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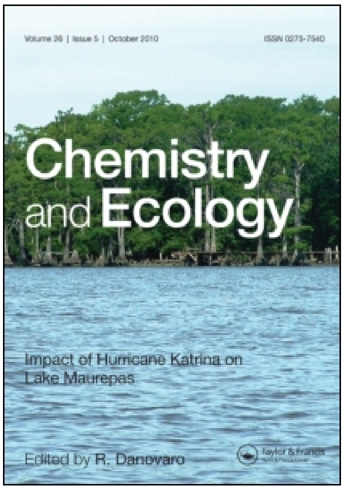

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REASSESSMENT OF THE OCEAN-TO-ATMOSPHERE FLUX OF CARBON MONOXIDE

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Carbon monoxide (CO) in the surface sea waters is produced predominantly by photochemical processes, oxidized by micro-organisms and outgassed to the atmosphere. To assess carbon monoxide flux from the oceans to the atmosphere, the photochemical production and microbial oxidation of carbon monoxide in the oceanic mixed-layer was investigated during several oeanographic cruises and in the laboratory. The photoproduction rate of carbon monoxide was found to be well correlated to the concentration of dissolved organic carbon (DOC) in coastal and open ocean surface waters. Taking a global average carbon monoxide production rate of 10 ± 2 nmole $\text{litre}^{-1}(\text{mg DOC hr})^{-1}$ in the surface open ocean water, and 25 ± 7 nmole litre^{-1} $(\text{mg DOC hr})^{-1}$ in coastal sea water, at cloud-free summer solar noon, the photochemical production of carbon monoxide in the global oceans is estimated to be at a rate of 1200 ±200 Tg CO y^{-1}. The microbial carbon monoxide turnover time in the mixed-layer was observed to range from hours in a coastal estuary to 16 days in the Pacific along 105° W in dark incubations. Natural sunlight can largely inhibit the microbial consumption of carbon monoxide in surface water. On a global scale, microbial consumption is responsible for the loss of less than 10% of photochemical produced carbon monoxide in the surface ocean. Field measurements have shown that the net transport of carbon monoxide from the euphotic zone to the underlying deeper ocean water is limited and that the overall life time in surface sea waters is less than 3–4 hours. When combined, these field measurements with the photoproduction and microbial consumption rates obtained, we estimate the oceanic flux to the atmosphere is about 1000 ± 200 Tg CO y^{-1}, which represents the largest single source of atmospheric carbon monoxide.

Keywords: Carbon monoxide; marine chemistry; sea-to-air gas exchange; natural dissolved organic matter

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INTRODUCTION

Carbon monoxide (CO) is the third most abundant carbon species in the atmosphere. It plays an important role in controlling the concentrations of hydroxyl radical (OH) via the reaction

$$OH + CO \rightarrow H + CO_2, \tag{1}$$

which is the major sink for both atmospheric carbon monoxide and hydroxyl radicals (Logan *et al.*, 1981; Thompson and Cicerone, 1986; Warneck, 1988; Crutzen, 1995). Hydroxyl radicals are the dominant atmospheric oxidizing species which is responsible for removing many natural and anthropogenic trace gases, including greenhouse gases such as methane and nitrous oxide. The reactions of carbon monoxide substantially increase or decrease the levels of tropospheric ozone (O_3), depending on the levels of nitric oxide present (Logan *et al.*, 1981; Crutzen, 1995). Any change in the tropospheric carbon monoxide concentration, for instance, by increasing or decreasing emission rates of anthropogenic carbon monoxide, will therefore lead to a change in the distribution and abundance of hydroxyl radical and ozone which, in turn, will have a significant impact on the tropospheric cycle of a variety of trace gases, and affect atmospheric photochemistry and climate change. Thus, accurate estimates of the sources of carbon monoxide to the atmosphere is critical to the development of quantitative models of atmospheric processes, such as the transformation rates for atmospheric pollutants, climate change, and ozone depletion.

The global budget of atmospheric carbon monoxide has been estimated repeatedly during the past decades by different research groups (Logan *et al.*, 1981; Volz, 1981; Seiler and Conrad, 1987; Khalil and Rasmussen, 1990; Crutzen, 1995). It is generally agreed that carbon monoxide comes from both natural and anthropogenic sources. Of the anthropogenic sources, the burning of fossil fuels and biomass is considered by far the most important source, producing carbon monoxide at a rate of approximately 1100 Tg per year (Crutzen, 1995). Natural sources include oxidation of methane and non-methane hydrocarbons and direct emission from the oceans. A summary of the estimated global carbon monoxide budget is

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presented in Table I. However, there is still large uncertainty in the estimates of strength of individual sources. The observed sharp increase in the early 1980's (Khalil and Rasmussen, 1984), the unexpected decrease started in the late 1980's (Khalil and Rasmussen, 1994; Novelli *et al.*, 1994), the recent reversed downward trends (Crutzen, 1995), and current discrepancies in carbon monoxide budget (Bakwin *et al.*, 1994) indicate that improved estimates of sources and sinks for atmospheric carbon monoxide are needed for understanding basic atmospheric chemistry and related environmental issues.

The concentration of carbon monoxide in surface ocean waters has long been known to be supersaturated with respect to atmospheric equilibrium. This supersaturation results in a net flux from the ocean into the atmosphere that has been estimated by several investigators to be in the order of 10–220 Tg y^{-1} (Linnenbom *et al.*, 1973; Conrad *et al.*, 1982; Erickson, 1989; Erickson and Taylor, 1992; Bates *et al.*, 1995). However, all these estimates have been based on measurements of carbon monoxide in the surface water and in the air above, and a simple physical model for sea-to-air transfer which does not apply to the gases, such as carbon monoxide and carbonyl sulphide (COS), being photochemically produced in the surface waters. The use of such simple physical liquid-to-gas transfer model might have significantly underestimated the carbon monoxide flux from the oceans into the atmosphere (Zuo and Jones, 1995).

We have investigated the photochemical and microbial cycling of carbon monoxide in the surface marine and fresh waters (Vanzella *et al.*, 1989; Jones, 1991; Jones and Amador, 1993; Zuo and Jones,

TABLE I The global budget of carbon monoxide in the troposphere (in Tg CO y^{-1})

Type of Source	*Seiler* (1974)	*Logan et al.* (1981)	*Volz et al.* (1981)	*Seiler and Conrad* (1987)	*Khalil and Rasmussen* (1990)
1. Combustion					
Fossil Fuels	640	450	640	440–840	400–1000
Biomass Burning	60	655	300–2200	400–1600	340–1400
2. Oxidation					
Methane	1500–4000	810	600–1300	300–900	400–1000
Nonmethane HCs	60	650	200–1800	400–1400	300–1400
3. Other Sources					
Plants	–	130	50	50–100	50–200
Oceans	100	40	100	10–190	20–80
Total	2400–4900	2700	1900–3700	1600–5000	2000–3000

1994, 1995, 1997). Carbon monoxide in the surface water is mainly produced by photochemical degradation of dissolved organic matter (DOM). The major carbon monoxide sinks are microbial consumption and emission into the atmosphere. The diurnal variation of concentration is due to the balance between photoproduction and loss of carbon monoxide from the surface layer by microbial degradation, sea-to-air exchange, and downward mixing. If we assume that no significant amount of carbon monoxide is accumulated in the surface ocean waters, then:

the amount of photochemically produced
= the amount of microbially consumed
+ the amount of downward transported + the amount of effluxed to the atmosphere. (2)

To calculate the total net flux from the oceans to the atmosphere with this material balance model, it is necessary to estimate the other three quantities in the equation. In this paper, first we present the results of recent studies of photochemical production, microbial consumption, and spatial and temporal changes of carbon monoxide in surface sea waters. Then we combine these results with the above material balance equation to assess the flux of carbon monoxide from the global oceans into the atmosphere.

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EXPERIMENTAL

Investigations of photochemical production and microbial oxidation of carbon monoxide were undertaken aboard the RV "Columbus Iselin" off the southwest coast of Florida and in oligotrophic waters during cruises to the southwestern Sargasso Sea (June, 1987; August, 1989), to the Gulf Stream (May, August, 1991; August, 1992) and to Pacific Ocean (RITS cruise February–March, 1989) and also in the laboratory. Photochemical production rates were examined by exposing surface sea water in sealed quartz tubes to the radiation of a 300-W solar simulator or to natural sunlight. The radiation of the solar simulator has a spectrum similar to the tropospheric sunlight with a light intensity of approximately four times that of summer sunlight in Miami. The light intensity (400–1100 nm) for both light sources were recorded using an International Light Model IL 1700 radiometer with a SED 033 probe. Surface water samples were collected from a teflon-lined bow pumping system every 30 min while the ship was underway and every 60 min when the ship was on station. Florida and Ponce De Leon Bay sea water samples were taken by hand with glass bottles. The samples were filtered (0.45 µm) and degassed to remove ambient carbon monoxide immediately before irradiation. Carbon monoxide concentrations were measured by an automated stripping/gas chromatographic system as described elsewhere (Butler *et al.*, 1987; Jones, 1991). Dissolved organic carbon (DOC) was measured on a Shimadzu TOC-5000 Total Organic Carbon Analyzer, using a high-temperature catalytic oxidation technique.

Microbial oxidation rates of carbon monoxide were measured using the ^{14}C techniques described by Jones (1991). Some oxidation rates were also determined using unlabelled incubations. The inhibitory effect of sunlight on the consumption of carbon monoxide was examined using unlabelled incubation in the same quartz tubes employed for the determination of photoproduction rate. Sea water samples filtered (0.2 µm) and samples wrapped with aluminum foil were exposed to the same conditions as light and dark controls. Carbon monoxide concentrations were measured at various time intervals. The photo-inhibition was estimated by comparing the carbon monoxide concentration change rates in the unfiltered, and filtered sea waters with respect to the dark controls.

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RESULTS AND DISCUSSION

Photochemical Formation of Carbon Monoxide in the Surface Sea Waters

Photochemical formation was observed in all of the water samples irradiated. The formation of carbon monoxide was a linear function of the light exposure time. Dark controls showed no detectable accumulation of carbon monoxide. Figure 1 illustrates a typical plot of photochemical carbon monoxide formation in a Gulf Stream (Gulf of Mexico) water with sunlight illumination. Several unfiltered sea

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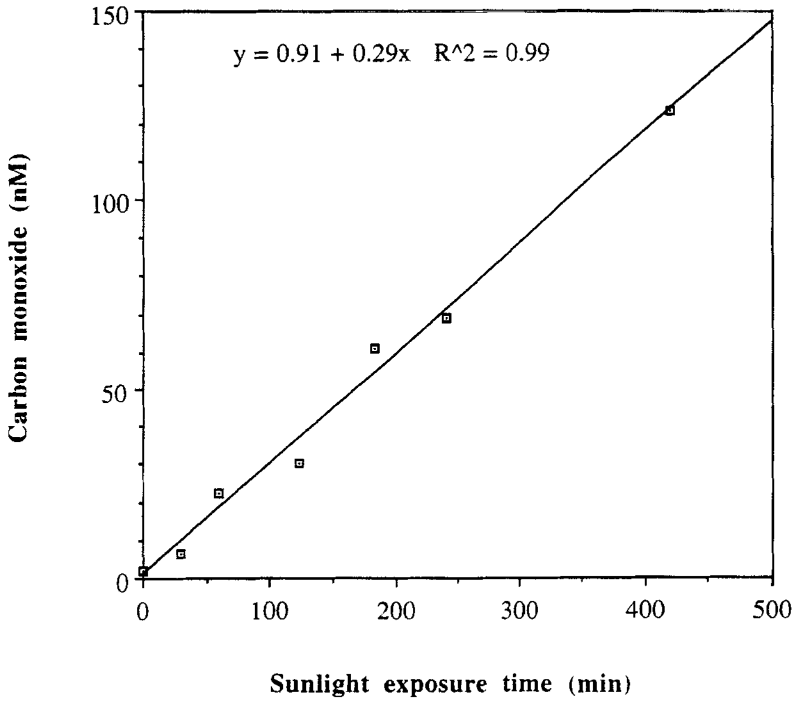

FIGURE 1 Photoformation of carbon monoxide as a function of sunlight exposure time. The samples were collected in Gulf Stream of Mexico at 24° 58′ N, 85°53′ W. Illuminations were performed at solar noon on October 30, 1992. The sunlight intensity $I_0 = 540$ W-h m^{-2}.

water samples and samples filtered through 0.2 μm filters (to remove bacteria) were also irradiated to test possible role of photobiological processes in the production of carbon monoxide. No detectable difference was observed in production rate compared with 0.45 μm filtered samples, indicating that carbon monoxide is produced predominantly in surface sea water by photochemical processes. This is in agreement with Valentine and Zepp's results (1993), but not with Conrad *et al.*'s (1982).

Figure 2 depicts the kinetic curves for carbon monoxide formation using the solar simulator as light source in four sea water samples with different dissolved organic carbon concentrations. Photoformation rates of carbon monoxide, as calculated from the early slopes of the kinetic curves, varied between samples from different regions (Tab. II).

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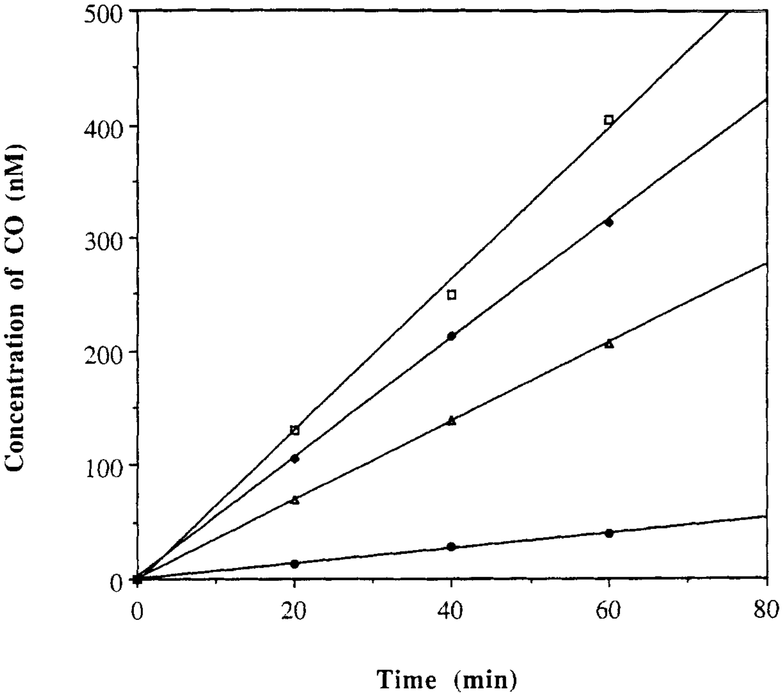

FIGURE 2 Photoformation of carbon monoxide as a function of illumination time with a solar simulator. Sample sources: closed circles, Gulf Stream; triangles, near Shark River outflow; diamonds, Ponce De Leon bay; open squares, Florida Bay near Highway Creek.

Higher formation rates were observed in coastal sea water samples with higher concentrations of dissolved organic carbon relative to the formation rates observed for the water samples taken from oligotrophic, open ocean stations. For example, humic-rich sea water from Florida Bay exhibited a much greater carbon monoxide photoformation rate than humic-poor water taken from the Gulf Stream. When the photochemical formation rate is plotted as a function of the concentrations of dissolved organic carbon (DOC), a good correlation between the carbon monoxide formation rate and the dissolved organic carbon concentration is achieved (Fig. 3). The samples from Florida and Ponce De Leon Bay are not included in this correlation because these near-coastal samples contain extremely high concentrations of dissolved organic carbon which has a very different history of

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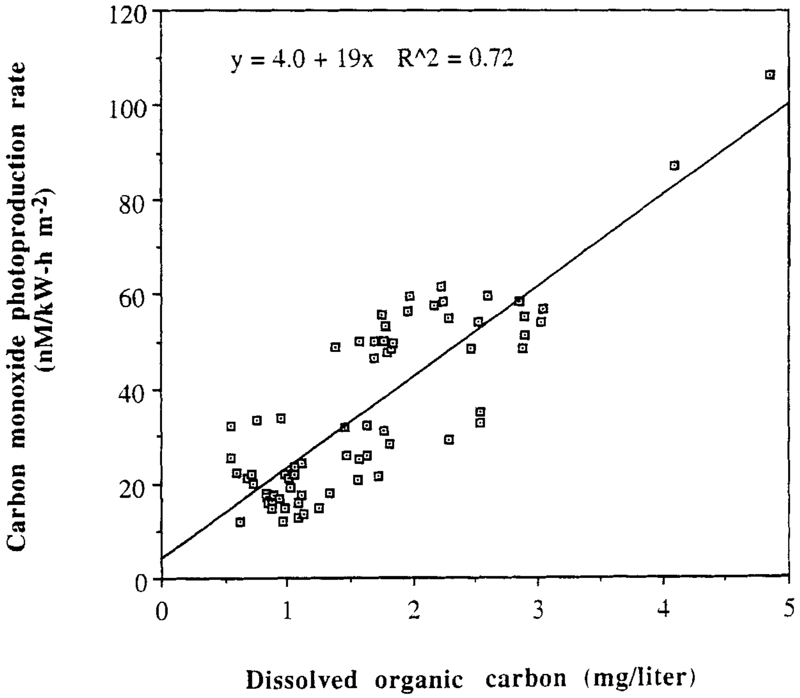

FIGURE 3 Relationship between photochemical production of carbon monoxide and the concentration of dissolved organic carbon (DOC) in marine water.

previous sunlight exposure from the open ocean and offshore sea waters. In coastal surface sea water, carbon monoxide is photochemically formed at an average rate of 25 ± 8 nmol (mg DOC h)$^{-1}$, and in the open ocean, 10 ± 2 nmol (mg DOC h)$^{-1}$, at cloud-free summer solar noon. Based on these production rates, the globally averaged solar flux at the sea level of 178 Wm^{-2}, and an average concentration of dissolved organic carbon of 1.2 mg l^{-1} in the open ocean surface water, and 2 mg litre^{-1} in coastal water, we estimated that the world oceans photochemically produce 1200 ± 200 Tg CO each year. In this 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 is obtained from the action spectrum of sea water for the formation of carbon monoxide.

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TABLE II Summary of photochemical formulation of carbon monoxide in surface sea waters on four cruises. (From Zuo, Y. and Jones, R. D., 1995)

Sampling location		*DOC* *(mg litre^{-1})*	*CO production rate* *(n mol litre^{-1}h^{-1})*	*CO production rate/DOC* *(n mol mg^{-1}h^{-1})*	*Number 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*	27°N, 73°W	1.2 ± 0.3	13 ± 3	11	6

* 300 km northeast of Bahamas.

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Microbial Consumption of Carbon Monoxide and Light Inhibition on Consumption

Although carbon monoxide in surface sea water is predominantly produced by photochemical processes, the microbial oxidation is the only documented pathway for the consumption of carbon monoxide in the ocean (Conrad *et al.*, 1982; Jones, 1991). Table III summarizes the examined turnover time of carbon monoxide in the ocean mixed-layer. In general, carbon monoxide turnovers are much slower in the oligotrophic regions than in the biologically productive coastal waters. Taking a Sargasso Sea average turnover time of 118 h, the mean first order-rate constant of microbial oxidation is 0.0085 h^{-1} in this water. If we further assume a mean mixed-layer depth of 75 m and an average mixed-layer concentration of 2.00 nM, the column oxidation rate is 110 μmol $y^{-1}dm^{-2}$, which is about 10% of the value of the column photochemical production rate of 1100 μmol $y^{-1}dm^{-2}$ in the Sargasso Sea. It should be noted that all values listed in Table III are derived from dark incubation experiments. During the daytime, natural sunlight may significantly inhibit microbial activities, and thereby inhibit the microbial oxidation in the surface sea water. To test this hypothesis, we incubated surface sea water samples under natural sunlight and in the dark. The results of an incubation experiment with surface water collected from Ponce De Leon Bay are presented in Figure 4. Surface water was degassed with carbon monoxide-free air.

TABLE III *In situ* microbial turnover times of carbon monoxide in the ocean mixed-layer

Sampling Location	*Date*	*CO Turnover Time* (*h*)	*N*	*Ref.*
Sargasso Sea	June 1986	71	4	(1)
	Sept. 1986	234	4	(1)
	June 1987	50	4	(1)
Pacific Ocean along 105°W	1989	400	60	(2)
Eastern Caribbean offshore	Spring 1991	57	5	(3)
	Fall 1991	27	6	(3)
Eastern Caribbean inshore	Spring 1991	23	9	(3)
	Fall 1991	4.1	12	(3)
Recife Coast	Fall 1980	26		(4)

(1) Jones, 1991; (2) this work; (3) Jones and Amador, 1993; (4) Conrad *et al.*, 1982, Conrad and Seiler, 1982.

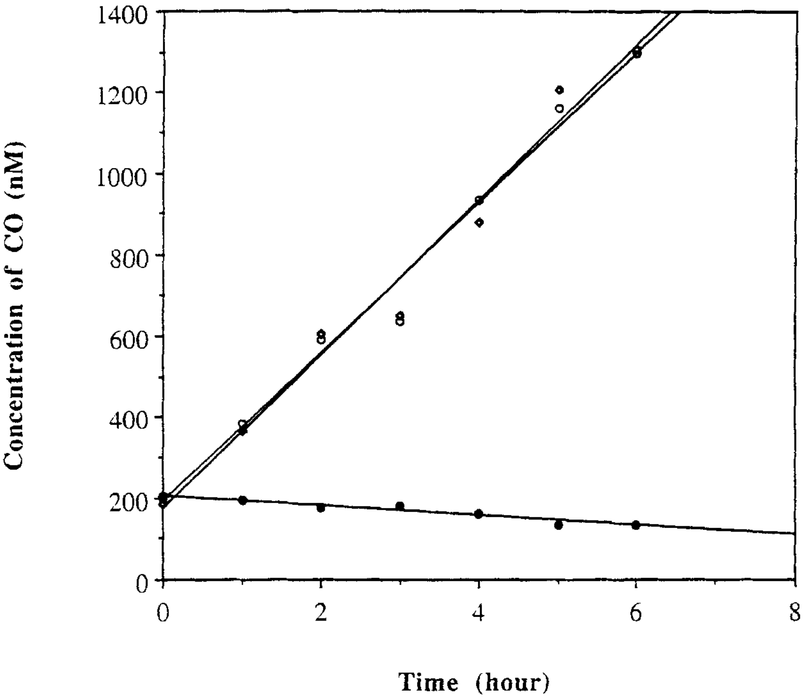

FIGURE 4 Inhibition effect of sunlight on microbial consumption of carbon monoxide in sea water. Water samples were collected from Ponce De Leon Bay. Irradiations were performed on March 12, 1997 ($I_0 = 580$ W-h m^{-2}).

An aliquot was then filtered (0.2 μm) to remove algae and bacteria. After re-establishing a carbon monoxide concentration of 10–20 nM by adding sterile sea water enriched with carbon monoxide, the aliquots, including those with unfiltered sea water, were incubated under natural sunlight or in the dark. Carbon monoxide concentrations were analyzed at varying intervals. As shown in Figure 4, the carbon monoxide concentration in the unfiltered sea water decreased at a rate of about 1 nM h^{-1}. In contrast, the concentrations increased in both the filtered and unfiltered sea waters exposed to sunlight at almost the same rate of 190 nM h^{-1}, indicating that natural sunlight can indeed significantly, if not completely, inhibit the microbial consumption in the surface sea water. At the present time, it is not clear which species of microorganisms are responsible for the observed *in situ* carbon monoxide consumption. Several research lines have

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suggested that the chemolithotrophic ammonium oxidizers *Nitrosomonas*, and methane oxidizers, may be possible candidates (Jones and Morita, 1983, 1984; Dalton and Stirling, 1982; Butler *et al.*, 1987; Jones *et al.*, 1984; Jones and Amador, 1992); they are able to co-oxidize carbon monoxide and exhibit a relatively high affinity for this gas in natural waters. Previous studies have also shown that natural sunlight inhibits significantly the activities of these microbial groups (Alleman *et al.*, 1987; Vanzella *et al.*, 1989; Sieburth, 1986), which is in agreement with our observation. It should also be noted that the observed carbon monoxide turnover time in the Pacific Ocean is much longer than those in the Sargasso Sea. It is, therefore, reasonable to assume that microbial oxidation is responsible for the loss of less than 10% of the photochemically produced carbon monoxide in the world's surface oceans.

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Spatial and Temporal Variation of Carbon Monoxide in the Ocean and its Flux into the Atmosphere

Extensive oceanographic measurements have shown that in near-surface waters dissolved carbon monoxide is not only supersaturated with respect to atmospheric mixing ratios, dissolved concentrations also vary diurnally with light intensity, and regionally with dissolved organic carbon concentration and with other physical, chemical and biological factors (Swinnerton *et al.*, 1969, 1970, 1976; Lamotagne *et al.*, 1971; Linnenbom *et al.*, 1973; Seiler and Schmidt, 1974; Conrad *et al.*, 1982; Jones, 1991; Bates *et al.*, 1993; Jones and Amador, 1993; Johnson and Bates, 1996). Vertical profiles of dissolved carbon monoxide reveal usually smooth gradients within the euphotic zone with the highest carbon monoxide concentration occurring at or near the surface, and decreasing to levels just above saturation below the euphotic zone. Carbon monoxide concentrations throughout the rest of the water column remain fairly constant, except for higher concentrations found near the sediment/water interface or occasional anomalies observed at intermediate depths (Swinnerton and Lamontagne, 1974; Conrad *et al.*, 1982; Jones, 1991; Johnson and Bates, 1996). Two typical vertical profiles of dissolved carbon monoxide are given in Figure 5, which were measured at different times during a

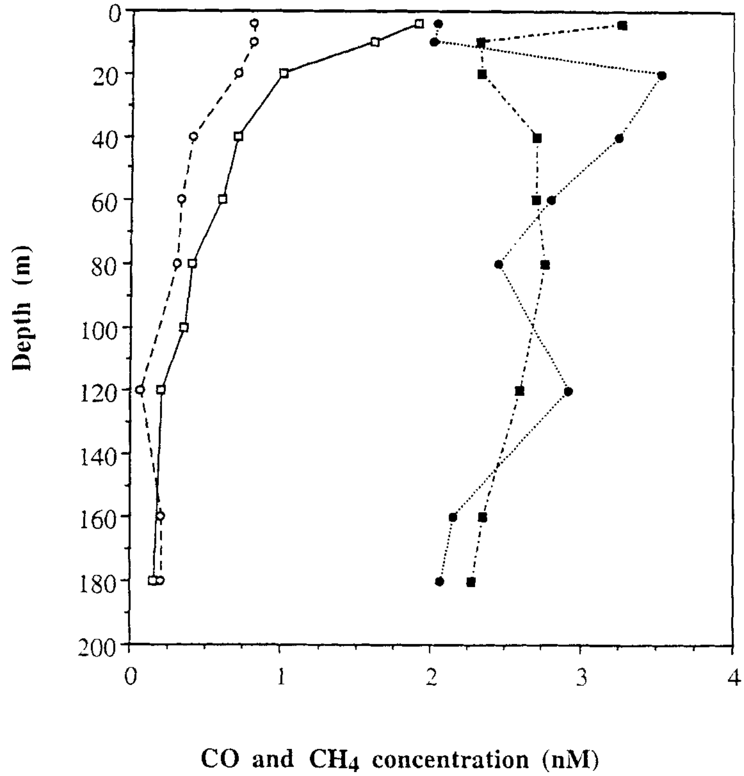

FIGURE 5 Vertical profiles of carbon monoxide and methane. Open symbols for carbon monoxide, closed symbols for methane; circles, 21:00, 31 May, and squares, 18:30, 1 June, 1987.

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cruise to the Sargasso Sea (June, 1987). Figure 6 is taken from Conrad *et al.* (1982) and shows the concentration as a function of the time of day at several depths. The data show clearly that dissolved concentrations within the euphotic zone follow a diel rhythm with maxima in the afternoon and minima in the early morning. The overall life time in surface sea waters is less than 3–4 hours. In contrast, the carbon monoxide concentration remains constant with time in the deeper sea water (below 100 m), indicating that the net transport from the euphotic zone to the underlying deeper ocean water is limited. This means that the third term of the balance equation (2) is approximately zero, and the carbon monoxide flux from the oceans to the atmosphere is the difference between the photochemical production and *in situ*

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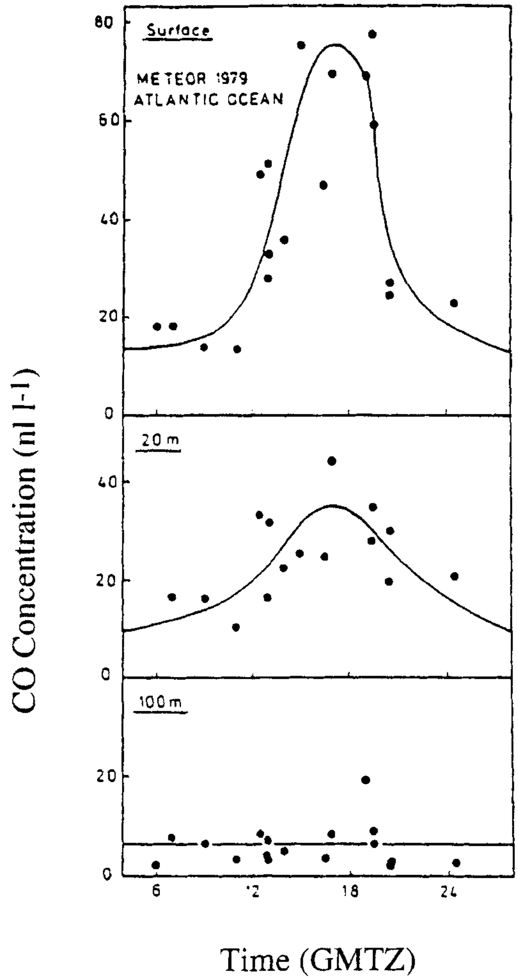

FIGURE 6 Diurnal variation of carbon monoxide concentration in sea water. (From Conrad *et al.*, 1982).

microbial consumption. Thus, the net contribution of the global oceans to atmospheric carbon monoxide is 1000 ± 200 Tg y^{-1}, which is about one order of magnitude greater than the previously estimated value of 100 ± 90 Tg by the simple physical air–sea transfer model. This production accounts for more than one third of the current global budget of atmospheric carbon monoxide of 2000–3200 Tg y^{-1}.

Considered this improved estimate of the ocean source for atmospheric carbon monoxide, the global budget of tropospheric carbon monoxide should be modified to a range of 3000–4200 $\text{Tg}\,\text{y}^{-1}$ (see Tab. I for more information on the budget).

These results suggest that the ocean is a more important source of atmospheric carbon monoxide than thought previously. When this oceanic production is combined with other natural sources, it is clear that the global level of carbon monoxide is governed by natural sources, while human activities determine atmospheric abundance locally. This study also indicates that photochemical processes play an important role in the marine biogeochemical cycling of carbon. These processes could potentially convert about 500 Tg dissolved organic carbon per year to carbon monoxide in the world ocean.

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