



The influence of dissolved organic matter on the marine production of carbonyl sulfide (OCS) and carbon disulfide (CS₂) in the Eastern Tropical South Pacific

Correspondence to [REDACTED] [REDACTED] [REDACTED] [REDACTED] [REDACTED]



1 Introduction



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5□ 2 Material and Methods

2.1 Study area

2.2 Measurement of trace gases



2.3 Chromophoric dissolved organic matter (CDOM)

25□ 2.4 Fluorescent dissolved organic matter (FDOM)



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

2.6 Shortwave radiation in the water column

250 18 1950 10 1M 7 6 200 10 1



10□ 2.7 Determination of gas diffusivity with microstructure profiles

$\Phi_{dia} \approx \rho \cdot K_\rho \cdot \frac{\partial c}{\partial z}$

15 K_ρ [m²s⁻¹] is the diapycnal turbulent diffusivity, and ρ [kg m⁻³] is the density of the fluid. The value of K_ρ is often taken to be constant at approximately 10 m²s⁻¹, although it may vary with depth and temperature. The term $\frac{\partial c}{\partial z}$ represents the vertical gradient of the concentration, which is positive in the direction of the flow. The sign of the flux is determined by the sign of the vertical gradient. If the concentration increases with depth, the flux is downward, and if it decreases with depth, the flux is upward.

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2.8 Determination of OCS dark production rates

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

$$k_h = e^{(24.3 - \frac{10450}{T})} + e^{(22.8 - \frac{6040}{T})} \cdot \frac{K_w}{a[H^+]} \quad -\log_{10} K_w = \frac{3046.7}{T} + 3.7685 + 0.0035486 \cdot \sqrt{S}$$

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



2.9 Surface box models to estimate photoproduction rate constants

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

2.10 1D water column modules for OCS and CS,



3 Results

3.1 CDOM, FDOM and DOS_{SPE}



3.2 Carbonyl Sulfide (OCS)

3.2.1 Horizontal and vertical distribution

15. 16. 17. 18. 19. 20. 21. 22. 23. 24. 25. 26. 27. 28. 29. 30. 31. 32. 33. 34. 35. 36. 37. 38. 39. 40. 41. 42. 43. 44. 45. 46. 47. 48. 49. 50. 51. 52. 53. 54. 55. 56. 57. 58. 59. 60. 61. 62. 63. 64. 65. 66. 67. 68. 69. 70. 71. 72. 73. 74. 75. 76. 77. 78. 79. 80. 81. 82. 83. 84. 85. 86. 87. 88. 89. 90. 91. 92. 93. 94. 95. 96. 97. 98. 99. 100.

3.2.2 Dark production

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



Medrano 2001 d 8

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

5 □ 3.2.3 Diapycnal fluxes

3.2.4 Photoproduction

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



3.3 Carbon Disulfide (CS_2)

3.3.1 Horizontal and vertical distribution

3.3.2 Diapycnal fluxes

15 d₂r₂rd_drd_{rd}in-situ₂₇d₁₈d_din-situ_dr_d
d₂rd_d2d₁₈r_rr_drd_dr_d
25 7d₁₈d₁rd_rrd_dr_rr_dr₁₈d_d
M_dr_rr_td₀₉₈d₁₀d₁¹₂r

20□ 3.3.3 Photoproduction of CS₂



4 Discussion

10 □ 4.1 Carbonyl Sulfide





4.2 Carbon Disulfide





20□ 5 Summary and conclusion

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r d r d r d r d r d r d r d
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Author contributions



Acknowledgements

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Figures

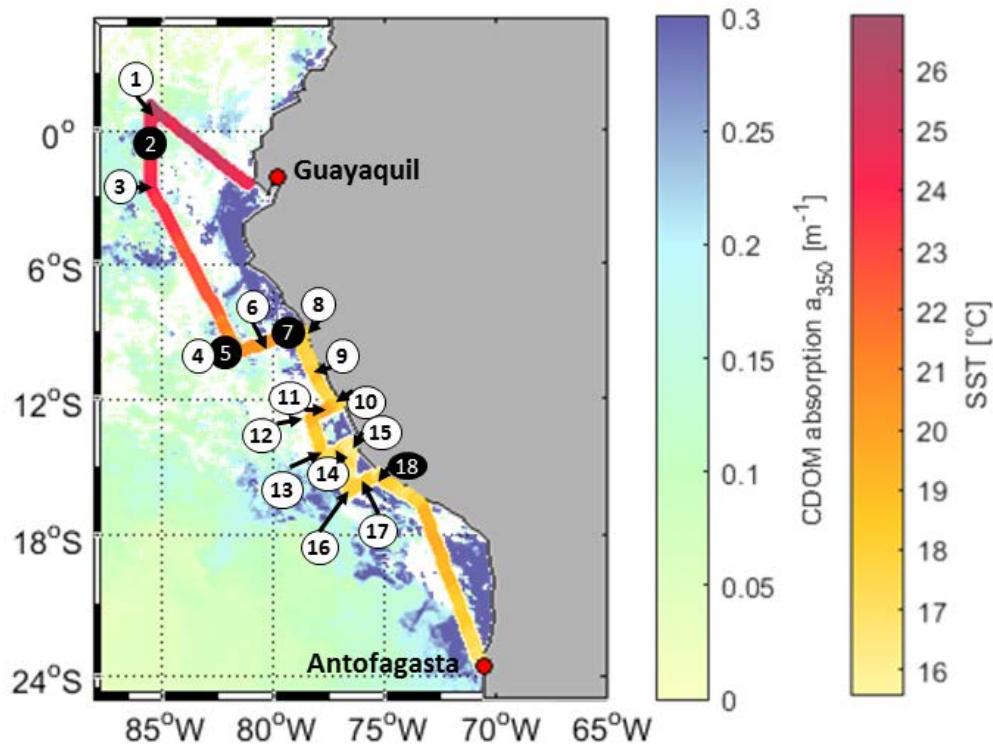


Figure 1: Cruise track of ASTRA-OMZ with stations 1-18 (in black circles: stations where OCS profiles were taken). The cruise track shows sea surface temperature (SST) measured onboard. For visualization only, the background is Aqua MODIS satellite data for the absorption of CDOM and detritus corrected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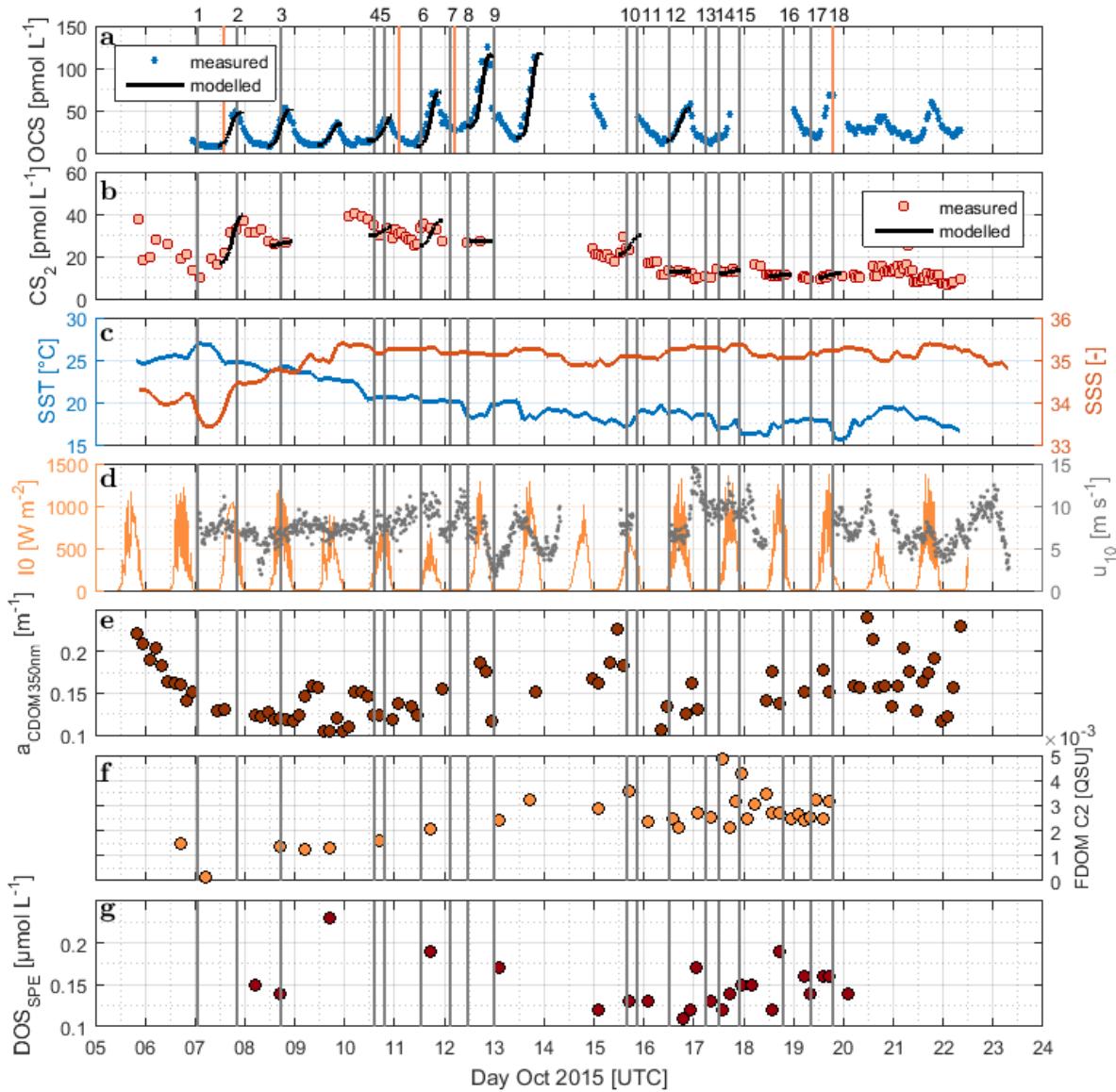
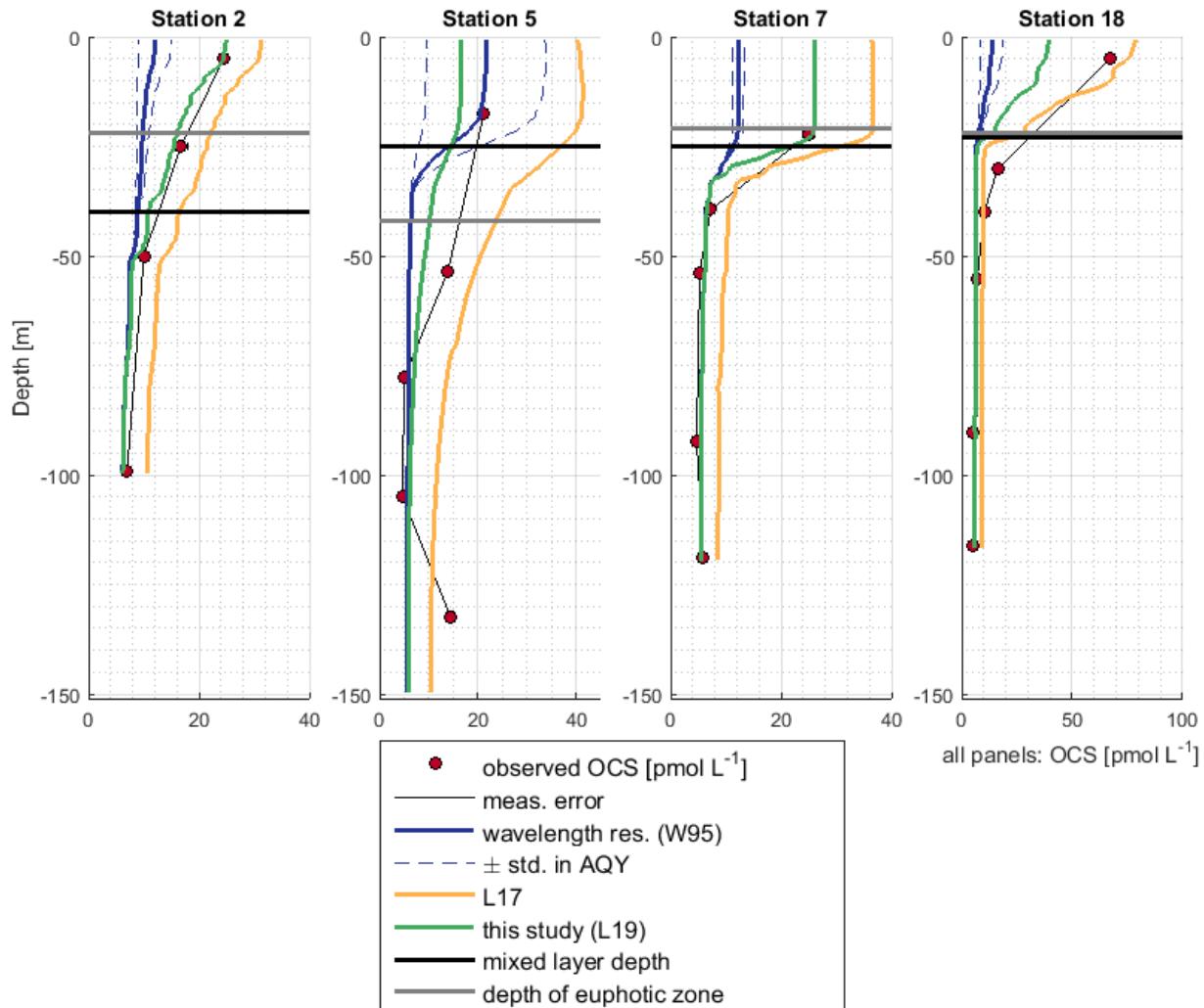


Figure 2: Time series of a) OCS, b) CS₂, c) SST and SSS, d) I₀ and wind speed at 10m, e) absorption coefficient of CDOM at 350 nm, f) humic-like FDOM component 2, and g) DOS_{SPE} sampled from the underway system along the cruise track of ASTRA-OMZ from 5 to 23 October 2018. Vertical lines indicate stations 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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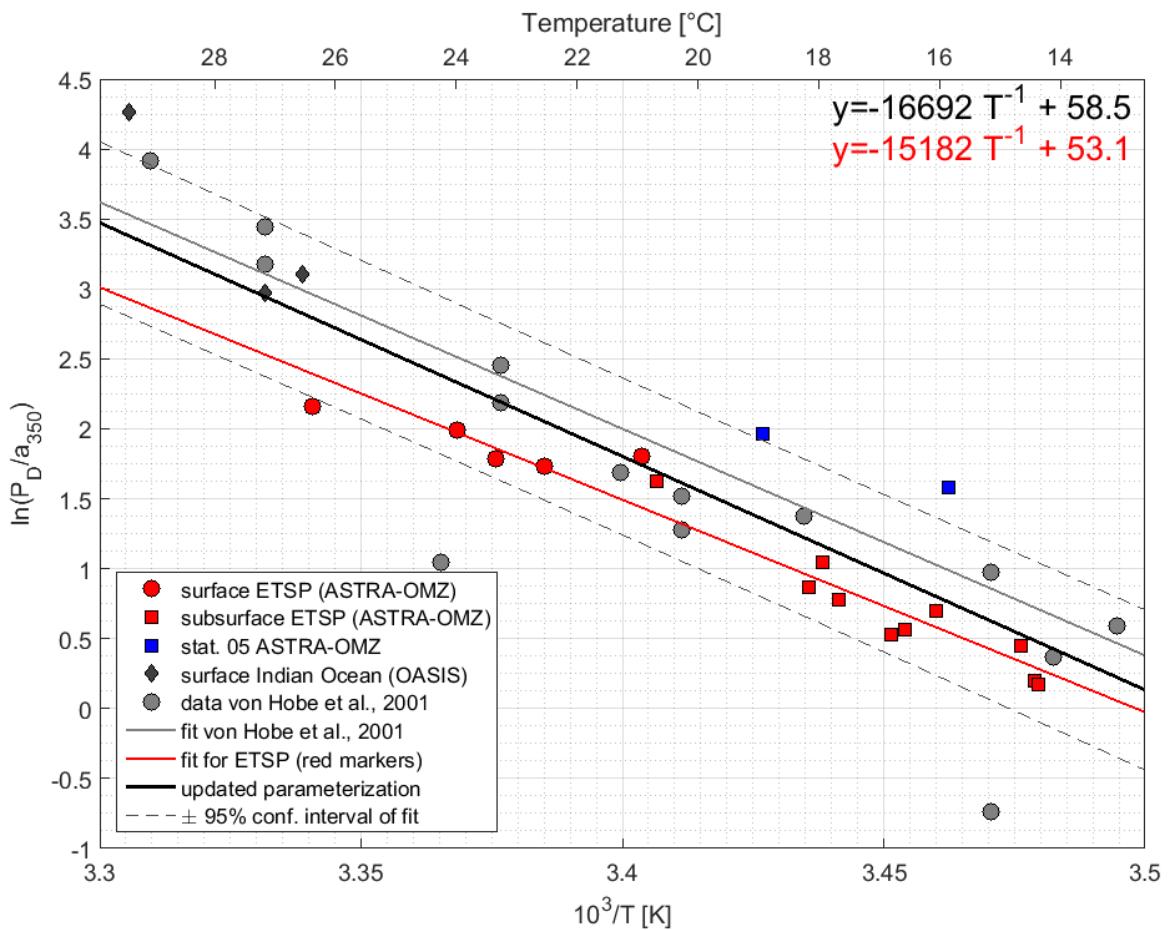
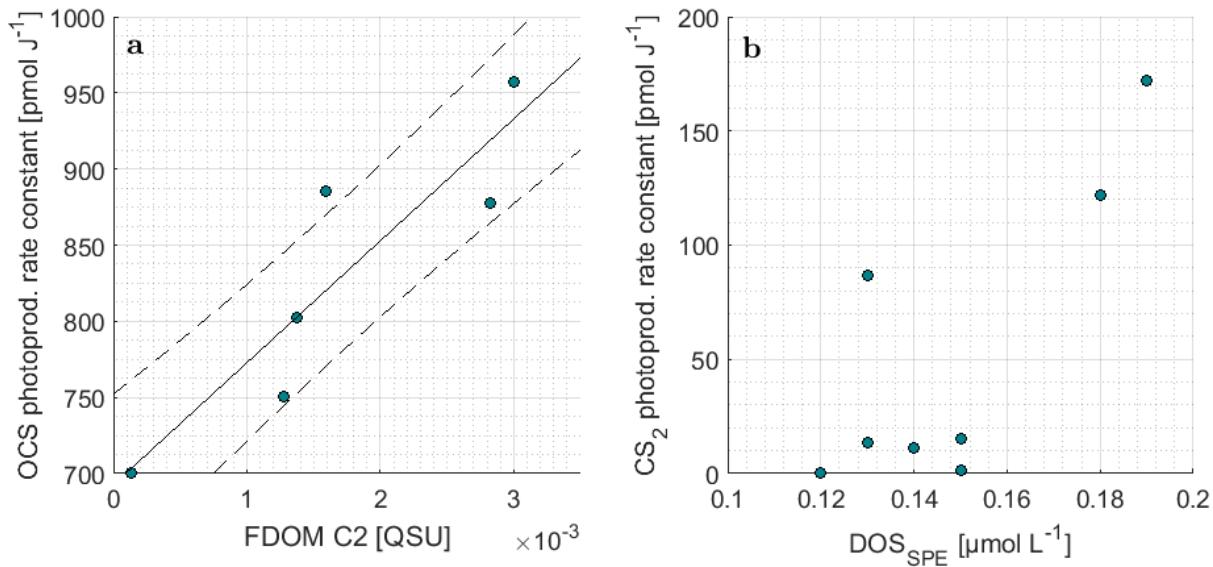


Figure 4: Arrhenius-plot of dark production rates from ASTRA-OMZ (this study, red and blue markers), data from the Indian Ocean (OASIS cruise, Lennartz et al. (2017)) and previously published rates (von Hobe et al., 2001, grey markers, note that P_D was converted from original units of $\text{pmol m}^{-3}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

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Figure 5: Correlations of the photoproduction rate constant from inverse surface box modelling for a) OCS and b) CS₂ and DOS_{SPE}.

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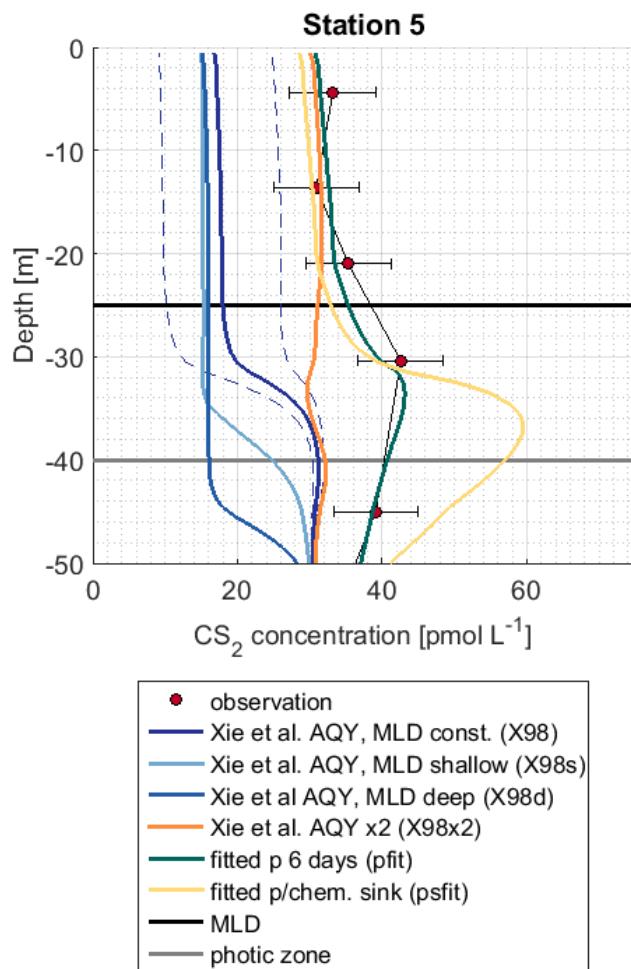


Figure 6: Observation and model sensitivity simulations at station 5. AQY=apparent quantum yield, MLD=mixed layer depth, chem. Simulations in brackets refer to Table 1. Dashed lines indicate confidence interval of AQY as reported in Xie et al. (1998).

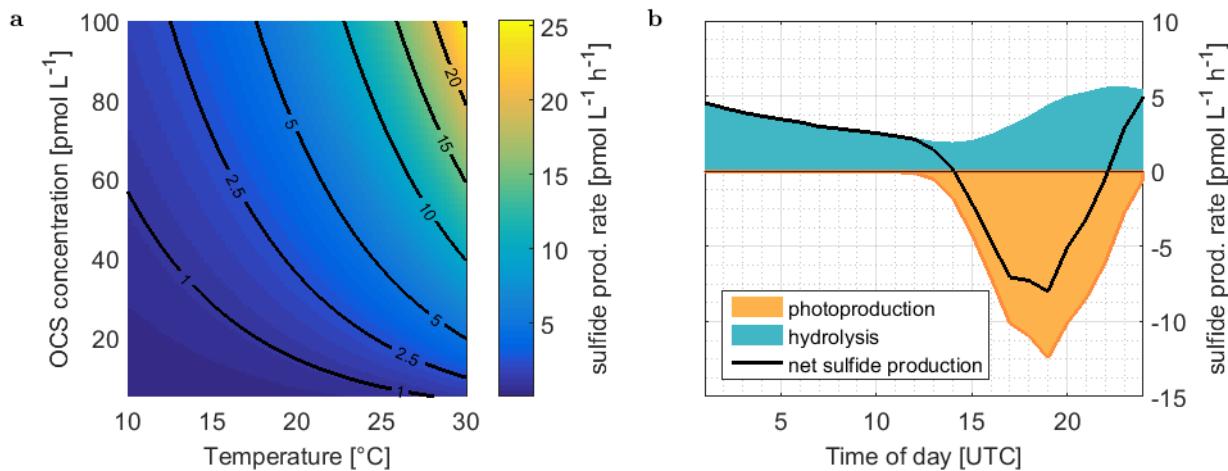


Figure 7: a) Rate of sulfide production due to OCS hydrolysis as a function of temperature and OCS concentration, calculated with eq. (3)-(4). b) Average consumption of S (organic or inorganic sulfide) by OCS photoproduction and production of sulfide during hydrolysis of ASTRA-OMZ (average 7 October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





Tables

1

Table. 1: Model experiments with 1D GOTM/FABM Modules for OCS and CS₂. AQY=apparent quantum yield.

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