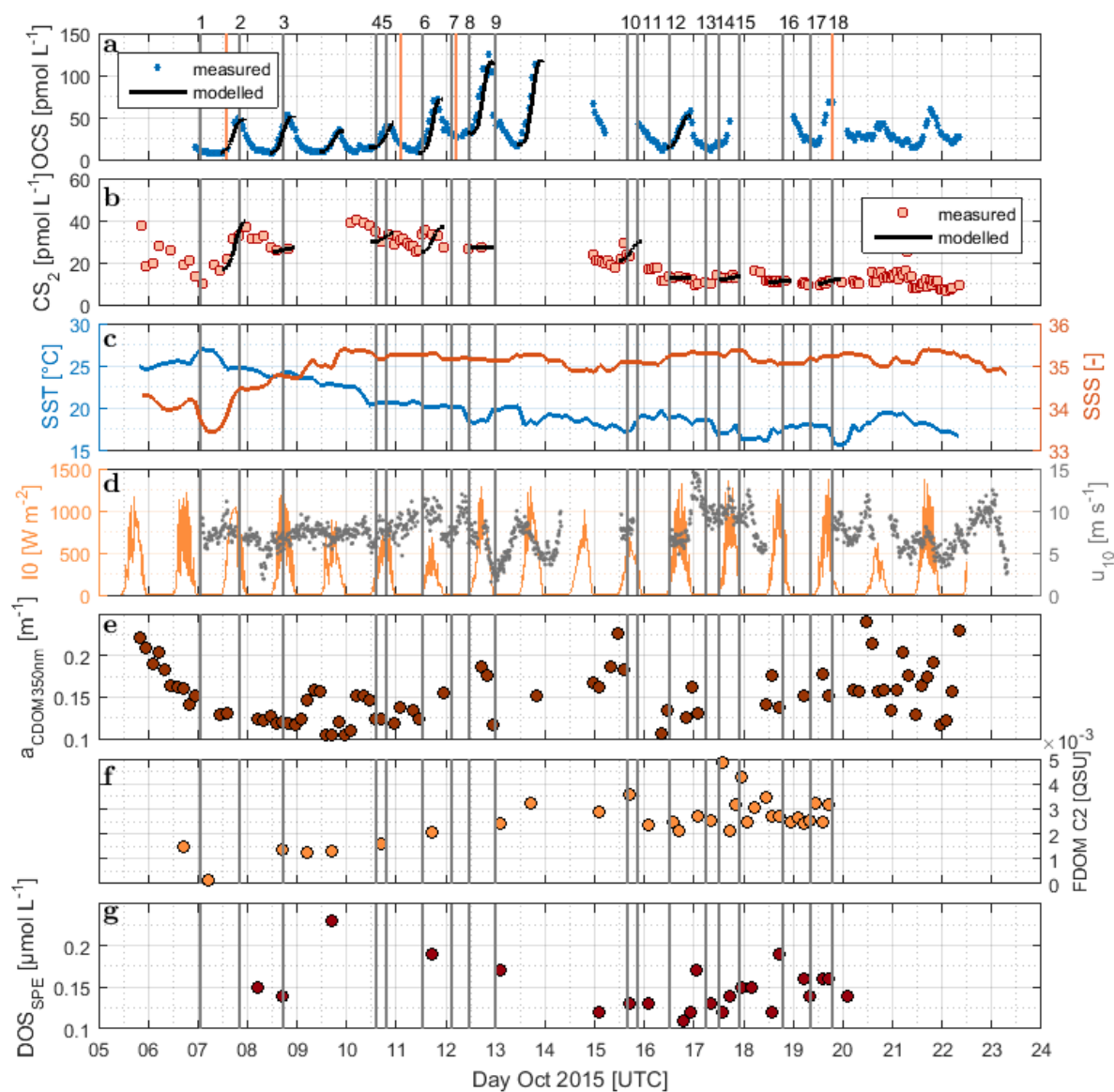
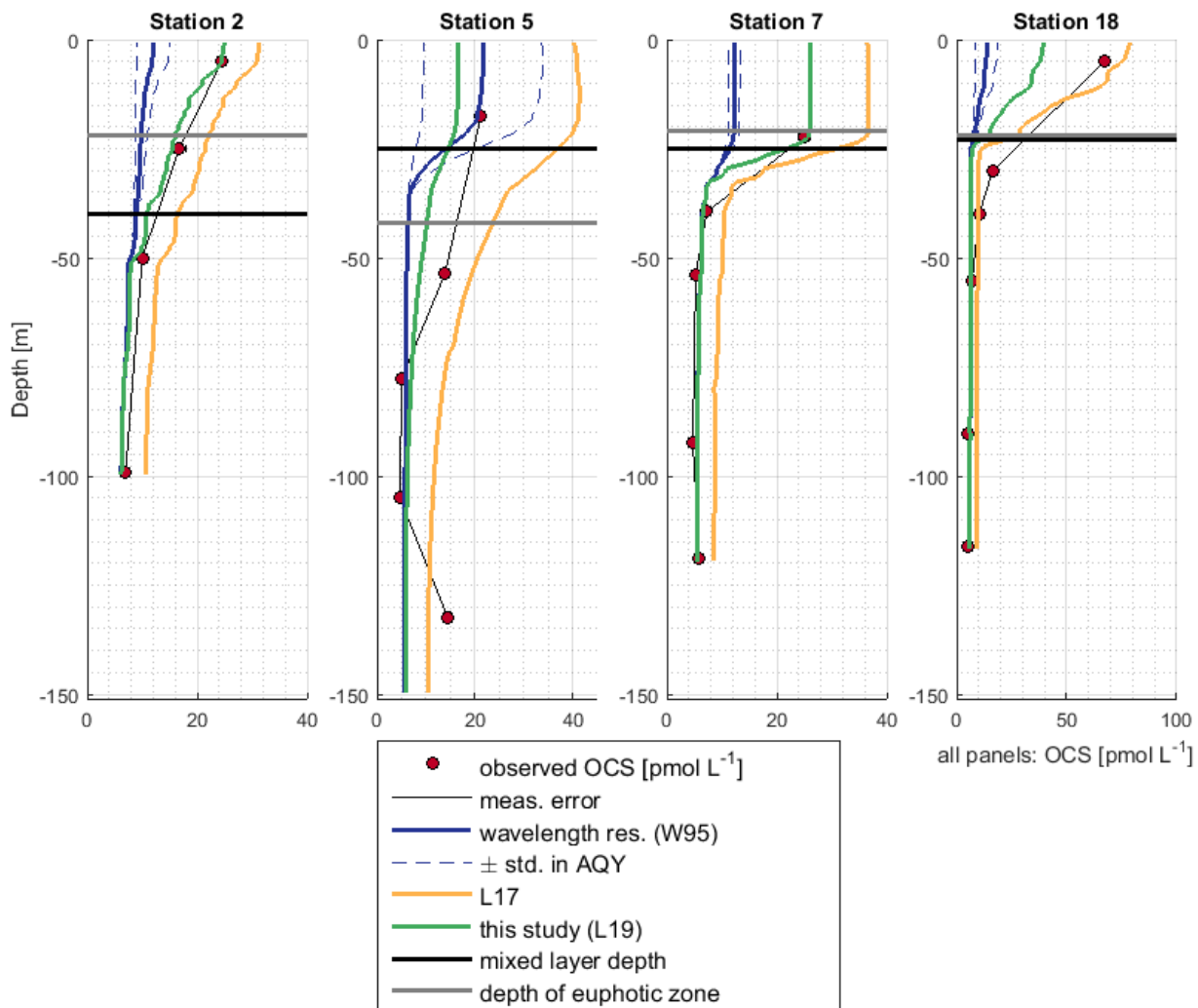


Figure 2: Time series of a) OCS, b) CS<sub>2</sub>, c) SST and SSS, d) I<sub>0</sub> and wind speed at 10m, e) absorption coefficient of CDOM at 350 nm, f) humic-like FDOM component 2, and g) DOS<sub>SPE</sub> sampled from the underway system along the cruise track of ASTRA-OMZ from 5 to 23 October 2018. Vertical lines indicate stations of ASTRA-OMZ for comparison with location (see Fig. 1).



□  
**Figure 3: Profile measurements of OCS concentrations and 1D model results for the OCS model experiments described in Table 1.**

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 □  
 □

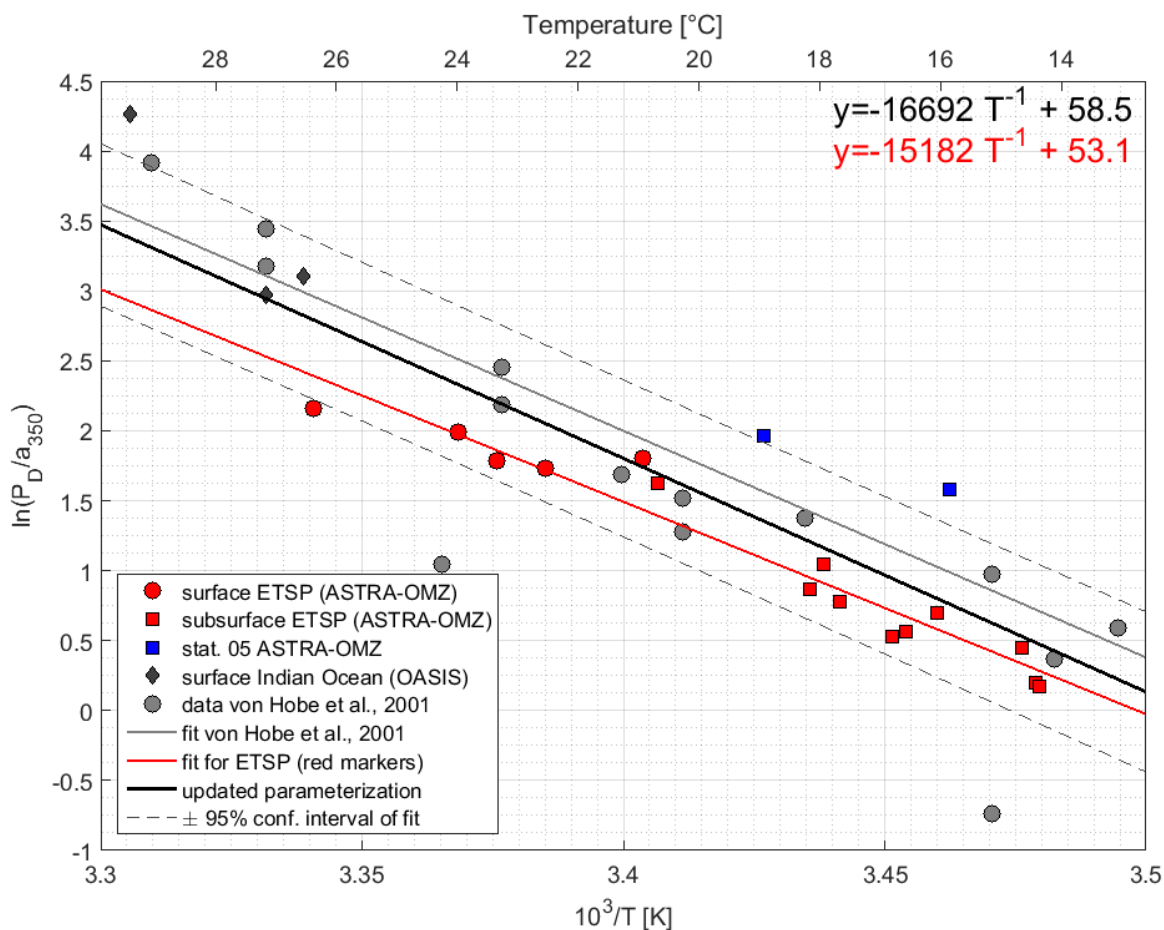
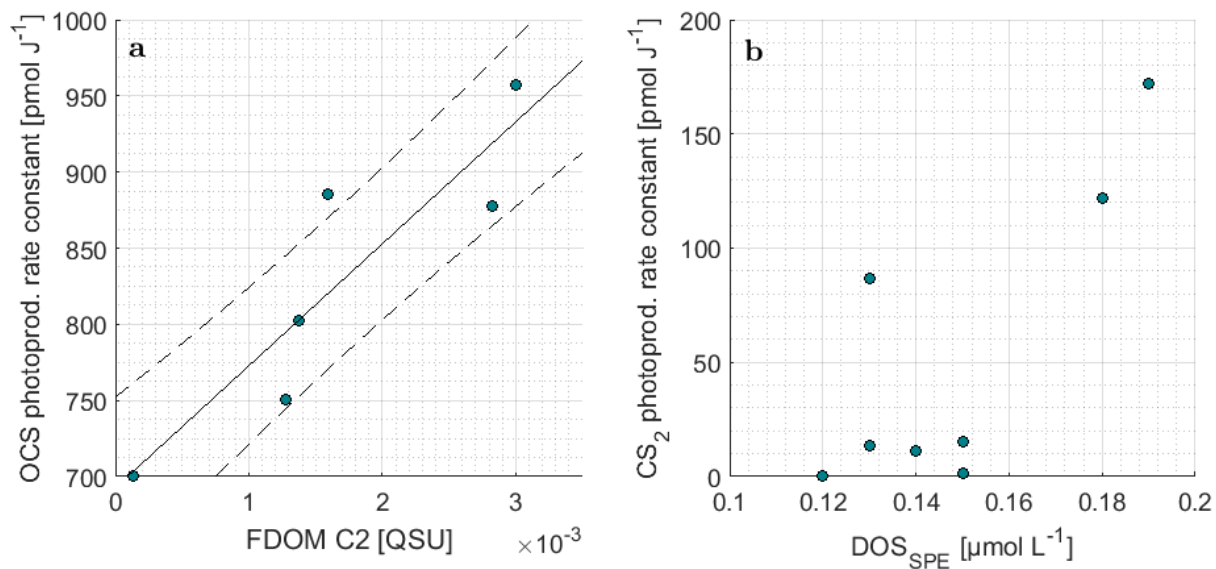


Figure 4: Arrhenius-plot of dark production rates from ASTRA-OMZ (this study, red and blue markers), data from the Indian Ocean (OASIS cruise, Lennartz et al. (2017)) and previously published rates (von Hobe et al., 2001, grey markers, note that  $P_D$  was converted from original units of  $\text{pmol m}^{-3} \text{s}^{-1}$  to  $\text{pmol L}^{-1} \text{h}^{-1}$ , for reversion subtract 1.28). The red linear fit and equation shows the parameterization for ASTRA-OMZ only, whereas the black fit and equation is an updated parameterization including dark production rates from this and previous studies (see Von Hobe et al. (2001)).



□

**Figure 5: Correlations of the photoproduction rate constant from inverse surface box modelling for a) OCS and FDOM component C2 and b) CS<sub>2</sub> and DOS<sub>SPE</sub>.**

□

□

□

5 □ □

□

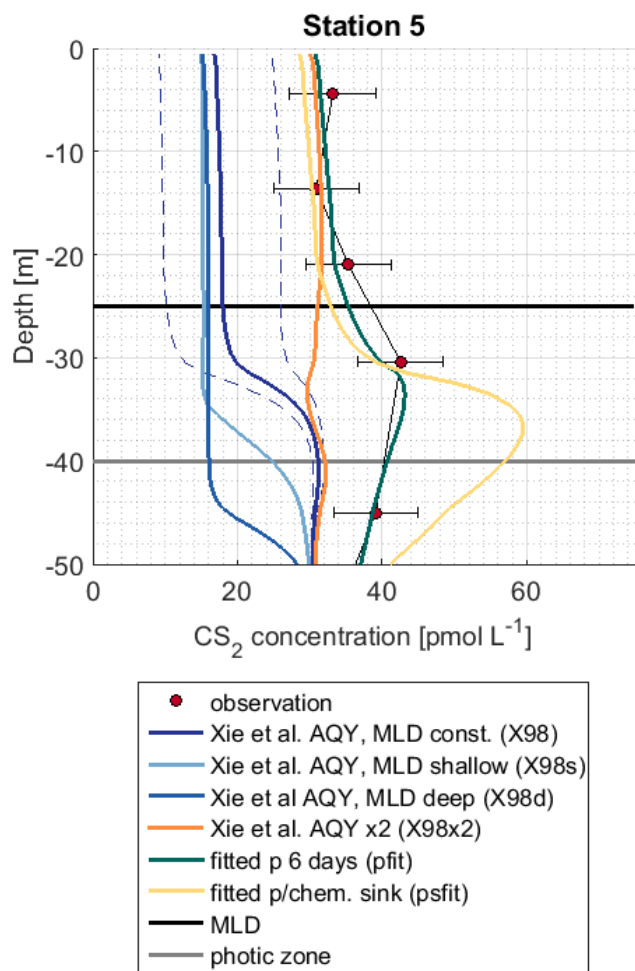


Figure 6: Observation and model sensitivity simulations at station 5. AQY=apparent quantum yield, MLD=mixed layer depth, chem. Simulation names in brackets refer to Table 1. Dashed lines indicate confidence interval of AQY as reported in Xie et al. (1998).

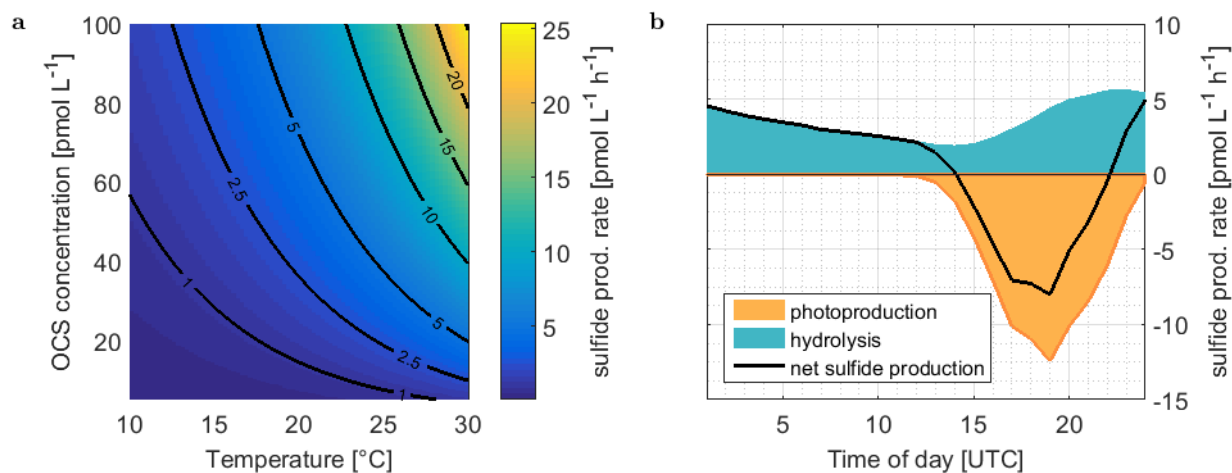


Figure 7: a) Rate of sulfide production due to OCS hydrolysis as a function of temperature and OCS concentration, calculated with eq. (3)-(4). b) Average consumption of S (organic or inorganic sulfide) by OCS photoproduction and production of sulfide during hydrolysis of ASTRA-OMZ (average 7 October – 14 October).

□  
□  
□

□



Tables

□

Table 1: Model experiments with 1D GOTM/FABM Modules for OCS and CS<sub>2</sub>. AQY=apparent quantum yield.

<b>Carbonyl Sulfide (OCS)</b>				
Exp	Photoproduction	Dark prod.	Station	Description
W95	□□□□ □ □□□□ □□ □□□ □□□□□d□□ □1995□□	□□□□□□□□□□□□	25718□	□ □□□□□□□□□ □ r□□□□□d□ □□□□□r□d□□□□□□ □ □□d□ □□□r□□□□□□□□
L17	□□□□r□□□□□□□□2017□□	□□□□□ □□□□□□□□□□ □2001□□	25718□	□ □□□□□□□□□ □□□□r□□d□ □□□□□r□d□□□□□□ □ □□d□ □□□r□□□□□□□□
L19	□□□□□□□□d□□p□□□□□d□□□□ □□□□□□□□ □□□M□□2□□	□□□□□□□□□□	25718□	□ □□□□□□□□□ □□□□r□□d□ □□□□□r□d□□□□□□ □ □□d□ □□□r□□□□□□□□
	□	□	□	□
<b>Carbon disulfide (CS<sub>2</sub>)</b>				
Exp	Photoproduction	Station	Description	
X98	□□□□□ □□□□□□□□□□1998□□	5□ 2718□	□ □□□□□□□□□ r□□□□□d□ □□□□□r□d□□□□□□□□ □ □□d□□□□r□d□□□□□□□□□□□□□□□□□□□□□□□□□□□□□□□□ □□□□□□ □□□□	
X98d	□□□□□ □□□□□□□□□□1998□□	5□	□ □□□□□□□□□ r□□□□□d□ □□□□□r□d□□□□□□□□ d□□□□d□r□□□□□ □□d□□□□r□□r□□□□□□□25□ 50□ □□□□□□□ □□□□□□□□	
X98s	□□□□□ □□□□□□□□□□1998□□	5□	□ □□□□□□□□□ r□□□□□d□ □□□□□r□d□□□□□□□□ □□□□□□□d□r□□□□□ □□d□□□□r□□r□□□□□□□10□ 25□ □□□□□□□ □□□□□□□□	
X98x2	□□□□□ □□□□□□□□□□1998□□ □2□	5□	□ □□□□□□□□□ r□□□□□d□ □□□□□r□d□□□□□□□□ □ □□d□□□□r□d□□□□□□□□□□□□□□□□□□□□□□□□□□□□□□□□ □□□□□	
pfit	□□□□d□□□□□r□□□□	5□	□ □□□□□□□□□□□□□r□□□d□□□00□□00□□□ □□□□□□□□ □r□□□□ □□□□□□□□□□□□□□□□□□□□□□□□□□□□□□□□□□□□□□ □□□□□ □□d□□□□□□r□d□□□□□□□r□□□□□□□□□□□□□□□□□□□□ □□□□□□6□□□□□□□□ □□□□□□□□	
psfit	□□□□d□□□□□r□□□□	5□	□ □□□□□□□□□□□□□r□□□d□ □00□00□ □□ □□□□□□□□ □□□□□ □□d□□□□□□r□d□□□□□□□r□□□□□□□□□□□□□□□□□□□□ □□□□□□6□□□□d□□r□□□□rd□r□□□□□ □□□□□□□□□□□□□□□□□□□□□	

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