SENSITIVITY STUDIES OF COS PRODUCTION
IN THE OCEAN

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INTRODUCTION

Carbonyl Sulfide (COS) is the most abundant and longest lived sulfur gas in the atmosphere. COS is transported from the troposphere to the lower stratosphere where it is thought to be a major contributor to the sulfate aerosol layer (Crutzen 1976). This layer affects the radiative balance of the atmosphere (Turco et al, 1980) and may increase the destruction of stratospheric ozone.

The oceans are perhaps the largest single source of COS emissions to the atmosphere (Khalil and Rasmussen, 1984). According to Andreea and Ferek (1992) COS is produced by reactions involving UV light and dissolved organic matter (referred to as DOM). As the destruction of the ozone layer increases, more UV radiation will reach the ocean surface, possibly causing an increase in the amount of COS produced. This increased production of COS may cause the sulfate aerosol layer to increase and stratospheric ozone to decrease. Thus a possible positive feedback exists (Fig. 1).

The purpose of this project was to study the spectral distribution of COS production in the ocean and its sensitivity to various environmental parameters. Specifically, we investigated how spectral COS production varies with 1) the solar zenith angle, 2) the concentration of chlorophyll in the ocean, and 3) the amount of ozone in the atmosphere. Future work will also be discussed since all factors in COS production were not considered.
METHODS

The first step in the study was to determine the wavelength-dependant spectral dose rate, \( SD(\lambda) \), given in \( \text{mol m}^{-2} \text{s}^{-1} \text{nm}^{-1} \). \( SD(\lambda) \) was found by integrating the product of the action spectrum for COS production, \( A(\lambda) \), given in \( \text{mol m}^{-2} \text{quanta}^{-1} \), and the downwelling spectral irradiance \( E(z,\lambda) \) given in quanta \( \text{s}^{-1} \text{m}^{-2} \text{nm}^{-1} \) over depth:

\[
(1) \quad SD(\lambda) = \int A(\lambda)E(\lambda,z)dz.
\]

The action spectrum for COS production was obtained from measurements made by Zepp and Andreae (1990). Their data were fit with an exponential function using least squares (Fig 2), yielding the equation

\[
(2) \quad A(\lambda) = 3.3161 \times 10^{14} \cdot 10^{(-0.0048\lambda)},
\]

where \( \lambda \) has units of nm.

The downwelling spectral irradiance at depth was computed from the downwelling spectral irradiance just above the surface \( E_0(\lambda) \) using

\[
(3) \quad E(z,\lambda) = E_0(\lambda) \cdot e^{-k_t(\lambda)z},
\]

where \( k_t(\lambda) \) is the total diffuse attenuation coefficient given in
m$^{-1}$. In this formulation, reflection of downwelling irradiance has been ignored. The diffuse attenuation coefficient can be divided into components due to clear water ($k_o$), chlorophyll-like pigments ($k_c$), and dissolved substances ($k_d$) (Baker and Smith, 1982). Since little is known about the distribution of DOM in the ocean and its optical characteristics, the latter component will not be considered in this project. Thus

\begin{equation}
 k_e(\lambda) = k_o(\lambda) + k_c(\lambda).
\end{equation}

As cautioned by Baker and Smith (1982), this model does not include the effect of non-living particulate matter which may be important in waters affected by terrigenous inputs. Baker and Smith (1982) express the attenuation of light due to chlorophyll-like pigments as

\begin{equation}
 k_c(\lambda) = k_{c1}(\lambda) \cdot [\text{chl}] \exp[-k_{c2}^2(\lambda)(\log[\text{chl}] - \log[\text{chl}_o])^2]
 + 0.001 \cdot [\text{chl}]^2,
\end{equation}

where [chl$_o$] is constant at 0.50 mg m$^{-3}$ and chlorophyll is given in mg m$^{-3}$. The values for $k_o$, $k_{c1}$, and $k_{c2}$ were taken from Baker and Smith (1982) with the exception of the values in the range of 280 - 295 nm which were extrapolated from their data.

After integration the equation (from Eqn.1) for the spectral dose rate is

3
\[ SD(\lambda) = \left[ A(\lambda) \cdot E_0(\lambda) \right] / k_c(\lambda), \]

where \( E_0(\lambda) \) is the sum of the irradiance of the direct solar beam and the irradiance of downwelling diffuse light at a specific wavelength. These values were obtained from the UV atmospheric radiative transfer model of Madronich (1992). The equation for the spectral dose rate was added to this model, and three different sensitivity tests were run with two variables being held constant while the third changed over a given range at a set interval. In the first test the chlorophyll concentration was set to 1.0 mg m\(^{-3}\), the ozone column was set to 350.0 DU, and the zenith angle varied between 10.0° and 70.0° at 20.0° intervals. In the second test the ozone column remained at 350.0 DU, the zenith angle was set to 30.0° and the chlorophyll concentration varied between 0.0 and 5.0 mg m\(^{-3}\) at 1.0 mg m\(^{-3}\) intervals. This range was determined using a global plot of chlorophyll concentrations in the oceans (Fig. 3). In the third test the zenith angle remained at 30.0°, the chlorophyll concentration was reset to 1.0 mg m\(^{-3}\), and the ozone column varied between 250.0 DU and 450.0 DU at 50.0 DU intervals.

RESULTS

The results from the first test showed that as the zenith angle increased (as the sun moved closer to the horizon) the wavelength for peak COS production increased (Fig. 4). This is due to the fact that as the zenith angle increases, the shorter
wavelengths responsible for COS production reach the ocean surface with more difficulty than the longer wavelengths (Fig. 5).

The results from the second test showed that as the chlorophyll concentration increased, the overall COS production rate decreased. This is due to the fact that chlorophyll absorbs the UV light necessary for the production of COS. Also it was found that the wavelength of peak production remained the same. This is because spectral distribution of UV light attenuation varies very little with chlorophyll concentration.

The results from the third test showed that the wavelength of peak production increased with ozone (Fig. 6). This is due to the fact that ozone preferentially absorbs shorter wavelength UV light (Fig. 7).

FUTURE STUDIES

This study assumes that there is no reflection of light at the sea surface, therefore the consideration of this aspect of COS production is recommended. The downward spectral irradiance just below the sea surface can be computed from the downward spectral irradiance just above the sea surface from

\[
E(\phi^-, \theta, \lambda) = \tau(\theta) \cdot E_{\text{sun}}(0^+, \theta, \lambda) + \tau_d \cdot E_{\text{diff}}(0^+, \theta, \lambda),
\]

where \(\theta\) is the solar zenith angle, \(E_{\text{sun}}(0^+, \theta, \lambda)\) is the direct component of the downward spectral irradiance just above the sea
surface, and $E_{\text{diff}}(0^*,\theta,\lambda)$ is the diffuse component of the downward spectral irradiance just above the sea surface. $\tau(\theta)$ is the transmittance of the air-sea interface for direct (sun) radiation, and $\tau_d$ is the transmittance of the air-sea interface for diffuse (sky) radiation. $\tau_d$ was found by Preisendorfer (1976) to be a constant equal to 0.94. $\tau(\theta)$ can be computed using the Fresnel’s equation

\begin{equation}
\tau(\theta) = 1 - 1/2 \cdot [(\sin^2(\theta-\phi)/\sin^2(\theta+\phi)) \\
+ (\tan^2(\theta-\phi)/\tan^2(\theta+\phi))].
\end{equation}

Here $\phi$ is the angle of refraction given by Snell’s law:

\begin{equation}
\sin \phi = \sin \theta / n,
\end{equation}

where $n$ is the relative index of seawater. Since the dependence of $n$ on temperature, salinity, and wavelength is minimal, it can be assumed to be constant at 1.34.

**CONCLUSIONS**

The purpose of this project was to study the sensitivity of marine COS production to solar zenith angle, chlorophyll concentration, and atmospheric ozone over the wavelength range 280-400 nm. Within this range it was shown that as the sun approaches the horizon, the UV wavelength of peak COS production gets longer.
When the chlorophyll concentrations were increased, it was shown that the overall COS production rate decreased. However, the spectral distribution of COS production remained the same. Finally, when the amount of atmospheric ozone increased, it was shown that wavelength of peak COS production increased.
FIGURES

Figure 1. Possible positive feedback between COS production in the ocean and stratospheric ozone depletion.

Figure 2. Action spectrum for COS production. Squares are data of Zepp and Andreae (1990). Line is a least squares fit to data (Eqn. 2).

Figure 3. Global plot of average chlorophyll concentrations of a given month (arbitrary) over a ten year period.

Figure 4. Effect of solar zenith angle on spectral COS production.

Figure 5. Effect of solar zenith angle on downwelling spectral irradiance.

Figure 6. Effect of ozone column on spectral COS production.

Figure 7. Effect of ozone column on downwelling spectral irradiance.
Fig. 1
Fig. 4
Fig. 6
REFERENCES


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