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CS₂ Cycling in Seawater: Dark Production and UV Light Driven Consumption

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Key Points:

- Carbon disulfide in seawater is degraded by UV light at time scales of days
- Carbon disulfide is produced in seawater without UV light at rates comparable to photochemical production
- Carbon disulfide dark production is limited by dissolved organic sulfur

Supporting Information:

Supporting Information may be found in the online version of this article.

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Abstract Carbon disulfide (CS₂) has recently gained attention as an important precursor for the atmospheric trace gas carbonyl sulfide (OCS), which delivers sulfur to the stratospheric sulfur layer and impacts the radiative budget of the Earth. CS₂ is naturally produced in the ocean and emitted to the atmosphere. However, the magnitude of its marine emissions is only poorly constrained due to lacking understanding of its production and consumption processes. Here, we present incubation experiments with and without UV light treatment and provide evidence for a previously not considered UV-light-driven degradation process of CS₂ in seawater, following first-order kinetics. In addition to its already known photochemical production process, CS₂ production is found in the dark, depending on the amount of dissolved organic sulfur present in seawater. We provide novel production and consumption rates of CS₂ in seawater that pave the way toward mechanistically quantifying marine emissions of this important trace gas.

Plain Language Summary The gas carbon disulfide (CS₂) impacts the climate system of our planet as a precursor for sulfate aerosols. CS₂ is naturally produced in the ocean, but how much marine CS₂ is emitted to the atmosphere is not well known. In our study, we have experimentally derived production and degradation rates of CS₂ in seawater and found processes that have previously not been considered: CS₂ is degraded by UV radiation in seawater, and is produced in the absence of light. This dark production increases with the amount of dissolved organic sulfur in the water. Our results help to understand the production and degradation of CS₂ in seawater, which is needed to quantify its emissions to the atmosphere.

1. Introduction

The short-lived trace gas carbon disulfide (CS₂) is oxidized to carbonyl sulfide (OCS) in the atmosphere (Stickel et al., 1993). Although its atmospheric mixing ratio is usually on the order of a few parts per trillion (ppt) (Khan et al., 2017; Lennartz et al., 2020), its contribution to the atmospheric budget of OCS is equal to or higher than direct marine emissions of OCS to the atmosphere, that is, 40–135 Gg S yr⁻¹ (Kettle et al., 2002; Whelan et al., 2018). CS₂ has recently gained attention as a precursor of OCS, because a missing source of 400–800 Gg S yr⁻¹ in the atmospheric budget of OCS was identified (Berry et al., 2013; Glatthor et al., 2015; Kuai et al., 2015; Suntharalingam et al., 2008). This missing source hampers our understanding on the temporal evolution of the stratospheric aerosol layer, to which OCS, and thus indirectly also CS₂, deliver sulfur and which impacts the radiative budget of the Earth by increasing Earth's albedo (Kremser et al., 2016). In addition, OCS has been suggested as a promising proxy for terrestrial gross primary production, but uncertainties in oceanic emissions of OCS, and its precursors CS₂ and dimethylsulfide, currently prevent the application of this proxy on a global scale (Whelan et al., 2018). Inverse atmospheric modeling studies rely on an accurate quantification of sources and sinks of CS₂ in this regard (Cartwright et al., 2023; Glatthor et al., 2015; Kuai et al., 2015; Stinecipher et al., 2022). However, production and consumption processes of CS₂ in seawater are not sufficiently understood to quantify its global emissions (Kettle et al., 2002; Lennartz et al., 2021). Uncertainties of marine emissions of CS₂ are as high as current emission estimates (Whelan et al., 2018).

CS₂ is photochemically produced by UV light and chromophoric dissolved organic matter (CDOM, (Gharehveran & Shah, 2018; Xie et al., 1998)). An apparent quantum yield of about a fourth of that of OCS has been reported for the Pacific Ocean (Xie et al., 1998), but this ratio seems to vary across space and time (Lennartz et al., 2019, 2021). Specific precursor molecules like cysteine and cysteine have been identified (Gharehveran & Shah, 2018; Xie et al., 1998). However, given the huge diversity of organic compounds in seawater (Zark & Dittmar, 2018) and the petagram inventory of marine dissolved organic sulfur (Ksionzek et al., 2016), the precursor pool

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presumably comprises a range of different molecules. Dissolved organic sulfur is photosensitive and exhibits considerable alteration under UV light treatment (Gomez-Saez et al., 2017). Whether or not CS₂ is also produced by a light-independent production pathway, like the structurally similar molecule OCS (von Hobe et al., 2001), is unknown. Previous studies show ambiguous results with (Gharehveran & Shah, 2018) and without (Xie et al., 1998) production in the dark. Here, we are testing the hypothesis whether such a light-independent production process occurs.

Sink processes are also not well constrained. Except for the emission to the atmosphere, the only known sink process for CS₂ in seawater is hydrolysis, which equates to a theoretical lifetime of about 2 years (Elliott, 1990). Due to this long lifetime in comparison to the lifetime of a few days due to air-sea exchange, hydrolysis rates have been neglected in previous model approaches that quantified marine CS₂ emissions (Kettle, 2000; Lennartz et al., 2019). In short-term (2–4 days) incubation experiments in the dark, no loss process was detected, but since these experiments were not performed with isotopically labeled CS₂, a concurrent production cannot be excluded (Kim & Andreae, 1987; Shooter et al., 1992). However, an additional, but so far unknown, first-order sink process was needed in a modeling study for an Atlantic transect cruise (AMT7) to reproduce CS₂ observations (Kettle, 2000). CS₂ is known to be photosensitive (Nicholes et al., 1936). Here we test the hypothesis that such a photodegradation process occurs in seawater at time scales significant for marine cycling, that is, days.

In this study, we present controlled incubation experiments in which we quantify production and consumption rates of CS₂ in seawater as well as their dependency on UV light and chemical properties of DOM separately. We test two hypotheses: First, to test whether there is a light-driven degradation process, we incubate isotopically labeled CS₂ (¹³CS₂) to determine gross degradation rates. Second, we assess whether a light-independent, “dark” production process occurs. By incubating natural extracts of marine DOM instead of specific precursors, we move toward a more environmentally relevant setting.

2. Materials and Methods

Incubation experiments were carried out in a custom-made UV photoincubator as described in Miranda et al. (2020). The photoincubator was equipped with 8 UVA lamps (Q-Lab Co. Saarbrücken, Germany) with a spectrum of 280–365 nm and a spectral peak at 340 nm (24 W/m² UVA). These light conditions have been found to simulate natural UV light conditions and represent the light spectrum most relevant for alteration of DOM (Mopper & Kieber, 2000; Stubbins et al., 2008, 2010). Incubations were performed in vessels of ca. 200 mL made of quartz glass for light treatments and borosilicate glass wrapped in aluminum foil for dark treatments. Light conditions were constant during the experiment, that is, no diel cycles, in order to obtain reaction rate constants and reaction rates in stable conditions. Temperature of the water bath was 21.5 ± 0.9°C (lower initial ¹³CS₂), 22.76 ± 0.3°C (higher initial ¹³CS₂) and 19.2 ± 1.2°C for the production rate experiment (Hobo, Melbourne, Australia).

Degradation rate experiments were performed with artificial seawater spiked with ¹³CS₂. Two different initial ¹³CS₂ concentrations were used to test for reaction kinetics. MilliQ water was mixed with salt (Pro-Reef Sea Salt, Tropic Marine, Switzerland, 35 g L⁻¹) and spiked with 5 (lower initial ¹³CS₂) or 10 (higher initial ¹³CS₂) μL of a solution of ¹³CS₂ in ethylene glycol (1 mmol L⁻¹). The absorption coefficient of ethylene glycol at the incubated concentration is negligible (Figure S1 in Supporting Information S1). Incubation vessels were filled without headspace to exclude loss to the gas phase. Samples were taken after 0, 4, 24, 72, 144, and 196 (referred to as t0–t5) hours and immediately stored in cool and dark conditions to preserve concentrations of the sampling time point until further analysis (<10 hr). At sampling times, two or three incubation vessels were sacrificed and from each, three 60 mL samples were filled directly into glass vials without headspace and crimped gas tight. The degradation rate experiment, t0 and t5 of the production rate experiment were sampled in experimental triplicates, t1–t4 of production rate experiments in duplicates.

Production rate experiments were performed similarly, except that artificial seawater was spiked with natural extracts of dissolved organic matter (DOM). These extracts were taken from three different regions of the ocean, to cover a large natural variability (Table S1 in Supporting Information S1): deep Pacific Ocean (674 m, North Equatorial Pacific Intermediate Water), surface Pacific Ocean (21 m), both from Natural Energy Laboratory of Hawaii Authority (NELHA; www.nelha.org) on the island of Hawaii, USA, near Kailua-Kona (19°44′N, 156°04′W) and North Sea porewater (German Wadden Sea, 53°44′N, 7°43′E). Pacific extracts are the same as described in Green et al. (2014), North Sea pore water has been taken at the same location and by the same method

as described in Seidel et al. (2014). Methanol extracts were obtained via solid phase extraction (Dittmar et al., 2008), remaining methanol was evaporated by aeration with N₂ gas and dried extracts were redissolved into MilliQ water. This method allowed for controlled conditions, because extraction efficiencies of 90%–100% of the redissolved extracts could be obtained. In addition, pure MilliQ water was incubated as a blank, and pure artificial seawater was incubated as a negative control. A carryover of living microorganisms from natural seawater during extraction is very unlikely, as DOM is extracted over PPL cartridges in methanol (Dittmar et al., 2008) and stored at −18°C before the methanol is evaporated and extracts are redissolved in artificial seawater.

Solid-phase extractable dissolved organic sulfur (SPE-DOS) was measured for all incubated extracts using ICP-OES (iCAP 6000, Thermo Fisher Scientific GmbH, Bremen, Germany). A specific volume, estimated according to findings by Gomez-Saez et al. (2017, 2021), of each methanol extract was dried in 1.5 mL precombusted (450°C, 4 hr) glass vials at 50°C and redissolved in 1 mL of 2% nitric acid (Suprapure). Analytical precision and accuracy, both better than 5%, were tested with in-house reference material. The dissolved organic carbon (DOC) concentration of the extracts (SPE-DOC) was measured by high temperature catalytic oxidation on a Shimadzu TOC-VCPH instrument. A subsample of each extract (max. 100 μL) was evaporated in 15 mL precombusted (450°C, 4 hr) glass vials at 50°C. The dry extract was then redissolved in 10 mL of acidified ultrapure water (final concentration 2% HCl, Suprapure). The analytical precision and accuracy of the DOC analyses were checked in each run using deep Atlantic seawater reference material (DSR, Florida Strait, 700 m, D. Hansell, USA) and ranged from 3% to 5%.

CS₂ was measured with a purge-and-trap system attached to a gas chromatograph and mass spectrometer (GC-MS; Agilent 7890A, Agilent 5975C; inert XL MSD with triple axis detector) running in single-ion mode (Lennartz et al., 2017). The 50 mL samples were purged for 15 min with helium (80 mL min^{−1}) and dried with a Nafion® membrane drier (Gasmeter Perma Pure). CS₂ was trapped with liquid nitrogen for preconcentration and subsequently injected into the GC-MS using boiling water to heat the trap. The retention time for both CS₂ ($m/z = 76, 78$) and ¹³CS₂ ($m/z = 77, 79$) was 4.9 min. A gravimetrically prepared liquid CS₂ standard in ethylene glycol was used for calibration at each day of measurement. The limit of detection was 1 pmol L^{−1} using a sample volume of 50 mL.

3. Results and Discussion

3.1. Loss Rates of CS₂

Degradation rate experiments revealed a light driven consumption process of CS₂. While concentrations did not change significantly in both experiments in the dark treatment (Pearson's correlation, $p \gg 0.5$), ¹³CS₂ concentrations in the light treatment declined significantly (Pearson's correlation, $p = 0.0016$ for lower initial ¹³CS₂ concentration, $p = 0.0009$ for higher initial ¹³CS₂ concentration) (Figure 1). For photodegradation at constant light levels, an exponential decay following a first-order reaction is expected. Hence, we fitted a degradation rate constant k in the equation for each light treatment time series separately (Figure 1, Table S3 in Supporting Information S1):

$$[CS_2](t) = [CS_2]_{t_0} \cdot \exp(-k \cdot t) \quad (1)$$

¹³CS₂ concentrations declined with a similar rate constant of $0.00348 \pm 0.001 \text{ hr}^{-1}$ (higher initial ¹³CS₂ concentration) and $0.00351 \pm 0.0008 \text{ hr}^{-1}$ (lower initial ¹³CS₂ concentration), that is, on average 0.0035 hr^{-1} . This degradation rate constant has been derived from measurements of isotopically labeled ¹³CS₂, so that any systematic bias due to concurrent production of CS₂ can be excluded. The rate constant therefore describes the gross degradation of CS₂ under UV light. It equates to a lifetime $[1/k]$ of ca. 12 days under constant irradiation. Diel cycles of UV light in the surface ocean would increase the lifetime by a factor of ca. 3, assuming a sinusoidal light curve and a day length of 12 hr.

CS₂ has known absorption bands in the UV spectrum, from 180 to 230 nm and 280–360 nm (Zhang et al., 2021), and is photodegraded in the gas phase (Nicholes et al., 1936). In the few studies that discuss marine cycling of CS₂, a photochemical sink has never been explicitly included (Kettle, 2000; Kettle et al., 2001; Lennartz et al., 2019, 2021). Here we show that photochemical degradation in seawater is a significant process on time scales of days to weeks, depending on the location and light conditions. This degradation time scale is much faster than the 2 years lifetime of CS₂ hydrolysis (Elliott, 1990) and on a similar order of magnitude as a constant

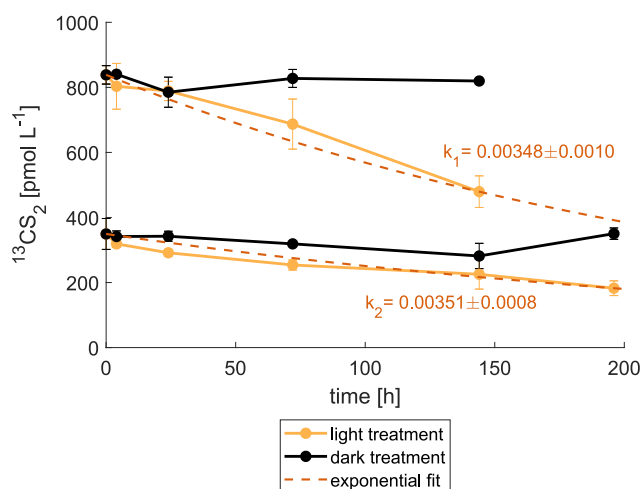


Figure 1. Time series of incubation experiments with different initial $^{13}\text{CS}_2$ concentrations and light and dark treatment. Error bars indicate standard deviation of triplicates. Red dashed line shows exponential fit for light treatments, with k_1 and k_2 indicating the respective fitted degradation rate constant \pm confidence interval. Data in Table S2 in Supporting Information S1.

first-order sink processes (9–13 days) needed in a modeling study by Kettle (2000) to reproduce observations. In that modeling study, Kettle fitted a model including air-sea exchange and photochemical production to time series measurements along an Atlantic cruise track, but had to invoke an additional first order degradation process in order to fit the model to the observed data. Whether or not photodegradation fully explains the missing degradation cannot be concluded based on our findings, but it most likely contributed to this unknown sink process.

In our experiments, we could not detect a significant degradation process in the dark treatments. This, however, does not rule out that potentially microbial driven processes may occur in natural seawater, as our experiments were carried out using artificial seawater only.

3.2. Production Rates of CS_2

The overall time series of CS_2 concentrations in the production rate experiments was qualitatively similar for all extracts (Figure 2): CS_2 concentrations increased steeply within the first day (t0-t1), and leveled off toward the end of the experiment. CS_2 concentrations in the light treatments were higher than in the dark treatment after 4 hours for each extract. However, after 6 days, this trend was reversed in all extracts, and CS_2 concentrations in the dark treatments were always higher.

The time point at which CS_2 concentrations in the dark treatment exceeded those in the light treatments differed: In the Pacific deep and surface DOM treatment, CS_2 concentrations in the dark were already higher than in the light treatment after 24 hr, whereas CS_2 concentrations in the North Sea porewater extracts showed this reversal only after 5 days.

Reaction rates have been calculated for a net production rate (change in concentration per hour) (Figures 3a and 3c). From this, the dark production rate was subtracted and CS_2 lost to photochemical degradation was added to the light treatment, to obtain the gross photochemical and light-independent production rates separately (Figures 3c and 3d). This calculation, however, relies on the assumption that light and dark reactions do not compete, but are additive. Hence, the gross photochemical production rate calculated here is a theoretical lower limit.

Photochemical production rates dominate at the beginning of the experiment (Figures 3a and 3b). When averaged over the whole duration of the experiment, dark production rates dominate (Pacific deep and surface), or are in the same range as photochemical production rates (North Sea porewater) (Figure 3d). These findings indicate that photochemical production is a faster process than dark production, but its intensity may decrease after the organic matter has been exposed to UV light, for example, due to the DOM becoming photobleached.

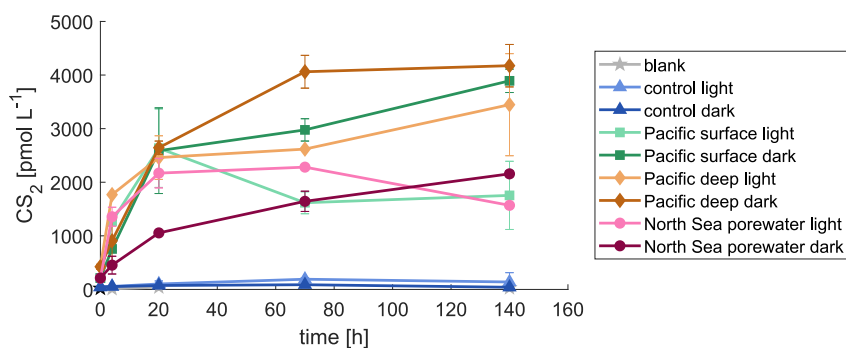


Figure 2. Time series of the CS_2 incubation experiment with natural DOM extracts. Dashed lines and triangle markers show dark treatment, solid lines and circles show UV light treatment. Error bars indicate standard deviation. Data in Table S4 in Supporting Information S1.

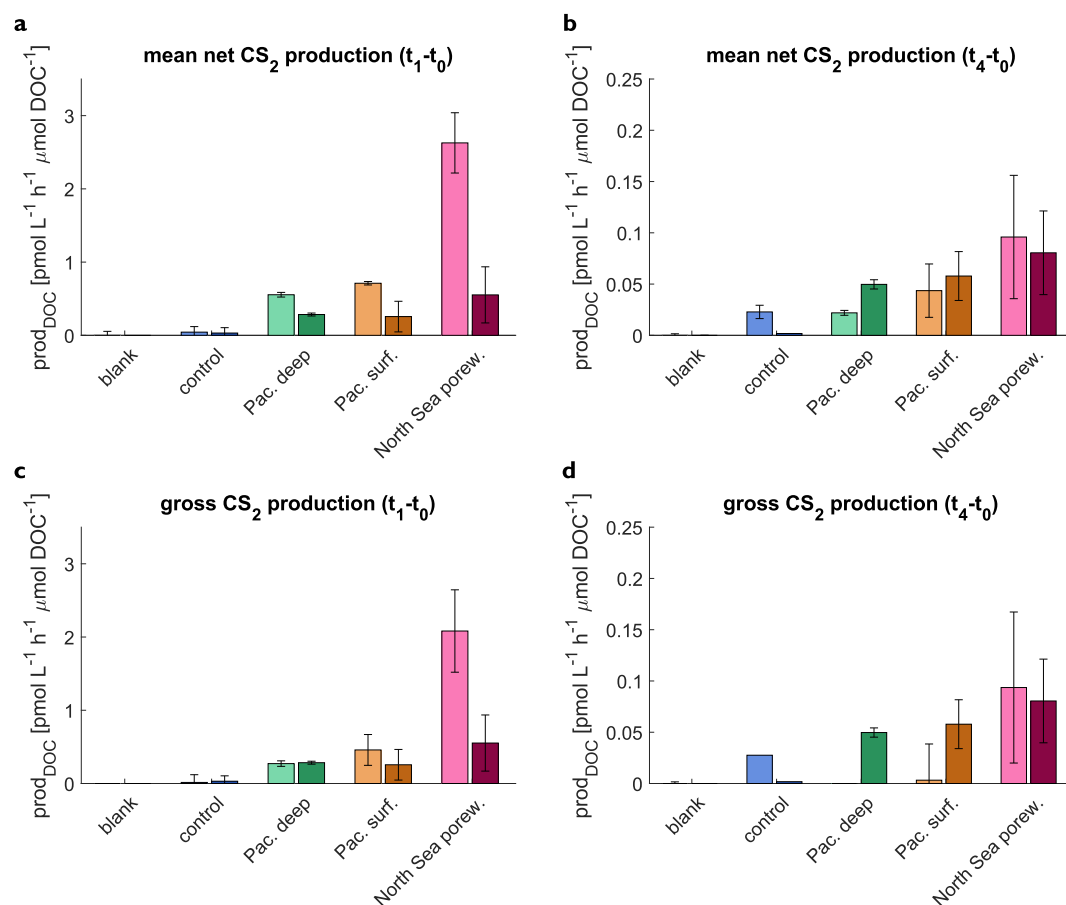


Figure 3. Average UV-light-dependent (light treatment, bright colors) and UV-light-independent (dark treatment, dark colors) production rates of CS₂ for natural dissolved organic matter extracts normalized to DOC content. (a) Net production rates, that is, change in concentration light (bright colors) and dark treatments (dark colors) for the first 4 hr of the experiment (sampling t₁ and t₀). Panel (b) same as (a) but for the total duration of the experiment. (c) Photochemical production (bright colors) and dark production (dark colors) separated by subtracting the dark production rate from the light treatment and adding the light loss, for the first 4 hr of the experiment. Panel (d) same as (c) but for the total duration of the experiment. Data in Table S5 in Supporting Information S1.

Our results are in line with previous studies, but provide the first assessment of gross rates because they are the first using isotopically labeled CS₂. The dark control of a previous irradiation experiment showed only marginal increases of CS₂ concentrations, but in light of the process rates determined here, their irradiation time of 100 min might have been too short to detect dark production of CS₂ (Xie et al., 1998). In another study in which natural water samples were spiked with cysteine and irradiated for 12 hr, dark controls showed an increase in CS₂ concentration, confirming our findings of a light-independent production of CS₂ (Gharehveran & Shah, 2018).

The absolute maximum CS₂ concentrations reached during the experiment differed among extracts, with highest CS₂ concentrations in the Pacific deep extract followed by the Pacific surface extract and the North Sea porewater extract (Figure 2). The treatments differed in the amount of natural extract incubated. When normalized to the measured DOC concentration in the light treatment, this ranking results in highest CS₂ concentrations per μmol DOC in the North Sea pore water (28.1 pmol CS₂ L⁻¹ (μmol DOC L⁻¹)⁻¹ at t₂), followed by the Pacific surface (7.9 pmol CS₂ L⁻¹ (μmol DOC L⁻¹)⁻¹ at t₂) and finally the Pacific deep extract (3.9 pmol CS₂ L⁻¹ (μmol DOC L⁻¹)⁻¹ at t₂). Maximum concentrations followed the same ranking in light and corresponding dark treatments (27.8, 9.4 and 8.6 pmol CS₂ L⁻¹ (μmol DOC L⁻¹)⁻¹ at t₄).

The difference in maximum CS₂ concentrations suggests that production rates depend on the composition of the DOM. Production rates were tested for their dependency on organic matter properties such as DOC, SPE-DOS and absorption coefficient for CDOM (Table S6 in Supporting Information S1). The absorption coefficient for

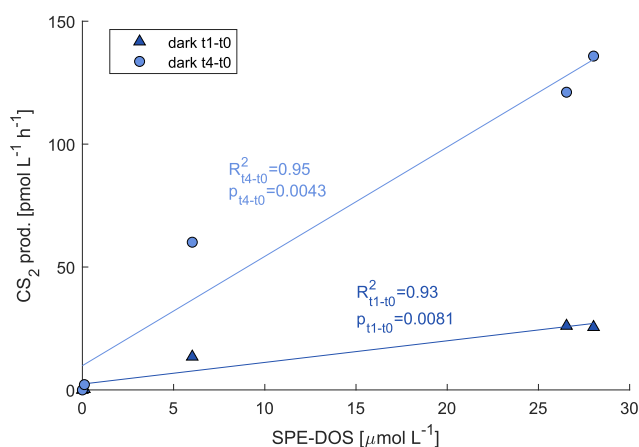


Figure 4. Correlation of CS₂ dark production rates with solid-phase extractable dissolved organic sulfur (SPE-DOS). Statistics for Pearson's correlation coefficient are given in respective color for the complete duration of the experiment (t0–t4 in light blue) and the first 4 hr (t0–t1 in dark blue). Note that these production rates have not been normalized to DOC, as they are correlated here with SPE-DOS.

CDOM was not significantly correlated with photochemical production rates ($p \gg 0.05$). This finding is surprising, because the absorption coefficient of CDOM at 350 nm correlates well with the dark and photochemical production rate of the structurally similar molecule OCS (von Hobe et al., 2001, 2003), and is therefore used as a proxy for global modeling studies (Lennartz et al., 2021). The results from this incubation experiment suggest that a more suitable proxy should be chosen for CS₂, and may explain the disagreement between global modeling approaches and observations which rely on CDOM as a proxy (Lennartz et al., 2021). The correlation with SPE-DOS for the calculated photochemical production rate is not significant ($p \gg 0.05$) and only explains 4% (t0–t1) respectively 37% (t0–t4) of the variance. This finding suggests that the precursor pool of photochemically produced CS₂ may be rather constrained to a few molecular functional groups, which is not captured by bulk DOC and SPE-DOS measurements.

The dark production rates significantly scale with the amount of DOC and SPE-DOS in the extracts (Figure 4). Hence, production of CS₂ in the dark seems to be limited by organic sulfur. Presumably, thiol groups or disulfide groups as in the known precursor molecules cysteine and its oxidized derivative cystine may form CS₂, and represent a major fraction of the organic sulfur pool. Such purely chemical reaction pathways proposed by Ghar-

hveran and Shah (2018) are in line with our observations. Additional biotic processes may occur in the ocean (Xie et al., 1999), but have not been in the focus of this study, in which purely artificial seawater was used. The finding that dark production rates correlate with organic sulfur, while photochemical rates do not, suggests that both reactions have different precursor molecules, that is, photochemical production may need more specific precursors than dark production. This finding indicates that different reaction pathways to form CS₂ may occur in the light and in the dark.

4. Conclusions

We provide evidence for a UV-light-driven degradation process of CS₂ in seawater, and show that a previously not considered light-independent production process occurs on magnitudes similar to the photochemical production pathway. Both processes have implications for estimating marine emissions with dynamical models.

Since photochemical production and degradation are co-occurring, photodegradation can be seen as an attenuation of the photoproduction. However, the processes do not depend on the same environmental parameters, that is, photoproduction depends on the composition of DOM whereas the degradation most likely does not. Hence, the attenuation of the photoproduction rate by photodegradation will vary in space and time. UV light exposure at the Earth's surface is highest in low latitudes, and penetrates deepest in the clear water of the subtropical gyres (Vasilkov et al., 2001). CDOM, as a proxy for optically active substances that may undergo photochemical reactions and produce CS₂, shows lowest concentrations in subtropical gyres. Based on our findings, we would expect relatively larger photodegradation in subtropical gyres compared to, for example, tropical upwelling regions with high UV light exposure and high CDOM, where photoproduction is expected to outweigh photochemical degradation. We provide evidence for the significance of the process and a first rate constant for specific physicochemical conditions, which may become refined in the future if dependence on other physicochemical conditions in the ocean become evident. Future studies should assess such dependencies, for example, on temperature dependence, which has been reported for the photochemical degradation of DOM (Porcal et al., 2015).

Our results also show that the light-independent production of CS₂ in seawater is a process that could be ubiquitously present in the ocean. While we provide a first quantitative correlation between dark production rates and organic sulfur content, the low global data coverage of dissolved organic sulfur makes a direct implementation into global numerical models to assess marine emissions of CS₂ difficult at this time. Along an oceanic transect, Ksionzek et al. (2016) report highest concentrations of SPE-DOS in tropical regions, and a depth gradient with decreasing SPE-DOS concentration below 200 m depth. Based on the results shown here, we expect a similar pattern for the dark production rates of CS₂. With a light-independent production process that may occur ubiquitously in the ocean, the existence of a concurrent, dark loss process becomes likely, although we could not detect

such a process in our artificial seawater incubations at a time scale of a week. However, without such a concurrent dark loss process, CS₂ concentrations would accumulate over time in the deep ocean. Such an accumulation has not been observed (Lennartz et al., 2020). Our experiments here do not allow conclusions about biotic processes. Hence, future studies would need to assess whether CS₂ might be degraded biologically. CS₂ serves as a substrate for several strains of bacteria, but can also be toxic (Jordan et al., 1995; Kiene, 1996; McDonald et al., 1997; Smeulders et al., 2013). Whether bacterial influence for the cycling of CS₂ is significant in the oxic water column remains to be tested, especially in the light of the projected decreasing marine oxygen concentrations in the future.

In summary, the hypothesis of photochemical degradation can be confirmed. A light-independent production rate was found to scale with SPE-DOS, and was at the same order of magnitude or higher than the photochemical production rate. Our results suggest that future modeling studies of CS₂ in the ocean need to take dark production and photochemical degradation into account in addition to photochemical production. The close link of CS₂ production to the organic sulfur content of DOM and its impact on stratospheric aerosol formation implies that the cycling of CS₂ critically depends on ocean biogeochemistry, suggesting potential feedback mechanisms in a changing climate.

Conflict of Interest

The authors declare no conflicts of interest relevant to this study.

Data Availability Statement

All underlying data, that is, measurements of CS₂ concentrations and DOC, are provided in Supporting Information S1 to this publication, and can be accessed at <https://doi.org/10.5281/zenodo.10684084> (Lennartz et al., 2024).

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