

Formation of Carbon Monoxide by Photolysis of Dissolved Marine Organic Material and Its Significance in the Carbon Cycling of the Oceans

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The importance of carbon monoxide (CO) as a major sink for the OH radical in the atmosphere is well established [1]. However, comparatively little is known about its role in the world oceans. In surface ocean waters, dissolved CO is typically supersaturated with respect to atmospheric equilibrium, and the dissolved concentration varies diurnally with light intensity [2–4]. It has, therefore, been assumed that the formation of CO in seawater is due to photooxidation of dissolved organic carbon (DOC). Recent oceanographic studies have further implied that CO may occupy a key position in the oceanic carbon cycling as an intermediate in the photochemical mineralization of marine-dissolved organic matter (DOM) which is resistant to biological decomposition. Among all identified photoproducts of DOM, CO is a predominant species and accounts for about $70 \pm 10\%$ of total carbon transfer from DOM to the identified low-molecular-weight carbon products [5–7]. In this paper we present experimental results which first show a strong correlation between photochemical formation of CO and dissolved organic carbon (DOC) in seawater, and then estimate the quantity of the global photochemical production of CO in the oceans as well as its significance in global oceanic carbon cycling. During cruises to the Gulf Stream (May, August, 1991; August, 1992) and to the southwestern Sargasso Sea (Au-

gust, 1989), seawater samples were collected off the southwest coast of Florida and in oligotrophic waters. Surface samples were taken every 30 min while the ship was underway and every 60 min when the ship was on station, from an all-Teflon, bow-mounted pumping system permanently installed in the RV Columbus Iselin. The samples were filtered ($0.45 \mu\text{M}$) and the absorbance at 350 nm was measured immediately before irradiation. For measurement of DOC, seawater samples were stored refrigerated in clean glass bottles and returned to the laboratory for analysis using a Shimadzu TOC 5000.

Irradiation experiments were carried out within 90 min of sampling for the samples from the cruise of August

1992. Sample waters were degassed to remove ambient CO before irradiation. Two hundred ml of the degassed seawater in sealed quartz tubes was exposed to the radiation of a 300-W solar simulator. Samples from the other cruises were stored in clean glass bottles at 4°C and shipped to the laboratory and irradiated in the same tubes with solar noon sunlight (26°N) or with the solar simulator. No detectable difference in the photoformation rate of CO was found for the same seawater samples irradiated on board or later in the laboratory, indicating that no change in the photochemical CO formation capacity occurred during the storage and transportation of seawater samples. All results were corrected for dark controls, which were always less than 10% of the photochemically formed CO.

When seawater samples from different sites were irradiated, carbon monoxide was formed (Table 1). A typical time course is depicted in Fig. 1. The rate of the photochemical production of CO was dependent on the amounts of DOC. The relationship between the formation rate of CO and the concentration of DOC for the coastal surface waters is shown in Fig. 2a. The correlation coefficient (r^2) for 70 sample points is

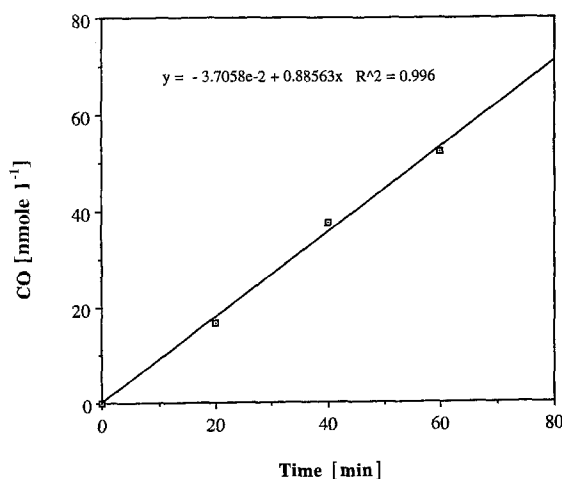


Fig. 1. Photochemical production of CO as a function of irradiation time. The samples were collected at Moser Channel station. $[\text{DOC}] = 2.0 \text{ mgC l}^{-1}$

Table 1. Summary of photochemical production of CO in surface seawaters on four cruises. The detailed sampling, irradiation, and analytical procedures have been described elsewhere [3]. Dissolved organic carbon (DOC) was measured on a Shimadzu TOC-5000 Total Organic Carbon Analyzer, using a high-temperature catalytic oxidation technique. Light intensity (400–100 nm) was recorded using an International Light Model IL 1700 radiometer, and all production rates of CO were normalized to 1000 Wh m⁻²

Sampling location		DOC [mg l ⁻¹]	CO production rate [nmol l ⁻¹ h ⁻¹]	CO production rate/DOC [nmol mg ⁻¹ h ⁻¹]	No. of samples
Fowey Rocks	25.6°N, 80.1°W	0.8 ± 0.2	21 ± 9	26	5
Triumph Reef	25.5°N, 80.1°W	0.9 ± 0.2	26 ± 5	29	6
Turtle Reef	25.3°N, 80.2°W	0.9 ± 0.3	22 ± 4	24	6
Carysfort Reef	25.2°N, 80.2°W	0.8 ± 0.2	21 ± 3	26	6
Alligator Reef	24.9°N, 80.6°W	1.0 ± 0.2	19 ± 3	19	8
Tennessee Reef	24.8°N, 80.8°W	1.1 ± 0.2	16 ± 2	15	8
Moser Channel (near Molassas Key)	24.7°N, 81.2°W	2.3 ± 0.7	55 ± 7	24	25
Near Shark River Outflow	25.3°N, 81.2°W	4.9 ± 1.0	106 ± 20	22	5
	25.3°N, 81.3°W	4.1 ± 1.0	87 ± 20	21	4
	25.3°N, 81.4°W	1.7 ± 0.5	32 ± 10	19	8
Florida Straits	24.5°N, 81.6°W	1.2 ± 0.4	12 ± 4	10	3
Gulf Stream/ Gulf of Mexico	24.5°N, 84.0°W	1.2 ± 0.3	11 ± 3	9.2	8
Sargasso Sea ^a	27°N, 73°W	1.2 ± 0.3	13 ± 3	11	6

^a 300 km northeast of the Bahamas

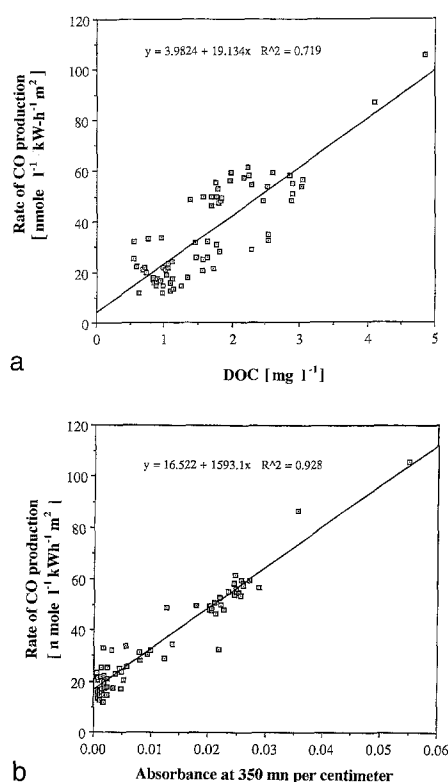


Fig. 2. a) Correlation between photochemical production of CO and the concentration of dissolved organic carbon (DOC) in seawater. b) Correlation between photochemical formation of CO and the absorbances of seawater samples at 350 nm

0.72. The discrepancy is most likely caused by the different extent of the photochemical bleaching of DOC, which decreases the photochemical reactivity of natural dissolved organic substances [5, 8, 9]. When photochemical formation of CO is plotted against the absorbance of the seawater at 350 nm, a better correlation is achieved with a correlation coefficient of 0.93 (Fig. 2b). Photobleaching may also explain why open-ocean waters have a lower photochemical formation rate of CO per unit DOC (10 ± 2 nmol [mgC h]⁻¹, see Table 1) than coastal seawater. When considering the absorption or fluorescence of DOC in these waters, however, a relatively higher rate of photochemical formation of CO was observed in open-ocean waters.

To assess the significance of CO photoproduction in the oceanic carbon cycle, we calculated the global photochemical formation of CO in the oceans, using the globally averaged solar flux at sea level of 178 W m^{-2} , which based on the solar constant $I_{sc} = 1367 \text{ W m}^{-2}$. Of this solar energy, 24% is reflected from the atmosphere back to space, clouds absorb 4%, and atmospheric gases about 20%, leaving 52% incident at the earth's surface [10]. In our calculation we also used an

average photochemically effective light penetration (1/e) depth of 6 m in the open ocean, and 1 m in the coastal ocean, which derived from the action spectrum of seawater for the formation of CO ([8] and Y. Zuo, R. D. Jones, unpubl. results); the average concentrations of DOC of 1.2 mg l^{-1} in the open ocean surface water, and 2 mg l^{-1} in the coastal water were employed [11]. The results indicated that the world ocean photochemically produces some $1200 \pm 200 \text{ Tg CO}$ per year, of which $100 \pm 20 \text{ Tg}$ is formed in coastal areas and $1100 \pm 200 \text{ Tg}$ in the open ocean. Thus, the photochemical processes convert about 500 Tg of oceanic dissolved organic carbon per year to CO. The field studies have shown that, in contrast to the strong diurnal variations within the euphotic zone, the CO concentration remains constant with time in water below 100 m, indicating that the net transport of CO from the euphotic zone to the underlying deeper ocean water is lacking [2, 3]. Thus, the photochemically formed CO must be either effluxed to the atmosphere, where it plays a very important role in tropospheric chemistry by reacting with the OH radical, or consumed in situ. The uptake by microorganisms is currently the only documented pathway

for the consumption of CO in the ocean. However, recent field studies in the Sargasso Sea, Lake Constance, the Okefenokee Swamp, and coastal sampling sites indicated that biological consumption is comparatively slow in the water column [3, 7, 12]. In the mixed layer of the Sargasso Sea and the Gulf of Mexico, the turnover times of CO range from 25 to 240 h [3]. In the Atlantic coastal areas, Conrad et al. [2, 13] have observed CO turnover times of 20 to 31 h. These microbial CO turnover times are much longer than the overall life time of CO in marine surface waters, which appears to be less than 3–4 h. Thus, one may assume that the production of CO is predominantly balanced by emission to the atmosphere. The estimated maximum fluxes of CO should be close to the photochemical production in the surface oceans, 1200 Tg/year, which is about one order of magnitude greater than the previously estimated value of 100 Tg by the simple physical air-sea transfer model [2, 14].

CO also plays an important role in situ in seawater. It is potentially inhibitory for nearly all aerobic organisms [15]. Its photoproduction in surface waters can further affect the cycling of carbon and other reactive elements in marine ecosystems by inhibiting the degradation of organic matter and other activities of aerobic bacteria. Field and laboratory studies have shown that the nitrification and oxidation of methane and other organic compounds are significantly inhibited by CO at concentration levels observed in natural surface waters [16]. It has also been argued that CO formation is in part responsi-

ble for photoinhibition of microbial activities in the upper oceans, especially in productive coastal areas. Finally, it is worth noting that the sunlight intensity in the UV-B region is increasing at a rate of more than 5% per year in summer at Toronto and may also be increasing in other regions due to the decrease of total ozone [17]. This could be leading to a corresponding increase in the photochemical formation of CO in the oceans.

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Identifizierung von Inhaltsstoffen aus Organen altägyptischer Mumien

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Der Totenkult in Altägypten übt auch auf die heutige Nachwelt noch große Faszination aus. Die Mumifizierungstechniken sind noch nicht in allen Einzelheiten verstanden und zählen daher zu den interessantesten Forschungsbereichen. Nach dem Verständnis der alten Ägypter war die Erhaltung des Körpers eine wichtige Voraussetzung für ein Weiterleben nach dem Tod. Deshalb wurden schon früh ausgefeilte Mumifizierungsmethoden entwickelt, die eine dauerhafte Erhaltung ermöglichen soll-