Spectral efficiencies of carbon monoxide photoproduction from particulate and dissolved organic matter in laboratory cultures of Arctic sea ice algae

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ABSTRACT

Recent evidence has demonstrated that carbon monoxide (CO) is enriched in the bottom layer of first-year Arctic sea ice during ice algal blooms, but the processes responsible for this enrichment are not well understood. This study presents spectral apparent quantum yields (AQYs) of CO photoproduction from chromophoric dissolved organic matter (CDOM) and particulate organic matter (POM) harvested from three monocultures of ice algae (*P. taeniata*, *A. septentrionalis*, and *N. frigida*) and a natural ice algal assemblage collected from Resolute Bay, Canada. The AQYs for both CDOM and POM declined with increasing wavelength. Prolific CO photoproduction was observed from POM at wavelength (λ) > 600 nm, while little CO was photochemically produced from CDOM at λ > 500 nm. Although POM-based CO AQY spectra exhibit considerable dependence on ice algal species and growth stage, POM collected from all cultures and from both the exponential and senescent phases were far more efficient at CO photoproduction than the corresponding CDOM, particularly at visible wavelengths. AQY-based modeling suggests that POM

dominates over CDOM in controlling CO photoproduction in bottom sea ice during ice algal blooms due to a combination of much higher photoreactivity of POM relative to CDOM at visible wavelengths, higher transmission of visible radiation in sea ice, and higher ratios of particle to CDOM absorption.

Key words: ice algae; CDOM and POM; photochemistry; carbon monoxide

1. Introduction

Sea ice plays an important role in carbon cycling in polar oceans via biological production by ice algae. Ice algae can provide 3-25% of the total primary production in seasonally ice covered Arctic seas and >50% in the central Arctic Ocean (Gosselin et al., 1997). Dissolved organic carbon (DOC) production by ice algae accounts for about 40% of the total organic carbon fixation in sea ice (Gosselin et al., 1997; Smith et al., 1997). During ice algal blooms, dissolved organic matter (DOM) in bottom sea ice is highly enriched relative to the underlying seawater; the abundance of sea-ice DOM, as indicated by the concentration of DOC and the absorbance of chromophoric DOM (CDOM), is correlated with the ice algal standing stock or the concentration of particulate organic carbon (POC) (Smith et al., 1997; Riedel et al., 2008; Song et al., 2011; Xie et al., 2014).

Notably, biological activity of sea ice communities and/or the associated cycling of DOM are sources of certain atmospherically and/or climatically reactive trace gases, such as dimethylsulfide (Levasseur et al., 1994; Levasseur, 2013; Turner et al., 1995), nitrous oxide (Randall et al., 2012; Lovely et al., 2015), and carbon monoxide (CO) (Xie and Gosselin, 2005; Song et al., 2011). During ice algal blooms, large amounts

of CO can accumulate in the lowermost layer of sea ice where ice algae thrive (Xie and Gosselin, 2005; Song et al., 2011). As sea ice is permeable at temperatures above -15°C (Gosink et al., 1976), it has been posited to be a potentially significant source of atmospheric CO (Song et al., 2011). CO regulates the oxidizing capacity of the atmosphere (Thompson, 1992) and acts as an indirect greenhouse gas (Zepp et al., 2011) through its reaction with the hydroxyl radical. Brine drainage and ice melting also bring CO down to the water column where it is consumed by CO-oxidizing bacteria (Moran and Miller, 2007; Xie et al., 2009a) and/or emits to the atmosphere.

Seasonal variations in CO concentration ($[\text{CO}]$) in the bottom layer of Arctic first-year sea ice generally parallels those in chlorophyll *a* concentration ($[\text{Chl } a]$) and CDOM absorption coefficient (a_{CDOM}) (Xie and Gosselin, 2005; Song et al., 2011; Xie et al., 2014). Given that photooxidation of CDOM is the main CO production pathway in open seawater (Conrad and Seiler, 1980; Zafiriou et al., 2003), the correlation between $[\text{CO}]$ and a_{CDOM} in sea ice suggests that CDOM photodegradation could be an important contributor to CO accumulation in sea ice during ice algal blooms. This supposition is supported by the study of Xie and Gosselin (2005) demonstrating that irradiation of sea ice refrozen from Arctic sea ice meltwater can produce considerable amounts of CO. More recently, particulate organic matter (POM) photodegradation has been identified to be an important source of CO in open seas (Xie and Zafiriou, 2009; Song et al., 2013, 2015). Considering the correspondence between $[\text{CO}]$ and $[\text{Chl } a]$ in sea ice, the enormous ice algal biomass during the vernal bloom, and the ability of algal pigments to absorb photosynthetically available radiation (PAR, 400-700 nm), we hypothesize that POM photochemistry can be the dominant source of CO in sea ice during ice algal blooms. Here we determined and compared the apparent quantum yield (AQY) spectra of CO photoproduction (Φ_{λ})

from particles and CDOM collected from laboratory ice algal cultures. Furthermore, the relative contributions of CDOM and particles to total CO photoproduction in bottom sea ice during ice algal blooms were estimated based on the obtained Φ_{λ} and absorption spectra of particles and CDOM. Results from this study help better understand the importance of photochemistry in carbon and trace gas cycling in sea ice.

2. Methods

2.1. Culture incubations

Eighty milliliters of non-axenic monocultures of *P. taeniata*, *A. septentrionalis*, *N. frigida* and a natural ice algal assemblage (NIAA) collected from bottom sea ice in Resolute Bay (Table 1) were inoculated into 0.8 L sterilized f/2 medium contained in 1 L Erlenmeyer flasks. The f/2 medium, containing vitamins and silica, was prepared according to the recipe of Natural Center for Marine Algae and Microbiota (NCMA) at Bigelow Laboratory. The stock solutions of the chemicals for preparing the f/2 medium were purchased from NCMA and added to 0.2- μ m filtered deep seawater collected from Canada Basin. The selected species are dominant diatoms in sea ice on the shelves of Chukchi Sea and Beaufort Sea (von Quillfeldt et al., 2003; Poulin et al., 2011). The NIAA was chosen to investigate potential differences in photoreactivities of CDOM and POM produced by monocultures and natural algal assemblages. All cultures were incubated in duplicate at 4°C under illumination of cool white fluorescent light. Light intensities and durations of light:dark cycles are shown in Table 1. A parallel medium-only control served to assess any potential alterations of the organic matter photoreactivity in the medium. The temporal progression of [Chl *a*] was monitored to examine the growth stages of the cultures. Biomass in terms of [Chl

a] in duplicate flasks for each culture agreed within 10% throughout the incubation periods.

2.2. Sample collection

A schematic description of sample collection and processing is shown in Fig. A1 in Appendix A. Briefly, at about the middle of the exponential phase (EP) in each culture (see sampling dates in Fig. A2 in Appendix A), ~10 mL of culture was collected from one of the duplicate cultures and the particulate matter in the culture was filtered onto a combusted Whatman GF/F filter (pore size: 0.7- μ m; diameter: 25 mm) for determining the absorption spectra of particles. Moreover, ~600 mL of the above culture was gravity-filtered through a clean 10- μ m Nitex screen to separate the ice algal cells from the liquid phase and bacteria. The filtrate as well as the culture's medium control, was sequentially filtered through GF/F (diameter: 47 mm) and 0.2- μ m polyethersulfone (PES) filters under low vacuum (<50 kPa). The remaining culture (~100 mL) was left in the flask for further incubation in order to compare its [Chl *a*] with that in the other duplicate culture which was sampled during the senescent phase (SP) in the same manner as that for the exponential phase. The final filtrate was stored cool (4°C) in the dark before being analyzed for CDOM absorption spectra and CO AQYs. The particles (i.e. algal cells plus detritus) retained on the Nitex screen were gently rinsed several times with artificial seawater (ASW) until the absorption coefficient of CDOM at 330 nm ($a_{\text{CDOM},330}$) in the rinsing solution reached <0.03 m⁻¹. The rinsing was purported to diminish bacteria and DOM retained on the ice algal cells, thereby minimizing potential microbial CO consumption and DOM-based CO photoproduction during irradiation of the particle-containing samples (see below).

The ASW was prepared according to the protocol of Berges et al. (2001) and composed of Na^+ , K^+ , Ca^{2+} , Mg^{2+} , SO_4^{2-} and Cl^- with a salinity ~ 34 . NaCl , KCl , and Na_2SO_4 were combusted at 400°C for ca. 4 h to remove any organic impurities. Before use, the ASW was vacuum-filtered with $0.2\text{-}\mu\text{m}$ PES filters and then irradiated for 24 h under solar-simulated radiation emitted from an XLS+ solar simulator to further reduce the ASW's DOM content (final $[\text{DOC}]$: $12\text{ }\mu\text{mol L}^{-1}$, $a_{\text{CDOM},330}$: 0.004 m^{-1}).

2.3. Irradiation

After flushing with the ASW, the particles retained on the mesh were immediately dispersed into $\sim 2.5\text{ L}$ ASW (herein referred to as particle sample or particle-containing sample), gently stirred with a Teflon-skinned magnetic bar and bubbled with CO -free air to minimize the background $[\text{CO}]$. After $\sim 30\text{ min}$ bubbling, part of the water was transferred into 44 mL quartz-windowed cells (ID: 24 mm , length: 140 mm); the cells were closed without headspace after sample filling. Eight sample-filled cells were vertically placed in a temperature-controlled (4°C) water bath and irradiated with a CPS solar simulator under full spectrum to determine CO photoproduction as a function of irradiation time. Two cells were sacrificed at a time for $[\text{CO}]$ determination. The wavelength-dependence of CO photoproduction was assessed with successive Schott long-band cutoff filters of WG280, WG295, WG305, WG320, WG345, GG395, GG435, GG495 and OG570, where the numeric values signify the nominal 50% transmittance cutoff wavelengths ($\lambda_{50\%T}$) in nanometers. The sidewalls of the cells were wrapped with black electric tape to prevent lateral light interference between the cells. Irradiation lasted $<40\text{ min}$ for the WG280, WG295, WG305 and WG320 cutoff filters, and $<1.5\text{ h}$ for the rest. The quartz cells were

shaken gently before irradiation and every 30 min thereafter to minimize particle settlement.

The remaining part of the bubbled, unirradiated particle-containing water was filtered through pre-combusted GF/F filters under low vacuum (<50 kPa) for determining the particle and CDOM absorption spectra and [DOC]. The filtrate was irradiated in the same manner as above to determine the wavelength-dependent CO photoproduction from residual CDOM remaining in the ASW plus that potentially released from particles during bubbling. All irradiations were accompanied with parallel dark controls.

After irradiation, [CO] was determined using the headspace method reported by Xie et al. (2002). Briefly, samples were transferred to a 50-mL glass syringe, into which 5 mL CO-free air was introduced to obtain a 1:6 gas:water ratio. The syringe was shaken for 3 min using a Burrell Wrist-Action Shaker (model: DD) and the equilibrated headspace gas was injected into a Trace Analytical Reduction Gas Analyzer (model: TA3000) for CO quantification. The analyzer was calibrated by frequent injections of a National Institute of Standards and Technology (NIST)-traceable gaseous CO standard of 1.23 parts per million by volume (Praxair). The uncertainty of CO measurement was within $\pm 2\%$ and the detection limit was 0.02 nmol L⁻¹. The particle-containing samples left after [CO] determination were filtered under low vacuum (<50 kPa) through 25-mm pre-combusted GF/F (Whatman) filters for determining the absorption spectra of particles and CDOM and [DOC]. It was found that these quantities did not change significantly (<6%) during irradiation and [CO] analysis. The absorption spectra of particles and CDOM used for retrieving CO AQY (see section 2.5) were the averages of before- and after-irradiation. Note that the dissolved and particulate phases here were demarcated by the GF/F (i.e. 0.7- μ m pore

size) filtration, as required by the use of GF/F filters to retain particles for particulate absorbance measurement. To distinguish the GF/F filtration-based CDOM absorption coefficients from those based on the 0.2- μm filtration (see section 2.2.), the former is designated as a'_{CDOM} herein. However, no significant difference in CDOM absorbance (<4%) was observed between the two-filtration procedures (GF/F vs. 0.2- μm PES).

The 0.2- μm filtrates from the medium control and the algal cultures were bubbled and irradiated in the same manner as described above to determine the AQY spectra of CO photoproduction from CDOM. The OG570 cutoff filter was not used for the CDOM-only samples, given no CO photoproduction observed at wavelength > 600 nm (Xie et al., 2009b; Song et al., 2013).

2.4. Sample analyses

Chlorophyll *a* was extracted in 10 mL of 90% acetone in scintillation vials for at least 18 h in darkness at $\sim 4^{\circ}\text{C}$. The supernatant was measured for fluorescence, before and after being acidified with 5% HCl, using a Turner Designs fluorometer (model 10-AU) according to the method of Parsons et al. (1984). [Chl *a*] was calculated using the equation of Holm-Hansen et al. (1965).

The optical density (*OD*) of particles retained on the filters was measured using a Perkin Elmer Lambda 850 dual beam spectrometer fitted with a 150-mm integrating sphere accommodating a filter holder (Röttgers and Gehnke, 2012). The spectral optical density of the filter, $OD_{f,\lambda}$, where λ is wavelength in nanometers, was recorded from 800 nm to 290 nm at 1-nm increments and a scanning speed of 120 nm min⁻¹. $OD_{f,\lambda}$ was converted to the spectral particulate absorption coefficient, $a_{p,\lambda}$ (m⁻¹), using Eq. 1,

$$a_{p,\lambda} = 2.303 \times (A/V) \times (OD_{f,\lambda} - OD_{blank,\lambda}) \times (1/\beta_{\lambda}) \quad (1)$$

where $OD_{blank,\lambda}$ is the optical density of a blank filter, A the clearance area of particles on the filter (m^2), V the volume of sample water filtered (m^3), and β_{λ} the pathlength amplification factor. β_{λ} was nonlinearly correlated with $OD_{f,\lambda}$ (Röttgers and Gehnke, 2012):

$$\beta_{\lambda} = 2.9 \times OD_{f,\lambda}^2 - 4.76 \times OD_{f,\lambda} + 4.5 \quad (2)$$

Upon the completion of $a_{p,\lambda}$ determination, the filter was dipped in 10 mL methanol for ~18 h to bleach pigments, leaving only the non-algal particles (i.e. detritus) on the filter. The absorption coefficient of the non-algal particles, $a_{nap,\lambda}$ (m^{-1}), was determined in the same manner as that for $a_{p,\lambda}$. Subtracting $a_{nap,\lambda}$ from $a_{p,\lambda}$ gave the phytoplankton absorption coefficient, $a_{phy,\lambda}$ (m^{-1}).

The beam attenuation coefficient, c (m^{-1}), of the particle-containing sample was determined after bubbling (section 2.3) using a Perkin-Elmer Lambda 35 dual beam spectrophotometer coupled with 10-cm cylindrical quartz cells with the same diameter of the irradiation cells. The scattering coefficient, b (m^{-1}), of particles at each wavelength is calculated by subtracting a_t from c (i.e. $b = c - a_t$). Here a_t is the total absorption coefficient of the sample, i.e. the sum of a_p , a'_{CDOM} and the absorption coefficient of pure water (a_w) (Buiteveld et al., 1994; Pope and Fry, 1997).

The spectral optical density of CDOM, $OD_{CDOM,\lambda}$, was scanned from 800 nm to 200 nm at 1-nm intervals with a Perkin Elmer Lambda 35 dual beam spectrometer fitted with a 5-cm flow-through quartz cuvette and referenced to MilliQ water. Samples were allowed to warm up to room temperature before analysis. The sample cuvette was rinsed with methanol, pure water, and sample water between individual scans. A baseline correction was applied by subtracting the optical density averaged over 683-687 nm from all $OD_{CDOM,\lambda}$ values (Babin et al., 2003). The spectral CDOM

absorption coefficient, $a_{\text{CDOM},\lambda}$ was calculated as 2.303 times $OD_{\text{CDOM},\lambda}$ divided by the light pathlength of the cell in meters (0.05 m).

For [DOC] determination, 8 mL sample was transferred into a 9 mL clean glass vial, added with 100 μL 2N HCl, and stored in the refrigerator until analysis. [DOC] was analyzed in triplicate using a Shimadzu TOC-5000A Total Carbon Analyzer calibrated with potassium biphthalate. The system was checked, every seven consecutive sample analyses, against Hansell's low-carbon ([DOC]: 1–2 $\mu\text{mol L}^{-1}$) and deep Sargasso Sea ([DOC]: 44–46 $\mu\text{mol L}^{-1}$) reference waters. The mean coefficient of variation of triplicate measurements was 1.3% (0.1% - 13.5%).

2.5. Retrieval of CO AQY spectra

The amount of CO photochemically produced was calculated as the difference between an irradiated sample and its parallel dark control. The spectral CO AQY, Φ_λ , is defined as the number of moles of CO produced per mole of photons absorbed by a given set of light-absorbing materials at wavelength λ . Here the light-absorbing materials refer to CDOM or particles, corresponding to Φ_λ for CDOM ($\Phi_{\text{CDOM},\lambda}$) or particles ($\Phi_{\text{p},\lambda}$), respectively. According to Hu et al. (2002), the number of photons absorbed by CDOM or particles at wavelength λ , $Q_{\text{a},\lambda}$ (mol photons $\text{s}^{-1} \text{ nm}^{-1}$), can be calculated as follows:

$$Q_{\text{a},\lambda} = Q_\lambda \times S \times (a_\lambda / a_{\text{t},\lambda}) \times [1 - \exp(-a_{\text{t},\lambda} \times L)] \quad (3)$$

Q_λ (mol photons $\text{m}^{-2} \text{ s}^{-1} \text{ nm}^{-1}$) denotes the photon flux just below the frontal quartz window of the irradiation cell; a_λ (m^{-1}) stands for $a_{\text{CDOM},\lambda}$ for the 0.2- μm filtered samples or $a_{\text{p},\lambda}$ for the particle-containing samples; $a_{\text{t},\lambda}$ (m^{-1}) is the total absorption coefficient, i.e. $a_{\text{CDOM},\lambda}$ plus $a_{\text{w},\lambda}$ (Buiteveld et al., 1994; Pope and Fry, 1997) for the 0.2- μm filtered samples, or the sum of $a_{\text{p},\lambda}$, $a'_{\text{CDOM},\lambda}$, and $a_{\text{w},\lambda}$ for the particle-

containing samples. S (m^2) and L (m) are, respectively, the cross section and the pathlength of the irradiation cell. Particles can scatter photons out of the irradiation cell and change the effective pathlength of light transmission (Miller and Zepp, 1979; Estapa et al., 2012). Following the procedure published by Song et al. (2013), we estimated the contribution of particle scattering to light attenuation in the particle-containing samples using Monte Carlo simulations run by the SimulO software (Leymarie et al., 2010). The particle scattering effect decreased with increasing wavelength for samples collected from both the exponential and senescent phases but a shoulder over 450–670 nm was evident for the exponential-phase samples (Fig. A3 in Appendix A).

CDOM- and particle-based CO AQY spectra were retrieved using the iterative fitting method reported previously (e.g. Xie et al., 2009b; Song et al., 2013), and the forms of Eqs. 4 (quasi-exponential) and 5 (simple exponential) were employed for Φ_λ retrieval:

$$\Phi_\lambda = m_1 \times \exp(m_2/(m_3 + \lambda)) \quad (4)$$

$$\Phi_\lambda = m_4 \times \exp(m_5 \times (\lambda - 290)) \quad (5)$$

where m_1 – m_5 are fitting parameters. The amount of CO produced in an irradiation cell over the exposure time could then be predicted as the product of the assumed Φ_λ function and the number of absorbed photons integrated over 290–600 nm for CDOM and over 290–700 nm for particles. The optimum values of m_1 – m_5 were identified by varying their initial estimates until the difference between the predicted CO production rate and the measured one for an entire set of irradiation reached a minimum. Tests indicated that Eq. 4 worked much better than Eq. 5 for particles, while vice versa for CDOM, based on R^2 for the regression of CO production rates calculated from the retrieved Φ_λ against the measured rates and the normalized root-

mean-squared errors (Koehler et al., 2016) (Table A2 in Appendix A). Therefore, Eqs. 4 and 5 were chosen for particles and CDOM, respectively.

Notably, the parallel control experiments showed CO photoproduction from the residual CDOM in the ASW and the CDOM potentially released from particles during bubbling (see section 2.3) was $3.1\% \pm 2\%$ ($0.4\% - 7.5\%$) of the total CO photoproduction (particles plus CDOM) under each cutoff filter for all cultures; the CO photoproduction rate from particles was corrected for this artifact and for any thermal CO production occurring in the dark controls, which ranged from $< 2\%$ of the CO photoproduction under the WG280 cutoff filter to $< 15\%$ under the OG 570 cutoff filter.

To facilitate comparison of various Φ_λ spectra, a solar irradiance spectrum-weighted mean apparent quantum yield, $\bar{\Phi}$, was computed for each individual CO AQY spectrum following the procedure of Zhang et al. (2006):

$$\bar{\Phi} = (\int_{290}^{600} Q_{0,\lambda} \times \Phi_\lambda \times d\lambda) / (\int_{290}^{600} Q_{0,\lambda} \times d\lambda) \quad (6)$$

$\bar{\Phi}$ denotes $\bar{\Phi}_{\text{CDOM}}$ for CDOM and $\bar{\Phi}_p$ for particles, respectively. $Q_{0,\lambda}$ (mol photons $\text{m}^{-2} \text{h}^{-1} \text{nm}^{-1}$) is the surface spectral solar photon fluxes at 70°N , 133°W at 14:00 local time on 01 July, simulated using the SMARTS model (Simple Model of the Atmospheric Radiative Transfer of Sunshine; Gueymard, 2001) under mid-summer Arctic atmospheric and cloudless conditions with an ozone column burden of 330 Dobson Units. This normalization reduces the full AQY spectrum to a single value corresponding to the amount of CO produced in an idealized water column divided by the amount of photons absorbed by CDOM or particles; in this water column, CDOM or particles are the sole light absorber. Although $\Phi_{p,\lambda}$ was modeled in the wavelength range from 290 nm to 700 nm, $\bar{\Phi}_p$ was integrated from 290 nm to 600 nm to facilitate

comparison with $\bar{\Phi}_{\text{CDOM}}$ and with $\bar{\Phi}_p$ published in a previous study (Song et al., 2013).

3. Results and discussion

For simplicity, symbols of absorption coefficients and CO AQYs are followed by EP and SP in parentheses, if needed, to distinguish the exponential and senescent phases, respectively, e.g. $a_{\text{CDOM},330}(\text{EP})$ and $\bar{\Phi}_p(\text{EP})$ denoting $a_{\text{CDOM},330}$ and $\bar{\Phi}_p$ obtained from the exponential phase. It is further stipulated that symbols of absorption coefficients and CO AQYs can be used herein as both a singular and a plural form. Units of CO AQYs ($\text{mol CO (mol photons)}^{-1}$) are omitted.

3.1. General chemical, biological and optical properties

All cultures reached exponential growth, in 1-4 weeks after inoculations. The maximum [Chl *a*] was $714 \mu\text{g L}^{-1}$ for *P. taeniata*, $234 \mu\text{g L}^{-1}$ for *A. septentrionalis*, $74.8 \mu\text{g L}^{-1}$ for *N. frigida*, and $347 \mu\text{g L}^{-1}$ for NIAA. Incubations lasted sufficiently long (94 to 166 d, Table 1) to allow significant Chl *a* decay to occur (Fig. A2 in Appendix A).

[Chl *a*]s in the particle samples for irradiation experiments were ~3-4 times lower than their corresponding concentrations in the cultures due to dilution (~1:3) and potential pigment losses during the cell rising with ASW. [Chl *a*]s in the EP particle samples were 3 to 8 times higher than those in the SP samples (Table 2). Likewise, the particle absorption coefficients at 443 nm ($a_{p,443}$) for the EP samples were also higher than their SP counterparts. The $a_p(\text{EP})$ spectra displayed a clear pigment peak at ~676 nm and a shoulder spanning from 380 nm to 500 nm and centered at ~443 nm. During the SP, the decay of algal cells diminished (Fig. 1A) or nearly eliminated (Fig. 1B) the characteristic pigment absorption peak and shoulder, thereby leading to a smaller

$a_{\text{phy},443}:a_{\text{p},443}$ ratio relative to that for the EP (Table 2).

Both [DOC] and $a_{\text{CDOM},330}$ in the cultures were higher than those in the medium control (Table 2), indicative of production of DOC and CDOM by the ice algae. The net accumulations of DOC and $a_{\text{CDOM},330}$ were 39.2-253.4 $\mu\text{mol L}^{-1}$ and 0.22-1.57 m^{-1} within the EP and 155.9-1359 $\mu\text{mol L}^{-1}$ and 0.72-6.12 m^{-1} during the SP. CDOM absorption coefficients in three of the four cultures were higher than those in the medium control throughout the wavelength range from 300 nm to 600 nm, as exemplified by NIAA (Fig. 1D). CDOM absorption coefficients for the exponential growth phase of *P. taeniata* were nonetheless lower than those in the medium control at $\lambda \geq 375$ nm (Fig. 1C) due probably to bacterial DOM consumption surpassing algal DOM production during the relatively early stage of the algal growth.

3.2. Confirmation of CO photoproduction from particles

Compared with the dark controls, a_{p} did not significantly decrease after irradiation under all light filters while [DOC] and a'_{CDOM} did not substantially increase (Table A3 in Appendix A). Hence, CO should be produced primarily from particles not from POM-derived DOM, consistent with the results of Song et al. (2013). In addition, [DOC] and a_{CDOM} did not change significantly in the particle-free (0.2- μm filtered) samples before and after irradiation (<3%). A time-course test demonstrated that [CO] in the particle samples increased linearly over 1.5 h (the longest exposure for CO AQY determinations) of full-spectrum irradiation (Fig. 2A). [CO] in the parallel dark controls either increased linearly (*P. taeniata* and NIAA) or remained nearly constant (*A. septentrionalis* and *N. frigida*) with time (Fig. 2B), confirming that the filtration and flushing procedure (see section 2.2) essentially eliminated microbes, at least the CO-oxidizing bacteria. The increase in [CO] in the

cultures of *P. taeniata* and NIAA could be attributed to thermal and/or biological production of CO from particles. However, the dark CO production rates were only < 2% and <1% of the rates in the light treatments of *P. taeniata* and NIAA, respectively.

CO photoproduction rates for both particles and CDOM decreased with increasing $\lambda_{50\%T}$ of the cutoff filters (Fig. 3). However, the production rate for particles decreased more slowly than that for CDOM. Under filter GG495 ($\lambda_{50\%T}$: 495 nm), the particle-based CO production rate was 5-130 times the CDOM-based rate for the EP and 1.2-7.3 times for the SP. Moreover, significant CO formation from particles occurred under filter OG570 ($\lambda_{50\%T}$: 570 nm). Gros et al. (2009) reported that CO could be produced by phytoplankton via biological processes. To test if there was significant biological CO production by ice algae during irradiation, a *N. frigida*-containing particle sample was poisoned with potassium cyanide (final concentration: 4.2 $\mu\text{mol L}^{-1}$) and irradiated under conditions identical to those for the parallel unpoisoned sample. CO production rates in the poisoned sample were <7% lower than in the unpoisoned sample under filters GG495 and OG570 and <4% under the other light filters. Given that cyanide with a concentration of 4.2 $\mu\text{mol L}^{-1}$ inhibits CO photoproduction by a similar range (Song et al., 2013), the <7% difference could be ascribed to the cyanide inhibitory effect instead of biological CO production. Hence, CO production in the particle samples predominantly originated from particle photochemistry within the short irradiation durations (≤ 1.5 h) adopted in the present study.

3.3. CO AQY spectra and $\bar{\Phi}$

Notably, CDOM in each culture was composed of two pools: the algal-derived CDOM and CDOM originally contained in the f/2 medium. The CO AQY of CDOM

determined in this study represents the mixture of these two CDOM pools, designated as total CDOM herein. The CO AQY of the algal-derived CDOM ($\Phi_{\text{CDOM,alga},\lambda}$) can be expressed as follows (see Eqs. A1-A8 in Appendix A for the detailed procedure of derivation):

$$\Phi_{\text{CDOM,alga},\lambda} = \Phi_{\text{CDOM,t},\lambda} + (\Phi_{\text{CDOM,t},\lambda} - \Phi_{\text{CDOM,medium},\lambda}) \times (a_{\text{CDOM,medium},\lambda} / a_{\text{CDOM,alga},\lambda}) \quad (7)$$

where $\Phi_{\text{CDOM,t},\lambda}$ and $\Phi_{\text{CDOM,medium},\lambda}$ denote CO AQYs for the total CDOM and the medium-based CDOM, respectively, and $a_{\text{CDOM,alga},\lambda}$ and $a_{\text{CDOM,medium},\lambda}$ are absorption coefficients of the algal-derived CDOM and the medium-based CDOM, respectively. $\Phi_{\text{CDOM,t},\lambda}$ was determined with the culture filtrates, and $\Phi_{\text{CDOM,medium},\lambda}$ with the medium control, assuming that CO AQY for the medium-based CDOM in the cultures was comparable to that in the medium control. The ratio of $a_{\text{CDOM,medium},\lambda}$ to $a_{\text{CDOM,alga},\lambda}$ in the culture filtrates is unknown, because $a_{\text{CDOM,medium},\lambda}$ for the medium control, which was determined experimentally, may not be equated to $a_{\text{CDOM,medium},\lambda}$ in the cultures due to very likely faster consumption and degradation of the medium-based CDOM in the cultures linked to the presence of algae and larger populations of bacteria as compared to the medium control. Besides, in separate incubations using the same ice algal species to investigate algal CDOM production, we found similar losses of CDOM absorbance in the f/2 medium control and the cultures during the first 2-d incubations (G. Li et al., unpublished data), which might also occur in the present study. We suspect that this early loss of CDOM was due to photobleaching of very reactive CDOM constituents contained in the f/2 medium under cool white fluorescent illumination used for culture incubations. However, since the CDOM losses associated with photobleaching in the medium control and the cultures were similar, they should not affect the CDOM abundance in the cultures relative to that in

the medium control.

Although the lack of knowledge of the $a_{\text{CDOM,medium},\lambda}/a_{\text{CDOM,alga},\lambda}$ ratio in Eq. 7 makes it impossible to precisely determine $\Phi_{\text{CDOM,alga},\lambda}$, the lower and upper limits of $\Phi_{\text{CDOM,alga},\lambda}$ can be estimated under appropriate assumptions. Given that $\Phi_{\text{CDOM,t},\lambda}$ was greater than $\Phi_{\text{CDOM,medium},\lambda}$ (see below), the lower limit can be obtained by assuming the total CDOM in the culture filtrates to be entirely algal-derived (i.e. $a_{\text{CDOM,medium},\lambda} = 0$ in Eq. 7), while the upper limit corresponds to the condition where the loss of the medium-based CDOM in the cultures equaled to that in the medium control, rendering $a_{\text{CDOM,medium},\lambda}$ in the cultures to be identical to $a_{\text{CDOM,medium},\lambda}$ in the medium control at the end of incubations. In terms of $\bar{\Phi}_{\text{CDOM}}$, the upper limit was 1.5 to 1.8 times the lower limit for the exponential phase and 1.2 to 1.5 times for the senescent phase, depending on species. In the discussion herein, Φ_{CDOM} refers to the lower limit unless otherwise specified.

The fitted parameters for $\Phi_{\text{p},\lambda}$ and $\Phi_{\text{CDOM},\lambda}$ in Eqs. 4 and 5, along with $\bar{\Phi}$, are shown in Table 3. Φ_{p} was higher than its corresponding Φ_{CDOM} for each culture and the difference increased with wavelength and up to several orders in the band of 500-600 nm (Fig. 4), which was consistent with the higher particle-based CO photoproduction rates at the visible wavelengths (Fig. 3). The $\Phi_{\text{p}}(\text{EP})$ and $\Phi_{\text{p}}(\text{SP})$ spectra were similar in both shape and magnitude for *A. septentrionalis* and NIAA, while the EP spectrum for *P. taeniata* sat well above the SP spectrum and became flatter than the latter at $\lambda > 350$ nm (Fig. 4A,B,D). The Φ_{CDOM} spectra for *P. taeniata* showed no substantial difference between the two growth phases (Fig. 4A), whereas the $\Phi_{\text{CDOM}}(\text{EP})$ spectra for *A. septentrionalis* and NIAA gradually diverged from the corresponding SP spectra towards longer wavelengths (Fig. 4B,D). The $\Phi_{\text{CDOM}}(\text{EP})$ spectra for *N. frigida* was above its corresponding SP spectra at shorter wavelengths

but converged at longer wavelengths (Fig. 4C). Φ_{CDOM} of the cultures was far higher than that of the medium control across the spectral range covered, particularly at longer wavelengths (Fig. 4), suggesting that CDOM produced by ice algae was more photoreactive than that contained in the medium in terms of CO photoproduction.

$\bar{\Phi}_p$ (EP) was higher than $\bar{\Phi}_p$ (SP) for *P. taeniata*, while the sequence was reversed for *A. septentrionalis* and NIAA, especially for the latter, with its $\bar{\Phi}_p$ (SP) ~3 times $\bar{\Phi}_p$ (EP) (Table. 3). These patterns remain the same even if the integration wavelength range is changed from 290-600 nm to 290-700 nm (data not shown). $\bar{\Phi}_p$ (EP) in descending order was: *P. taeniata* (10.6×10^{-6}) > NIAA (6.74×10^{-6}) > *A. septentrionalis* (3.40×10^{-6}) > *N. frigida* (2.83×10^{-6}), while $\bar{\Phi}_p$ (SP) in descending order was: NIAA (18.2×10^{-6}) > *P. taeniata* (5.75×10^{-6}) $\approx$ *A. septentrionalis* (5.51×10^{-6}). The between-culture difference reached up to a factor of 3.7 for $\bar{\Phi}_p$ (EP) and 3.3 for $\bar{\Phi}_p$ (SP). Note that $\bar{\Phi}_p$ for the natural assemblage was the second highest for the EP and the highest for the SP. $\bar{\Phi}_{CDOM}$ for the cultures exhibited little phase-dependence, except *N. frigida* whose $\bar{\Phi}_{CDOM}$ (EP) was approximately twice $\bar{\Phi}_{CDOM}$ (SP) (Table 3). Comparisons among different cultures revealed that NIAA had the highest $\bar{\Phi}_{CDOM}$ (EP) (3.61×10^{-6}) followed sequentially by *N. frigida* (2.18×10^{-6}), *P. taeniata* (1.99×10^{-6}) and *A. septentrionalis* (1.79×10^{-6}). NIAA also possessed the highest $\bar{\Phi}_{CDOM}$ (SP) (2.91×10^{-6}) followed sequentially by *A. septentrionalis* (1.94×10^{-6}), *P. taeniata* (1.88×10^{-6}) and *N. frigida* (1.18×10^{-6}) (Table 3).

$\bar{\Phi}_p$ was consistently higher than $\bar{\Phi}_{CDOM}$ for all cultures and both growth phases, with the mean $\bar{\Phi}_p$ ~3 times $\bar{\Phi}_{CDOM}$ for the EP and ~5 times for the SP. Even compared with the upper limits of $\bar{\Phi}_{CDOM}$, the mean $\bar{\Phi}_p$ was still 1.5 and 3.5 times the mean $\bar{\Phi}_{CDOM}$ for the EP and SP, respectively. The higher $\bar{\Phi}_p$ relative to $\bar{\Phi}_{CDOM}$ demonstrated

that algal particles were more efficient at CO photoproduction than the algae-derived CDOM, consistent with previous results showing that particles are more photoreactive than CDOM in Arctic offshore seawater (Song et al., 2013). It is worth pointing out that Φ_{CDOM} and Φ_{p} were determined in different matrices, i.e. f/2 medium for Φ_{CDOM} and ASW for Φ_{p} (see section 2.3). The f/2 medium contained high concentrations of nitrate ($880 \mu\text{mol L}^{-1}$) and dissolved iron ($11.7 \mu\text{mol L}^{-1}$) and normal seawater concentrations of carbonate/bicarbonate and bromide, while these compounds were absent or negligible in the ASW. Both photolysis of nitrate (Zafiriou, 1974; Zafiriou and True, 1979) and iron-mediated CDOM photochemistry (Gao and Zepp, 1998) can produce reactive oxygen species, notably hydroxyl radicals, whose reaction with DOM is known to produce significant amounts of CO in freshwater samples (Gao and Zepp, 1998; Stubbins et al., 2008). Although hydroxyl radicals could be largely scavenged by halide and carbonate ions (principally bromide ions) (Zafiriou et al., 1987) in the f/2 medium, it was likely that the highly elevated concentrations of nitrate and iron increased Φ_{CDOM} to some extent. Hence, the difference between Φ_{p} and Φ_{CDOM} could be even larger if the dissimilarity in the composition of the two matrices is taken into account.

3.4. Comparison with previous studies

Song et al. (2013) reported the only available wavelength-resolved Φ_{p} for water samples collected from the western Canadian Arctic, including the Mackenzie River estuary, the Mackenzie Shelf, and the Canada Basin. The Canada Basin was chosen for comparison due to the least riverine influence and hence the highest proportion of phytoplankton-derived POM among the three sampling areas (Doxaran et al., 2012; Song et al., 2013). The average Φ_{p} spectra for surface water and the deep chlorophyll

maximum (DCM) layer in the Canada Basin are shown in Fig. 5A, alongside the average $\Phi_p(\text{EP})$ and $\Phi_p(\text{SP})$ spectra from this study. Clearly, both $\Phi_p(\text{EP})$ and $\Phi_p(\text{SP})$ are much higher than those obtained from the Canada Basin throughout the wavelength range of interest but the divergence increases with wavelength. Consequently, $\bar{\Phi}_p$ for the cultures exceed those for the Canada Basin by a factor of 1.4-12.4, depending on species and growth phases. The large discrepancy in Φ_p between the cultures and the Canada Basin could arise from many factors but potential differences in POM properties of pelagic vs. sympagic organisms may have played a role. However, the difference between the cultures and field samples falls into the range of variations associated with phase- and species-dependences of the cultures, as described above in this section.

Our lab had previously determined the Φ_{CDOM} spectrum for meltwater of a first-year drifting sea ice sample taken on 26 April 2008 from the bottommost 10-cm section of an ice core extracted at a site (70.59°N, 122.44°W; station D43-1 in Song et al., 2011) located in the Amundsen Gulf of the western Canadian Arctic. The sea ice sampling took place during the vernal ice algal bloom and [Chl *a*] in the bottom section reached 573.0 $\mu\text{g L}^{-1}$ (Song et al., 2011). The procedure and experimental conditions for determining Φ_{CDOM} for the sea ice meltwater were identical to those for determining Φ_{CDOM} for the cultures, save that the meltwater was irradiated at 1°C, 3°C lower compared with this study (see section 2.3). Φ_{CDOM} averaged on the lower limits of all cultures and both growth phases is considerably lower, at $\lambda > 350$ nm, than that of the sea ice meltwater but again the difference widens with wavelength (Fig. 5B). The lower- and upper-limit average $\bar{\Phi}_{\text{CDOM}}(\text{SP})$ for the cultures are 42% and 25% lower than that for the meltwater, respectively. Additionally, the lower-limit average $\bar{\Phi}_{\text{CDOM}}(\text{EP})$ for the cultures is 30% lower, but the upper-limit one is slightly higher

(16%) than that for the meltwater. Sea ice in the Canada Basin may contain terrigenous CDOM (Xie et al., 2014), which is a more efficient substrate of CO photoproduction than marine CDOM of biological origin, especially in visible regime (Zhang et al., 2006; White et al., 2010; Stubbins et al., 2011).

3.5. Relative contributions of CDOM and POM to CO in bottom sea ice

During vernal ice algal blooms, CO is enriched in the lowermost layer of first-year sea ice in the western Canadian Arctic (Xie and Gosselin, 2005; Song et al., 2011). Xie and Gosselin (2005) proposed that CO photoproduction from CDOM, combined with slow microbial CO consumption, in the bottom ice may be an important mechanism underlying this CO enrichment. The present study indicates that CO photoproduction from ice algal-derived POM may play a significant role as well. Here we assessed the relative contributions of these two CO source pathways at station D43-1 in Song et al. (2011), based on the Φ_{CO} spectra from this study, assuming that the selected ice algae are dominant species at this area during ice algal blooms (Poulin et al., 2011). The absorption spectrum of sea-ice CDOM used for this assessment was obtained from the study by Xie et al. (2014), and that of particles was retrieved according to the relationship between $a_{p,\lambda}$ and [Chl *a*] reported by Ehn and Mundy (2013). This estimation can be mathematically expressed as:

$$P_{POM,\lambda} = Q'_{0,\lambda} \times (a_{p,\lambda}/a_t) \times (1 - \exp(-a_t \times Z)) \times \Phi_{p,\lambda} \quad (7)$$

$$P_{CDOM,\lambda} = Q'_{0,\lambda} \times (a_{CDOM,\lambda}/a_t) \times (1 - \exp(-a_t \times Z)) \times \Phi_{CDOM,\lambda} \quad (8)$$

where $P_{POM,\lambda}$ and $P_{CDOM,\lambda}$ denote CO photoproduction rates ($\mu\text{mol CO m}^{-2} \text{d}^{-1} \text{nm}^{-1}$) for POM and CDOM, respectively, $Q'_{0,\lambda}$ ($\text{mol photons m}^{-2} \text{d}^{-1} \text{nm}^{-1}$) is the in-ice spectral solar photon flux at the depth of 10 cm from the ice-water interface, $a_{t,\lambda}$ (m^{-1}) is the total absorption coefficient, i.e. the sum of $a_{CDOM,\lambda}$, $a_{p,\lambda}$ and the absorption

coefficient of pure ice (Grenfell and Perovich, 1981; Perovich and Govoni, 1991), and Z (m) is the light pathlength of the bottommost 10-cm sea ice layer. Z is unknown due to the highly scattering property of sea ice (Ehn and Mundy, 2013; Katlein et al., 2014). Dividing Eq. 7 by Eq. 8 gives the ratio of $P_{POM,\lambda}$ to $P_{CDOM,\lambda}$ ($R_{POM/CDOM,\lambda}$):

$$R_{POM/CDOM,\lambda} = (a_{p,\lambda} \times \Phi_{p,\lambda}) / (a_{CDOM,\lambda} \times \Phi_{CDOM,\lambda}) \quad (9)$$

The $\Phi_{CO}(EP)$ values are assigned to the parameters on the right-hand side of Eq. 9 in order to be in line with the spring bloom in the field.

$R_{POM/CDOM}$ is thus dictated by the ratios of $a_{p,\lambda}/a_{CDOM,\lambda}$ and $\Phi_{p,\lambda}/\Phi_{CDOM,\lambda}$. The ratio of $a_{p,\lambda}/a_{CDOM,\lambda}$ generally increased with increasing wavelength, with the values < 1 at $\lambda < 340$ nm (Fig. 6A). Moreover, there is a broad shoulder between 340 and 560 nm, which is mainly induced by the pigment absorption. The ratio of $\Phi_{p,\lambda}/\Phi_{CDOM,\lambda}$ first decreased with increasing wavelength, with the minima located at 345-375 nm depending on species, and then increased approximately exponentially at longer wavelength (Fig. 6B). The modeled results demonstrate that $R_{POM/CDOM}$ in bottom sea ice slightly decreases with wavelength from 300 nm to ~330 nm and increases approximately exponentially with further increasing wavelength from 330 nm to 600 nm (Fig. 6C). $R_{POM/CDOM}$ is >1 within the entire wavelength range from 300 nm to 600 nm and for all cultures except *N. frigida* whose $R_{POM/CDOM}$ values are <1 (range: 0.64 to 1) at $\lambda < 345$ nm. Averaged on all cultures, $R_{POM/CDOM}$ increases from 2.1 ± 1.2 (0.8-3.6) in the UVB to 6.9 ± 5.4 (3.7-15) in the UVA to $1.6 \times 10^4 \pm 2.0 \times 10^4$ ($510-4.3 \times 10^4$) in the visible (Fig. 7). Given that the transmittance and hence the solar irradiance are highest at ~500 nm in the bottom sea ice (Ehn et al., 2008), particles far exceed CDOM in contributing CO photoproduction. The results are similar when the upper-limits of $\Phi_{CDOM}(EP)$ are used for calculating $R_{POM/CDOM,\lambda}$. However, $R_{POM/CDOM,\lambda}$ based on the upper-limits of $\Phi_{CDOM}(EP)$ is 19%-77% lower than those

calculated from the lower-limits of $\Phi_{\text{CDOM}}(\text{EP})$, depending on species and wavelength. Although $R_{\text{POM/CDOM}}$ was estimated only for station D43-1, the general conclusion should hold for the rest of the western Canadian Arctic during spring blooms of ice algae, since the ratio of $a_p/a_{\text{CDOM},\lambda}$ fell in a relatively small range (e.g. 1.2-4.8 at 330 nm) (Ehn and Mundy, 2013; Xie et al., 2014).

Notably, $\Phi_{\text{CDOM},\lambda}$ used in this study likely overestimates $R_{\text{POM/CDOM}}$, since Φ_{CDOM} of the cultures are usually lower than those of sea-ice meltwater at $\lambda > 350$ nm (Fig. 5). Furthermore, $\Phi_{p,\lambda}$ of the cultures may also cause overestimation, given that sea ice may contain terrigenous particles (Rachold et al., 2004), which are less efficient than marine-derived POM at CO photoproduction (Song et al., 2013). On the other hand, the relative contributions of POM and CDOM were assessed only for the wavelength range from 300 nm to 600 nm, which excludes the POM-photosensitive band of 600-700 nm (Fig. 4). The omission of this part underestimates $R_{\text{POM/CDOM}}$.

4. Summary

We detected CO photoproduction from ice algal-derived CDOM and particles, with the particle-based pathway extending into the much longer wavelengths (>600 nm) than the CDOM-based one. The magnitude and shape of the AQY spectra of CO photoproduction from particles were dependent on ice algal species and growth stage. The particle-based CO AQY was more than several times higher than the CDOM-based one, irrespective of the ice algal species and growth stage, with the difference increasing with increasing wavelength. Particles are expected to dominate over CDOM in controlling CO photoproduction in bottom sea ice during ice algal blooms due to a combination of much higher photoreactivity of POM relative to CDOM at visible wavelengths, higher transmission of visible radiation in sea ice, and higher

ratios of particle to CDOM absorption.

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Figure captions

Fig. 1. Examples of absorption spectra of particles (A: *P. taeniata*; B: NIAA) and CDOM (C: *P. taeniata*; D: NIAA). Particle absorption spectra refer to those in the particle-containing artificial seawater samples prepared for the irradiation experiments, while CDOM absorption spectra refer to those in the cultures used for preparing the particle-containing artificial seawater samples (see details in the text). EP and SP stand for exponential phase and senescent phase, respectively; a_p and a_{nap} denote absorption coefficients of total particles and non-algal particles, respectively. Note that the vertical scales for the four panels are different.

Fig. 2. [CO] in NIAA particle-containing samples versus exposure time under full-spectrum irradiation (A) and [CO] in dark controls of particle-containing samples versus incubation time for all the cultures (B). In panel A, error bars, which are smaller than the symbols, represent the range of the duplicate [CO] measurements. Data for cultures other than NIAA are not shown but also show linear increases in [CO] with irradiation time. In panel B, data shown are for exponential phase (EP) only; data for the senescent phase (SP) are not shown but similar in pattern, with lower slopes (i.e. production rates).

Fig. 3. Examples of CO photoproduction from CDOM and particles collected from the culture of *A. septentrionalis* as a function of the nominal 50% cutoff wavelength.

Fig. 4. Spectra of $\Phi_{CDOM,\lambda}$ and $\Phi_{p,\lambda}$ obtained in the present study. In panel (A), spectra of $\Phi_{CDOM,\lambda}(EP)$ and $\Phi_{CDOM,\lambda}(SP)$ are overlapped. No data available for $\Phi_{p,\lambda}(SP)$ of *N. frigida*.

765

766 **Fig. 5.** Comparison of the mean $\Phi_{p,\lambda}$ spectra obtained in this study with those reported
767 by Song et al. (2013) for surface and deep-chlorophyll *a*-maximum (DCM) water
768 samples collected from Canada Basin (A) and comparison of the mean lower- and
769 upper-limits of $\Phi_{CDOM,\lambda}$ spectra with that for the bottommost 10-cm layer of sea ice
770 collected from station D43-1 in the study of Song et al. (2011) (B).

771

772 **Fig. 6.** The ratios of a_p to a_{CDOM} (A) and Φ_p to Φ_{CDOM} (B), and the modeled ratio of
773 $P_{POM,\lambda}$ to $P_{CDOM,\lambda}$ ($R_{POM/CDOM}$) (C) as a function of wavelength in bottom sea ice for
774 each culture. The lower-limits of $\Phi_{CDOM,\lambda}$ were used for calculation.

775

776 **Fig. 7.** Wavelength integrated $R_{POM/CDOM}$ for UVB (300-330 nm), UVA (330-400 nm),
777 visible (400-600 nm), and full-spectrum (300-600 nm) radiations for each culture. The
778 lower-limits of Φ_λ of CDOM were used for the calculation.

Table 1 Incubation conditions of selected ice algae

Ice algae	CCMP strain	Taxon	Cell size ^a (μm)		Light		Incubation duration (d)
			Length	Width	Intensity (μmol m ⁻² s ⁻¹)	Cycle	
<i>Pauliella taeniata</i> ^b	1115	Pennate diatoms	20-22	5-7	60-70	14:10	166
<i>Attheya septentrionalis</i>	2083	Centric diatoms	14-20	3-4	40	Continuous	94
<i>Nitzschia frigida</i>	NA	Pennate diatoms	NA	NA	40	Continuous	124
Natural ice algal assemblage	NA	NA	NA	NA	40	Continuous	120

^aCell sizes of *P. taeniata* and *A. septentrionalis* are obtained from the webpage of National Center for Marine Algae and Microbiota (NCMA) (<https://ncma.bigelow.org>). No size data is available for *N. frigida* and natural ice algal assemblage (NIAA).

^bIncubation conditions for *P. taeniata* were the same as those adopted by NCMA and for other species (including NIAA) followed those employed by the providers of the ice algae (C. Lovejoy and A. R. Juhl, personal communications).

Table 2 Biological, chemical, and optical properties of particles (GF/F filtered) and CDOM (0.2- μm filtered) samples. Here [Chl *a*], $a_{\text{p},443}$, and $a_{\text{phy},443}/a_{\text{p},443}$ refer to the mean values of duplicate dark controls for samples of particles dispersed into the artificial seawater (see text for details). [DOC] and CDOM absorption spectra of the medium were determined only for the exponential phase and did not show significant variations during the incubation (Li et al., unpublished data). EP: exponential phase; SP: senescent phase; ND: no data is available.

Growth phase	f/2 medium	<i>P. taeniata</i>	<i>A. septentrionalis</i>	<i>N. frigida</i>	NIAA
Chl <i>a</i> ($\mu\text{g L}^{-1}$)					
EP	ND	73.7	60.6	15.0	92.7
SP	ND	22.6	13.0	ND	12.0
$a_{\text{p},443}$ (m^{-1})					
EP	ND	0.93	1.10	0.29	1.33
SP	ND	0.85	0.68	ND	0.13
$a_{\text{phy},443}/a_{\text{p},443}$					
EP	ND	0.92	0.92	0.89	0.85
SP	ND	0.84	0.86	ND	0.47
DOC ($\mu\text{mol L}^{-1}$)					
EP	283.3	410.0	322.5	340.0	536.7
SP	ND	1542	603.3	439.2	1642
$a_{\text{CDOM},330}$ (m^{-1})					
EP	1.45	1.67	1.67	1.70	3.02
SP	ND	7.57	2.94	2.17	6.09

Table 3 Fitted parameters for Eq. 4 (particles) and Eq. 5 (CDOM) in the text, along with $\bar{\Phi}$. NA: no data available.

Ice algae	Particles							
	Exponential phase				Senescent phase			
	m_1 $\times 10^{10}$	m_2	m_3	$\bar{\Phi}$ $\times 10^6$	m_1 $\times 10^{10}$	m_2	m_3	$\bar{\Phi}$ $\times 10^6$
<i>P. taeniata</i>	1883	805.1	-209.4	10.6	0.92	3965	-45.8	5.75
<i>A. septentrionalis</i>	38.1	2024	-116.6	3.40	3.04	3611	-43.2	5.51
<i>N. frigida</i>	291.1	987.8	-193.9	2.83	NA			
NIAA	2249	641.6	-222.3	6.74	181.1	2271	-91.2	18.2
	CDOM							
	Exponential phase			Senescent phase				
	m_4 $\times 10^6$	m_5	$\bar{\Phi}$ $\times 10^6$	m_4 $\times 10^6$	m_5	$\bar{\Phi}$ $\times 10^6$		
Medium	104.4	-0.058	0.42		NA			
<i>P. taeniata</i>	238.6	-0.044	1.99	221.9	-0.043	1.88		
<i>A. septentrionalis</i>	105.5	-0.033	1.79	227.8	-0.047	1.94		
<i>N. frigida</i>	306.3	-0.047	2.18	137.8	-0.043	1.18		
NIAA	136.7	-0.027	3.61	159.2	-0.032	2.91

Fig. 1. Examples of absorption spectra of particles (A: *P. taeniata*; B: NIAA) and CDOM (C: *P. taeniata*; D: NIAA). Particle absorption spectra refer to those in the particle-containing artificial seawater samples prepared for the irradiation experiments, while CDOM absorption spectra refer to those in the cultures used for preparing the particle-containing artificial seawater samples (see details in the text). EP and SP stand for exponential phase and senescent phase, respectively; a_p and a_{nap} denote absorption coefficients of total particles and non-algal particles, respectively. Note that the vertical scales for the four panels are different.

Fig. 2. [CO] in NIAA particle-containing samples versus exposure time under full-spectrum irradiation (A) and [CO] in dark controls of particle-containing samples versus incubation time for all four cultures (B). In panel A, error bars, which are smaller than the symbols, represent the range of the duplicate [CO] measurements. Data for cultures other than NIAA are not shown but also show linear increases in [CO] with irradiation time. In panel B, data shown are for exponential phase (EP) only; data for the senescent phase (SP) are not shown but similar in pattern, with lower slopes (i.e. production rates).

Fig. 3. Examples of CO photoproduction from CDOM and particles collected from the culture of *A. septentrionalis* as a function of the nominal 50% cutoff wavelength.

Fig. 4. Spectra of $\Phi_{\text{CDOM},\lambda}$ and $\Phi_{\text{p},\lambda}$ obtained in the present study. In panel (A), spectra of $\Phi_{\text{CDOM},\lambda}(\text{EP})$ and $\Phi_{\text{CDOM},\lambda}(\text{SP})$ are overlapped. No data available for $\Phi_{\text{p},\lambda}(\text{SP})$ of *N. frigida*.

Fig. 5. Comparison of the mean $\Phi_{p,\lambda}$ spectra obtained in this study with those reported by Song et al. (2013) for surface and deep-chlorophyll *a*-maximum (DCM) water samples collected from Canada Basin (A) and comparison of the mean lower- and upper-limits of $\Phi_{CDOM,\lambda}$ spectra with that for the bottommost 10-cm layer of sea ice collected from station D43-1 in the study of Song et al. (2011) (B).

Fig. 6. The ratios of a_p to a_{CDOM} (A) and Φ_p to Φ_{CDOM} (B), and the modeled ratio of $P_{POM,\lambda}$ to $P_{CDOM,\lambda}$ ($R_{POM/CDOM}$) (C) as a function of wavelength in bottom sea ice for each culture. The lower-limits of $\Phi_{CDOM,\lambda}$ were used for calculation.

Fig. 7. Wavelength integrated $R_{\text{POM/CDOM}}$ for UVB (300-330 nm), UVA (330-400 nm), visible (400-600 nm), and full-spectrum (300-600 nm) radiations for each culture. The lower-limits of Φ_{λ} of CDOM were used for the calculation.

Appendix A

Table A1 List of symbols and abbreviations

Abbreviation	Meaning	
AQY	Apparent quantum yield	
ASW	Artificial seawater	
CDOM	Chromophoric dissolved organic matter	
Chl <i>a</i>	Chlorophyll <i>a</i>	
CO	Carbon monoxide	
DOC	Dissolved organic carbon	
DOM	Dissolved organic matter	
EP	Exponential phase	
NIAA	Natural ice algal assemblage	
PAR	Photosynthetically available radiation	
POC	Particulate organic carbon	
POM	Particulate organic matter	
SP	Senescent phase	
UVA	Ultraviolet-A (320-400 nm)	
UVB	Ultraviolet-B (290-320 nm)	
Symbol	Meaning	Unit
a_{CDOM}	Absorption coefficient of CDOM	m^{-1}
a'_{CDOM}	Absorption coefficient of CDOM based on GF/F filtration	m^{-1}
$a_{\text{CDOM},330}$	Absorption coefficient of CDOM at 330 nm	m^{-1}
$a_{\text{CDOM,alga}}$	Absorption coefficient of algal-derived CDOM	m^{-1}
$a_{\text{CDOM,medium}}$	Absorption coefficient of medium-based CDOM	m^{-1}
a_{nap}	Absorption coefficient of non-algal particles	m^{-1}
a_{p}	Absorption coefficient of total particles	m^{-1}
$a_{\text{p},443}$	Absorption coefficient of total particles at 443 nm	m^{-1}
a_{phy}	Absorption coefficient of ice algal pigment	m^{-1}
$a_{\text{phy},443}$	Absorption coefficient of ice algal pigment at 443 nm	m^{-1}
a_{t}	Absorption coefficient of the sum of a_{cdom} , a_{p} and a_{w}	m^{-1}
a_{w}	Absorption coefficient of pure water	
A	Clearance area of filters for retaining particles	m^2
b	Scattering coefficient of particles	m^{-1}
β	Pathlength amplification factor	unitless

c	Beam attenuation coefficient	m^{-1}
λ	Wavelength	nm
$\lambda_{50\%T}$	50%-transmittance wavelength	nm
L	Light pathlength of irradiation cells	m
OD	Optical density	unitless
OD_{blank}	Optical density of blank GF/F filter	unitless
OD_{CDOM}	Optical density of CDOM	unitless
OD_{f}	Optical density of particles	unitless
$P_{\text{CDOM},\lambda}$	Rate of CO photoproduction from CDOM in bottommost 10-cm sea ice	$\mu\text{mol CO m}^{-2} \text{d}^{-1} \text{nm}^{-1}$
$P_{\text{POM},\lambda}$	Rate of CO photoproduction from POM in bottommost 10-cm sea ice	$\mu\text{mol CO m}^{-2} \text{d}^{-1} \text{nm}^{-1}$
$P_{\text{CDOM,alga},\lambda}$	CO photoproduction rate from algal-derived CDOM in culture filtrates	$\text{mol CO s}^{-1} \text{nm}^{-1}$
$P_{\text{CDOM,medium},\lambda}$	Rate of CO photoproduction from medium-based CDOM in culture filtrates	$\text{mol CO s}^{-1} \text{nm}^{-1}$
$P_{\text{CDOM,t},\lambda}$	Rate of CO photoproduction from total CDOM in culture filtrates	$\text{mol CO s}^{-1} \text{nm}^{-1}$
Φ	CO apparent quantum yield (AQY)	$\text{mol CO (mol photons)}^{-1}$
$\Phi_{\text{CDOM},\lambda}$	CO AQY for CDOM	$\text{mol CO (mol photons)}^{-1}$
$\Phi_{\text{CDOM,alga},\lambda}$	CO AQY for algal-derived CDOM in culture filtrate	$\text{mol CO (mol photons)}^{-1}$
$\Phi_{\text{CDOM,medium},\lambda}$	CO AQY for medium-based CDOM in medium control	$\text{mol CO (mol photons)}^{-1}$
$\Phi_{\text{CDOM,t},\lambda}$	CO AQY for total CDOM in culture filtrate	$\text{mol CO (mol photons)}^{-1}$
$\Phi_{\text{p},\lambda}$	CO AQY for particles	$\text{mol CO (mol photons)}^{-1}$
$\bar{\Phi}$	Solar irradiance spectrum-weighted mean Φ	$\text{mol CO (mol photons)}^{-1}$
$\bar{\Phi}_{\text{CDOM}}$	Solar irradiance spectrum-weighted mean Φ for CDOM	$\text{mol CO (mol photons)}^{-1}$
$\bar{\Phi}_{\text{p}}$	Solar irradiance spectrum-weighted mean Φ for particles	$\text{mol CO (mol photons)}^{-1}$
Q_{λ}	Photon flux just below the frontal quartz window of irradiation cells	$\text{mol photons m}^{-2} \text{s}^{-1} \text{nm}^{-1}$
$Q_{0,\lambda}$	Modeled surface solar photon flux	$\text{mol photons m}^{-2} \text{h}^{-1} \text{nm}^{-1}$
$Q'_{0,\lambda}$	In-ice spectral solar photon flux at the depth of 10 cm from the ice-water interface	$\text{mol photons m}^{-2} \text{d}^{-1} \text{nm}^{-1}$
$Q_{\text{a},\lambda}$	Photons absorbed by CDOM or CDOM plus particles	$\text{mol photons m}^{-2} \text{s}^{-1} \text{nm}^{-1}$

$Q_{a(\text{CDOM,algal}),\lambda}$	Photons absorbed by algal-derived CDOM in culture filtrates	mol photons $\text{m}^{-2} \text{s}^{-1} \text{nm}^{-1}$
$Q_{a(\text{CDOM,medium}),\lambda}$	Photons absorbed by medium-based CDOM in culture filtrates	mol photons $\text{m}^{-2} \text{s}^{-1} \text{nm}^{-1}$
$Q_{a(\text{CDOM,t}),\lambda}$	Photons absorbed by total CDOM in culture filtrates	mol photons $\text{m}^{-2} \text{s}^{-1} \text{nm}^{-1}$
$R_{\text{POM/CDOM}}$	Ratio of CO photoproduction from particles to that from CDOM (i.e. $P_{\text{POM},\lambda}:P_{\text{CDOM},\lambda}$)	unitless
S	Cross-section area of irradiation cells	m^2
V	Filtered volume of water samples through GF/F filters	m^3
Z	Light pathlength of the bottommost 10-cm sea ice	m

Table A2 Fitted parameters for linear regression ($y = a \cdot x + b$) between measured and predicted CO photoproduction for the simple and quasi-exponential CO AQY models. R^2 : coefficient of determination; nRMSE: normalized root-mean-squared error; ND: no data available (i.e. the model does not converge).

Ice algae	Simple exponential model				Quasi-exponential model			
	a	$b (\times 10^{-11})$	R^2	nRMSE (%)	a	$b (\times 10^{-11})$	R^2	nRMSE (%)
CDOM (EP)								
<i>P. taeniata</i>	1.01	-1.66	0.997	5	ND	ND	ND	ND
<i>A. septentrionalis</i>	1.02	-2.94	0.998	6	ND	ND	ND	ND
<i>N. frigida</i>	0.99	0.46	0.996	6	0.98	1.95	0.993	8
NIAA	1.02	-4.48	0.998	4	ND	ND	ND	ND
CDOM (SP)								
<i>P. taeniata</i>	1.02	-8.27	0.997	5	1.00	0.26	0.999	3
<i>A. septentrionalis</i>	1.02	-0.51	0.999	5	ND	ND	ND	ND
<i>N. frigida</i>	0.99	0.75	0.998	4	ND	ND	ND	ND
NIAA	1.02	-15.1	0.995	6	ND	ND	ND	ND
Particles (EP)								
<i>P. taeniata</i>	ND	ND	ND	ND	1.04	-23.5	0.991	8
<i>A. septentrionalis</i>	ND	ND	ND	ND	1.04	-7.50	0.994	6

<i>N. frigida</i>	ND	ND	ND	ND	1.03	-2.37	0.991	8
NIAA	ND	ND	ND	ND	1.04	-17.7	0.991	7
Particles (SP)								
<i>P. taeniata</i>	ND	ND	ND	ND	0.98	7.00	0.995	7
<i>A. septentrionalis</i>	ND	ND	ND	ND	1.01	-2.16	0.997	4
NIAA	ND	ND	ND	ND	1.03	-7.30	0.995	6

Table A3 Values of $a_{p,443}$, $a'_{\text{cdom},330}$ and [DOC] after irradiation and in dark controls. Dark: dark controls; light: after irradiation under cutoff filter WG 280 (i.e. full spectrum); EP: exponential phase; SP: senescent phase; ND: no data available.

	<i>P. taeniata</i>		<i>A. septentrionalis</i>		<i>N. frigida</i>		<i>NIAA</i>	
	dark	light	dark	light	dark	light	dark	light
$a_{p,443} (\text{m}^{-1})$								
EP	0.93	0.94	1.10	1.08	0.29	0.29	1.33	1.32
SP	0.85	0.84	0.68	0.68	ND	ND	0.13	0.13
$a'_{\text{CDOM},330} (\text{m}^{-1})$								
EP	0.11	0.11	0.08	0.08	0.06	0.06	0.22	0.23
SP	0.08	0.10	0.09	0.09	ND	ND	0.07	0.08
[DOC] ($\mu\text{mol L}^{-1}$)								
EP	26.7	25.2	16.7	16.3	22.5	20.8	36.7	36.7
SP	53.3	51.7	43.3	44.2	ND	ND	25.0	26.7

Equations A1-A8 (derivation of CO AQY for algal-derived CDOM)

This derivation is based on the approach identical to that published by Song et al. (2013). In culture filtrates containing algal-derived CDOM and CDOM originally existing in the f/2 medium:

$$P_{\text{CDOM},t,\lambda} = P_{\text{CDOM},\text{alga},\lambda} + P_{\text{CDOM},\text{medium},\lambda} \quad (\text{A1})$$

$$P_{\text{CDOM},t,\lambda} = \Phi_{\text{CDOM},t,\lambda} \times Q_{a(\text{CDOM},t),\lambda} \quad (\text{A2})$$

$$P_{\text{CDOM},\text{alga},\lambda} = \Phi_{\text{CDOM},\text{alga},\lambda} \times Q_{a(\text{CDOM},\text{alga}),\lambda} \quad (\text{A3})$$

$$P_{\text{CDOM},\text{medium},\lambda} = \Phi_{\text{CDOM},\text{medium},\lambda} \times Q_{a(\text{CDOM},\text{medium}),\lambda} \quad (\text{A4})$$

where

$P_{\text{CDOM},t,\lambda}$: total CO photoproduction from algal-derived CDOM and CDOM added from the f/2 medium ($\text{mol CO s}^{-1} \text{ nm}^{-1}$);

$P_{\text{CDOM},\text{alga},\lambda}$: CO photoproduction from algal-derived CDOM ($\text{mol CO s}^{-1} \text{ nm}^{-1}$);

$P_{\text{CDOM,medium},\lambda}$: CO photoproduction from CDOM added from the f/2 medium (mol CO s⁻¹ nm⁻¹);

$\Phi_{\text{CDOM,t},\lambda}$: CO AQY for total CDOM (i.e. algal-derived CDOM plus medium-based CDOM) determined with culture filtrates (mol CO (mol photons)⁻¹);

$\Phi_{\text{CDOM,alga},\lambda}$: CO AQY for algal-derived CDOM (mol CO (mol photons)⁻¹);

$\Phi_{\text{CDOM,medium},\lambda}$: CO AQY for medium-based CDOM determined with the medium control (mol CO (mol photons)⁻¹);

$Q_{\text{a(CDOM,t)},\lambda}$: flux of photons absorbed by total CDOM (mol photons s⁻¹);

$Q_{\text{a(CDOM,alga)},\lambda}$: flux of photons absorbed by algal-derived CDOM (mol photons s⁻¹);

$Q_{\text{a(CDOM,medium)},\lambda}$: flux of photons absorbed by medium-based CDOM (mol photons s⁻¹).

The fluxes of absorbed photons can be computed according to Hu et al. (2002):

$$Q_{\text{a(CDOM,t)},\lambda} = Q_{\lambda} \times S \times ((a_{\text{CDOM,alga},\lambda} + a_{\text{CDOM,medium},\lambda})/a_{\text{t},\lambda}) \times [1 - \exp(-a_{\text{t},\lambda} \times L)] \quad (\text{A5})$$

$$Q_{\text{a(CDOM,alga)},\lambda} = Q_{\lambda} \times S \times (a_{\text{CDOM,alga},\lambda}/a_{\text{t},\lambda}) \times [1 - \exp(-a_{\text{t},\lambda} \times L)] \quad (\text{A6})$$

$$Q_{\text{a(CDOM,medium)},\lambda} = Q_{\lambda} \times S \times (a_{\text{CDOM,medium},\lambda}/a_{\text{t},\lambda}) \times [1 - \exp(-a_{\text{t},\lambda} \times L)] \quad (\text{A7})$$

where

Q_{λ} : photon flux just below the frontal quartz window of the irradiation cell (mol photons m⁻² s⁻¹);

$a_{\text{CDOM,alga},\lambda}$: absorption coefficient of algal-derived CDOM (m⁻¹);

$a_{\text{CDOM,medium},\lambda}$: absorption coefficient of medium-based CDOM (m⁻¹);

$a_{\text{CDOM,t},\lambda}$: absorption coefficient of total CDOM plus that of pure water (m⁻¹);

L : pathlength of the irradiation cell (m);

S : cross-section area of the irradiation cell (m²);

Substituting Eqs. A2) to A7 into Eq. A1 and rearranging it give

$$\Phi_{\text{CDOM,alga},\lambda} = \Phi_{\text{CDOM,t},\lambda} + (\Phi_{\text{CDOM,t},\lambda} - \Phi_{\text{CDOM,medium},\lambda}) \times (a_{\text{CDOM,medium},\lambda}/a_{\text{CDOM,alga},\lambda}) \quad (\text{A8})$$

Fig. A1. Flow chart of the main procedures of sample collection and processing. Diamonds denote samples obtained at different sample processing stages, rectangles designate parameters measured, and text next to arrows indicates sample manipulations. See Table A1 for definitions of symbols and abbreviations.

Fig. A2. Temporal progression of [Chl *a*] in ice algal cultures. Solid points in each panel denote collecting times of DOM and particle samples for CO photoproduction experiments.

Fig. A3. Particle scattering effect expressed by R as a function of wavelength. R denotes the ratio of the number of absorbed photons calculated from Hu et al. (2002) (Eq. 3 in the main text) to that modeled using Monte Carlo simulation. Refer to Song et al. (2013) for details in the calculation of R .