

Review of manuscript os-2019-1

"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"  
by Lennartz et al.

## 1. General comments

This manuscript presents a comprehensive set of results from a cruise into the Peruvian upwelling area. Observational data are of high quality and unique in that the report OCS and CS<sub>2</sub> concentrations together with a wider range of complementary information such as dissolved organic sulfur (DOS), DOM optical characteristics and diapycnal diffusivities. This comprehensive data set is complemented by applications of 1D models of trace gas biogeochemistry and mixed layer dynamics. This approach can allow for near synoptic interpretation although there are of course limitations arising from our incomplete understanding of underlying production mechanisms.

The manuscript is clearly appropriate for publication in Ocean Science, not least due the unique combination of comprehensive data and modeling applications. However, I do have some concerns about presentation, and about some aspects of data interpretation and modeling results.

**Title:** The term 'Eastern Tropical South Pacific' used in the title suggests a study area much larger than that covered in the actual cruise track. I therefore suggest replacing ETSP with 'Peruvian upwelling'.

**OCS photoproduction:** Interestingly the manuscript reports that OCS photoproduction is well correlated with colored dissolved organic matter (CDOM) characteristics such as humic-like fluorescence emission but not with DOS. This leads authors to speculate that the sulfur needed for OCS production may come from its hydrolysis product H<sub>2</sub>S and not from organic fractions. However, there are several issues the authors neglect to discuss.

Firstly, the absence of a correlation between sulfur from the DOS pool and OCS photo production *per se* does not exclude that DOS fractions are involved in OCS production. Reported DOS concentrations exceed OCS concentrations 1000-fold (see figure 2 in MS). Therefore, only a tiny DOS fraction is required as the source of OCS sulfur. This tiny fraction might not necessarily correlate with bulk DOS.

Secondly, although laboratory experiments showed that both H<sub>2</sub>S and free sulfur-bearing amino acids such as cysteine may act as OCS precursors, precursor concentrations in these experiments were unrealistically high (10 μM) (Pos et al., 1998). S-OCS may well be derived from DOM itself given that irradiations of both unaugmented seawater and solutions of reconstituted DOM produced OCS (Zepp and Andreae, 1994; Pos et al., 1998).

Thirdly, regarding H<sub>2</sub>S, available data suggest concentration levels of free sulfide below 100 pM (see e.g. Andreae et al., 1991). Although this may be similar to OCS concentrations, it is unrealistic to assume near complete conversion of

sulfide to OCS. Clearly formation of the thermodynamically stable end product sulfate would be favored here. And finally, although the authors state that sulfur-bearing amino acids '*are rare*' (p 17, lines 9-11), they are still likely to occur at levels high enough to sustain picomolar OCS levels.

I recommend that the authors rewrite the corresponding sections in the light of my comments above.

**OCS dark production:** The manuscript presents OCS dark production rates derived using a steady state assumption (methods, p 8). I agree that a steady state assumption may be made for samples "*below the euphotic zone*" or better for samples collected from below the MLD because sea surface OCS shows a pronounced diel cycle. However, I am not entirely convinced that "early morning" samples always reflect steady state. Half lives of OCS with respect to hydrolysis removal range from > 80 hours at 5°C to ~3 hours at 30°C (Elliott et al., 1989). For most of the cruise track half-lives were likely in the order of 10 hours. Given that OCS concentrations peak in the afternoon, and that early morning sampling will occur less than 2 half-lives later, OCS levels are likely biased i.e. more than 25% higher than 'steady state' assuming that hydrolysis is the main removal process. According to equation (2) artificially high OCS levels directly translate into artificially high dark production rates.

Therefore, I would welcome some additional detail on sample selection, and some quantitative considerations of possible bias in section 2.8.

**CS<sub>2</sub> vertical profiles:** On p 13 ff the authors present CS<sub>2</sub> depth profiles which are then further discussed on p 17 line 22 ff together with modeled profiles. Unfortunately, the full set of profiles is only shown in the supplement, although these are clearly needed to support the results and discussion section. I therefore recommend moving figure S2 into the main paper.

I also have some issues with the modeling results shown both in figures 6 and S2. All simulations in S2 and most in Fig 6 show MLD concentrations below those in underlying waters. To me this seems to indicate that photoproduction in the MLD (the only source term used here) is lower than air sea gas exchange losses. However, if photoproduction is the only source term, why do these profiles indicate increasing concentrations with increasing depth across the thermocline? The modeled profiles in S2 all suggest a CS<sub>2</sub> flux from below the TC into the mixed layer, although photoproduction should clearly be constrained to the MLD. Do these profiles show a non-steady state solution? Is it possible that the 1D model was initiated with a homogenous CS<sub>2</sub> depth distribution rather than with CS<sub>2</sub> free water? I think here the manuscript needs to give a much more detailed explanation of the modeling setup and a more cogent explanation of the resulting profiles.

I am also not entirely convinced of the authors' idea that 'deep' photoproduction below the MLD may have caused the observed subsurface maxima at stations 5 and 18. The statement on p 17 lines 34-5 "*substantial production takes place at higher wavelengths penetrating deeper into the water column*" needs to be put into context: based on apparent quantum yields used (Xie et al., 1998), light levels and K<sub>D</sub>, what is the depth dependence of CS<sub>2</sub> photoproduction? How much

of the total occurs below the MLD?

I wonder how this likely very small source term would compare to diapycnal transfer, and I very much doubt that it could sustain the elevated CS<sub>2</sub> levels below the MLD.

Of course, the limited understanding of CS<sub>2</sub> cycling hinders the modeling here. However, the treatment of CS<sub>2</sub> depth profiles is rather unbalanced, with some data shown only in the supplement and not fully discussed, while Figure 6 only shows results for one station. The authors might want to consider rebalancing the reporting of their CS<sub>2</sub> results.

## 2. Specific and editorial comments

**Abstract:** The abstract is rather vague, does not give details on time period, sample numbers, and areal extent of the study area, and avoids any quantitative statements. Please rewrite.

### Introduction

**Page 2 lines 26-7:** “[CDOM...] and contains the photosensitizers that absorb light and form radicals for photochemical reactions”. This statement should be revised: not all reactive species formed during irradiation of natural water DOM are ‘radicals’ (e.g. singlet oxygen, triplet states, solvated electrons) nor does CDOM act solely as a photosensitizer given that it undergoes photodegradation itself.

**Page 2 lines 31-2:** “The method favors the retention of polar molecules, which comprise approximately 40 % of the total dissolved organic carbon (DOC) in marine waters”. Please add supporting reference.

**Page 3 lines 5 ff:** “the CDOM absorption 5 coefficient at 350 nm (a<sub>350</sub>) can serve as a proxy for both photoexcitable carbonyl-groups and organic sulfur precursors making the overall photoproduction rate second-order dependent on a<sub>350</sub> (von Hobe et al., 2003)”.

(i) a<sub>350</sub> may be a proxy for DOM but not specifically for carbonyl groups and DOS. Simple carbonyls show absorption maxima well below 350 nm (e.g. acetone: ~265 nm).

(ii) Relationships between OCS photoproduction and a<sub>350</sub> were initially proposed by Uher and Andreae (1997) and subsequently applied to a global model by Preiswerk and Najjar (2000). This should be reflected here.

(iii) It would be worth clarifying that ‘second order’ here should not be understood in terms of chemical kinetics. Instead, this statement refers to the dual roles of CDOM in light absorption and photochemistry.

**Page 3 lines 20 ff:** Preiswerk and Najjar (2000) should be added here.

**Page 3 lines 31 ff, CS<sub>2</sub> lifetime:** Please clarify if this 'CS<sub>2</sub> sink' should be air-sea gas exchange or an additional unknown process. Gas exchange would have a matching lifetime in the order of weeks.

## Methods

**Page 4 lines 23 ff, OCS calibration:** Please provide a quantitative comparison of calibrations before and after the cruise.  
Why is the stated LOD (180 pptv) 12 times higher than the stated precision?  
What did you mean by "NOAA scale"?

**Page 4 line 29:** Does "ca. 35 m" refer to the height of the inlet above sea level? It would also be interesting to see atmospheric OCS mixing ratios reported somewhere.

**Page 5 lines 26 ff:** Replace "spectrophotometer" with "spectrofluorometer". I suspect your statement in line 29 refers to photomultiplier voltage? Please state this clearly.  
Explain why you list two conversion factors for conversion between QSU and Raman units.  
How did you apply the QSU scale to fluorophores that do not show significant overlap with quinine sulphate emission?

**Page 6 line 30:** "*downwelling irradiance profiles were corrected for incident sunlight*". This statement is worded incorrectly. I suspect you adopted the profile from station 6 after normalization to sea surface irradiance? Please clarify.

**Page 7 line 7:** Reference to equation 1 is incorrect. Equation 1 refers to diapycnal flux, not to underwater irradiance. Please insert appropriate equation and update equation numbering.

**Page 7 lines 23-25:** Please add a supporting reference.

**Page 8 lines 1-2, dark OCS production:** Please spell out the units used in equations (2) and (5).

**Page 10 lines 13-15:** Given MLDs in the order of 30-40 m and piston velocities of maybe 1-2 m d<sup>-1</sup>, CS<sub>2</sub> lifetimes with respect to ventilation losses should be in the order of weeks not days. Please revise your statement.

**Page 10 lines 17-19:** Explain why "*air-sea gas exchange is absent*" at station 5.

## Results

**Page 10 lines 28ff, description of results in figure 2:** Your statement that “DOM showed strong spatial variability in FDOM, but less in the  $DOS_{SPE}$  concentration and CDOM absorbance” is not supported by data in figure 2. All three variables vary roughly 3-fold during your cruise, including FDOM component 2, particularly if highest & lowest FI were excluded from analysis. Unfortunately, however,  $\text{mean} \pm \text{stdev}$  are not reported for component 2 (nor for any other components).  
You stated that DOS decreased with depth but did not quantify this.  
Please rewrite this section and include the required statistical and quantitative information.

**Page 11, OCS distribution:** The authors should clearly state here and in their introduction that OCS sea surface concentrations from this cruise were already published in Lennartz et al (2017).

**Page 12, OCS photoproduction, lines 12 ff:** It is interesting that OCS production rates only covary with humic-like fluorescence but not with  $a_{350}$ . Please give further details of your analysis: how did you bin C2 and  $a_{350}$  data into days? Did you only use samples obtained between sunrise & sunset? Figure 6 only shows data for 6 days. How many days were available to test for  $p_{OCS} - a_{350}$  correlations? Given that your experiment was not Lagrangian, how could changes in CDOM characteristics during diurnal cycles have affected your relationships?  
I would also be interested to see if  $a_{350}$  and C2 fluorescence were correlated with each other as they usually are (Ferrari and Dowell, 1998). If not, the authors should give possible explanations for this unusual trend.

**Page 12, diapycnal fluxes, line 6 ff:** Why does the air-sea flux have a different algebraic sign? Please clarify.  
Explain what condition might have caused the large diapycnal flux at stn 18.

**Page 13, CS<sub>2</sub> distribution:** Reference to Fig 3 in line is incorrect. This should be Fig 2. CS<sub>2</sub> depth profiles from the supplement should be moved into this section, because they are needed here to support the discussion.

**Page 13, diapycnal fluxes:** “Small in-situ sinks (stations 2, 7, and 18) and in-situ sources at different water depths (stations 2 and 18) within the water column were required to maintain convergences/divergences under a steady state assumption.”  
This statement is unclear. Please explain how your statement relates to your CS<sub>2</sub> depth profiles.

**Page 13, CS<sub>2</sub> photoproduction:** Did you test for possible correlations between production rates and chl a or SST?

## Discussion

**Page 14, Carbonyl sulfide, lines 11-12:** “[profiles] *do not indicate any connection to a significant redox-sensitive process*”. This should be expected given that OCS photoproduction was found to be independent of dissolved oxygen concentration (Zepp and Andreae, 1994; Uher and Andreae, 1997). Please refer to previous work.

**Page 14, line 17:** Please remove reference to Ulshöfer et al. (1995) because they did not report dark production rates.

**Page 14, “radical production pathway”, lines 25 ff:** “*A strong similarity across different biogeochemical regimes favors the hypothesis of a radical production pathway, which would be indifferent to the prevailing biological community*”. This statement is simply wrong and should be removed together with other associated statements.

Available evidence clearly shows that rate constants of reactive radical species with DOM can vary significantly as a function of DOM source / composition (see e.g. McKay et al., 2011). Furthermore, DOM and its colored fraction are indirectly derived from primary production and therefore reflect its distribution pattern (see e.g. Carder et al., 1989), although not necessarily short terms variations.

This unsupported speculation should be replaced by appropriate references to previous work. Kamysny et al. (2003) for example, proposed a mechanism for dark production of OCS.

That aside, possible differences in dark production rates between stations inside & outside the OMZ more likely reflect DOM compositional differences related to the microbial food web.

**Page 15, line 5:** “[...] *internal waves led to high diffusivities*”. Explain how you arrived at this conclusion. What is the evidence?

**Page 15, correlations, lines 10 ff:** see my previous comments on correlation results section 3.2.4.

Lines 18-20: give references supporting your statement regarding covariation of humic like fluorescence and  $a_{350}$ .

**Page 15, lines 21 ff:** see my previous comments regarding  $H_2S$  as a possible substrate or OCS production.

**Page 16, lines 7 ff:** This discussion of 1D model results refers to ‘*scaling factors*’ for AQYs. Note that AQYs cannot be assumed to be ‘constant’. There is now clear evidence that AQY can vary with CDOM absorbance, presumably due to changes in DOM composition reflected by optical properties. See for example Gali et al. (2016) and Stubbins et al. (2011). The authors’ own pocs-CDOM relationships do reflect this as well.

Establishing AQY-CDOM relationships for OCS would be useful and should be discussed in this section.

**Page 16, CS<sub>2</sub> vs SST, lines 30 ff:** Report the CS<sub>2</sub> vs SST relationship in your data and compare this to Xie et al (1999).

**Pages 17-18, CS<sub>2</sub> photoproduction:** see my previous comments regarding CS<sub>2</sub> production and vertical profiles.

**Page 18, lines 7-9:** Sustained subsurface maxima cannot be caused by 'downward mixing' because the CS<sub>2</sub> gradient would cause transfer into the surface layer. Please remove this statement.

#### **Editorial:**

The wording could be improved by careful editing.

#### **References**

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**End of review**