

Photoproduction of carbonyl sulfide in south Pacific Ocean waters as a function of irradiation wavelength

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Abstract. Carbonyl sulfide (OCS) photoproduction rates were measured at selected wavelengths of ultraviolet light between 297 and 405 nm in sea water samples from the southern Pacific Ocean. Near-surface and column production rate spectra for natural sunlit waters were calculated using sea-surface sunlight data measured near the austral summer solstice. These plots show that photoproduction rates are at a maximum at 313 nm in tropical waters and at 336 nm in Antarctic waters. Tropical surface and column rates were found to be 68 pM/day and 360 nmol/m²/day, respectively, and Antarctic surface and column rates were found to be 101 pM/day and 620 nmol/m²/day, respectively. A high degree of variability was observed between photoproduction rates from different ocean regions, with coastal rates being the highest, suggesting that natural environmental variability is an important factor. Photoproduction rates at 297 nm were found to be constant at individual locations with increasing irradiation time. Relative photoproduction rates from this work are compared to previously measured rates from coastal sea water.

Introduction

Carbonyl sulfide (OCS) is naturally present in the earth's atmosphere at an average concentration of 500 pptv and a residence time of greater than 1 year [Khalil and Rasmussen, 1984]. This long lifetime allows it to enter the stratosphere and act as the major non-volcanic source of stratospheric sulfate aerosols [Crutzen, 1976]. Considerable research has focused on the role of these stratospheric aerosols in enhancing ozone destruction through heterogeneous chemistry with chlorine and nitrogen species [Rodriguez *et al.*, 1991; Hofmann and Oltmans, 1992; Solomon *et al.*, 1993]. Presently, the proposed atmospheric budget for OCS is quite unbalanced, with the total sources exceeding the total sinks by a factor of near 2 [Chin and Davis, 1993]. The oceans are believed to be an important source of atmospheric OCS [Andreae and Ferek, 1992], but the magnitude is still uncertain (0.16–0.64 Tg OCS/yr, or 20–40% of total flux) [Chin and Davis, 1993].

OCS is produced in marine surface waters from photolysis of dissolved organic material (DOM) [Ferek and Andreae, 1984]. Zepp and Andreae [1990] have postulated that OCS formation

results from DOM chromophores acting as photosensitizing agents in the oxidation of dissolved organic sulfur (DOS) compounds. Since photosensitized reactions are generally more rapid in coastal waters than in the open ocean, their results may explain why dissolved OCS concentrations are usually highest in coastal, sunlit waters. However, photoproduction rates of OCS from open ocean waters have not previously been reported.

We present here the first OCS action spectra measurements for surface waters of the open ocean. These data provide a basis for estimating total photochemical production rates under natural sunlight conditions. With the observed losses of stratospheric ozone, especially over the Antarctic region, a knowledge of the action spectra of OCS is essential for determining the enhancement of OCS production from increased UV-B flux to the surface ocean.

Experimental

Photoproduction rates were measured on a cruise aboard the NOAA Ship *Surveyor* during the '93-'94 austral summer (Figure 1). Surface water was sampled from the ship's "clean" seawater pumping system with an intake about 5 meters below the surface. Samples were taken only while underway to reduce

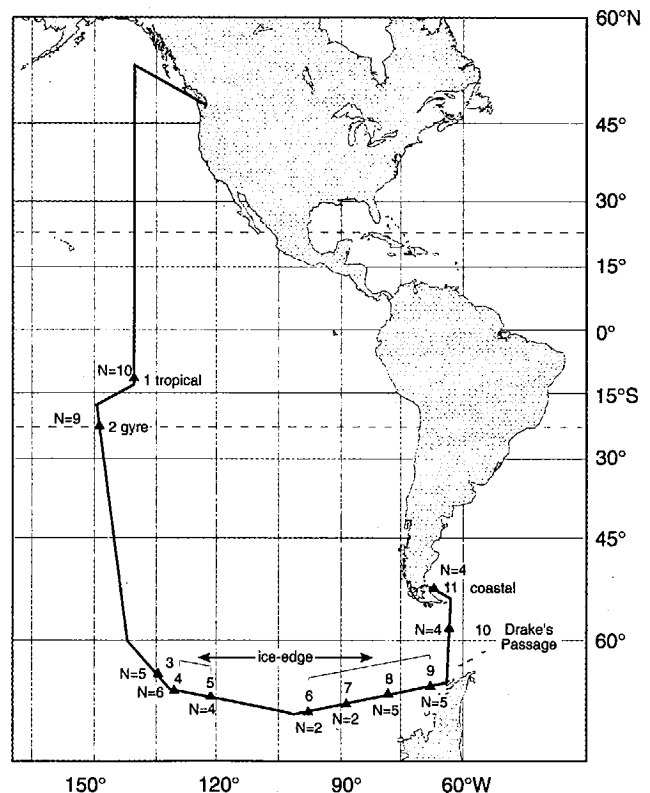


Figure 1. Cruise track of the NOAA Ship *Surveyor* from Seattle, Washington, USA to Punta Arenas, Chile (November 20, 1993 to January 7, 1994). Sampling locations are denoted by numbers and N refers to the number of samples taken at each location.

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Table 1. Photoproduction of OCS in Sea Water (mean \pm 1 σ)

Wavelength (nm)	N ¹	Production Rate (pM OCS/J/cm ²)	Relative Production Rate ²	Absorption Coefficient ³ (a_λ) (meter ⁻¹)	Quantum Yield ⁴
297	26	4.96 \pm 1.93	1.00	0.36 \pm 0.02	5.80e-7 \pm 2.26e-7
306	2	2.63 \pm 0.51	0.53	0.30 \pm 0.02	3.71e-7 \pm 0.72e-7
313	8	1.59 \pm 0.73	0.32	0.25 \pm 0.01	2.46e-7 \pm 1.13e-7
336	7	0.78 \pm 0.79	0.16	0.17 \pm 0.01	1.64e-7 \pm 1.66e-7
365	8	0.34 \pm 0.29	0.069	0.12 \pm 0.01	9.33e-8 \pm 8.02e-8
405	2	0.058 \pm 0.008	0.012	0.09 \pm 0.02	1.94e-8 \pm 0.26e-8

¹ N is the number of distinct samples irradiated at each wavelength.

² Relative production rate = prod. rate / prod. rate at 297 nm in pM/J/cm².

³ $a_\lambda = 2.303 A_\lambda / r$, where A_λ is absorbance and r is the pathlength in meters. a_λ was measured (mean \pm 1 σ , N = 6 for each λ) in the same water types but not the exact locations as samples taken for irradiations.

⁴ Quantum yield = μ mole OCS produced / μ einstein absorbed.

contamination by the ship. Irradiations were performed with a Spectral Energy 1-kW Monochromatic Illumination System with a mercury-xenon lamp and a monochromator with a 10.0 nm bandwidth. Samples were held in a gas-tight, cylindrical quartz cell with a 31-cm pathlength and a 2.2-cm inside diameter. Relative light intensity was measured with an International Light model IL1700 radiometer and corrected to absolute light doses by ferrioxalate actinometry [Hatchard and Parker, 1956]. Sea water absorption, referenced to Milli-Q water (Millipore Corp.), was measured on 0.2- μ m filtered water with a Hewlett-Packard model 8452A diode array spectrophotometer, using a 10-cm pathlength quartz cell. Spectra were corrected for refractive index effects by subtracting the average apparent absorption from 700 to 800 nm from each spectrum [Blough *et al.*, 1993; Green, 1992]. All samples were found to be optically thin with $A_{350\text{nm}} < 0.05 \text{ cm}^{-1}$ [Valentine and Zepp, 1993]. Sea surface light intensity was measured with a LI-1800UW spectro-radiometer (LI-COR, Inc.) at 2-nm intervals between 300 nm and 850 nm, with an 8-nm bandwidth, and also with an Epply radiometer.

Duplicate samples were analyzed without UV-irradiation to determine initial OCS concentrations; some irradiations were performed on sea water that was degassed with OCS-free air in a 1-liter sparging vessel. Degassed samples showed no significant difference in photoproduction versus unmodified sea water. Sample temperatures were initially between -1 and 28°C , and warmed during irradiations to near room temperature (15 – 29°C). Changes in photoproduction rates due to warming were assumed to be small based on Kieber *et al.* [1990]. Typical irradiation times were 30 min at 297 nm, 306 nm, and 313 nm, 60 min at 336 nm and 365 nm, and 12 hours at 405 nm. These wavelengths were selected for high energy output from the lamp.

Hydrolysis of dissolved OCS [Elliot *et al.*, 1987] did not significantly affect photoproduction rate measurements between 297 and 365 nm since irradiation times were 1 hour or less and OCS concentrations in dark control samples decreased by less than 10% ($< 1 \text{ pM}$) during this time. For the measurements at 405 nm (using degassed water only), it was necessary to subtract a significant concentration increase ($\sim 50\%$ of OCS concentration after irradiation) which occurred in the dark control samples after ~ 12 -hour incubations. The reason for this increase is unclear since there was no measurable room light below 415 nm. OCS production by a mechanism other than UV photolysis cannot be ruled out, however, on the basis of this study.

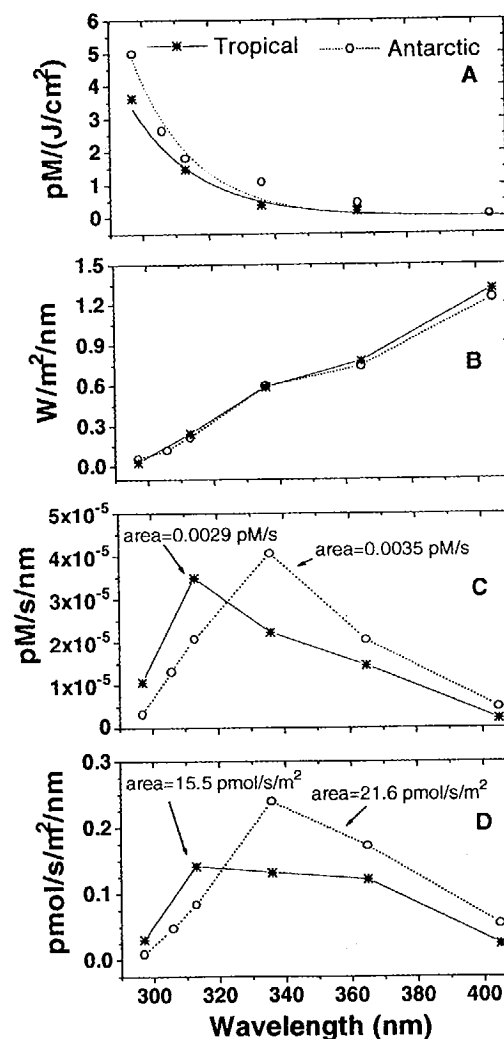


Figure 2. (A) Average action spectra of OCS in sea water from tropical (10° – 22°S) and Antarctic (58° – 70°S) regions, not including coastal data. Lines are exponential fits to the data (tropical: $y = 2.87e^{-(0.049)(x-300)}$, Antarctic: $y = 4.08e^{-(0.055)(x-300)}$). (B) Measured downward solar irradiance at the sea surface (tropical: local noon, 4°S , 19° zenith angle; Antarctic: local noon, 61°S , 38° zenith angle). (C) Surface production rate spectra with estimated areas under the curves. (D) Column production rate spectra with estimated areas under the curves. The points at 405 nm for the tropical curves in C and D are from the exponential fit data in (A).

Water samples were transferred by ground-glass syringe to a purge-and-trap system, described in detail by *Johnson and Harrison* [1986]. Differences in the present system include using about 12 ml of sample water, a stainless steel cold finger held at -40°C to dehydrate the sample, and a cryotrap loop filled with Porapak Q (80/100, Alltech). Condensed gases were then injected onto a gas chromatograph with an electron capture detector (VICI, 140BN), referred to as the electron capture sulfur detector (ECD-S). The instrument is described in detail in *Johnson and Lovelock* [1988] and *Johnson and Bates* [1993]; the operating temperature of the catalysts was lowered from 150°C to 40°C to improve the signal-to-noise ratio without loss of selectivity.

OCS levels ranged from 2 to 200 pM in irradiated samples where the ECD-S showed a linear response to standards of better than 96%. Standards were made by diluting a 512 ± 38 ppbv tank standard (Scott Specialty Gases) with OCS-free air, to make a secondary standard of about 1 ppbv OCS in dry air. The tank standard was calibrated using two permeation devices whose weight loss histories are known from bi-monthly weighings. The instrument blank was about 4% of the standard peak, or about 1 pM in a 12-ml water sample. Measurement accuracy was about 15% based on the permeation tube weight-loss data and the precision was about 15% based on the reproducibility of standard peak heights over a 1-day period.

Results and Discussion

Table 1 shows the mean of all measurements of photoproduction rates of OCS as a function of wavelength. Figure 2A is a plot of the average action spectra from tropical and Antarctic regions (on Figure 1, locations 1–2 and 3–10, respectively). These rates fall off approximately exponentially with increasing wavelength, as noted previously for OCS [*Zepp and Andreae*, 1990], CO [*Valentine and Zepp*, 1993] and formaldehyde [*Kieber et al.*, 1990]. Additionally, photoproduction rates from Antarctic waters are consistently higher than those from tropical waters. By normalizing these action spectra with available UV sunlight measured at local noon at the sea surface (Figure 2B), the result is the near-surface production rate spectra shown in Figure 2C. Note that in the tropics, production rates are at a maximum around 313 nm, whereas in Antarctic waters the maximum is closer to 340 nm. Figure 2D shows column production rate spectra that were obtained using quantum yields and assuming that all incident light is absorbed in the water column. Figure 2D represents an upper limit for production rates since in "blue waters" a significant fraction of the total absorption of light includes sea water absorption and backscattering of light out of the ocean. However, these curves do show that column integrated production rates are enhanced at longer wavelengths compared to surface rates.

To estimate daily near-surface and column photoproduction rates, it was assumed that 6.5 and 8 hours of noon sunlight at the tropical and Antarctic locations, respectively, were equivalent to an entire day's radiation. These times result from dividing the measured total insolation at each location by the maximum insolation intensity, occurring around local noon, depending on cloud cover. No corrections were made for high albedo at the sea-surface at large zenith angles, and the fact that a higher fraction of UV light is diffuse than that of the rest of the spectrum. However, to a first approximation, these effects will cancel, giving an estimate of tropical surface and column rates of 68 pM/day and 360 nmol/m²/day, respectively, and Antarctic

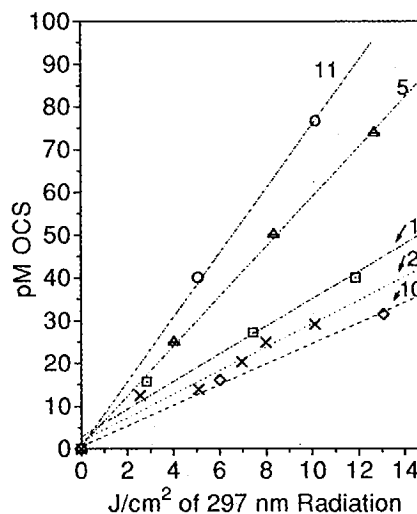


Figure 3. Photoproduction of OCS with 297 nm radiation in samples from five locations (see Figure 1). Linear fits to each sample set, with an origin point added, are also shown.

surface and column rates of 101 pM/day and 620 nmol/m²/day, respectively.

Photoproduction was measured on samples from different locations as a function of irradiation time, up to 75 minutes (Figure 3). Irradiation intensity remained constant during these studies. No significant departure from linearity was observed, indicating that only a small fraction of the DOS pool was being photolyzed and significant photobleaching was not occurring. The distinctly different slopes of the lines demonstrate the natural variability of OCS photoproduction rates. Note that the highest production occurred in the coastal sample, consistent with previous speculation [*Zepp and Andreae*, 1990]. Figure 4A shows action spectra from different locations plotted on a log scale to facilitate slope comparisons. Although the lines are offset from each other, the slopes are relatively constant, suggesting that photochemical mechanisms are similar between locations, and other factors such as OCS precursor concentrations are influencing production rates. Weak correlations between photoproduction rates and dissolved dimethyl sulfide and chlorophyll-*a* concentrations ($R^2 = 0.41$ and 0.46 , respectively), indicate that these species are not directly involved in OCS formation.

The average action spectrum from this work (data from Table 1) is compared to that for OCS from a coastal North Sea sample [*Zepp and Andreae*, 1990] in Figure 4B. An exponential fit to each data set gives log slopes of -0.017 and -0.048 nm^{-1} for this work and *Zepp and Andreae* [1990], respectively. Differences in DOM origins between the two works may explain this pronounced discrepancy. *Zepp and Andreae* [1990] collected samples in an area influenced by riverine inputs, rich in terrestrial DOM, whereas this work was dominated by measurements in open waters presumably containing mostly marine DOM. Because the two types of DOM are suspected to have very different photoresponses [*Mopper et al.*, 1991], this difference is not surprising. Further studies should focus on the dependence of action spectra on sampling site with the intention of understanding the number and origins of OCS-forming DOM pool(s) and their relationship(s) to the DOM pools involved in other photophysical (absorption, fluorescence) and photochemical processes.

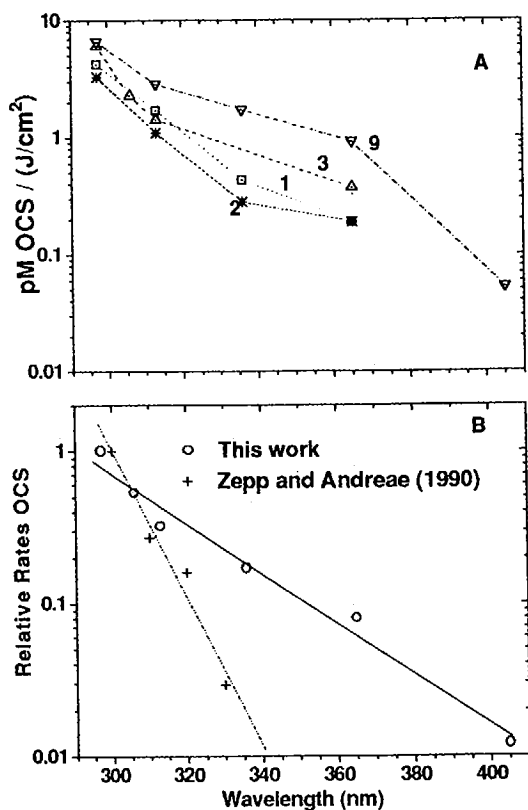


Figure 4. (A) Action spectra from four locations, denoted in Figure 1. (B) Action spectra expressed as relative production rates from this work compared to Zepp and Andreae [1990], with exponential fits. Absolute production rates were not reported in Zepp and Andreae [1990].

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