

## Reply to

Interactive comment on “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 Sinikka T. Lennartz et al.

### **We thank Dr. Cutter for his review, and reply to the comments below.**

Given interest in the global radiation balance in a changing world, this manuscript examines the production of carbonyl sulfide and related gas carbon disulfide in waters off Chile using a combined field and modeling approach. It is a relevant and needed compilation for ocean and atmospheric scientists. One of the issues driving any recent examination of sulfur gas fluxes from the ocean is the apparent imbalance between known/established source fluxes, the atmospheric inventories, and residence times – the known fluxes cannot account for the measured inventories. In this respect, this Discussion paper doesn't solve the problem, but in fact they also missed the papers by Cutter and Radford-Knoery (Mar. Chem., 43: 225-233, 1993) that clearly demonstrate the importance of coastal OCS fluxes, and another by Zhang and Cutter (Mar. Chem., 61:127- 142, 1998) that shows coastal sediments are a large source to the water column of OCS via sulfate reduction and enhance the sea-air flux. Another interesting feature in this 1998 paper is that low depth-resolution bottle sampling that have acquired OCS depth profiles to date, and that used here with a pump, may be missing large subsurface maxima in OCS that would then radically change the calculated fluxes. These same features could be present for CS<sub>2</sub> as well.

**We are aware that such a comprehensive, but locally constrained study cannot solve the problem on global emissions alone, but we believe that increased process understanding and testing of model parameterizations in different biogeochemical regimes helps to improve global modeling approaches and, hence, global emission estimates.**

**Concerning emission estimates:** Emission estimates that are derived from modelling approaches (i.e. not simply scaling oceanic OCS measurements to the global ocean area) already account for elevated OCS emissions at the coasts, because they take into account input data with e.g. elevated  $a_{350}$  in coastal areas (Lennartz et al., 2017). Coastal emissions, although important, are unlikely to account for the whole missing source of 400-600 Gg S yr<sup>-1</sup>.

**We thank Dr. Cutter for pointing us to the studies, and we include them in the following.**

**p. 3, l. 1:** OCS is produced in the surface ocean by interaction of UV radiation with CDOM (Uher and Andreae, 1997), making coastal and shelf regions a hot spot for OCS production (Cutter and Radford-Knoery, 1993).

**p. 14, l. 15:** Profiles at station 7 and 18 reached down to the sediment, but did not show increased concentrations towards the bottom. Increased sediment inputs, as e.g. reported from estuarine regions (Zhang et al., 1998), apparently do not play a large role in the studied region, and fluxes to the atmosphere are not affected.

**P 14, l. 15ff:** The latter study also raises the question of near surface gradients, suggesting that our shallowest measurement depth of 5 m in both profile and underway sampling might underestimate the flux of OCS. On the other hand, strong near surface stratification acts as a barrier for air-sea exchange (Fischer et al., 2019) and could lead to a bias of the OCS flux, if the

sampling depth is below the barrier. Since it is difficult to perform underway sampling at shallower depths than a few meters, we cannot fully resolve this issue. However, given the low  $a_{350}$  compared to coastal and estuary regions as in Zhang et al. (1998), irradiation likely penetrates deeper into the water column in our study region than in the estuary in their study. Hence, photochemical production likely extended further down into the water column, which reduces the problem of underestimating the flux.

In these authors' computations of photochemical and dark production, it would have been beneficial to examine the carefully measured and calculated rates in the Sargasso Sea (Cutter et al., 2004). In this respect, the Sargasso Sea dark production not only depends on the abundance of particulate organic matter, but also is ca. 3x higher than those reported here. Since they have endeavored to compare their results with others, this bears mentioning.

**We added a paragraph to discuss these results:**

p. 14, l. 18: Only incubation experiments in the Sargasso Sea showed higher production rates than reported here, ranging between 4-7  $\text{pmol L}^{-1} \text{h}^{-1}$  (Cutter et al., 2004). Therein, the authors concluded that particulate organic matter heavily influences dark production. Although no sample-to-sample comparison to particulate organic carbon (POC) is possible for our OCS data, the general range of POC during our cruise was  $12.1 \pm 6.1 \text{ } \mu\text{mol L}^{-1}$  ( $145.2 \text{ } \mu\text{g L}^{-1}$ ), which is much higher than the POC (ca.  $41 \text{ } \mu\text{g L}^{-1}$ ) reported from the Sargasso Sea (Cutter et al., 2004). We thus cannot confirm the influence of POC on dark production in the Peruvian upwelling, and do not find a direct biotic influence.

Interestingly, their photochemical model using Weiss et al.'s 1995 Apparent Quantum Yields is 3-6 times lower than required based on field data (p. 12, line 22), but the Cutter et al. (2004) AQY parameters would nicely fit their field results. Thus, expanding their search for parameterizations would have solved some of their problems.

**We added:**

**Methods:**

p. 10, l. 4: We use the AQY by Weiss et al., since they were measured at the location closest to our study region (i.e. South Pacific). We assume they reflect the DOM composition in our study region best due to their similarity in  $a_{350}$ . We note other observed AQYs (Zepp and Andreae, 1994; Cutter et al., 2004), which vary by up to two orders of magnitude.

**Discussion:**

p. 16, l. 11: Photoproduction rates based on the wavelength-resolved simulation W95 underestimated observed concentrations in all cases. Other AQYs were not tested, but can be interpreted in a relatively straightforward way, since the AQYs of a given spectral shape is proportional to the OCS production and concentration (in steady state). Higher wavelength-resolved AQY as reported by Zepp and Andreae (1994) from the North Sea and the Gulf of Mexico, as well as by Cutter et al. (2004) ranged from twofold to up to two magnitudes higher than the ones reported by Weiss et al. (1995). These differences in magnitude were attributed to the composition of the DOM pool. To reflect this influence of the DOM composition, Lennartz et al. (2017) parameterized the photoproduction rate constant (corresponding to an integrated AQY) to

$\alpha_{350}$ , following the suggestion by von Hobe et al. (2003) that  $\alpha_{350}$  can be used as a proxy for OCS precursors on larger spatial scales. Using this parameterization for photochemical production in the 1D water column model (simulation L19) yielded simulated concentrations closer to, but higher than, observations (Fig. 3). Although the absolute concentrations for the AQY W95 did not match observations due to the reasons outlined above, the shape of the profile fits observations well. The simulations thus support the experimental findings in most of the previously published AQY work, i.e. the highest OCS yield at UV wavelengths for in-situ conditions.

Finally, their speculation on p. 15 that dissolved H<sub>2</sub>S in the surface ocean could maintain OCS abundances is interesting, but in fact the major pathway for oxic H<sub>2</sub>S production is phytoplankton emissions coupled to assimilatory sulfate reduction, not OCS hydrolysis, and most of the resulting H<sub>2</sub>S is complexed with trace metals such as zinc (Walsh et al., *Limnol. Oceanogr.*, 39: 941-948, 1994; Radford-Knoery [NOTE CORRECT SPELLING] and Cutter, 1994; Cutter et al., *Deep-Sea Res. II*, 46: 991-1010, 1999).

We have rewritten the whole paragraph for clarity:

An interesting finding is the significant correlation of the photoproduction rate constant  $p$  with FDOM C2 (humic-like FDOM), but not with  $\text{DOS}_{\text{SPE}}$ , given a reported correlation of OCS and DOS in the Sargasso Sea where much higher DOS concentrations of ca.  $0.4 \mu\text{mol S L}^{-1}$  were present (Cutter et al., 2004). It should be noted that the method to extract  $\text{DOS}_{\text{SPE}}$  in our study does not recover all DOS compounds, and we cannot exclude the possibility that this influences the missing correlation between  $p$  and DOS. In the studied area, OCS photoproduction is apparently not limited by the bulk organic sulfur, but rather by humic substances. The humic-like FDOM component C2 is an abundant fluorophore in marine (Catalá et al., 2015; Jørgensen et al., 2011), coastal (Cawley et al., 2012) and freshwater (Osburn et al., 2011) environments. This FDOM component seems to be especially abundant in the deep ocean (Catalá et al., 2015), which might be the reason for higher C2 surface concentrations in regions of upwelling, as evident in our study (Fig. 2) and reported by Jørgensen et al. (2011). The significant correlation of  $p$  with humic-like fluorophores in our study highlights the importance of upwelling and coastal regions for OCS photoproduction.

A significant correlation (i.e., a limitation) of OCS photoproduction with humic-like substances, but not with bulk  $\text{DOS}_{\text{SPE}}$  can be explained by two scenarios: Under the assumption that only organic sulfur is used to form OCS, the limiting factor is contained in the humic-like C2 fraction of the FDOM pool. The sulfur demand ( $75.8 \text{ pmol L}^{-1}$ , the orange area in Fig. 7b) would need to be covered entirely by organic, sulfur-containing precursors. The limiting driver of this process is either organic molecules acting as photosensitizers or a sulfur-containing fraction of the DOM pool that correlates with FDOM C2, but not bulk  $\text{DOS}_{\text{SPE}}$ . In that scenario, FDOM C2 can be used as a proxy for the OCS photoproduction rate constant. More data from other regions would help to quantify such a relationship. In a second possible scenario under the assumption that both organic and inorganic sulfur can act as a precursor, the sulfur demand could theoretically be covered by the sulfur generated by hydrolysis of OCS (i.e.  $85.8 \text{ pmol L}^{-1}$ , Fig. 7). In this case, FDOM C2 would only be limiting as long as enough organic or inorganic sulfur is present, for example when temperatures are high enough to recycle sulfur directly from OCS, or when other inorganic sulfur sources are present.

Incubation experiments have shown that inorganic sulfur is a precursor for OCS (Pos et al., 1998). It is not clear whether the mechanism proposed therein occurs under environmental conditions,

because sulfide concentrations were higher than in most marine areas, but also yielded much higher OCS production rates in the magnitude of  $\text{nM hr}^{-1}$  compared to the magnitude of  $\text{pM hr}^{-1}$  under natural conditions. Furthermore, the conversion of sulfide to sulfate, rather than to OCS, is thermodynamically favored. Based on our data, we cannot resolve the question about the role of anorganic sulfur in OCS photoproduction, but our results are consistent with the reaction mechanism suggested by Pos et al. (1998). Incubation experiments at environmentally relevant sulfide concentrations, as well as *p*-DOS relationships across different temperature and DOM regimes will help to resolve this issue.

We have corrected the spelling mistake.

## References

Catalá, T. S., Reche, I., Fuentes-Lema, A., Romera-Castillo, C., Nieto-Cid, M., Ortega-Retuerta, E., Calvo, E., Álvarez, M., Marrasé, C., Stedmon, C. A., and Álvarez-Salgado, X. A.: Turnover time of fluorescent dissolved organic matter in the dark global ocean, *Nature Communications*, 6, 5986, 10.1038/ncomms6986

<https://www.nature.com/articles/ncomms6986#supplementary-information>, 2015.

Cawley, K. M., Butler, K. D., Aiken, G. R., Larsen, L. G., Huntington, T. G., and McKnight, D. M.: Identifying fluorescent pulp mill effluent in the gulf of maine and its watershed, *Marine Pollution Bulletin*, 64, 1678-1687, 2012.

Cutter, G. A., and Radford-Knoery, J.: Carbonyl sulfide in two estuaries and shelf waters of the western north atlantic ocean, *Marine Chemistry*, 43, 225-233, [http://dx.doi.org/10.1016/0304-4203\(93\)90228-G](http://dx.doi.org/10.1016/0304-4203(93)90228-G), 1993.

Cutter, G. A., Cutter, L. S., and Filippino, K. C.: Sources and cycling of carbonyl sulfide in the sargasso sea, *Limnology and Oceanography*, 49, 555-565, 2004.

Fischer, T., Kock, A., Arévalo-Martínez, D. L., Dengler, M., Brandt, P., and Bange, H. W.: Gas exchange estimates in the peruvian upwelling regime biased by multi-day near-surface stratification, *Biogeosciences*, 16, 2307-2328, 10.5194/bg-16-2307-2019, 2019.

Jørgensen, L., Stedmon, C. A., Kragh, T., Markager, S., Middelboe, M., and Søndergaard, M.: Global trends in the fluorescence characteristics and distribution of marine dissolved organic matter, *Marine Chemistry*, 126, 139-148, 2011.

Lennartz, S. T., Marandino, C. A., von Hobe, M., Cortes, P., Quack, B., Simo, R., Booge, D., Pozzer, A., Steinhoff, T., Arevalo-Martinez, D. L., Kloss, C., Bracher, A., Röttgers, R., Atlas, E., and Krüger, K.: Direct oceanic emissions unlikely to account for the missing source of atmospheric carbonyl sulfide, *Atmos. Chem. Phys.*, 17, 385-402, 10.5194/acp-17-385-2017, 2017.

Osburn, C. L., Wigdahl, C. R., Fritz, S. C., and Saros, J. E.: Dissolved organic matter composition and photoreactivity in prairie lakes of the us great plains, *Limnology and Oceanography*, 56, 2371-2390, 2011.

Pos, W. H., Riemer, D. D., and Zika, R. G.: Carbonyl sulfide (ocs) and carbon monoxide (co) in natural waters: Evidence of a coupled production pathway, *Marine Chemistry*, 62, 89-101, [http://dx.doi.org/10.1016/S0304-4203\(98\)00025-5](http://dx.doi.org/10.1016/S0304-4203(98)00025-5), 1998.

Uher, G., and Andreae, M. O.: Photochemical production of carbonyl sulfide in north sea water: A process study, *Limnology and Oceanography*, 42, 432-442, 1997.

von Hobe, M., Najjar, R. G., Kettle, A. J., and Andreae, M. O.: Photochemical and physical modeling of carbonyl sulfide in the ocean, *Journal of Geophysical Research*, 108, 10.1029/2000jc000712, 2003.

Weiss, P. S., Andrews, S. S., Johnson, J. E., and Zafiriou, O. C.: Photoproduction of carbonyl sulfide in south pacific ocean waters as a function of irradiation wavelength, *Geophysical Research Letters*, 22, 215-218, 1995.

Zepp, R. G., and Andreae, M. O.: Factors affecting the photochemical production of carbonyl sulfide in seawater, *Geophysical Research Letters*, 21, 2813-2816, 10.1029/94gl03083, 1994.

Zhang, L., Walsh, R. S., and Cutter, G. A.: Estuarine cycling of carbonyl sulfide: Production and sea-air flux, *Marine Chemistry*, 61, 127-142, 1998.