ARTICLE IN PRESS

Marine Chemistry xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Marine Chemistry

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

MoDIE: Moderate dissolved inorganic carbon (DI^{13}C) isotope enrichment for improved evaluation of DIC photochemical production in natural waters

Leanne C. Powers[a,*], Jay A. Brandes[a], Aron Stubbins[a], William L. Miller[b]

[a] *Skidaway Institute of Oceanography, Department of Marine Sciences, University of Georgia, 10 Ocean Science Circle, Savannah, GA 31411, United States*
[b] *Department of Marine Sciences, University of Georgia, Athens, GA 30602, United States*

ARTICLE INFO

Keywords:
Dissolved organic carbon
Dissolved inorganic carbon
Photochemistry
Stable carbon isotopes

ABSTRACT

Photochemical reactions in natural waters are a sink for dissolved organic carbon (DOC) and a source of dissolved inorganic carbon (DIC). Although considered significant to the carbon budget of the oceans, DIC photoproduction rates remain poorly constrained due to the analytical challenge involved in accurately measuring very low production rates (likely sub-μM h^{-1} for blue ocean waters) relative to high background DIC concentrations (~2 mM). In an attempt to overcome this analytical limitation, almost all previous DIC photoproduction studies in marine systems have relied on the stripping of background DIC prior to irradiation, with unknown consequences for the integrity of the DOC pool and its photoreactivity, and none have resulted in a satisfactory determination of photoproduced DIC in open ocean waters. Here, we use small additions of NaH^{13}CO$_3$ (< 10% of background DIC concentrations) to achieve moderate DI^{13}C isotope enrichment (MoDIE) of river, estuarine, and seawater samples. We then quantify the shift in δ^{13}C of DIC in irradiated samples via liquid chromatography - isotope ratio mass spectrometry (LC-IRMS) and use these shifts to calculate photoproduced DIC. MoDIE provides a new method to more precisely (± 56 to ± 340 nM DIC) and more rapidly quantify DIC photoproduction compared to previous methods. MoDIE was evaluated by determining initial DIC photoproduction rates, along with associated broadband photochemical efficiency data (ranging from 144 to 280 μmol DIC per mol photons absorbed), in riverine to offshore waters, and produced the earliest time point and most precise measurement of DIC photoproduction in unmodified, low-CDOM, blue water (a_g(325) = 0.30 m^{-1}) reported to date. In addition to measuring small DIC changes from photochemistry, the use of MoDIE could provide a major advance for other ocean carbon cycling studies, including examination of oceanic respiration, carbonate mineral precipitation/dissolution, and assessment of ocean acidification.

1. Introduction

The pool of reduced carbon stored in the ocean as dissolved organic carbon (DOC) is of approximately the same magnitude as the pool of oxidized carbon present in the atmosphere as CO$_2$ (Hansell et al., 2009). Despite the pressing need to understand the biological and abiotic controls on exchange between these active reservoirs, the sources, sinks, and transformations for the oceanic DOC pool remain poorly quantified. Photochemical reactions, driven by the absorption of sunlight by colored dissolved organic matter (CDOM), were suggested by Mopper et al. (1991) to oxidize a significant fraction of oceanic DOC to carbon monoxide (CO). Miller and Zepp (1995) subsequently reported that the photochemical oxidation of DOC to dissolved inorganic carbon (DIC) in nearshore waters proceeds at rates more than an order of magnitude faster than the sum of CO plus all other identified carbon photoproducts. To date, there have been no direct efficiency measurements of DIC photoproduction in blue waters (i.e. for the clearest of marine waters with CDOM absorption coefficients at 325 nm (a_g325) < 0.25 m^{-1}; Siegel et al., 2002; Stedmon and Nelson, 2015). Instead, estimates of oceanic DOC photooxidation to DIC have relied upon easier to measure proxy photoproducts, and their associated DIC photoproduction ratios. Most commonly, CO has been used as the proxy photoproduct since its photoproduction efficiency can be readily measured for blue waters (Stubbins et al., 2006; Zafiriou et al., 2003). The modeled rates of CO photoproduction are then multiplied by an assumed ratio of DIC:CO photoproduction to estimate total DOC photooxidation rates of 0.6 to 1.3 Pg C yr^{-1} for the global ocean (Stubbins et al., 2006; Zafiriou et al., 2003). As DIC photoproduction cannot be measured directly in blue waters, the ratios of DIC:CO are obtained in CDOM-enriched fresh and coastal waters, where the ratio of DIC:CO varies across a broad range (2 to > 60; Miller and Zepp, 1995; Powers and Miller, 2015a; White et al., 2010). Consequently, the

---

[*] Corresponding author at: University of Maryland Center for Environmental Science, Chesapeake Biological Laboratory, 146 Williams St, Solomons, MD 20688, United States
E-mail addresses: lpowers@umces.edu (L.C. Powers), Jay.Brandes@skio.uga.edu (J.A. Brandes), Aron.Stubbins@skio.uga.edu (A. Stubbins), bmiller@uga.edu (W.L. Miller).

http://dx.doi.org/10.1016/j.marchem.2017.03.007
Received 17 September 2016; Received in revised form 24 January 2017; Accepted 23 March 2017
0304-4203/

Please cite this article as: Powers, L.C., Marine Chemistry (2017), http://dx.doi.org/10.1016/j.marchem.2017.03.007

Table 1

Physical properties of South Atlantic Bight samples used in method development and sensitivity analysis. For salinity, pH and CDOM absorption coefficients at 325 nm (a_g(325); m^{-1}), the left column was recorded before MoDIE treatment ($NaH^{13}CO_3$ addition) and the right column was recorded after MoDIE treatment. δ^{13}C-DIC (‰) values are listed ± 1 SD and the left column contains the starting values before irradiation (darks) and the right column contains the final values after 25 h irradiation; values in parentheses are number of sample cells analyzed per measurement. The detection limits were determined as the 3 times the standard deviation of δ^{13}C-DIC (‰) darks, converted to DIC concentration using Eqs. (6) to (9) listed in the text.

Sample	Initial [DIC] ± 1 SD (μM)	[$NaH^{13}CO_3$] added (μM)	Salinity		pH		a_g(325) (m^{-1})		δ^{13}C-DIC (‰)		Detection limit (nM)
Skidaway R. Estuary	1935 ± 10	145.1	31	31	7.87	7.94	6.226	6.774	6351.0 ± 0.9 (3)	6333.1 ± 1.6 (5)	873
Midshelf	2120 ± 25	144.5	34	34.5	8.24	8.26	1.546	1.618	5306.1 ± 0.5 (2)	5303.8 ± 0.6 (2)	582
Offshore	2124 ± 11	138.7	37	36.5	8.36	8.38	0.450	0.377	5612.4 ± 0.6 (6)	5611.8 ± 0.3 (4)	668

oceanic photochemical sink for DOC remains poorly constrained and a persistent, fundamental analytical challenge in marine chemistry has been to directly quantify the role of photochemistry in the oceanic cycling of DOC.

The analytical challenge involves quantifying sub-μM DIC photoproduction against the 2000-fold greater background seawater DIC concentration (~2 mM). To date, the method most often employed to quantify DIC photoproduction in seawater involves pre-stripping the background DIC prior to irradiation (Powers and Miller, 2015a, 2015b; White et al., 2008). DIC-removal requires significant sample manipulation (acidification, sparging and pH readjustment) with unknown consequences for the integrity of the DOC pool and its photoreactivity (White et al., 2008). Even after modifying samples by stripping background DIC, the detection limit for the photoproduction of DIC remains at ~3 μM using typical IR detectors (Powers and Miller, 2015a; Powers et al., 2017) and can easily suffer from atmospheric contamination (DIC-free samples are far from equilibrium with atmospheric CO_2) if the whole process, from stripping to sample analysis, is not 100% gas-tight. Even with relatively high coastal photoproduction rates, it can take > 12 h to obtain detectable concentration changes (Powers and Miller, 2015a, 2015b), and the extremely low rates anticipated for blue water would necessitate exorbitantly long irradiations of unknown environmental relevance.

Currently, all direct measurements of marine DIC photoproduction, including determinations of DIC photochemical efficiency as defined using apparent quantum yield (AQY) spectra (and resulting photochemical rate models), have utilized data from DIC-stripped samples (Bélanger et al., 2006; Powers and Miller, 2015a; Reader and Miller, 2012; White et al., 2010). Furthermore, all these studies (Bélanger et al., 2006; Johannessen and Miller, 2001; Powers and Miller, 2015a; Reader and Miller, 2012; White et al., 2010) have been on waters containing significant amounts of terrigenous CDOM (Siegel et al., 2002; Stedmon and Nelson, 2015). This lack of blue water, oceanic data is problematic because to our knowledge, no credible initial DIC photoproduction rates have been measured in open ocean seawater ($a_g325 < 0.25\,m^{-1}$) even though the subtropical gyres intercept about 55% of global solar UV irradiance (290–400 nm; System for Transfer of Atmospheric Radiation model, Ruggaber et al., 1994) and the more broadly defined "open ocean" represents ~80% of the ocean's total surface area (Wollast, 2003). Consequently, there are no reported blue water DIC AQY spectra to assist in modeling the carbon cycle significance of more than half of the photochemically active photons that the sun rains down on earth each year.

In order to overcome current analytical limitations and examine photoproduction of DIC in seawater, we have developed a new isotope enrichment method. Our approach builds upon a previous alternative to sample stripping, a complete isotope enrichment method, or pool isotope exchange (PIE; Wang et al., 2009). PIE involves bubbling pure $^{13}CO_2$ at natural pH to replace all DI^{12}C in seawater prior to irradiation. The PIE DI^{13}C exchanger system employed a 16-way valve to fill and then flame-seal 16 quartz tubes with the DI^{13}C sample for irradiation experiments. Photoproduced DIC was then calculated as the difference in measured $^{13}CO_2/^{12}CO_2$ ratios before and after irradiation on a gas chromatography-isotope ratio mass spectrometer (GC-IRMS) with special modifications to measure changes in these highly enriched samples. However, by enriching the sample to 100% DI^{13}C, the same risk of atmospheric contamination found in the pre-stripping method is greatly magnified by PIE's heightened sensitivity to $^{12}CO_2$, which may explain why Wang et al. (2009) took extreme measures to avoid this issue.

To our knowledge, no study has used the Wang et al. (2009) method to measure photochemical DIC production since its publication, likely due to the technical challenges associated with the method. However, the PIE method did point out the utility of measuring δ^{13}C-DIC shifts as a means to calculate DIC photoproduction. Building upon the PIE method of Wang et al. (2009), we have developed a simplified isotope dilution method that allows high precision measurements of DIC photoproduction without the need for aggressive sample DIC-stripping or the custom-built equipment required for PIE. Our solution is a moderate DI^{13}C isotope enrichment (MoDIE) method achieved by adding small amounts of ^{13}C–labeled bicarbonate to seawater that result in δ^{13}C-DIC values ranging from 1350 to 8000‰ (Tables 1 and 2). At these levels, sub-μM photoproduced DIC (with expected δ^{13}C values ranging from − 25 to − 45‰; Franke et al., 2012; Lalonde et al., 2014; Opsahl and Zepp, 2001; Powers et al., 2017; Vähätalo and Wetzel, 2008) will significantly shift δ^{13}C values during irradiation experiments. Here we present MoDIE as a method that allows for the direct measurement of photoproduced DIC with minimal sample manipulation, by taking advantage of a liquid chromatography (LC) interface that acidifies the sample before extracting and transferring CO_2 to an isotope ratio mass spectrometer (IRMS). The combination of LC-IRMS analysis and an isotopic mass balance equation provides a new, higher precision, more rapid method to quantify initial rates and associated AQY spectra for DIC photoproduction in natural waters.

2. Methods

2.1. Sample collection and physical properties

Samples for preliminary experiments and method development were collected from stations located at the mid and outer shelf of the South Atlantic Bight off the coast of Georgia, USA, June 4 to 6, 2015 on board the *R/V* Savannah. Additional samples were collected dockside from the St. Marys River (June 15, 2015) and the Skidaway River Estuary (Sept 8, 2015 and March 25, 2016), and from the Gulf Stream (March 3, 2016) on board the *R/V* Savannah. All sampling equipment and containers were acid cleaned (0.01 M HCl, ACS grade, Fisher), rinsed five times with 18 MΩ ultrapure water (Milli-Q, Millipore) and dried before use. Samples were gravity filtered directly from Niskin bottles (*R/V* Savannah samples) or pumped from ~1 m depth through 0.2 μm Whatman Polycap 75 AS (aqueous solution glass microfiber prefilter with nylon membrane) or 75 TC (dual layer polyethersulfone) filters into either 10 or 20 L polyethylene carboys and stored at 4 °C in the dark within < 3 h of collection either on board the *R/V* Savannah or in the laboratory. Samples were stored for up to 3 months in this