Marine Chemistry 171 (2015) 21–35

Contents lists available at ScienceDirect

Marine Chemistry

journal homepage: www.elsevier.com/locate/marchem

Photochemical production of CO and CO_2 in the Northern Gulf of Mexico: Estimates and challenges for quantifying the impact of photochemistry on carbon cycles

Leanne C. Powers, William L. Miller *

[a] Department of Marine Sciences, University of Georgia, Athens, GA 30602, USA

ARTICLE INFO

Article history:
Received 9 September 2014
Received in revised form 1 February 2015
Accepted 9 February 2015
Available online 12 February 2015

Keywords:
Photochemistry
CDOM
Carbon dioxide
Carbon monoxide
Apparent quantum yield
Gulf of Mexico

ABSTRACT

The photochemical production of carbon dioxide (CO_2) and carbon monoxide (CO), derived from marine colored dissolved organic matter (CDOM), is considered a significant oceanic loss process for the large and variable fluxes of terrigenous dissolved organic carbon (DOC) in river dominated coastal systems. Using samples collected over 4 seasons (2009–2010) in a grid centered on the Mississippi–Atchafalaya River system in the Northern Gulf of Mexico, we attempt to improve constraints for these direct photochemical impacts on DOC cycles by contributing the largest coherent set of photochemical apparent quantum yield (AQY) spectra for CO to date ($n = 99$), 18 of which had CO_2 AQY spectra determined in the same sample for use in calculating CO_2:CO photoproduction ratios. Simple correlations, previously reported from much smaller data sets, between CO photoproduction and CDOM optical properties showed weak or no correlations within our much larger spatio-temporal study. However, grouping samples with an optical transition point ($a_g(320) = 1.3\ m^{-1}$) allowed definition of two distinct inshore and offshore CO AQY spectra. Inputting these in regional photochemical models that use remotely sensed ocean color data and modeled water optical properties dramatically improves results over using a single CO AQY spectrum (modeled vs. measured $r^2 = 0.73$ vs. 0.18 for single AQY), as has been done previously. Monthly average CO photoproduction rates ranged from 6.0 to 17.7 $\mu mol\ m^{-2}\ d^{-1}$, amounting to a conservative estimate of 3.35 Gg C yr^{-1} for our study region. Our data also shows that the efficiency for CO_2 photoproduction decreases over prolonged irradiations up to 48 h. Consequently, no assessable method exists for direct determination of initial rates in clear waters with low CO_2 photoproduction. Therefore CO_2 photoefficiency in the Gulf of Mexico was inferred using CO photoproduction estimates and CO_2:CO ratios. In agreement with previous studies, CO_2:CO ratios determined here were also poorly constrained, ranging from ~6 to 66 providing a median value of 24.4. This approach estimates that direct photochemical production of CO_2 plus CO can remineralize DOC on the order of 85 Gg C each year. This estimate provides an improvement over the use of a single inshore CO_2 AQY spectrum for a largely blue water system but caution should be used when interpreting CO_2 photochemical flux estimates that rely heavily on the selection of CO AQY spectra and/or poorly constrained relationships between CO_2 and CO photoproduction. Our results stress that the continued expansion of the CO_2:CO ratio database to new oceanic regimes is likely of very limited value and that assessable direct methods or better proxies to quantify CO_2 photochemistry in clear marine waters are needed.

1. Introduction

Terrestrial dissolved organic carbon (DOC) transported to the coast via rivers is photoreactive (Kieber et al., 1990; Miller and Zepp, 1995) and many irradiation studies on a variety of riverine waters suggest that 31–45% of this DOC is lost during long term photochemical exposure (Moran et al., 2000; Spencer et al., 2009). Specifically, solar ultraviolet radiation (UVR; 280–400 nm) absorbed by chromophoric dissolved organic matter (CDOM) results in significant oxidation of DOC to form carbon dioxide (CO_2), carbon monoxide (CO), and a variety of low molecular weight organic molecules (Kieber et al., 1990; Miller and Zepp, 1995; Mopper and Kieber, 2002). In the marine environment, the largest identified DOC photoproduct is "CO_2" which is most often analyzed as dissolved inorganic carbon (DIC) (i.e. the sum of dissolved CO_2, HCO_3^-, and CO_3^{2-}) (Bélanger et al., 2006; Miller and Moran, 1997; Miller and Zepp, 1995; White et al., 2010). Analytical challenges inherent in measuring low μM photochemical production of DIC in seawater containing ~2 mM DIC background concentrations results in almost all published CO_2 photochemical experiments removing DIC prior to irradiation of high CDOM coastal water to create measurable production. Consequently blue water CO_2 photoproduction rates are rare and very

* Corresponding author.
E-mail addresses: lcpowers@uga.edu (L.C. Powers), bmiller@uga.edu (W.L. Miller).

http://dx.doi.org/10.1016/j.marchem.2015.02.004

close to the analytical detection limit, making any large-scale estimates beyond nearshore environments speculative.

The second largest identifiable marine carbon photoproduct is CO, which also occupies a key position in oceanic carbon cycling (Zuo and Jones, 1995), acting both as a direct DOC removal pathway and as a substrate for bacterial DOM mineralization (Moran and Zepp, 1997; Xie et al., 2009; Zafiriou et al., 2008). Due to the analytical sensitivity of well refined headspace equilibration methods (e.g. Xie et al., 2002) and the fact that irradiations require no sample pretreatment beyond filtering, CO has become the most extensively studied marine carbon photoproduct, with flux calculations published for samples ranging from highly turbid (Stubbins et al., 2011; White et al., 2010; Zhang et al., 2006) to coastal (Xie et al., 2009; Ziolkowski and Miller, 2007) and oligotrophic waters (Stubbins et al., 2006; Zafiriou et al., 2003; Ziolkowski and Miller, 2007). Despite the extensive work on CO photochemistry, most studies examine the efficiency of CO photoproduction by determining apparent quantum yield (AQY) spectra using far fewer than 20 samples in only one or two sampling seasons.

For CO, a correlation between salinity and its photochemical production has been demonstrated in a variety of coastal zones (Reader and Miller, 2012; Stubbins et al., 2011; Xie et al., 2009; Zhang et al., 2006). However, Stubbins et al. (2011) showed that a simple 2 component-mixing model could not be used to predict CO photoefficiency in the Tyne Estuary, demonstrating non-conservative CDOM photoreactivity in terms of both the removal and addition of reactive and nonreactive CDOM in this coastal zone. Additionally, Reader and Miller (2012) found no correlation between CDOM-normalized photoproduction of either CO_2 or CO and salinity in coastal estuaries of the South Atlantic Bight. They did observe, however, that there was a seasonal trend in CO photoproduction rates, with lower CO production efficiency in the spring and summer and higher CO production efficiency in the fall and winter. Considering the contradictory reports and dynamic nature of these estuarine systems, the spatiotemporal variability in both CO_2 and CO photoproduction rates in fresh water impacted coastal zones requires further evaluation.

A recent multi-season coastal study by Reader and Miller (2012) has provided a much larger temporal CO dataset, including 38 paired CO_2 and CO experiments that determine both production rates and the spectral efficiency, as AQY spectra, for both reactions. This attempt to constrain not only the seasonal variability of each photoproduct but to quantify the link between photochemical CO_2 and CO flux estimates builds on previous work that suggests the *total* direct photochemical loss term for marine DOC might be estimated using relationships to the well-studied and analytically accessible CO results (Miller and Zepp, 1995; Reader and Miller, 2012; White et al., 2010) and a robust CO_2:CO ratio. Studies reporting CO_2:CO photoproduction ratios, however, have found a range from ~2 to >65 (Miller and Zepp, 1995; Johannessen 2000; White et al., 2010; Reader and Miller, 2012), suggesting that a single ratio is not appropriate for global or regional models of CO_2 photochemical fluxes. White et al. (2010), using only three ratios, explain some of this variability in CO_2:CO ratios noting correlations with AQY spectra and salinity in the Delaware Estuary. CO AQY spectra decreased with increasing salinity while CO_2 AQY spectra remained unchanged, thus altering the ratio with salinity related changes in CO AQY spectra.

To provide better estimates for the photochemical impact on DOM turnover in river-dominated coastal margins, we have greatly expanded the database for CO and CO_2 photoproduction rates in the Northern Gulf of Mexico. Our focus on this area is based on isotopic and elemental data that indicate in situ production, bacterial utilization and photo-oxidation could all regulate the removal of DOC (Wang et al., 2004) in this region of large and variable terrigenous carbon fluxes (~3 Tg C yr^{-1}; Bianchi et al., 2004; Shen et al., 2012). Collecting over 4 seasons, we have determined CO AQY spectra for 81 stations and CO_2:CO ratios using the photoproduction of both CO_2 and CO in 18 paired samples (99 total CO spectra) to assess the seasonal and spatial variability in AQY spectra appropriate for this region. Our initial goal was to link this CO variability to CO_2 photoproduction. The study reported here represents the largest coherent data set for CO AQY spectra gathered to date, thus allowing a comprehensive evaluation of trends in CO photoproduction in the Northern Gulf of Mexico. Based on these data, we optimized methods to estimate photochemical CO production from remotely sensed ocean color and modeled solar irradiances (Fichot and Miller, 2010). With associated CO_2 AQY spectra and their relationship to CO photoproduction, we estimated the average photochemical fluxes for both species and evaluate their overall role in carbon cycles for the Northern Gulf of Mexico.

2. Methods

2.1. Sampling

Surface water samples for photochemical experiments were collected in the Northern Gulf of Mexico as part of the GulfCarbon project on four separate 12 day research cruises onboard the R/V *Cape Hatteras* in April 2009, July 2009, and March 2010 and onboard the R/V *Sharp* in October/November 2009. 2 or 3 L of water were collected and 0.2 μm filtered (Whatman Polycap 75 AS nylon membrane) directly from 12 L Niskin bottles into 1 L acid-cleaned (2 M HCl, J.T. Baker) ashed borosilicate glass bottles (Kimax) at 20 stations, with the exception of October/November 2009 when 21 samples were collected, for a total of 81 samples (Figs. 1 and 1SI, supporting information). All samples were stored at 4 °C in the dark until use for a period of up to one year. CDOM absorption spectra have been shown to exhibit no significant changes when stored in this manner for up to 12 months (Johannessen and Miller, 2001; Swan et al., 2012).

2.2. Laboratory irradiations and optical measurements

All laboratory irradiation experiments were performed using a Suntest CPS solar simulator equipped with a 1.5 kW xenon lamp (Atlas), as detailed in Reader and Miller (2012). Each water sample was brought to room temperature, partitioned into 15 gas-tight 10 cm cylindrical quartz spectrophotometric cells, and sealed with no headspace using caps fitted with Teflon faced, butyl rubber septa (Microsolv) to minimize diffusion, particularly of CO_2, into the sample. The absorbance in each cell was measured from 250 to 800 nm with a dual beam UV–vis spectrophotometer (Lambda 40; Perkin Elmer) both prior to and postirradiation at room temperature. 18.0 MΩ Milli-Q water (Millipore) was used as the absorbance blank. For open ocean samples,

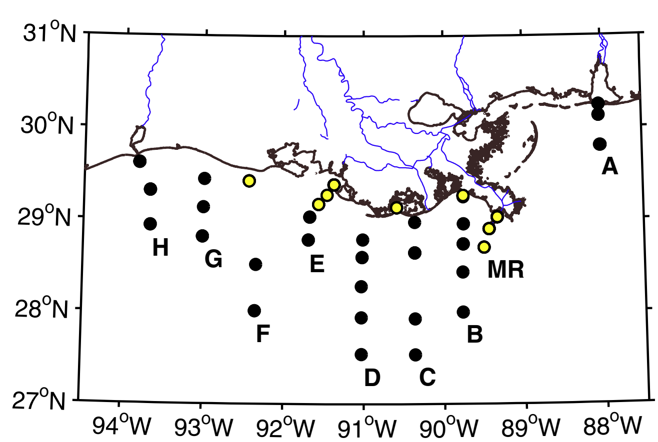

Fig. 1. Sampling locations in the Northern Gulf of Mexico over 4 separate research cruises between 2009 and 2010, with stations used for both CO_2 and CO AQY spectra determination highlighted in yellow. For CO AQY spectra, 20 or 21 samples were collected each cruise with repeat occupation of 11 stations. Transects MR and E start in the mouth of the Mississippi and Atchafalaya Rivers, respectively.