



Evidence for significant photochemical production of carbon monoxide by particles in coastal and oligotrophic marine waters

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[1] Carbon monoxide (CO) photoproduction from particulate and chromophoric dissolved organic matter (CDOM) was determined in seawater from open-ocean and coastal areas. In confirmatory tests, poisoned or non-poisoned filtered and unfiltered blue-water samples, were exposed to sunlight. CO photoproduction was 21–42% higher in the unfiltered than in the filtered samples. In a more thorough study utilizing concentrated particles prepared by 0.2- μm cross-flow filtration, samples containing varying levels of particles were irradiated under simulated solar radiation. Their CO photoproduction rates increased linearly with particle concentration factor. Particulate CO production was 11–35% of CDOM-based CO production. On an absorbed-photons basis, the former was 30–108% more efficient than the latter. This study suggests that in both coastal and blue waters these new-found particulate photoprocesses are of similar biogeochemical importance to the well-known CDOM photoproduction term. **Citation:** Xie, H., and O. C. Zafriou (2009), Evidence for significant photochemical production of carbon monoxide by particles in coastal and oligotrophic marine waters, *Geophys. Res. Lett.*, 36, L23606, doi:10.1029/2009GL041158.

1. Introduction

[2] Recent decades have witnessed growing evidence of the impacts of marine photochemistry on the cycling of dissolved organic carbon and trace gases (e.g., carbon monoxide, carbonyl sulfide, dimethyl sulfide) [Mopper and Kieber, 2002]. Photochemistry exerts a major control on the fate of biologically refractory dissolved organic matter (DOM) [Opsahl and Benner, 1997; Andrews et al., 2000] by labilizing refractory DOM to metabolic attack [Mopper and Kieber, 2002] and by oxidizing chromophoric DOM (CDOM) to small inorganic molecules, mainly carbon dioxide (CO₂) and carbon monoxide (CO) [Miller and Zepp, 1995]. Most previous marine photochemistry studies focused on DOM and ignored the particulate phase (POM), since POC is only ~12% of DOC in surface open ocean waters [Millero, 2002]. Exceptions include the photodegradation of chlorophyll and unsaturated lipids of phytoplankton [e.g., Llewellyn et al., 1990; Rontani, 2001; Cuny et al., 2002; Rontani et al., 2003]. However, earlier studies demonstrated that photodecomposition of vascular plants in air or water produces ample CO [Tarr et al., 1995] and CO₂ [Anesio et al.,

1999]. More recent works discovered photorelease of DOC from resuspended sediments and phytoplankton detritus [Kieber et al., 2006; Mayer et al., 2006; Riggsbee et al., 2008]. Stubbins et al. [2006, and references therein] presented preliminary evidence for photoproduction of CO from estuarine POM and recommended further work on the role of particles in CO photoproduction. These results indicate potentially important impacts of particle photochemistry in freshwater and estuarine environments.

[3] In contrast to this limited knowledge of POM photochemistry in fresh and estuarine waters, almost nothing is known of this process in oceanic waters, particularly blue waters, at least partly due to formidable methodological challenges posed by the much lower abundance of particles in oceanic waters. CO, however, is potentially an excellent species for studying seawater particle photochemistry (as is already well-known for DOM photochemistry), since almost uniquely, it can be measured easily and precisely ($\pm 2\%$) [Zafriou et al., 2008]. Hence even small signals due to particles should be detectable. Additionally, CO has been used to indicate DOM photoreactivity, since it is the second most abundant carbon photoproduct and a potential proxy for other major, more-difficult-to-measure photoproducts (e.g. CO₂, biolabile carbon) [Miller and Zepp, 1995; Miller et al., 2002]. Potentially, an analogous proxy role may hold for CO in particle photochemistry. We report here clear evidence of major particle-based CO photoproduction in both coastal and blue waters, and discuss its implications for the global ocean's CO budget.

2. Methods

[4] After indirect evidence strongly implicated CO photoproduction by POM at the Bermuda Atlantic Time-series Study (BATS) site (O. Zafriou, to be reported elsewhere), confirmatory work was performed using seawater from the surface mixed layer (20 m) at BATS in June 2007. Upon minimizing background CO by bubbling with CO-free air, filtered (0.2- μm) and unfiltered aliquots, either poisoned (2.7 mg KCN L⁻¹) or non-poisoned, were placed into 110-mL quartz ampoules (i.d. 5.08 cm) in triplicate and exposed to clear-sky sunlight (48.45°N) for 1–2 h near noon. CO concentrations ([CO]) before and after irradiation were quantified by a headspace method [Xie et al., 2002].

[5] A more thorough study was conducted in September 2007 on samples taken from BATS, Vineyard Sound (VS), Massachusetts, and Pointe-au-Père (PAP), on the south shore of the lower St. Lawrence estuary, Quebec (Table 1). Samples were treated immediately for PAP and within 1–3 d of collection for VS and BATS, respectively. Large particles were removed from VS by gravitational deposition and from PAP by pre-filtration through 20- μm glass-fiber membranes

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Table 1. Rates of CO Photoproduction From Particles (P_p) and CDOM (P_{cdom}) and the Corresponding Derived Apparent Photochemical Efficiencies, β_p and β_{cdom}

Sample ^b	Position	Depth (m)	Salinity	$a_{cdom}(330)$ (m^{-1})	$a_p(330)$ (m^{-1})	P_{cdom} ($nmol L^{-1} h^{-1}$)	P_p ($nmol L^{-1} h^{-1}$)	P_p / P_{cdom}	$\beta_{cdom}(330)^c$ ($nmol m L^{-1} h^{-1}$)	$\beta_p(330)^d$ ($nmol m L^{-1} h^{-1}$)	R (330) ^e
BATS	31.67°N, 64.17°W	40 ^f	36.2	0.103	0.012	0.14	0.034	0.24	1.36	2.83	2.08
VS	41.52°N, 70.68°W	0	32.0	1.58	0.43	2.35	0.83	0.35	1.49	1.93	1.30
PAP	48.45°N, 68.51°W	0	29.9	1.89	0.13	2.79	0.31	0.11	1.48	2.38	1.61

^aAlso shown are sampling position, depth, salinity, and the absorption coefficient of CDOM (a_{cdom}) and of total particles (a_p) at 330 nm.

^bBATS: Bermuda Atlantic Time-series Study site; VS: Vineyard Sound, Massachusetts; PAP: Pointe-au-Père, Rimouski, Quebec.

^c $\beta_{cdom}(330) = P_{cdom} / a_{cdom}(330)$.

^d $\beta_p(330) = P_p / a_p(330)$.

^e $R(330) = \beta_p(330) / \beta_{cdom}(330)$.

^fJust below the base of the surface mixed layer.

(Millipore). To increase sensitivity to particle vs. CDOM photoprocesses, particles were then concentrated using a MiniKros[®] cross-flow filtration (CFF) system fitted with a pre-cleaned 0.2- μ m disposable MiniKros[®] hollow fiber module. A particle concentration series was established, including the filtrate (particle concentration factor, PCF, = 0) and original water (PCF = 1). Samples in each concentration series were equilibrated with clean air and transferred into 40-mL cylindrical quartz cells (i.d. 2.0 cm) in duplicate, with a 1:3 headspace:water volume ratio. The cells were irradiated for 3–4 h under a SUNTEST XLS+ solar simulator in a water bath (21–23°C). To facilitate gas-water equilibration, samples were simultaneously rotated at \sim 35 rpm about an axis tilted from the vertical irradiance incident on the bath, measured to be 91 W m⁻² with an OL-754 spectroradiometer. As CO is sparingly soluble in seawater (Henry's law constant \sim 48:1 air:water at 21°C), rotation with a headspace rapidly transferred \sim 94% of photoproduced CO into the headspace, minimizing its microbial uptake (the main sink of CO in seawater [Zafiriou *et al.*, 2003; Xie *et al.*, 2005]). Parallel dark incubations showed negligible CO loss in BATS and PAP and 4–9% losses in VS. VS data were corrected in calculating CO photoproduction. If CO-consuming microbes were aggregated within CO-producing particles, this method may only give a lower limit on particle-based CO production.

[6] CDOM absorbance spectra, referenced to Nanopure water, were recorded at \sim 21°C in 10-cm quartz cells using a Perkin-Elmer lambda-35 UV-visible spectrometer. Napierian CDOM absorption coefficients at wavelength λ , $a_{cdom}(\lambda)$ (m^{-1}), were calculated as 2.303 times the absorbance divided by the light pathlength in meters. Suspended particles in untreated samples were collected onto GF/F filters, and their absorption coefficients, $a_p(\lambda)$ (m^{-1}), were determined following the method by Tassan and Ferrari [2002], using the same spectrometer fitted with a 50-mm integrating sphere. Baseline corrections for $a_{cdom}(\lambda)$ and $a_p(\lambda)$ measurements were made using the methods of Babin *et al.* [2003] and Babin and Stramski [2002], respectively.

3. Results and Discussion

[7] The unfiltered June 2007 BATS mixed-layer samples, cyanide-poisoned or not, displayed higher CO production rates than did their filtered counterparts (Figure 1), confirming

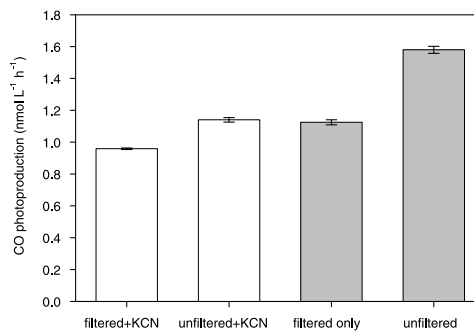


Figure 1. Rates of CO photoproduction for different treatments of a water sample collected in June 2007 from the BATS site. Cyanide-poisoned and non-poisoned treatments were irradiated on different days. Error bars are one standard deviation.

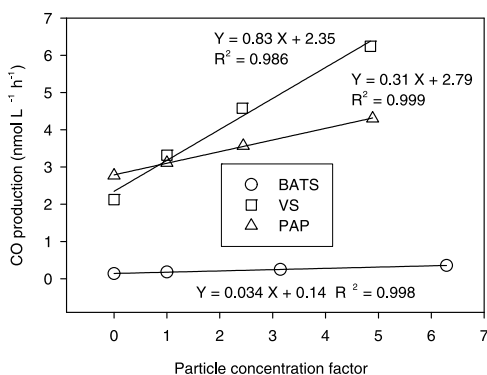


Figure 2. Rate of CO photoproduction as a function of particle concentration factor (PCF) for samples collected in September 2007 from the BATS site, Vineyard Sound (VS), Massachusetts, and Pointe-au-Père (PAP), Rimouski, Quebec. Lines are least-squares best fits of the data. PCF = 1 corresponds to untreated water.

particle-based CO production, CO_{part} , in these oligotrophic waters. In the poisoned sample, CO_{part} was 19% of that from CDOM; the proportion increased to 40% in the nonpoisoned sample. Since cyanide suppresses CO photoproduction from CDOM (H. Xie and O. Zafiriou, unpublished data, 2002), it may do so for particles as well. The lower proportion of particle-based production in the poisoned sample might then arise from a stronger cyanide effect on particles vs. CDOM and/or from living cells being more efficient at CO photoproduction than poisoned cells. Additionally, CO production by living cells could be effected by a photobiological mechanism, as assumed by some early researchers [e.g., Swinnerton *et al.*, 1977]. Subsequent studies, however, ascribe CO production by phototrophic organisms principally to photo-oxidation of plant tissues [Bauer *et al.*, 1980; King, 2001]. Microbial uptake in the nonpoisoned, unfiltered sample was negligible over the exposure period. Its bacterial activity may have been inhibited by solar UV radiation and/or by temperature changes during storage (in situ $\sim 26^{\circ}C$; storage $\sim 4^{\circ}C$).

[8] All particle concentration series irradiations exhibited increases in CO production rate that were linear with PCF (Figure 2). The excellent linearity of regressions through both the untreated samples (PCF = 1) and the filtrates (PCF = 0) proves that the CFF process did not cause significant artifacts. The intercepts and slopes of regressions in Figure 2 correspond to the rate of CO production by CDOM (P_{cdom}) and by particles (P_p), in the original sample (PCF = 1). In ascending order, P_{cdom} was: BATS < VS < PAP, and P_p : BATS < PAP < VS (Table 1). This order parallels the trends for a_{cdom} and a_p shown in Figure 3. P_p values corresponded to 11% of P_{cdom} for PAP, 24% for BATS, and 35% for VS, in line with the values of $a_p(330):a_{cdom}(330)$ ratios: PAP (7%) < BATS (12%) < VS (27%).

[9] Based on 3-D Monte Carlo simulations using Simulo version 1.3.6 (Laboratoire d'Océanographie de Villefranche), the amounts of photons in the UV and visible regimes absorbed by CDOM and particles in the irradiation cells were proportional to a_{cdom} and a_p , consistent with the linear relationships observed in Figure 2. The a_{cdom} - and a_p -normalized CO production rates then represent the efficiencies of the CDOM- and particle-based CO productions,

β_{cdom} and β_p , respectively. At 330 nm, the wavelength usually giving rise to the maximum CO production in the water column [Zhang *et al.*, 2006], the β_{cdom} values for VS and PAP are similar, but 10% higher than the β_{cdom} for BATS (Table 1). These data corroborate previous studies revealing higher efficiencies of CDOM-based CO photoproduction in coastal than in blue waters [Zhang *et al.*, 2006; Ziolkowski and Miller, 2007; Xie *et al.*, 2009]. In contrast, $\beta_p(330)$ for BATS is highest, 19 and 47% higher than those for PAP and VS, respectively (Table 1). $\beta_p(330)$ displayed a negative, linear correlation with $a_p(330)$ [$\beta_p(330) = -2.03 * a_p(330) + 2.77$, $R^2 = 0.941$, $n = 3$], opposite to the positive correlation between the efficiency of CO production by CDOM photochemistry and a_{cdom} [Xie *et al.*, 2009]. This inverse correspondence between β_p and a_p , if confirmed elsewhere, will lay a basis for developing satellite-based evaluation of marine particle photochemistry, as has recently been proposed and tested for CDOM photooxidation [Del Vecchio *et al.*, 2009; Fichot and Miller, 2009; Xie *et al.*, 2009]. Notably, despite the similarity of both spectra in shape, the particle absorption spectrum of VS was 3.7 (± 0.3) times that of PAP in magnitude in the range 300–500 nm. This contrasts the similarity of the CDOM absorption spectra of VS and PAP in both shape and magnitude (VS / PAP = 0.91 ± 0.06 from 300–500 nm) (Figure 3). The much bigger a_p for VS may have partly resulted from a higher proportion of large suspended particles, as gravity-deposition (performed on VS) was less effective than 20- μm pre-filtration (executed on PAP) in eliminating them. Perhaps then, large particles possessed low efficiencies of CO production.

[10] Another important parameter is the $\beta_p(330):\beta_{cdom}(330)$ ratio, $R(330)$ (Table 1), which varies substantially (range: 1.30–2.08) but is >1 for all samples: particles

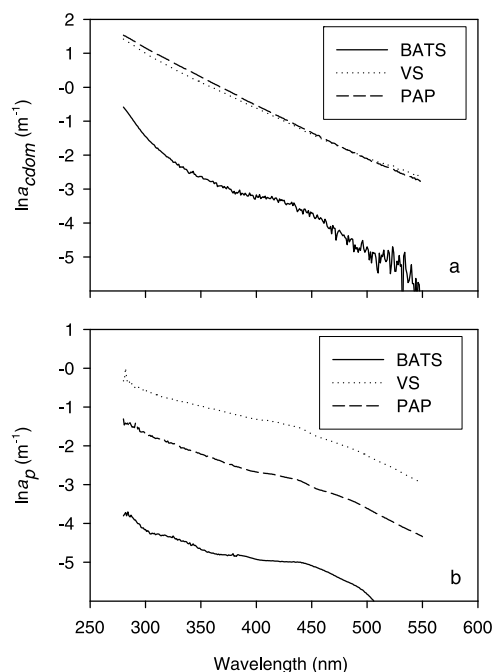


Figure 3. Absorption spectra of CDOM (a) and total particles (b) of the original (unconcentrated) samples tested in Figure 2. Keys for samples are the same as in Figure 2.

always produced CO more efficiently than did CDOM. This is consistent with the finding that chlorophyll-sensitized photodegradation processes are strongly favored in micro-environments such as senescent phytoplanktonic cells or phytodetritus [Nelson, 1993], where pigments remain in molecular-scale association at high local concentrations, strengthening their interactions in photosensitized processes. Moreover, the lifetime of the highly reactive singlet oxygen produced from sensitizers in lipid-rich hydrophobic micro-environments should be longer than in aqueous CDOM solutions. Photooxidative effects in such microenvironments might therefore be more efficient [Nelson, 1993], resulting in enhanced formation of photoproducts.

[11] Study of a PAP water sample collected in September 2009 was conducted under similar experimental conditions as those in September 2007 to examine whether increased CO production in particle-enriched samples might be partly caused by release of CDOM from particles prior to and/or during irradiation. No significant difference in $a_{cdom}(\lambda)$ ($<2\%$; λ : 300–500 nm) was observed between the unirradiated filtrate and the particle-enriched fraction (PCF = 5.0) and neither fraction's $a_{cdom}(\lambda)$ changed significantly after irradiation ($\leq 2\%$; λ : 300–500 nm). Particles thus did not add appreciable new CDOM to the particle-containing fraction, confirming that enhanced CO production was directly induced by particles. Although no tests were performed on the VS and BATS samples (due to logistic and financial constraints), the production of CDOM in the BATS sample was likely unimportant given its long turnover time in blue waters (order of months [Nelson *et al.*, 1998]) compared to the short irradiation durations (3–4 h) and intensity (91 W m^{-2}) employed here. The untested effect of particles on $a_{cdom}(\lambda)$ in the VS sample might also be comparable to that in the PAP sample. However, at larger absorbed light doses POM may generate CDOM whose photoreactivity differs from the original CDOM, as it becomes partially photobleached. Clearly, further mechanistic studies are needed to determine if the particle and CDOM pools behave independently, or to what extent the particle effect is mediated by release of CDOM and its subsequent photolysis.

[12] This study suggests that in blue waters CO photoproduction from particles is 20–40% of that from CDOM, or 8–16 Tg CO-C a^{-1} (Tg carbon from CO per year) based on recent estimates of the global blue-water CO photoproduction of $\sim 40 \text{ Tg CO-C a}^{-1}$ [Zafiriou *et al.*, 2003; Stubbins *et al.*, 2006; Fichot and Miller, 2009]. In coastal waters, the particle-produced proportion is 10–35%, or 0.3–1.0 Tg CO-C a^{-1} , based on the estimate of the global coastal-water CO photoproduction of 2.9 Tg CO-C a^{-1} [Fichot and Miller, 2009]. The total CO photoproduction (particles plus CDOM) in the global ocean is then 51–60 Tg CO-C a^{-1} . This value broadly agrees with a prior estimate of 53–84 Tg CO-C a^{-1} from POM plus CDOM [Stubbins *et al.*, 2006]. That estimate assumed that the photoreactivity of POM in the open ocean is similar to that of DOM and used approximate optical measurements that required equating the particulate absorption to the measured quantity, absorption plus scattering. Adding a global oceanic CO dark production of 5–16 Tg CO-C a^{-1} [Zhang *et al.*, 2008] yields a total global oceanic CO source of 56–76 Tg CO-C a^{-1} . While extrapolating our results to regional or global scales is fraught with large uncertainties due to limited

spatial and seasonal coverage, if the global extrapolation of our CO budget estimates above is robust, the balance of CO sources and sinks reported by Zafiriou *et al.* [2003] is thrown into serious imbalance, requiring faster CO consumption and/or outgassing, or implying new CO sinks. Obviously, more work is needed to refine the estimates given here.

[13] Future studies should also elucidate any differences among various particle types: living vs. nonliving particles, effects of particle size, and effects of environmental variables (e.g., spectral quality of the light field, temperature, salinity, pH). The implications of particle-based photoprocesses for other major photoproducts also require elucidation.

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