Ocean Sci. Discuss., https://doi.org/10.5194/os-2019-1
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The influence of dissolved organic matter on the marine production of carbonyl sulfide (OCS) and carbon disulfide (CS_2) in the Eastern Tropical South Pacific

[illegible]

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Correspondence to [illegible]

Abstract. [illegible]

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1 Introduction

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[illegible]

2 Material and Methods

2.1 Study area

[illegible]

2.2 Measurement of trace gases

[illegible]

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[illegible] 1 [illegible] 2 [illegible] 10 15 [illegible] 6 [illegible]

[illegible] 7890 [illegible] 5975 [illegible] 2017 [illegible] 50 [illegible] 1 [illegible] 15 [illegible] 70 [illegible] $\frac{m}{z}$ =76 [illegible] 78 [illegible] 9 [illegible] thylene glycol. During purging, 500 µL gaseous deuterated DMS (d3 [illegible] d5 [illegible] 1 [illegible] 2 [illegible] 2 [illegible] 2 [illegible]

2.3 Chromophoric dissolved organic matter (CDOM)

[illegible] a_{350} [illegible] 0 2 [illegible] 2 5 [illegible] 2002 [illegible] 270 [illegible] 700 [illegible] 2 [illegible] 2017 [illegible]

2.4 Fluorescent dissolved organic matter (FDOM)

[illegible] 2700 [illegible] 0 2 [illegible] 200 [illegible] 220 [illegible] 550 [illegible] 10 [illegible] 250 [illegible] 550 [illegible] 1 [illegible] 00 [illegible] 800 [illegible] 10 [illegible] 2015 [illegible] 5 [illegible] 0 [illegible] 0 9991 [illegible] 0 9971 [illegible]

[illegible]

2.5 Solid-phase extractable dissolved organic sulfur (DOS_{SPE})

[illegible]

2.6 Shortwave radiation in the water column

[illegible]

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[illegible] $K_d(\lambda, z)$ [illegible] $K_d(\lambda, z)$ [illegible] $E_d^-(\lambda, 0)$ [illegible] $E_d(\lambda, z)$ [illegible] $E_d^-(\lambda)$ [illegible] λ [illegible] λ [illegible] $E_d^-(\lambda)$ [illegible] *in-situ* [illegible]

2.7 Determination of gas diffusivity with microstructure profiles

[illegible] diffusive flux of a compound, φ_d [illegible]

$$\Phi_{dia} \approx \rho \cdot K_\rho \cdot \frac{\partial c}{\partial z} \quad (1)$$

[illegible] $\frac{\partial c}{\partial z}$ [illegible] K_ρ [$m^2\ s^{-1}$] is the diapycnal turbulent diffusivity, and ρ [kg m^{-3}] [illegible] K_ρ [illegible]

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2.8 Determination of OCS dark production rates

$$P_D = L_H = [OCS] \cdot k_h$$

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

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

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

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2.9 Surface box models to estimate photoproduction rate constants

[illegible]

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

[illegible]

[illegible]

2.10 1D water column modules for OCS and CS_2

[illegible]

[illegible]

[illegible]

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[illegible]

[illegible]

[illegible]

3 Results

3.1 CDOM, FDOM and DOS_{SPE}

[illegible]

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3.2 Carbonyl Sulfide (OCS)

3.2.1 Horizontal and vertical distribution

3.2.2 Dark production

$$P_D = a_{350} \cdot \exp\left(-\frac{15182}{T} + 53.1\right) \quad (7)$$

[illegible]

$$P_D = a_{350} \cdot \exp\left(-\frac{16692}{T} + 58.5\right) \quad (8)$$

3.2.3 Diapycnal fluxes

[illegible]

3.2.4 Photoproduction

[illegible]

$$p = 85.8 \cdot [\text{FDOM C2}] + 828.76 \quad (9)$$

[illegible]

[illegible]

3.3 Carbon Disulfide (CS_2)

3.3.1 Horizontal and vertical distribution

[illegible]

3.3.2 Diapycnal fluxes

[illegible]

3.3.3 Photoproduction of CS_2

[illegible]

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[illegible]

4 Discussion

4.1 Carbonyl Sulfide

[illegible]

[illegible]

[illegible]

4.2 Carbon Disulfide

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[illegible]

[illegible]

5 Summary and conclusion

[illegible]

[illegible]

[illegible]

[illegible]

[illegible]

Author contributions

[illegible]

Acknowledgements

[illegible]

References

[illegible]

[illegible] 79 [illegible] 95 [illegible] 105 [illegible] 2008 [illegible]

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[illegible]

[illegible] 200[illegible]

[illegible] 5 [illegible] 6557 [illegible] 6566 [illegible] 10 [illegible] 1160 [illegible] 201[illegible]

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[illegible] Knęry, J., and Cutter, G. A.: Biogeochemistry of dissolved hydrogen sulfide species and carbonyl sulfide in the [illegible] 58 [illegible] 5 [illegible] 21 [illegible] 5 [illegible] 1 [illegible] 10 [illegible] 1016 [illegible] 0016 [illegible] 70 [illegible] 7 [illegible] 9 [illegible] 902 [illegible] 9 [illegible] 9 [illegible] 199[illegible]

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[illegible] 2011 [illegible] 119 [illegible] 7882 [illegible] 7910 [illegible] 201[illegible]

[illegible] 2011[illegible]

[illegible] 67 [illegible] 72 [illegible] 10 [illegible] 1016 [illegible] 1 [illegible] 52 [illegible] 2 [illegible] 10 [illegible] 98 [illegible] 00 [illegible] 6 [illegible] 1 [illegible] 1999[illegible]

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[illegible] 2 [illegible] 2 [illegible] 2 [illegible] 1997[illegible]

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[illegible] 22 2601 260 1995

[illegible] 5 25 9 1996

[illegible] 25 795 827 2005

[illegible] 50 51 1999

[illegible] 106 1217 10 1029 2000 000567 2001

[illegible] 108 10 1029 2000 000712 200

[illegible] 22 215 218 1995

[illegible] 15 625 657 10 519 15 625 2018 2018

[illegible] 6 588 601 2018

[illegible] 10 56 5 56 10 1029 97 02885 1998

[illegible] 10 5 9 10 1029 1998 90007 1999

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[illegible] 7 9 67 10 1111 1751 908 201 002 2 201

[illegible] 21 281 2816 10 1029 9 0 08 199

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Figures

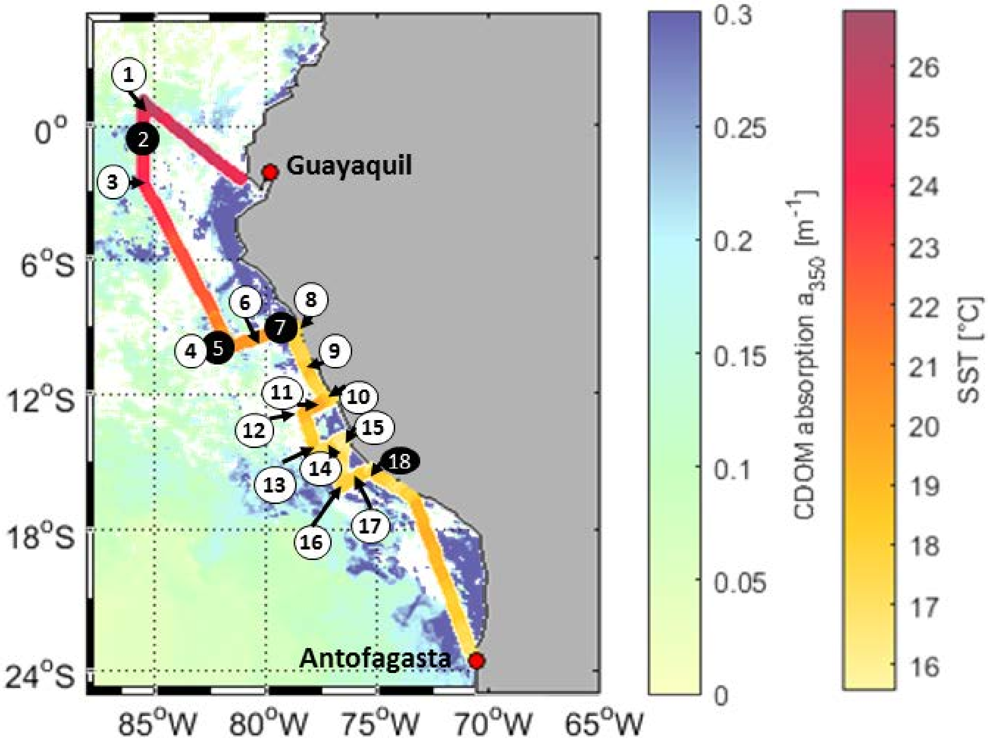

Figure 1: Cruise track of ASTRA-OMZ with stations 1-18 (in black circles: stations where OCS profiles were taken). The cruise track shows sea surface temperature (SST) measured onboard. For visualization only, the background is Aqua MODIS satellite data for the absorption of CDOM and detritus corrected 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.

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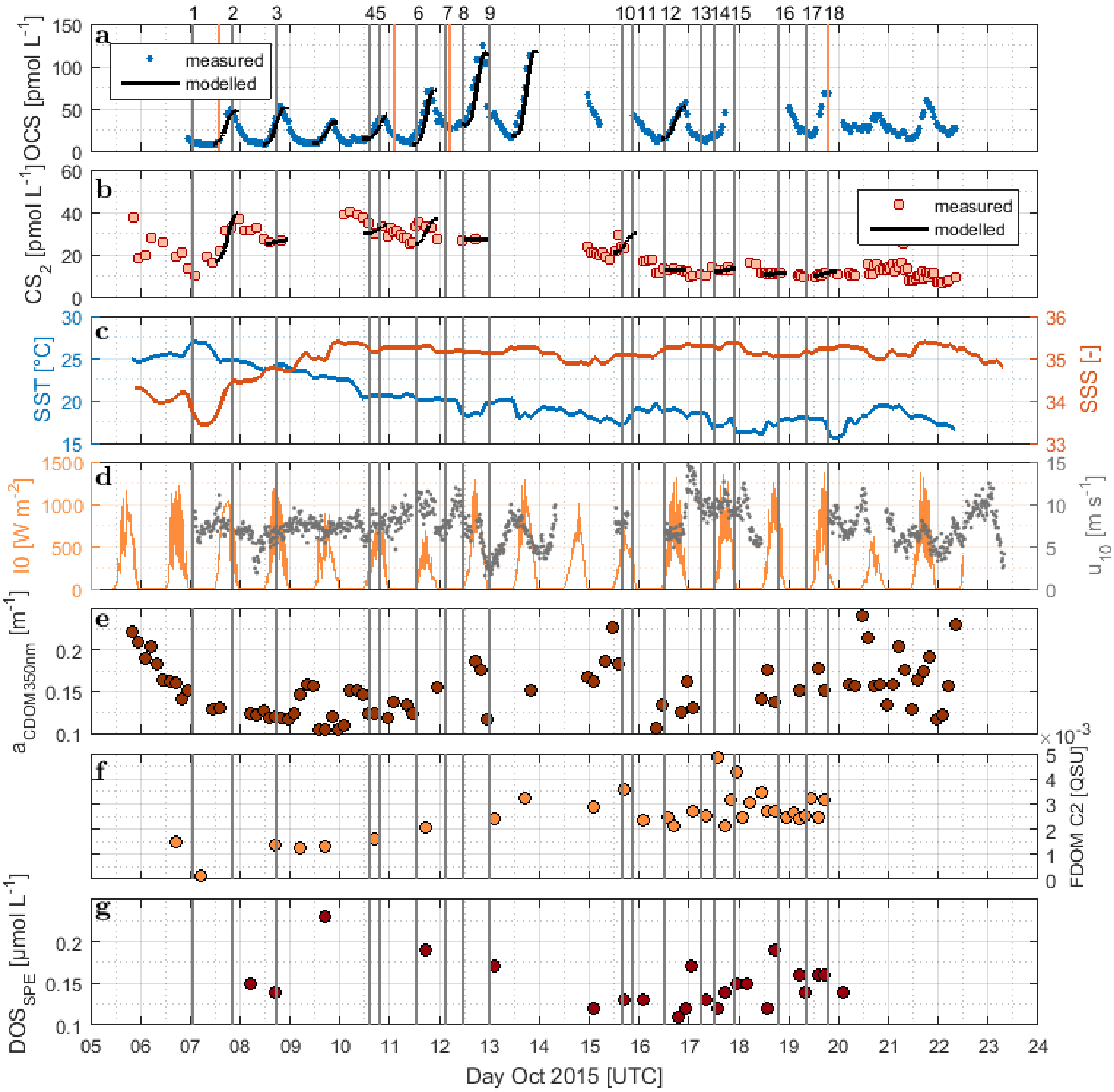

Figure 2: Time series of a) OCS, b) CS_2, c) SST and SSS, d) I0 and wind speed at 10m, e) absorption coefficient of CDOM at 350 nm, f) humic-like FDOM component 2, and g) DOS_{SPE} sampled from the underway system along the cruise track of ASTRA-OMZ from 5 to 23 October 2018.Vertical lines indicate stations of ASTRA-OMZ for comparison with location (see Fig. 1).

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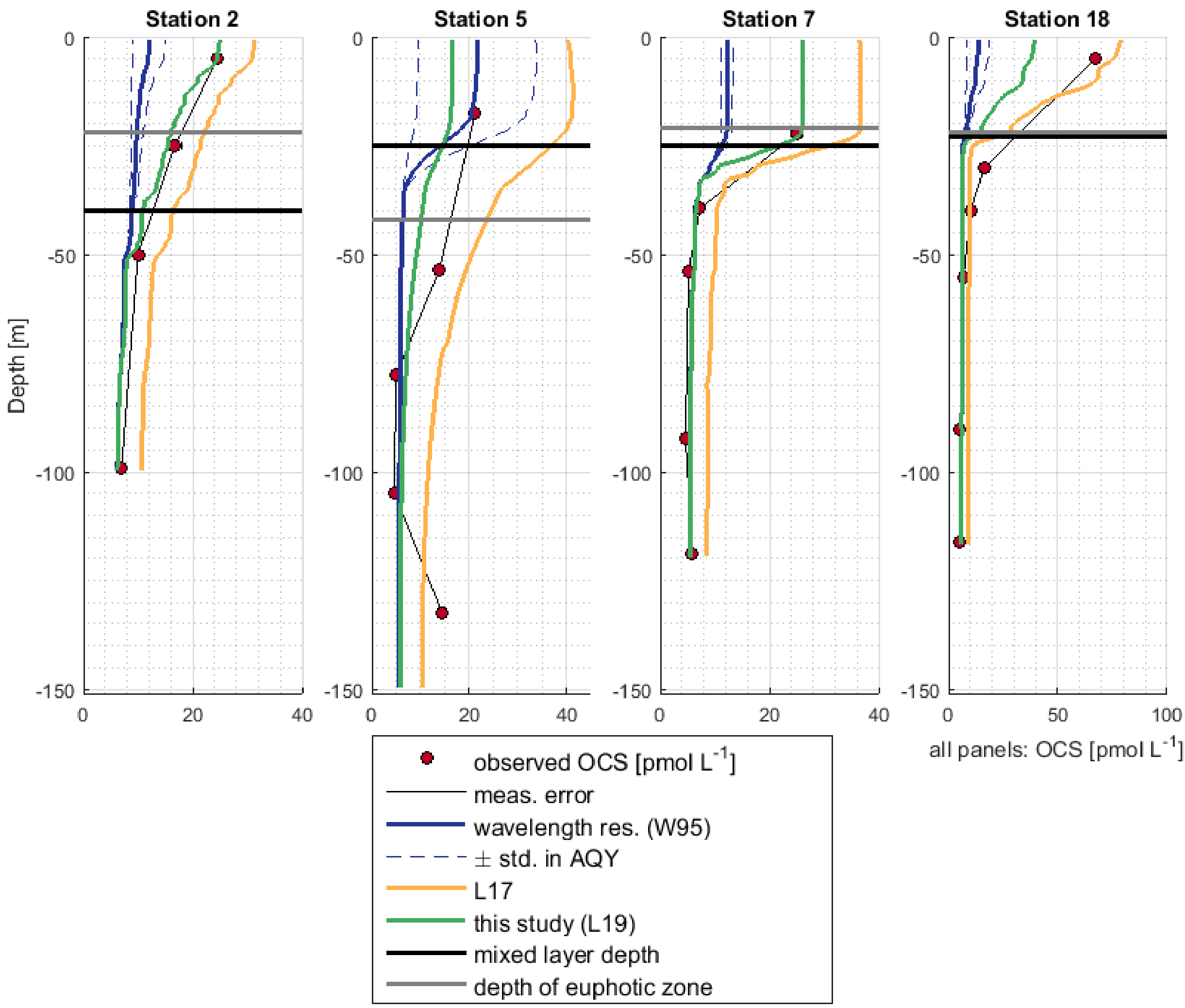

Figure 3: Profile measurements of OCS concentrations and 1D model results for the OCS model experiments described in Table 1.

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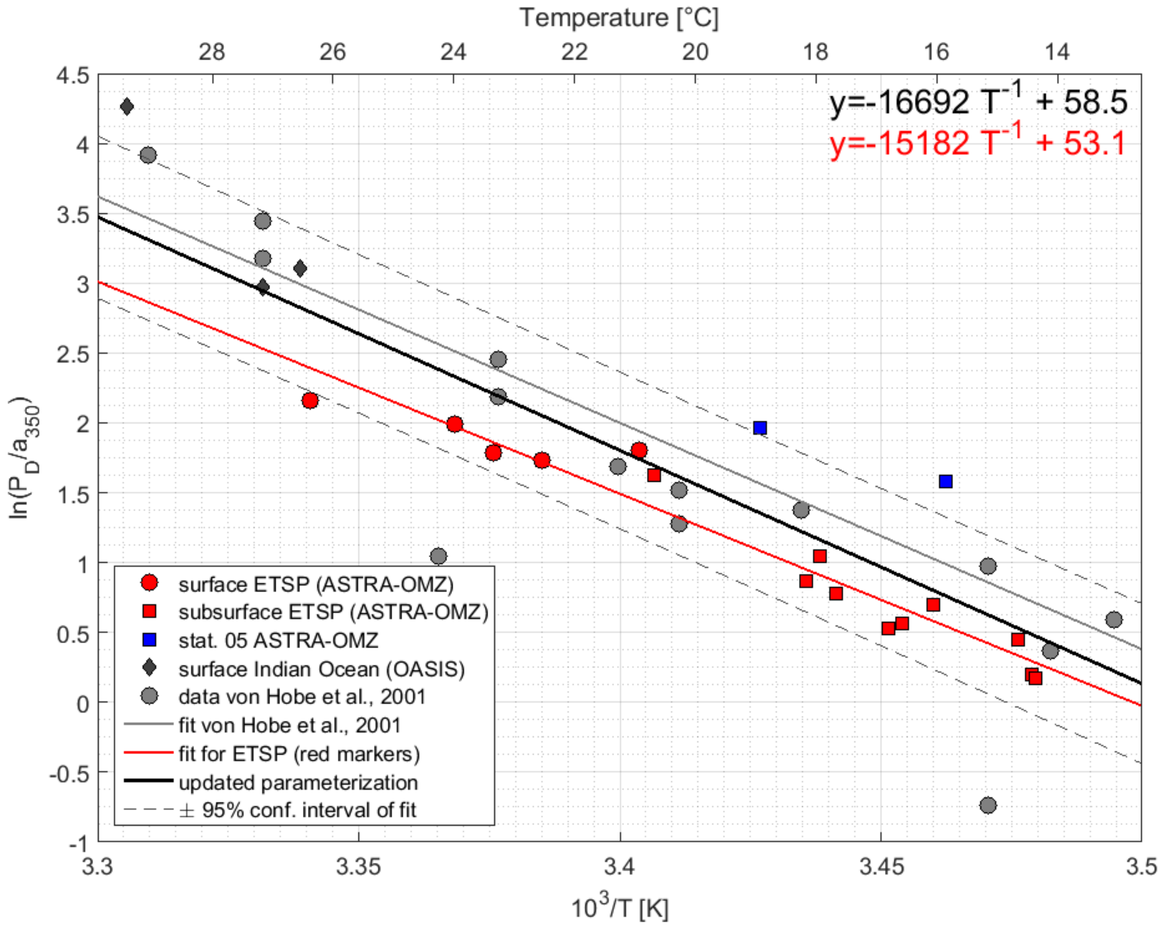

Figure 4: Arrhenius-plot of dark production rates from ASTRA-OMZ (this study, red and blue markers), data from the Indian Ocean (OASIS cruise, Lennartz et al. (2017)) and previously published rates (von Hobe et al., 2001, grey markers, note that P_D was converted from original units of pmol m^{-3} s^{-1} to pmol L^{-1} h^{-1}, for reconversion 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)).

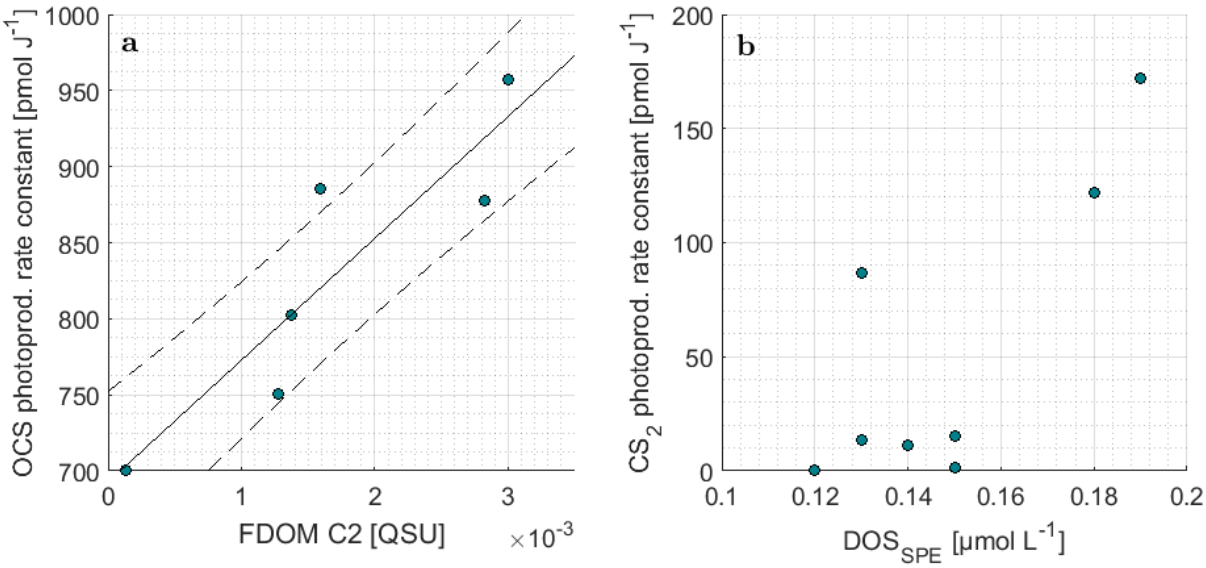

Figure 5: Correlations of the photoproduction rate constant from inverse surface box modelling for a) OCS and FDOM component C2 and b) CS_2 and DOS_{SPE}.

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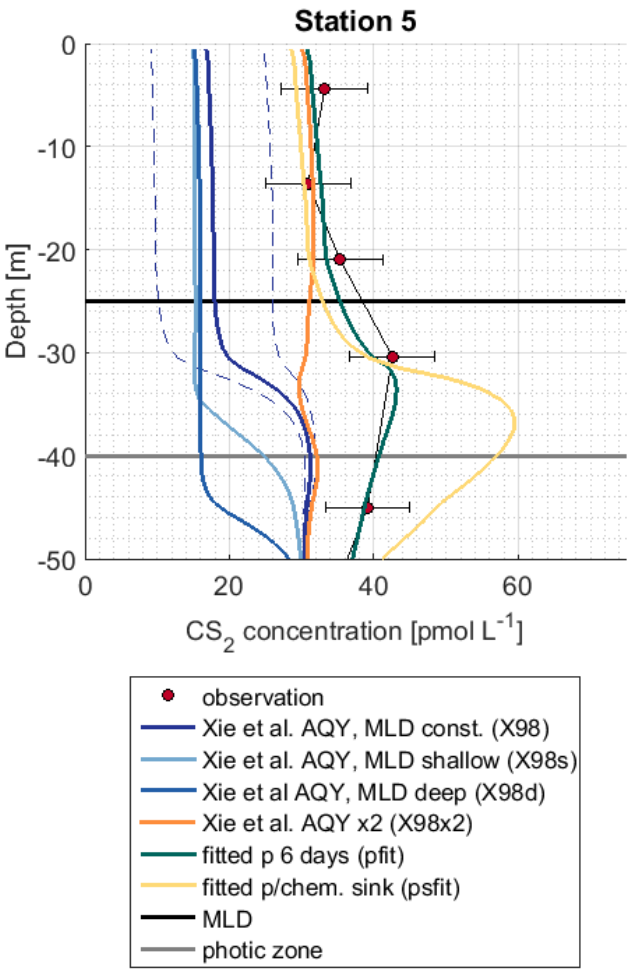

Figure 6: Observation and model sensitivity simulations at station 5. AQY=apparent quantum yield, MLD=mixed layer depth, chem. Simulation names in brackets refer to Table 1. Dashed lines indicate confidence interval of AQY as reported in Xie et al. (1998).

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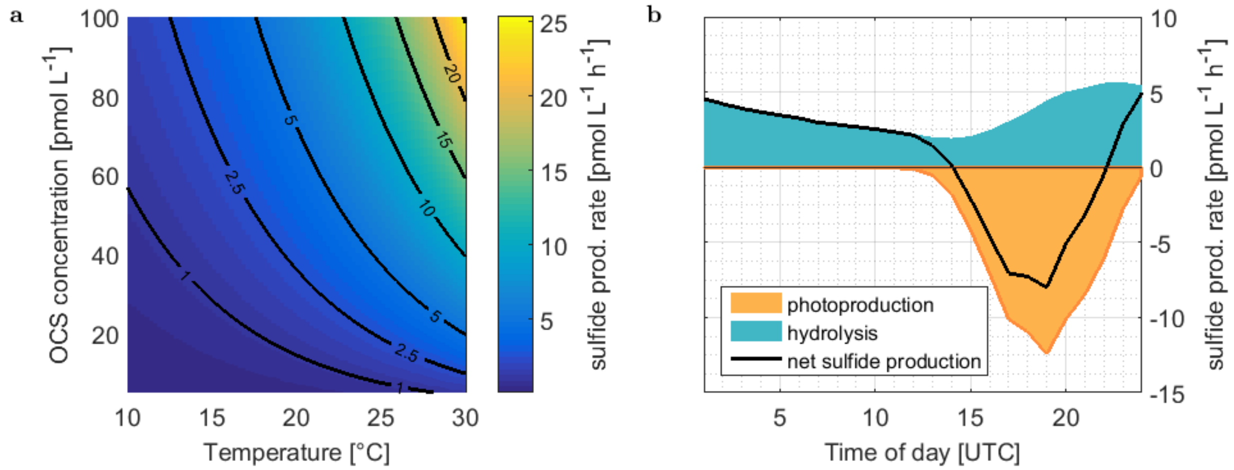

Figure 7: a) Rate of sulfide production due to OCS hydrolysis as a function of temperature and OCS concentration, calculated with eq. (3)-(4). b) Average consumption of S (organic or inorganic sulfide) by OCS photoproduction and production of sulfide during hydrolysis of ASTRA-OMZ (average 7 October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

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Tables

Table. 1: Model experiments with 1D GOTM/FABM Modules for OCS and CS_2. AQY=apparent quantum yield.

Carbonyl Sulfide (OCS)				
	Photoproduction	**Dark prod.**	**Station**	**Description**
W95	[illegible] (1995) [illegible]	[illegible]	2 5 7 18	[illegible]
L17	[illegible] 2017 [illegible]	[illegible] 2001 [illegible]	2 5 7 18	[illegible]
L19	[illegible] M 2 [illegible]	[illegible]	2 5 7 18	[illegible]

Carbon disulfide (CS_2)			
	Photoproduction	**Station**	**Description**
X98	[illegible] 1998 [illegible]	5 2 7 18 [illegible]	[illegible]
X98d	[illegible] 1998 [illegible]	5	[illegible] 25 50 [illegible]
X98s	[illegible] 1998 [illegible]	5	[illegible] 10 25 [illegible]
X98x2	[illegible] 1998 [illegible] 2	5	[illegible]
pfit	[illegible]	5	[illegible] 00 00 [illegible] 6 [illegible]
psfit	[illegible]	5	[illegible] 00 00 [illegible] 6 [illegible]