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# PHOTOCHEMICAL PROCESSES

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## Introduction

Life on Earth is critically dependent on the spectral quality and quantity of radiation received from the sun. The absorption of visible light (wavelengths from 400 to 700 nm) by pigments within terrestrial and marine plants initiates a series of reactions that ultimately transforms the light energy to chemical energy, which is stored as reduced forms of carbon. This complex photochemical process, known as photosynthesis, not only provides all of the chemical energy required for life on Earth's surface, but also acts to decrease the level of a major greenhouse gas, $CO_2$, in the atmosphere. By contrast, the absorption of ultraviolet light in the UV-B (wavelengths from 280 to 320 nm) and UV-A (wavelengths from 320 to 400 nm) by plants (as well as other organisms) can produce seriously deleterious effects (e.g. photoinhibition), leading to a decrease in the efficiency of photosynthesis and direct DNA damage (UV-B), as well as impairing or destroying other important physiological processes. The level of UV-B radiation received at the Earth's surface depends on the concentration of ozone ($O_3$) in the stratosphere where it is formed photochemically. The destruction of $O_3$ in polar regions, leading to increased levels of surface UV-B radiation in these locales, has been enhanced by the release of man-made chlorofluorocarbons (CFCs), but may also be influenced in part by the natural production of halogenated compounds by biota.

These biotic photoprocesses have long been recognized as critical components of marine ecosystems and air–sea gas exchange, and have been studied extensively. However, only within the last decade or so has the impact of abiotic photoreactions on the chemistry and biology of marine waters and their possible coupling with atmospheric processes been fully appreciated. Light is absorbed in the oceans not only by phytoplankton and water, but also by colored dissolved organic matter (CDOM), particulate detrital matter (PDM), and other numerous trace light-absorbing species. Light absorption by these constituents, primarily the CDOM, can have a number of important chemical and biological consequences including: (1) reduction of potentially harmful UV-B and UV-A radiation within the water column; (2) photo-oxidative degradation of organic matter through the photochemical production of reactive oxygen species (ROS) such as superoxide ($O_2^-$), hydrogen peroxide ($H_2O_2$), the hydroxyl radical (OH) and peroxy radicals ($RO_2$); (3) changes in metal ion speciation through reactions with the ROS or through direct photochemistry, resulting in the altered biological availability of some metals; (4) photochemical production of a number of trace gases of importance in the atmosphere such as $CO_2$, CO, and carbonyl sulfide (COS), and the destruction of others such as dimethyl sulfide (DMS); (5) the photochemical production of biologically available low molecular weight (LMW) organic compounds and the release of available forms of nitrogen, thus potentially fueling the growth of microorganisms from a biologically resistant source material (the CDOM). These processes provide the focus of this article.

## Optical Properties of the Abiotic Constituents of Sea Waters

CDOM is a chemically complex material produced by the decay of plants and algae. This material, commonly referred to as gelbstoff, yellow substance, gilvin or humic substances, can be transported from land to the oceans by rivers or be formed directly in marine waters by as yet poorly understood processes. CDOM is the principal light-absorbing component of the dissolved organic matter (DOM) pool in sea waters, far exceeding the contributions of discrete dissolved organic or inorganic light-absorbing compounds. CDOM absorption spectra are broad and unstructured, and typically increase with decreasing wavelength in an approximately exponential fashion (**Figure 1**). Spectra have thus been parameterized using the expression [1].

$$a(\lambda) = a(\lambda_0)\cdot e^{-S(\lambda-\lambda_0)} \qquad [1]$$

$a(\lambda)$ and $a(\lambda_0)$ are the absorption coefficients at wavelength $\lambda$ and reference wavelength $\lambda_0$,

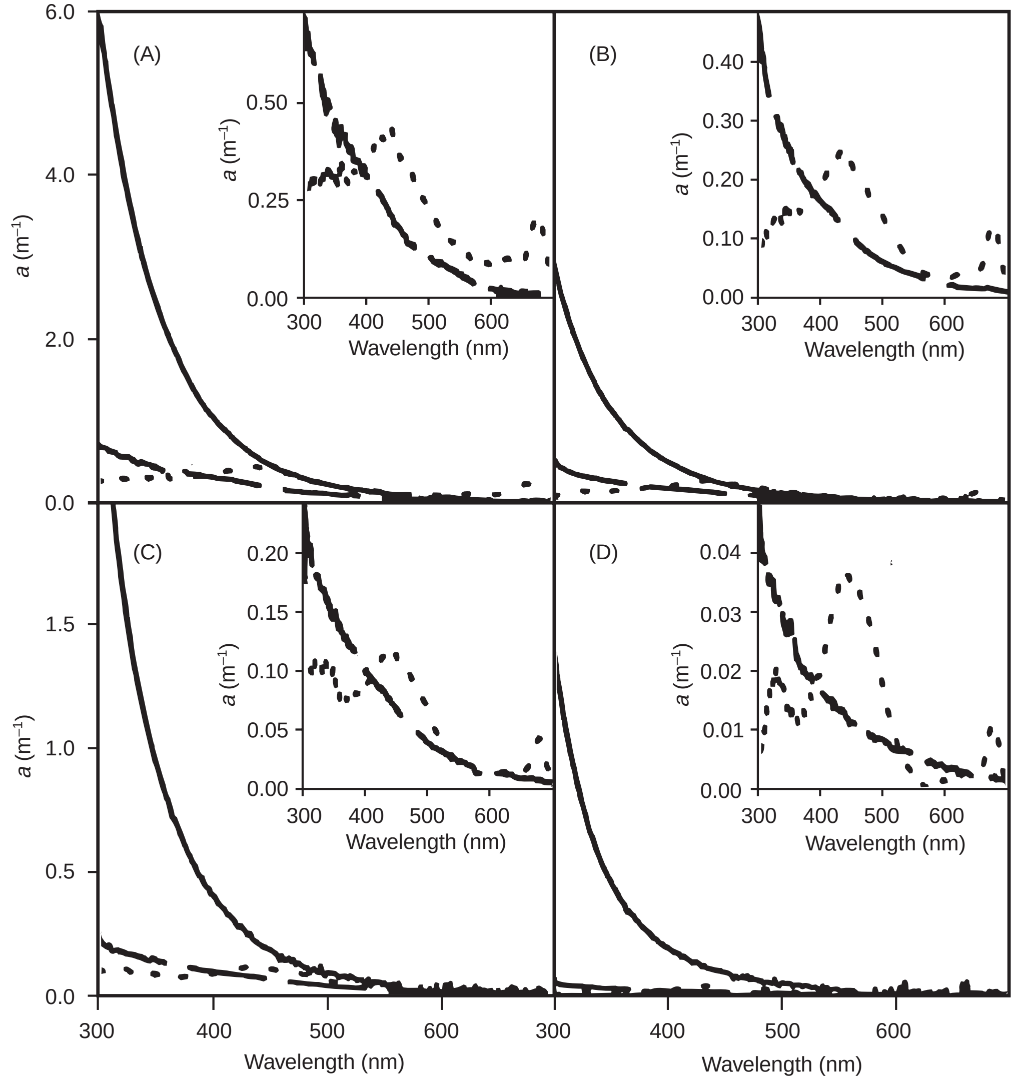

**Figure 1** Absorption spectra of CDOM ( — ), PDM (– – –) and phytoplankton (- - - -) from surface waters in the Delaware Bay and Middle Atlantic Bight off the east coast of the USA in July 1998: (A) mid-Delaware Bay at 39° 9.07′ N, 75° 14.29′ W; (B) Mouth of the Delaware Bay at 38° 48.61′ N, 75° 5.07′ W; (C) Mid-shelf at 38° 45.55′ N, 74° 46.60′ W; (D) Outer shelf at 38° 5.89′ N, 74° 9.07′ W.

respectively, and $S$ defines how rapidly the absorption increases with decreasing wavelength. Absorption coefficients are calculated from relation [2], where $A$ is the absorbance measured across pathlength, $r$.

$$a(\lambda) = \frac{2.303 \cdot A(\lambda)}{r} \qquad [2]$$

Due to the exponential increase of $a(\lambda)$ with decreasing $\lambda$, CDOM absorbs light strongly in the UV-A and UV-B, and thus is usually the principal constituent within marine waters that controls the penetration depth of radiation potentially harmful to organisms (**Figure 1**). Moreover, for estuarine waters and for coastal waters strongly influenced by river inputs, light absorption by CDOM can extend well into the visible wavelength regime, often dominating the absorption by phytoplankton in the blue portion of the visible spectrum. In this situation, the amount and quality of the photosynthetically active radiation available to phytoplankton is reduced, thus decreasing primary productivity and potentially affecting ecosystem structure. High levels of absorption by CDOM in these regions can also seriously compromise the determination of phytoplankton biomass through satellite ocean color measurements.

As described below, the absorption of sunlight by CDOM also initiates the formation of a variety of photochemical intermediates and products. The photochemical reactions producing these species ultimately lead to the degradation of the CDOM and the loss, or bleaching, of its absorption. This process can act as a feedback to alter the aquatic light field.

Particulate detrital material (PDM), operationally defined as that light-absorbing material retained on a GFF filter and not extractable with methanol, is a composite of suspended plant degradation products and sediment that also exhibits an exponentially rising absorption with decreasing wavelength (**Figure 1**); eqn [2] has thus been used to parameterize this material as well. However, the values of $S$ acquired for this material are usually smaller than those of the CDOM. In estuarine and near-shore waters, and in shallow coastal waters subject to resuspension of bottom sediments, PDM can contribute substantially to the total water column absorption. However, in most marine waters, the PDM is a rather minor constituent. Little is known about its photochemical reactivity.

Other light-absorbing trace organic compounds such as flavins, as well as inorganic compounds such as nitrate, nitrite, and metal complexes, do not contribute significantly to the total water column absorption. However, many of these compounds are quite photoreactive and will undergo rapid transformation under appropriate light fields.

## Photochemical Production of Reactive Oxygen Species

CDOM is the principal abiotic photoreactive constituent in marine waters. Available evidence suggests that the photochemistry of this material is dominated by reactions with dioxygen ($O_2$) in a process known as photo-oxidation. In this process, $O_2$ can act to accept electrons from excited states, radicals (highly reactive species containing an unpaired electron) or radical ions generated within the CDOM by the absorption of light. This leads to the production of a variety of partially reduced oxygen species such as superoxide ($O_2^-$, the one-electron reduction product of $O_2$), hydrogen peroxide ($H_2O_2$, the two-electron reduction product of $O_2$), peroxy radicals ($RO_2$, formed by addition of $O_2$ to carbon-centered radicals, R) and organic peroxides ($RO_2H$), along with the concomitant oxidation of the CDOM (**Figure 2**). Many of these reduced oxygen species as well as the hydroxyl radical (OH), which is generated by other photochemical reactions, are also quite reactive. These reactive oxygen species or ROS can undergo additional secondary reactions with themselves or with other organic and inorganic seawater constituents. The net result of this complex series of reactions is the light-induced oxidative degradation of organic matter by dioxygen (**Figure 2**). This process leads to the consumption of $O_2$, the production of oxidized carbon gases ($CO_2$, CO, COS), the formation of a variety of LMW organic compounds, the release of biologically available forms of nitrogen, and the loss of CDOM absorption. Through direct photochemical reactions and reactions with the ROS, the speciation of metal ions is also affected.

These photochemical intermediates and products are produced at relatively low efficiencies. About 98–99% of the photons absorbed by CDOM are released as heat, while another ~ 1% are re-emitted as fluorescence. These percentages (or fractions) of absorbed photons giving rise to particular photoresponses are known as quantum yields ($\Phi$). The $\Phi$ for the production of $H_2O_2$ and $O_2^-$, (the two reduced oxygen species produced with highest efficiency), are approximately one to two orders of magnitude smaller than those for fluorescence, ranging from ~ 0.1% at 300 nm to ~ 0.01% at 400 nm. The $\Phi$ for other intermediates and products range even lower, from ~ 0.01% to 0.000 0001% (see below). The $\Phi$ for most of the intermediates and products created from the CDOM are highest in the UV-B

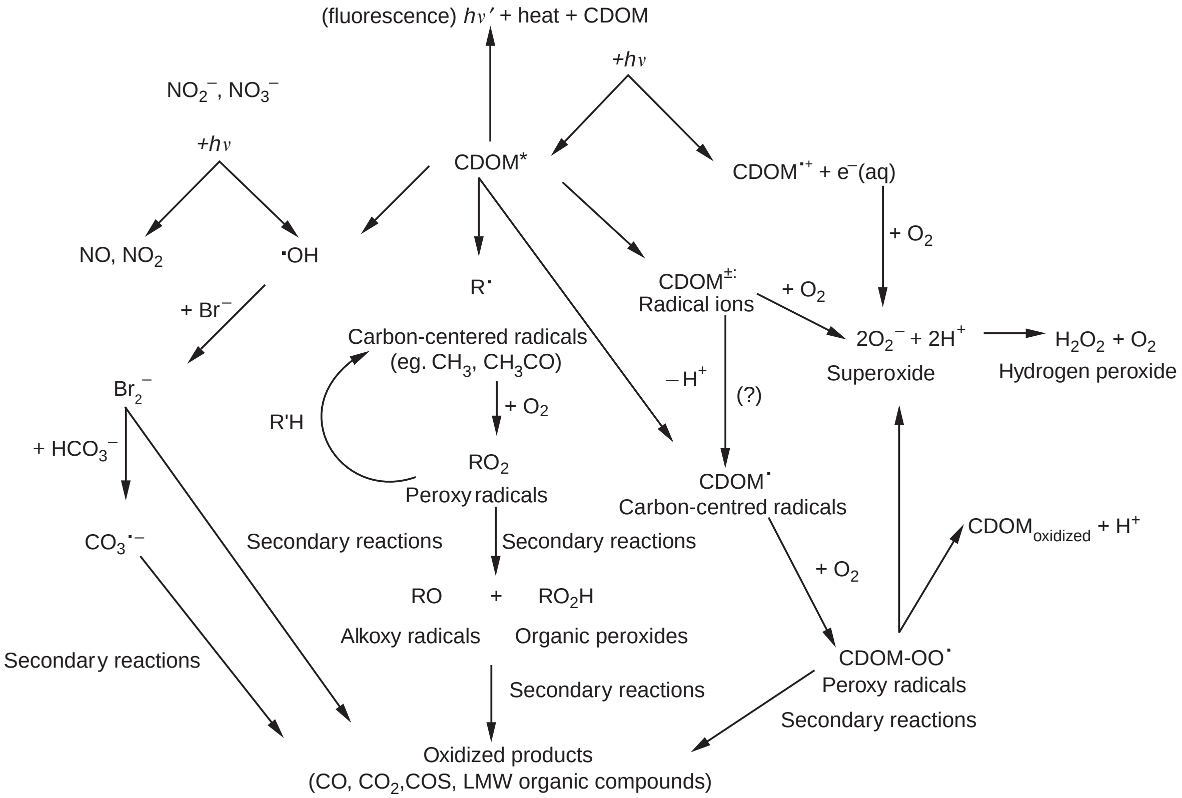

**Figure 2** Schematic representation of the photochemical and secondary reactions known or thought to occur following light absorption by CDOM. For a more detailed description of these reactions see the text, Blough and Zepp (1995), and Blough (1997). Not shown in this diagram are primary and secondary reactions of metal species; for a description of these processes, see Helz *et al.* (1994) and Blough and Zepp (1995).

and UV-A, and fall off rapidly with increasing wavelength; yields at visible wavelengths are usually negligible (see for example, **Figure 3**).

The hydroxyl radical, a very powerful oxidant, can be produced by the direct photolysis of nitrate and nitrite (eqns [I]–[III]).

$$NO_3^- + h\nu \rightarrow O^- + NO_2 \qquad [I]$$

$$NO_2^- + h\nu \rightarrow O^- + NO \qquad [II]$$

$$O^- + H_2O \rightarrow OH + OH^- \qquad [III]$$

The Φ values for these reactions are relatively high, about 7% for nitrite and about 1–2% for nitrate. However, because of the relatively low concentrations of these compounds in most marine surface waters, as well as their low molar absorptivities in the ultraviolet, the fraction of light absorbed is generally small and thus fluxes of OH from these sources also tend to be small. Recent evidence suggests that OH, or a species exhibiting very similar reactivity, is produced through a direct photoreaction of the CDOM; quinoid moieties within the CDOM may be responsible for this production. Quantum yields are low, ~ 0.01%, and restricted primarily to the ultraviolet. In estuarine and near-shore waters containing higher levels of iron, the production of OH may also occur through the direct photolysis of iron–hydroxy complexes or through the Fenton reaction (eqn [IV]).

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH + OH^- \qquad [IV]$$

Compounds that do not absorb light within the surface solar spectrum are also subject to photochemical modification through indirect or ‘sensitized’ photoreactions. In this case, the ROS or intermediates produced by direct photoreactions of a light-absorbing constituent such as CDOM can react secondarily with the nonabsorbing compounds. DMS and COS, two trace gases of some importance to the atmosphere, are thought to be destroyed and created, respectively, by sensitized photoreactions in marine surface waters.

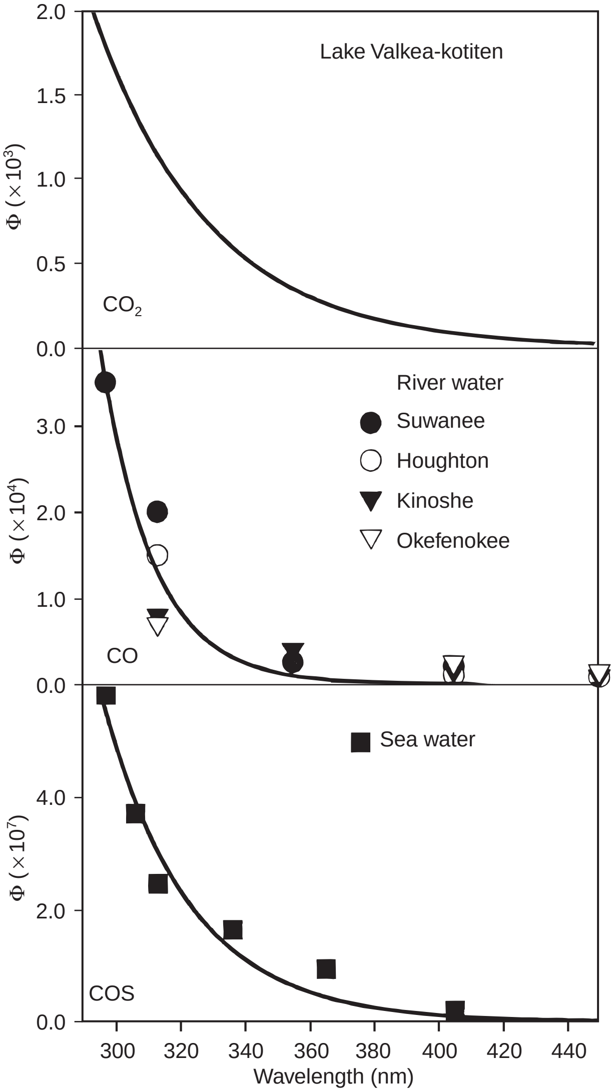

**Figure 3** Wavelength dependence of the quantum yields (Φ) for the photochemical production of $CO_2$, CO, and COS. Data have been replotted from those dependencies originally reported in Vähätalo *et al.* (2000), Valentine and Zepp (1993), and Weiss *et al.* (1995) for $CO_2$, CO, and COS, respectively.

## Photochemical Production and Consumption of LMW Organic Compounds and Trace Gases

The photolysis of CDOM produces a suite of LMW organic compounds and a number of trace gases. The production of these species presumably occurs through radical and fragmentation reactions arising from the net oxidative flow of electrons from CDOM to $O_2$ (see above), although the exact mechanism(s) have yet to be established. Most LMW organic compounds produced contain three or fewer carbon atoms and include such species as acetaldehyde, acetate, acetone, formaldehyde, formate, glyoxal, glyoxalate, methylglyoxal, propanal, and pyruvate. The Φ values for the production of individual compounds are low, ~0.001–0.0001%, with wavelengths in the UV-B the most effective; efficiencies decrease rapidly with increasing wavelength. Available evidence indicates that the Φ for $O_2^-$ and $H_2O_2$ production are about one to two orders of magnitude larger than those for the LMW organic compounds, so it appears that the sum of the production rates for the known LMW organic compounds is small with respect to the flux of photochemical equivalents from CDOM to $O_2$.

Most, if not all, of these products are rapidly taken up and respired by bacteria to $CO_2$. Numerous investigators have presented evidence supporting enhanced microbial activity in waters exposed to sunlight, with bacterial activities increasing from 1.5- to almost 6-fold depending presumably on the length and type of light exposure, and the concentration and source of the CDOM. Recently, biologically labile nitrogen-containing compounds such as ammonia and amino acids have also been reported to be produced photochemically from CDOM. Because CDOM is normally considered to be biologically refractive, this recent work highlights the important role that abiotic photochemistry plays in the degradation of CDOM, not only through direct photoreactions, but also through the formation of biologically available products that can be respired to $CO_2$ or used as nutrients by biota. A recent estimate suggests that the utilization of biologically labile photoproducts could account for as much as 21% of the bacterial production in some near-surface waters.

Carbon dioxide and carbon monoxide are major products of the direct photolysis of CDOM (**Figure 3**). Quantum yields for CO production are about an order of magnitude smaller than those for $O_2^-$ and $H_2O_2$ production, ranging from ~0.01% at 300 nm to ~0.001% at 400 nm. Available data indicate that the Φ for $CO_2$ range even higher, perhaps as much as 15–20-fold. The yields for $CO_2$ production must thus approach, if not exceed, those for $O_2^-$ and $H_2O_2$. This result is somewhat surprising, since it implies that about one $CO_2$ is produced for each electron transferred from the CDOM to $O_2$, further implying a high average redox state for CDOM. Although CDOM (i.e. humic substances) is known to contain significant numbers of carboxyl moieties that could serve as the source of the $CO_2$, the yield for $CO_2$ production, relative to $O_2^-$ and $H_2O_2$, would be expected to fall rapidly as these groups were removed photochemically; available evidence suggests that this does not occur. An alternative explanation is that other species, perhaps the CDOM itself, is acting as an electron acceptor. Regardless of mechanism, existing information indicates that $CO_2$ is the dominant product of CDOM photolysis (**Figure 3**).

A recent estimate suggests that the annual global photoproduction of CO in the oceans could be as high as $0.82 \times 10^{15}$ g C. Assuming that $CO_2$ photoproduction is 15–20 times higher than that for CO, values for $CO_2$ formation could reach from 12 to $16 \times 10^{15}$ g C y$^{-1}$. To place these numbers in perspective, the estimated annual input of terrestrial dissolved organic carbon to the oceans ($0.2 \times 10^{15}$ g C y$^{-1}$) is only 1.3–1.7% of the calculated annual $CO_2$ photoproduction, which is itself about 2–3% of the oceanic dissolved organic carbon pool. These calculated $CO_2$ (and CO) photoproduction rates may be high due to a number of assumptions, including (1) the complete absorption of UV radiation by the CDOM throughout the oceans, (2) constant quantum yields (or action spectra) for production independent of locale or light history, and (3) neglecting mass transfer limitations associated with physical mixing. Nevertheless, these estimates clearly highlight the potential impact of abiotic photochemistry on the oceanic carbon cycle. Moreover, the products of this photochemistry are generated in near-surface waters where exchange with the atmosphere can take place readily.

Like the LMW organic compounds, bacteria can oxidize CO to $CO_2$; this consumption takes place in competition with the release of CO to the atmosphere. Due to its photochemical production, CO exists at supersaturated concentrations in the surface waters of most of the Earth's oceans. Recent estimates indicate that global oceanic CO emissions could range from $0.013 \times 10^{15}$ g y$^{-1}$–$1.2 \times 10^{15}$ g y$^{-1}$ (see above). The upper estimate is based on calculated photochemical fluxes (see below) and the assumption that all CO produced is emitted to the atmosphere. The lower estimate was calculated using air–sea gas exchange equations and extensive measurements of CO concentrations in the surface waters and atmosphere of the Pacific Ocean. The source of the significant discrepancy between these two estimates has yet to be resolved. Depending on the answer, CO emitted to the atmosphere from the oceans could play a significant role in controlling OH levels in the marine troposphere.

Carbonyl sulfide (COS) is produced primarily in coastal/shelf waters, apparently by the CDOM-photosensitized oxidation of organosulfur compounds. UV-B light is the most effective in its formation, with $\Phi$ decreasing rapidly from $\sim 6 \times 10^{-7}$ at 300 nm to $\sim 1 \times 10^{-8}$ by 400 nm (**Figure 3**). The principal sinks of seawater COS are release to the atmosphere and hydrolysis to $CO_2$ and $H_2S$. Accounting for perhaps as much as one-third of the total source strength, the photochemical production of COS in the oceans is probably the single largest source of COS to the atmosphere, although more recent work has revised this estimate downward. Smaller amounts of carbon disulfide ($CS_2$) are also generated photochemically in surface waters through CDOM sensitized reaction(s); $\Phi$ values decrease from $\sim 1 \times 10^{-7}$ at 313 nm to $5 \times 10^{-9}$ at 366 nm. The $CS_2$ emitted to the atmosphere can react with OH to form additional COS in the troposphere. Although it was previously thought that the oxidation of COS in the stratosphere to form sulfate aerosol could be important in determining Earth's radiation budget and perhaps in regulating stratospheric ozone concentrations, more recent work suggests that other sources contribute more significantly to the background sulfate in the stratosphere.

Dimethyl sulfide (DMS), through its oxidation to sulfate in the troposphere, acts as a source of cloud condensation nuclei, thus potentially influencing the radiative balance of the atmosphere. DMS is formed in sea water through the microbial decomposition of dimethyl sulfonioproprionate (DMSP), a compound believed to act as an osmolyte in certain species of marine phytoplankton. The flux of DMS to the atmosphere is controlled by its concentration in surface sea waters, which is controlled in turn by the rate of its decomposition. Estimates indicate that 7–40% of the total turnover of DMS in the surface waters of the Pacific Ocean is due to the photosensitized destruction of this compound, illustrating the potential importance of this pathway in controlling the flux of DMS to the atmosphere.

In addition to these compounds, the photochemical production of small amounts of nonmethane hydrocarbons (NMHC) such as ethene, propene, ethane, and propane has also been reported. Production of these compounds appears to result from the photolysis of the CDOM, with $\Phi$ values of the order of $10^{-7}$–$10^{-9}$. The overall emission rates of these compounds to the atmosphere via this source are negligible with respect to global volatile organic carbon emissions, although this production may play some role in certain restricted locales exhibiting stronger source strengths, or in the marine environment remote from the dominant terrestrial sources.

The photolysis of nitrate and nitrite in sea water produces nitrogen dioxide ($NO_2$) and nitric oxide (NO), respectively (eqns [I] and [II]). Previous work indicated that the photolysis of nitrite could act as a small net source of NO to the marine atmosphere under some conditions. However, this conclusion seems to be at odds with estimates of the steady-state concentrations of superoxide and the now known rate constant for the reaction of superoxide with nitric oxide ($6.7 \times 10^9\ \mathrm{M^{-1}\,s^{-1}}$) to form peroxynitrite in aqueous phases (eqn [V]).

$$\mathrm{O_2^- + NO \rightarrow {}^-OONO} \qquad [\mathrm{V}]$$

The peroxynitrite subsequently rearranges in part to form nitrate (eqn [VI]).

$$\mathrm{{}^-OONO \rightarrow NO_3^-} \qquad [\mathrm{VI}]$$

Even assuming a steady-state concentration of $\mathrm{O_2^-}$ ($10^{-12}$ M) that is about two orders of magnitude lower than that expected for surface sea waters ($\sim 10^{-10}$ M), the lifetime of NO in surface sea waters would be only $\sim 150$ s, a timescale too short for significant exchange with the atmosphere except for a thin surface layer. Moreover, even in this situation, the atmospheric deposition of additional $\mathrm{HO_2}$ radicals to this surface layer (to form $\mathrm{O_2^-}$) would be expected to act as an additional sink of the NO (flux capping). It appears that most if not all water bodies exhibiting significant steady-state levels of $\mathrm{O_2^-}$, produced either photochemically or thermally, should act as a net sink of atmospheric NO and probably of $\mathrm{NO_2}$ as well. Further, although less is known about the steady-state levels of peroxy radicals in sea waters due largely to their unknown decomposition routes, their high rate constants for reaction with NO ($1\text{–}3 \times 10^9\ \mathrm{M^{-1}\,s^{-1}}$) indicate that they should also act as a sink of NO. In fact, methyl nitrate, a trace species found in sea waters, may in part be produced through the aqueous phase reactions (eqns [VII] and [VIII]) with the methylperoxy radical ($\mathrm{CH_3OO}$) generated through a known photochemical reaction of CDOM (or through atmospheric deposition) and the NO arising from the photolysis of nitrite (or through atmospheric deposition).

$$\mathrm{CH_3OO + NO \rightarrow CH_3OONO} \qquad [\mathrm{VII}]$$

$$\mathrm{CH_3OONO \rightarrow CH_3ONO_2} \qquad [\mathrm{VIII}]$$

The concentrations of NO and $\mathrm{NO_2}$ in the troposphere are important because of the involvement of these gases in the formation of ozone.

The atmospheric deposition of ozone to the sea surface can cause the release of volatile iodine compounds to the atmosphere. There is also evidence that methyl iodide can be produced (as well as destroyed) by photochemical processes in surface sea waters. The release of these volatile iodine species from the sea surface or from atmospheric aqueous phases (aerosols) by these processes may act as a control on the level of ozone in the marine troposphere via iodine-catalyzed ozone destruction.

## Trace metal photochemistry

A lack of available iron is now thought to limit primary productivity in cerain ocean waters containing high nutrient, but low chlorophyll concentrations (the HNLC regions). This idea has spurred interest in the transport and photochemical reactions of iron in both seawaters and atmospheric aerosols. Very little soluble Fe(II) is expected to be available at the pH and dioxygen concentration of surface seawaters due to the high stability of the colloidal iron (hydr)oxides. The photoreductive dissolution of colloidal iron oxides by CDOM is known to occur at low pH; this process is also thought to occur in seawaters at high pH, but the reduced iron appears to be oxidized more rapidly than its detachment from the oxide surface. However, some workers have found that CDOM-driven cycles of reduction followed by oxidation increases the chemical availability, which was strongly correlated with the growth rate of phytoplankton. Significant levels of Fe(II) are also known to be produced phytochemically in atmospheric aqueous phases (at lower pH) and could serve as a source of biologically available iron upon deposition to the sea surface.

Manganese oxides are also subject to reductive dissolution by light in surface seawaters. This process produces Mn(II), which is kinetically stable to oxidation in the absence of bacteria that are subject to photoinhibition. These two effects lead to the formation of a surface maximum in soluble Mn(II), in contrast to most metals which are depleted in surface waters due to biological removal processes. Other examples of the impact of photochemical reactions on trace metal chemistry are provided in Further Reading.

## Photochemical Calculations

Global and regional estimates for the direct photochemical production (or consumption) of a particular photoproduct (or photoreactant) can be acquired with knowledge of the temporal and spatial variation of the solar irradiance reaching the Earth's surface combined with a simple photochemical model (eqn [3]).

$$F(\lambda, z) = E_D(\lambda, z) \cdot \Phi_i(\lambda) \cdot a_{Di}(\lambda) \qquad [3]$$

Here $F(\lambda, z)$ is the photochemical production (or consumption) rate; $E_D(\lambda, z)$ is the downwelling irradiance at wavelength, $\lambda$, and depth, $z$, within the water column; $a_{Di}$ is the diffuse absorption coefficient for photoreactive constituent $i$; $\Phi_i(\lambda)$ is the quantum yield of this $i$th constituent. $E_D(\lambda, z)$ is well approximated by eqn [4].

$$E_D(\lambda, z) = E_{D0}(\lambda) \cdot e^{-K_d(\lambda) \cdot z} \qquad [4]$$

$E_{D0}(\lambda)$ is the downwelling irradiance just below the sea surface and $K_d(\lambda)$ is the vertical diffuse attenuation coefficient of downwelling irradiance. $K_d(\lambda)$ can be approximated by eqn [5].

$$K_d(\lambda) \approx \frac{\sum a_i(\lambda) + \sum b_{bi}(\lambda)}{\mu_D} \qquad [5]$$

where $\sum a_i(\lambda)$ and $\sum b_{bi}(\lambda)$ are the total absorption and backscattering coefficients, respectively, of all absorbing and scattering constituents within the water column, and $\mu_D$ is the average cosine of the angular distribution of the downwelling light. This factor accounts for the average pathlength of light in the water column, and for direct solar light is approximately equal to cos $\theta$, where $\theta$ is the solar zenith angle (e.g. $\mu_D \sim 1$ when the sun is directly overhead). The diffuse absorption coefficient, $a_{Di}$, is given by eqn [6].

$$a_{Di} = \frac{a_i}{\mu_D} \qquad [6]$$

This model assumes that the water column is homogeneous, that $K_d(\lambda)$ is constant with depth, and that upwelling irradiance is negligible relative to $E_D(\lambda, z)$. Combining eqns [3], [4] and [6] gives eqn [7].

$$F(\lambda, z) = \frac{E_{D0}(\lambda) \cdot e^{-K_d(\lambda) \cdot z} \cdot \Phi_i(\lambda) \cdot a_i(\lambda)}{\mu_D} \qquad [7]$$

This equation allows calculation of the spectral dependence of the production (consumption) rate as a function of depth in the water column, assuming knowledge of $E_{D0}(\lambda)$, $K_d(\lambda)$, $a_i(\lambda)$ and $\Phi_i(\lambda)$, all of which can be measured or estimated (**Figure 4**). Integrating over wavelength provides the total production (consumption) rate at each depth.

Integration of eqn [7] from the surface to depth $z$ provides the spectral dependence of the photochemical flux ($Y$) over this interval

$$Y(\lambda, z) = \frac{E_{D0}(\lambda) \cdot (1 - e^{-K_d(\lambda) \cdot z}) \cdot \Phi_i(\lambda) \cdot a_i(\lambda)/K_d(\lambda)}{\mu_D} \qquad [8]$$

which upon substitution of eqn [4] becomes,

$$Y(\lambda, z) = E_{D0}(\lambda) \cdot (1 - e^{-K_d(\lambda) \cdot z}) \cdot \Phi_i(\lambda) \cdot \frac{a_i(\lambda)}{\sum a_i(\lambda) + \sum b_{bi}(\lambda)} \qquad [9]$$

In most, but not all seawaters, the total absorption will be much greater than the total backscatter, $\sum a_i(\lambda) \gg \sum b_{bi}(\lambda)$, and thus the backscatter can be ignored; this approximation is not valid for most estuarine waters and some coastal waters, where a more sophisticated treatment would have to be applied. This approximation leads to the final expression for the variation of the spectral dependence of the flux with depth (**Figure 5**),

$$Y(\lambda, z) = E_{D0}(\lambda) \cdot (1 - e^{-K_d(\lambda) \cdot z}) \cdot \Phi_i(\lambda) \cdot \frac{a_i(\lambda)}{\sum a_i(\lambda)} \qquad [10]$$

The spectral dependence of the total water column flux ($z \to \infty$) is then given by,

$$Y(\lambda) = E_{D0}(\lambda) \cdot \Phi_i(\lambda) \cdot \frac{a_i(\lambda)}{\sum a_i(\lambda)} \qquad [11]$$

with the total flux obtained by integrating over wavelength,

$$Y = \int_\lambda E_{D0}(\lambda) \cdot \Phi_i(\lambda) \cdot \frac{a_i(\lambda)}{\sum a_i(\lambda)} d\lambda \qquad [12]$$

To obtain global estimates of photochemical fluxes, many investigators assume that the absorption due to CDOM, $a_{\mathrm{CDOM}}$, dominates the absorption of all other seawater constituents in the ultraviolet, and thus that $a_{\mathrm{CDOM}}(\lambda)/\sum a_i(\lambda) \approx 1$. While this approximation is reasonable for many coastal waters, it is not clear that this approximation is valid for all oligotrophic waters. This approximation leads to the final expression for flux,

$$Y = \int_\lambda \mathrm{E}_{D0}(\lambda) \cdot \Phi_i(\lambda) d\lambda \qquad [13]$$

which relies only on the surface downwelling irradiance and the wavelength dependence of the quantum yield for the photoreaction of interest. Uncertainties in the use of this equation for estimating global photochemical fluxes include (1) the (usual) assumption that $\Phi(\lambda)$ acquired for a limited number of samples is representative of all ocean waters, independent of locale or light history, and (2) differences in the spatially and temporally averaged values of $E_{D0}(\lambda)$ utilized by different investigators.

## Conclusions

The absorption of solar radiation by abiotic sea water constituents initiates a cascade of reactions leading to the photo-oxidative degradation of organic matter and the concomitant production (or consumption) of a variety of trace gases and LMW organic compounds (**Figure 2**), as well as affecting trace metal speciation. The magnitude and impact of these processes on upper ocean biogeochemical cycles and their coupling with atmospheric processes are just beginning to be fully quantified and understood. There remains the need

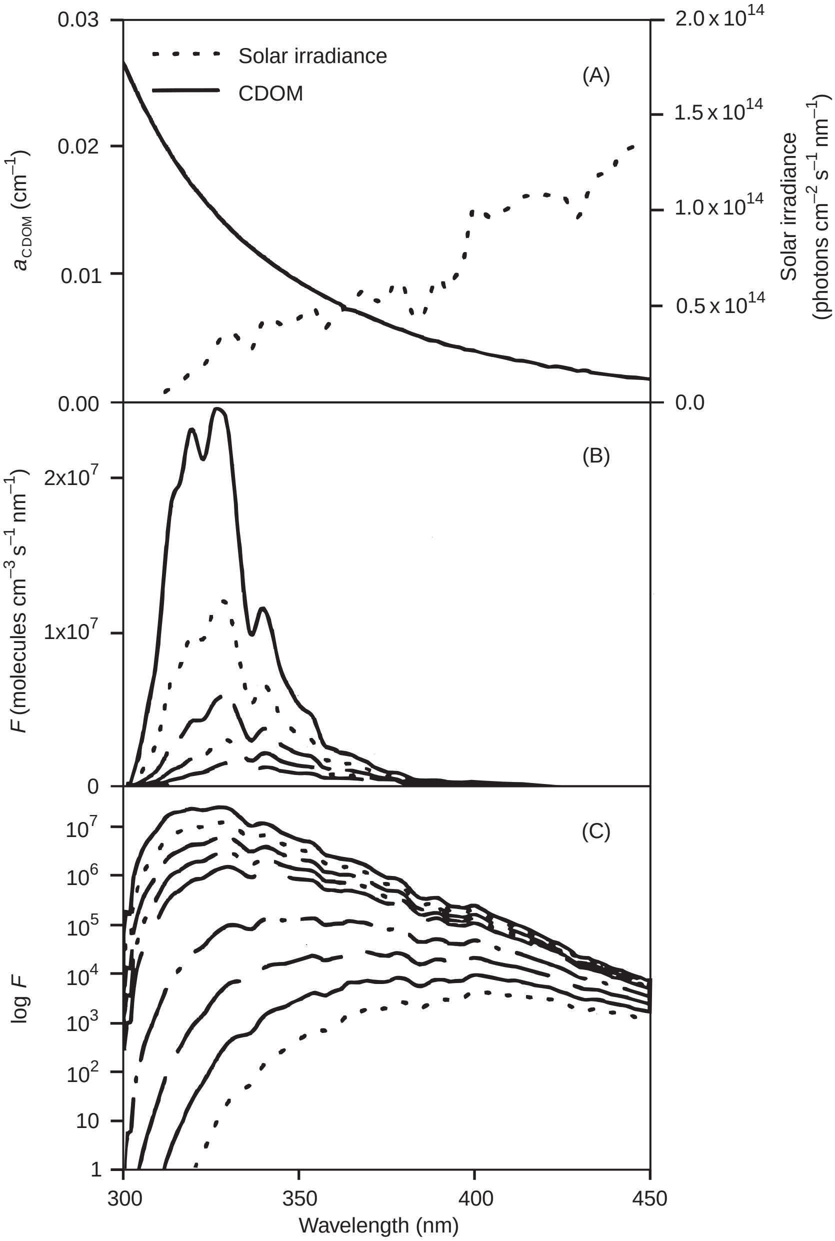

**Figure 4** Spectral dependence of CO photoproduction rates with depth, plotted on a linear (B) and logarithmic (C) scale. Depths in (B) are (from top to bottom): surface, 0.5, 1, 1.5, and 2 m. Depths in (C) are (from top to bottom): surface, 0.5, 1, 1.5, 2, 4, 6, 8, and 10 m. These spectral dependencies were calculated using eqn [7], the wavelength dependence of the quantum yield for CO shown in Figure 3, and the CDOM absorption spectrum and surface solar irradiance shown in (A). The attenuation of irradiance down the water column in this spectral region was assumed to be only due to CDOM absorption, a reasonable assumption for coastal waters (see **Figure 1**). Note the rapid attenuation in production rates with depth in the UV-B, due to the greater light absorption by CDOM in this spectral region.

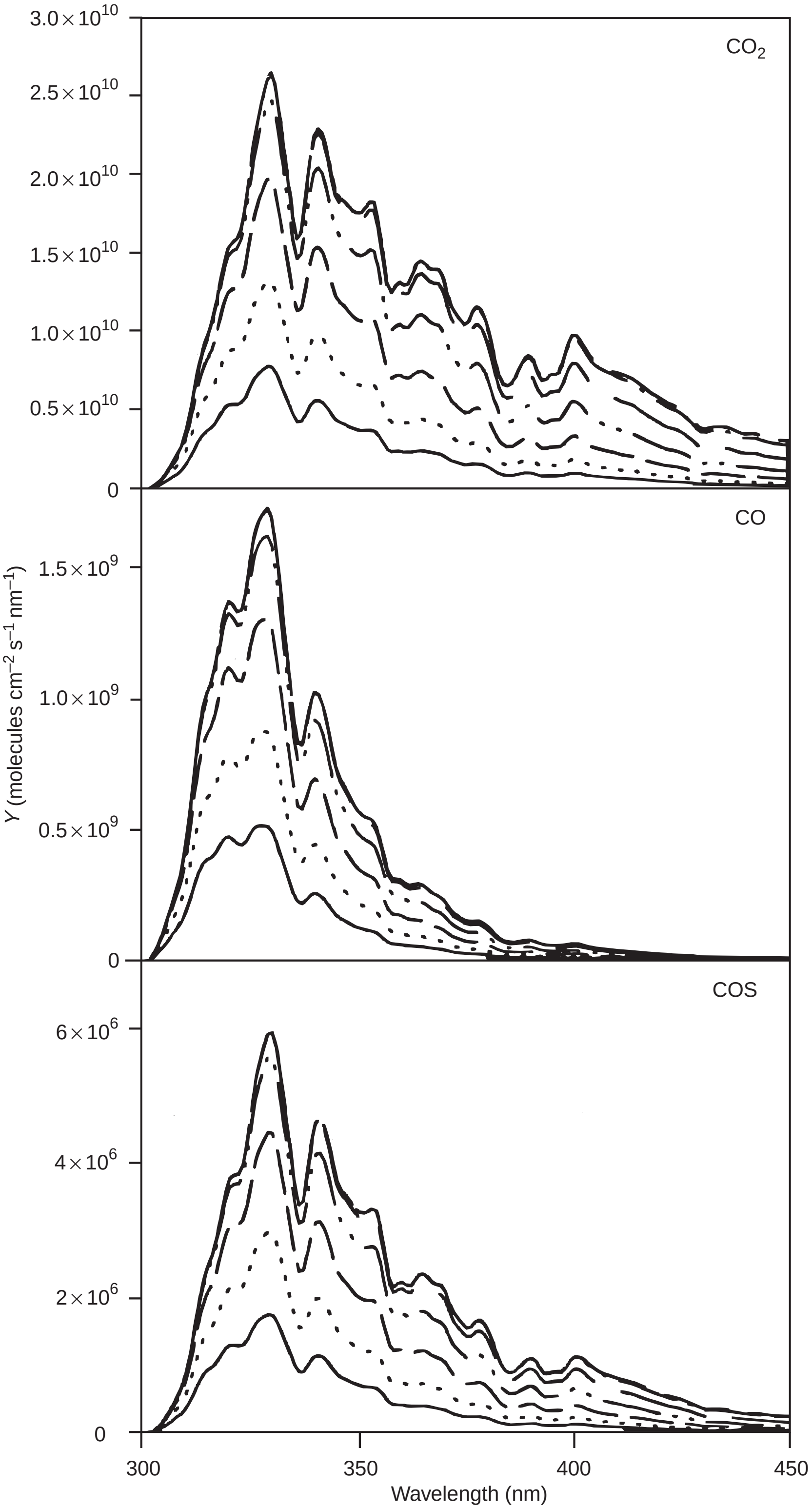

**Figure 5** Spectral dependence of the photochemical flux with depth for $CO_2$, CO, and COS. Fluxes with depth are from the surface to 0.25, 0.5, 1.0, 2.0, and 4 m, respectively (bottom spectrum to top spectrum). Below 4 m, increases in the flux are nominal. These spectral dependencies were calculated using eqn [10], the wavelength dependence of the quantum yields for $CO_2$, CO and COS shown in **Figure 3**, and the surface solar irradiance shown in **Figure 4A**. CDOM is assumed to absorb all photons in this spectral region (see **Figures 1** and **4**).

to examine possible couplings between atmospheric gas phase reactions and photochemical reactions in atmospheric aqueous phases.

## See also

**Air–Sea Transfer: Dimethyl Sulphide, COS, $CS_2$, $NH_4$, Non-methane Hydrocarbons, Organo-halogens; $N_2O$, NO, $CH_4$, CO.**

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# PHYTOBENTHOS

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## What is Phytobenthos?

'Phytobenthos' means plants of the seabed, both intertidal and subtidal, and both sedimentary and hard. Such plants belong almost entirely to the algae although seagrasses, which form meadows on some subtidal and intertidal areas, are flowering plants or angiosperms. Algae of sedimentary shores are usually microscopic, unicellular or filamentous, and are known as the microphytobenthos or benthic microalgae. Marine algae on hard surfaces can range from microscopic single-celled forms to large cartilaginous plants. Some use the term 'seaweed' for macroscopic forms whereas others also include the smaller algae of rocky seashores. This article is concerned with the nature, diversity, ecology, and exploitation of the marine benthic algae. Other plants of the shore are dealt with elsewhere in this encyclopedia as salt-marshes, mangroves, and seagrasses (*see* **Mangroves; Salt Marsh Vegetation**).

## What are Algae?

Algae were regarded as the least highly evolved members of the plant kingdom. Nowadays most classifications either regard the microscopic algae as