**Characteristics of colored dissolved organic material in first year landfast
sea ice and the underlying water column in the Canadian Arctic in the
early spring**

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Abstract

The absorption of solar energy by colored dissolved organic material (CDOM) in Arctic surface waters during the springtime is increasingly recognized as having profound impacts on seasonal retreat of ice from the Arctic Ocean. This study observed the production of CDOM within first year landfast sea ice, its contribution to light absorption within the water column and its photoreactivity, at a location near Ellef Ringnes Island in the Canadian Archipelago during the spring of 2011. CDOM was the optically dominant component of non-water absorption, increasing the energy absorption and heating potential in the top 8 m by 30% over pure seawater. CDOM absorption within sea ice brine channels increased with solar-stimulated ice algae production. This ice algal mediated production of CDOM exceeded photooxidation rates, potentiating a net delivery of CDOM to the immediately underlying water column from brine channels in the ice. The rates of production and loss of CDOM in Arctic waters during the early spring quantified here will help constrain a major uncertainty in modeling light absorption by surface waters that contributes to sea ice loss in the Arctic.

1. Introduction

The rapid retreat and thinning of Arctic sea ice over recent decades has been accompanied by increases in heat stored in the upper ocean, leading to positive anomalies in sea surface temperature, a decline in the Arctic ice pack and delays in fall freezing (Perovich et al. 2007; Steele et al. 2008; Stroeve et al., 2012; Stroeve et al., 2014). The decline in the Arctic ice pack extent and thickness has been related to solar energy deposition in the upper ocean, (Perovich et al., 2007; Nicolaus et al., 2012), but uncertainty in solar energy absorbed by surface waters limits our ability to predict sea ice thickness and upper ocean heat content (Kwok and

Untersteiner, 2011). Solar energy absorbed in the upper ocean early in the spring, especially in the ice-ocean boundary layer, is transported to the base of the ice via the ocean-to-ice heat flux where it enhances melting and negatively reinforces the ocean-ice-albedo feedback (Perovich et al., 2007; Stanton et al., 2012). Later in the season, solar radiation is trapped below the cold fresh surface layer produced by ice melt and gives rise to the near-surface temperature maximum which stores energy and inhibits fall freezing (Steele et al., 2011; Hudson et al., 2013; Timmermans, 2015). Understanding the factors controlling the vertical distribution of solar energy absorption will help constrain the effects of climate change on Arctic sea ice cover and subsequent impacts on Arctic marine ecosystems (Stroeve et al., 2014; Pavlov et al., 2015).

The absorption of solar energy by marine waters is driven by the absorption and scattering properties of seawater, phytoplankton, non-algal particles and colored dissolved organic material (CDOM). CDOM dominates absorption in late winter through early spring when phytoplankton presence is negligible (Scully and Miller, 2000; Pegau, 2002; Hill, 2008; Matsuoka et al., 2011; Gueguen et al., 2012). Phytoplankton absorption is more influential later in the spring and summer, during intense blooms that significantly reduce light penetration (Balch et al., 2014). The importance of CDOM driven energy absorption especially in early spring when other absorbing compounds are negligible has been increasingly recognized in the past decade due to its impact on energy budgets and ice melt (Pegau, 2002; Granskog et al., 2007; Hill, 2008; Pavlov et al., 2015). CDOM is the optically active fraction of the dissolved organic matter (DOM) pool present in natural waters, and is produced through degradation of organic material, both on land and in the ocean. Stedmon et al. (2011a) identified three CDOM pools in Arctic surface waters: (i) a background marine CDOM pool, (ii) a recently produced marine CDOM pool and (iii) a terrestrial CDOM pool which is often the dominant signal

(Stedmon et al., 2011a). The marine pool results from high primary production, particularly on the shelf seas (Mathis et al., 2007; Hill et al., 2013), the Chukchi Sea in particular has a strong marine signal that is exported to the adjacent surface waters of the Canada Basin (Stedmon et al., 2011a). The terrestrial pool mainly originates from Siberian and North American rivers (Gordeev et al., 1996; Amon et al., 2012; Holmes et al., 2012), and is dominant on the Eurasian shelves and Basin (Stedmon et al., 2011a; Granskog et al., 2012; Pavlov et al., 2015;), and close to the Mackenzie River outflow (Matsuoka et al., 2012).

Sea ice can also be an important source of CDOM to the under-ice ocean boundary layer. Absorption coefficients of CDOM within the ice can be up to 7 times greater than in the underlying water column (Belzile et al., 2000; Scully and Miller, 2000; Norman et al., 2011; Xie et al., 2014a) and this CDOM pool is delivered to the underlying water column during ice melt. CDOM compounds within sea ice include labile protein-like material generated as a by-product of ice algal growth (Smith et al., 1997; Xie et al., 2014a; Granskog et al., 2015; Jorgensen et al., 2015), and refractory humic- like material linked to the retention of dissolved organic material from the parent water mass during winter freeze-up (Stedmon et al., 2007a; Giannelli et al., 2001; Muller et al., 2011; Muller et al., 2013;). The relative combination of refractory and labile compounds impacts the residence time of the material in the natural environment. Both labile and refractory compounds can be diluted by vertical mixing, but labile compounds are lost more rapidly through photochemical and biological oxidation, lowering the absorption coefficient of CDOM in the water column by as much as 50% in as little as 120 h (Mopper et al., 1991; Mopper et al., 1991; Miller and Zepp, 1995; Stubbins et al., 2006). Therefore, the nature and source of DOM in Arctic surface waters ultimately determines the residence time and impact of CDOM on upper ocean warming.

Mechanisms for the flux of CDOM from sea ice into the underlying water column include brine convection which mixes the sea ice brine with underlying seawater, particularly in the lower most 5 to 10 cm (Vancoppenolle et al., 2010), and gravity drainage through the percolation of surface meltwater through the ice (Vancoppenolle et al., 2007; Tison et al., 2008; Petrich and Eicken, 2010). However, the rate of these fluxes in terms of CDOM remains unquantified. Studies on the bio-optical properties of the upper water column in spring show higher CDOM absorption close to the underside of the ice before ice melt, a result of convection or drainage of CDOM from brine channels (Ehn et al., 2004). Later in the season bulk ice melt and drainage of surface ponds also promotes the release of CDOM into the water column, but this is accompanied by a reduction in absorption due to the dilution effect of freshwater input (Pegau, 2002; Belanger et al., 2013).

The goals of this study were to quantify (i) the production of CDOM within first year sea ice in the Canadian Archipelago, (ii) the contribution of CDOM to light absorption within the water column, relative to pure water, and (iii) the photoreactivity of CDOM produced in sea ice. The rates of production and loss of CDOM in Arctic waters during the early spring generated by this work will be useful in constraining one of the major uncertainties in modeling light attenuation in surface waters of the Arctic Ocean.

2. Methods

2.1 Study site - Catlin Ice Base 2011 was occupied from 1 March through 29 April 2011, on a region of level, first year sea ice that extended westward from Ellef Ringnes Island, in the Canadian Arctic (N 78° 46.2' W 104° 43.3, Fig. 1). The camp was 4 km from the nearest land. At the start of the camp the undisturbed sea ice was between 1.6 and 1.9 m thick and a track of rubble ice ran north to south along the east side of the camp. A sampling hole (~ 1 m diameter)

was cut through the ice on 16 March 2011 on the western edge of the camp. All water column sampling was conducted through this ice hole. Water depth under the ice was at least 200 m, based on Canadian Hydrographic Chart ID 7000. Air temperatures at the site were well below freezing (March mean $\pm$ S.D = -27.7 ± 7.7 °C), ice thickness measured during ice coring varied from 172 to 189 cm, snow thickness was highly variable due to high winds with depths from 3 to 26 cm measured at ice core sites.

2.2 Sample Collection -Discrete water samples were collected approximately every four days between 19 March and 25 April using a 5 L Niskin bottle deployed through the ice hole to depths of 0, 3, 10 and 50 m (relative to the underside of the ice and measured by the amount of wire deployed). The winch drum was attached to a stationary bicycle, which was then cycled in place and the number of full pedal rotations counted to approximate depth. Additional samples were collected at depths of 100 and 200 m on 19, 24, 31 March and 25 April. Particles were captured onto Whatman GF/F filters under gentle vacuum and the filtrate was collected directly into acid washed clear borosilicate glass vials. CDOM was isolated by a second filtration of the initial filtrate through acid-washed, 0.2 μ m nucleopore polycarbonate filters (Mitchell et al., 2002).

Vertical profiles of beam attenuation [$c(\lambda)$, m^{-1}] and absorption [$a(\lambda)$, m^{-1}] coefficients were measured at nine wavelengths (412, 440, 488, 510, 532, 555, 650, 676 and 715 nm) every two days to 50 m depth, using an *ac-9* instrument package with integrated CTD (WETLabs/SeaBird). *ac-9* profiles were extended to between 100 and 200 m on 24, 28 March and 9, 21 and 25 April. The *ac-9* optical data were processed and corrected for ambient temperature, salinity, and scattering [Method 3 according to Pegau et al. (2003)]. The attenuation and absorption of particles plus CDOM (c_{pg} , a_{pg}) was calculated by subtracting the

absorption and scattering by pure water (Pope and Fry, 1997). The spectral scattering coefficient $[b_p(\lambda), \text{m}^{-1}]$ was calculated as $c_{pg}(\lambda) - a_{pg}(\lambda)$.

Ice cores were collected at predetermined random distances (< 20 m) and bearings from the main sampling hole every four days starting on 19 March. A total of 10 cores were collected (one core per day), ending on 26 April. Snow depth was measured with a stainless steel ruler and the snow removed before collecting each core with a Kovacs Mark II 9 cm diameter coring system. The top, middle and bottom 20 cm were cut from each core and the bottom 20 cm of each core was further subdivided into 5 cm sections, using a clean stainless steel saw. Nitrile gloves were used when handling the core and sections. All core samples were stored in acid washed borosilicate glass jars, placed inside a dark box for ~ 24 hours to melt within the science tent where the temperature was a few degrees above freezing. Due to the cold temperatures experienced in the tents, and difficulty controlling air temperature, water was added to the storage box around the jars to facilitate melting of the cores if they had not melted within 24 hours. The melting process was performed slowly to reduce the release of fresh DOM from phytoplankton cells due to rupturing from osmotic pressure. The melted core sections were then processed for particulate and dissolved absorbing components, as described above for discrete water column samples.

2.3 Analytical Methods -Chl *a* concentrations were determined spectrophotometrically after grinding the fresh filters in 5 ml of 90% acetone and extracting in the dark at above freezing temperatures for 12 hours (Jeffrey and Humphrey, 1975). The filter debris was pelleted using a hand cranked centrifuge before absorbance of the supernatant was measured in a 1 cm cuvette using an Ocean Optics DH-2000 lamp and TIDAS 1 spectrophotometer, blanked against 90% acetone.

Absorbance of CDOM (230 – 724 nm) was measured using a WPI Ultrapath system, equipped with a 50 cm pathlength, a TIDAS 1 spectrophotometer with a dynamic range of 0.002 - 230 m⁻¹ and an Ocean Optics DH-2000 lamp. The instrument was blanked with a solution of reagent grade sodium chloride (Fisher Scientific) dissolved in HPLC-grade water with a refractive index matching that of each sample to compensate for changes in the transmission properties of liquid waveguide cells that vary with the sample refractive index (Miller et al., 2002; Nelson et al., 2007). Absorption coefficients [$a_g(\lambda)$, m⁻¹] were calculated from measured absorbances [$A_g(\lambda)$] as;

$$a_g(\lambda) = \frac{2.303A_g}{0.5}$$

Absorption of CDOM from water column samples was designated $a_{gw}(\lambda)$, and that from bulk melted ice samples $a_{gi}(\lambda)$. Slopes of the CDOM absorption spectra (S_g) between 300 and 450 nm were calculated using least squares fits to a negative exponential model (Twardowski and Donaghay, 2002).

Select CDOM samples from melted ice core sections and discrete water column sampling were frozen and shipped back to Old Dominion University for measurement of fluorescence excitation-emission matrix spectroscopy (EEMS). All samples were analyzed using a Spex Industries FluoroMax-2 spectrofluorometer within 10 months of collection, with scans controlled by DataMax spectroscopy software. Three dimensional EEMS were obtained by collecting individual emission spectra (290 – 560 nm) over a range of excitation wavelengths (250 – 450 nm). The scan increments for excitation and emission wavelengths were 5 and 2 nm, respectively, and the data integration time was 0.1 s. Data acquisition was carried out in the S/R (signal/reference) mode, which normalizes the fluorescence emission signal to the intensity of

the excitation light, thereby accounting for wavelength-dependent variation in the intensity of the excitation lamp. A long pass filter (Corion, CG-431-01, wavelength cut-off: 290 nm) was placed in the emission light path to remove second order Rayleigh scattering and Raman scattering. Inner filter correction, Raman normalization, blank subtraction and quinine sulfate calibration of the raw fluorescence spectra were performed on each scan according to the EEMS correction procedures outlined in Murphy et al. (2010).

2.4 Experimental Methods - The dynamic relationship between CDOM production and ice algal growth was explored using a 1 m² patch of ice that was cleared of snow on 8 April and maintained snow-free for 18 days. Overlying snow cover can attenuate as much as 98% of the light before it reaches the ice (Perovich et al., 1998), severely limiting the growth of ice algae, and necessitating its removal for this experiment. The patch was maintained free of snow by covering it with an acrylic sheet angled into the prevailing wind direction so that drifting snow was blown up and off the sheet. The acrylic cover transmitted approximately 90% of the photosynthetically active radiation (PAR = 400 to 700 nm) but less than 5% of the UV ($\lambda < 400\text{nm}$). However, the transmission of UV through sea ice itself is less than 1% (Perovich, 2006), so the light environment experienced by algae in the bottom of the ice was not negatively impacted by the acrylic sheet covering the patch. Individual cores were collected from the cleared patch on 8, 16 and 26 April. Ice thickness of the patch during the experiment increased from 164 to 190 cm due to cold air temperatures, decreasing light transmission to the bottom of the ice by ~5% and possibly depressing potential photosynthetic rates of the ice algae.

A photooxidation experiment was completed using bulk melted ice samples obtained from core sections cut from the bottom 20 cm of six ice cores collected at a single randomly assigned location as described above, melted in the dark in the science tent, combined into a

single volume (to attain enough volume for the experiment) and filtered through acid-rinsed 0.2µm polycarbonate filters to remove all particulate material. The combined volume was then distributed among 36 acid washed borosilicate glass bottles (40 ml each) that were randomly assigned to light and dark incubation treatments. The glass bottles transmitted 50% of the UV radiation at 200 nm and 90% of the UV-visible radiation between 325 and 750 nm. Solar radiation was excluded from dark experimental bottles by wrapping them in black electrical tape. The bottles were incubated in a UV-Vis transparent polycarbonate rack at 1 m depth in a ~2 m diameter hole cut through the ice. Three bottles were collected from each treatment once a day for six days, and $a_{gi}(\lambda)$ was measured using a WPI Ultrapath system. Time zero was 22 April at 18:15 local time, sample collection occurred at 24 hour intervals.

Downwelling quantum irradiance [$E_d(0^+)$] integrated across the photosynthetically active portion of the spectrum (PAR = 400 to 700 nm) was measured throughout the experiment just above the ice surface using a Li-Cor LI-192 plane radiometer. Quantum scalar irradiance [$E_o(0^-)$] was simultaneously monitored at the level of the submerged incubation rack using a LI-193 spherical radiometer. Ice was removed from the hole using a sieve twice each day and the hole was covered with a tent at night to limit ice growth. A storm necessitated covering the hole continuously on 25 and 26 April. During the course of the experiment, the chamber experienced 3 daylight periods of 9, 11 and 8 hours, and 3 dark periods of 14.5 and 13.5 hours and 2.5 days (due to the storm).

2.5 Data Analysis -All CDOM from ice cores was assumed to be restricted to the brine channels, leading to much higher absorption values *in situ* than indicated by the optical properties of the bulk melted samples. As drainage of the CDOM-rich brine into the underlying water column would be the major source of CDOM into the ice-ocean boundary layer, we

applied a correction to calculate $a_g(\lambda)$ of the concentrated brine [$a_{gb}(\lambda)$]. The relative volume of undiluted brine (V_{brine}) in the ice channels was calculated for all melted ice core sections using equation 5 from Cox and Weeks (1983), assuming an air volume fraction of zero:

$$\frac{V_{brine}}{V} = \frac{\rho Sal}{F_1(T)}$$

where V was total ice and brine volume, Sal was bulk salinity (ppt), $F_1(T)$ was an empirical polynomial function based on phase relations and found in table II in Cox and Weeks (1983), T was temperature of the core section in °C and ρ was bulk density in kg m⁻³, calculated by

$$\rho = (917 - 0.1403T)/1000$$

The dilution factor of the bulk melted ice sections was defined as $100/V_{brine}$ and was used to calculate $a_{gb}(\lambda)$.

The temperature of each core was measured by inserting the probe of a NIST-traceable digital thermometer (Cole-Parmer Model 90080-12) into freshly drilled holes (4 mm diameter) in the center of the core at 5 cm intervals along the length of the ice core. Salinity was determined in all melted ice samples using a hand held conductivity meter (Symphony SP70C, VWR) calibrated one month prior to the field program using IAPSO standard seawater diluted over a salinity range of 0 to 32.6 (Practical Salinity Scale). Conductivity measurements made by the probe were compared against a Guildline Autosalinometer (Model 8400B) at the Institute of Ocean Sciences (Sidney, BC, Canada), and a correction factor of 1.0554 was applied to probe measured salinity values.

All data are presented as arithmetic means ± 1 standard error. Overall statistical significance of differences within and among sample types (water column, ice core) was

determined by 1-way ANOVA, followed by Tukey's honestly significant difference criterion for individual comparisons when ANOVA returned statistically significant results.

A data set of 60 EEMS was compiled and characterized by parallel factor analysis with the use of the DOMFluor MATLAB toolbox (Stedmon and Bro, 2008). Six outlier samples were identified and excluded from the dataset using outlier tests and leverage plots. The PARAFAC algorithm was run for 3 to 7 components and the 4 component model was identified as the most appropriate by a split-half validation and residual analysis (Stedmon and Bro, 2008) The model was uploaded to OPENfluro (Murphy et al., 2014) to look for matching PARAFAC model components.

Measured scalar PAR values at the incubation rack were transformed into spectral irradiances [$E_o(\lambda)$ = 300 to 700 nm] according to the spectral distribution provided by *Hydrolight* Ver 4.2 (Sequoia Scientific) simulations. *Hydrolight* was initialized with water column absorption and scattering properties measured by the *ac-9*, the study site latitude and longitude, experimental date and 0% cloud cover. The contribution of each wavelength to PAR [$E_f(\lambda)$] was calculated as:

$$E_f(\lambda) = \frac{E_{od}(\lambda)}{PAR}$$

Using measured PAR at the incubation rack spectral E_{od} was then calculated by :

$$E_{od}(\lambda) = E_f(\lambda) * PAR$$

The resulting irradiance was then converted from quantum units ($\mu\text{mol m}^{-2} \text{s}^{-1}$) to energy (W m^{-2}) by:

$$E_{od}(\lambda) = \frac{hc}{\lambda}$$

266 where h was Planck's constant (6.626×10^{-34} joule s) and c was the speed of light (2.998×10^8 m
 267 s^{-1}). The total radiant energy absorbed [E_a ($W\ m^{-3}$)] by the samples was then calculated by
 268 summing the energy absorbed over all wavelengths, where $a(\lambda)$ was the wavelength-specific
 269 absorptance $\{= 1 - \exp [-A(\lambda)]\}$ of each sample.

$$E_a = \sum_{\lambda=400}^{700} E_{od}(\lambda) a(\lambda)$$

270 *2.6 Radiative transfer modeling* – Above ice spectral surface irradiance was calculated
 271 using the method described in section 2.5, and propagated through bare sea ice and melt pond
 272 covered ice using sea ice transmission values from Light et al. (2008), and through snow covered
 273 ice using ice transmission values from Hamre et al. (2004). Sea ice thicknesses during the light
 274 transmission observations varied between 1.5 and 2 m. The penetration of visible solar radiation
 275 (400 to 700 nm) through the water column to a depth of 100 m was modeled using *HydroLight*.
 276 Water column optical properties were parameterized using average profiles of a_{gw} and a_{pg} , plus
 277 pure water absorption estimates from Pope and Fry (1997). The volume scattering function was
 278 parameterized using the Fournier-Forand phase function (Fournier and Forand, 1994)
 279 corresponding to a constant b_b/b value of 0.014. Energy absorption was calculated as the
 280 difference in solar radiation between each 1 m layer, potential temperature increase was
 281 calculated as:

$$pT = \frac{E}{mc_p}$$

282 where m was density of seawater (1.05 kg/L) and c_p was energy needed to raise the temperature
 283 of 1 g of seawater by 1°C (4184 J), and E was the energy absorbed in each 1 m thick layer.

Temperature increase was thus calculated as a maximum potential value with no mixing or heat loss.

3. Results

3.1 Physical conditions during the study – The water column beneath the ice was highly stratified during the study, with a clearly defined polar mixed layer (PML) down to ~40 m (Fig. 2A). Temperature within the PML was -1.7° C, increasing to -1.5° C just below the thermocline, and reached -0.3° C at 200 m. A staircase feature initially observed in in salinity profile degraded between 12 and 25 April, coincident with an increase in surface salinity from 30.4 to 30.8 (Fig. 2B). The salinity increase corresponded to an increase in density, and possibly mixing of the PML (Fig. 2C).

3.2 Water column optical properties – Phytoplankton concentration in the water column remained below 0.2 mg Chl *a* m⁻³ over the course of the study (Fig. 2D). $a_{pg}(440)$ within the PML was variable with a mean of 0.073 ($\pm$ 0.00018) m⁻¹. Although $a_{pg}(440)$ in the first cast was the highest of the study and $a_{pg}(440)$ in the last cast the lowest (Fig. 2E), there was no discernable decline with time between these dates. $a_{pg}(440)$ decreased sharply across the thermocline, and continued to decrease with increasing depth below the PML (Fig. 2E). Absorption by CDOM declined with depth from 0.054 ($\pm$ 0.004) m⁻¹ at the surface to 0.026 ($\pm$ 0.0029) m⁻¹ at 200 m, the contribution to $a_{pg}(440)$ was ~ 75% in the PML and approached 90% below the thermocline. The mean $S_{gw}(300-450)$ was significantly higher within the PML than below it (Table 1, ANOVA), indicating a difference in the composition of the CDOM pool between the two water masses.

Beam attenuation [$c_{pg}(440)$] was highest (0.16 m⁻¹) immediately under the ice, decreased between 5 and 20 m (0.122 to 0.134 m⁻¹) and then increased sharply to a peak of 0.15 m⁻¹ around

307 30 m (Fig. 2G). All casts featured an initial rapid decrease in $c_{pg}(440)$ at the base of thermocline
308 followed by a slow decay with depth below the thermocline. In the final two casts, $c_{pg}(440)$ was
309 constant throughout the surface mixed layer (40 - 50 m deep), this was concurrent with the loss
310 of the staircase feature in salinity. Scattering [$b_p(440)$] in the PML followed the same pattern as
311 $c_{pg}(440)$, values of $\sim 0.06 \text{ m}^{-1}$ were observed immediately under the ice (Fig. 2H), followed by
312 decreased values between 5 and 20 m (0.05 m^{-1}) and an increase just above the thermocline.
313 Below the thermocline, $b_p(440)$ was constant with depth. The vertical features in $b_p(440)$
314 disappeared by the end of the study (Fig. 2H), consistent with the loss of these features in the
315 $c_{pg}(440)$ profiles.

316 The presence of CDOM increased the daily depth integrated energy absorption in the
317 PML by 27% over optically pure seawater (Fig. 3A), reducing the 1% penetration depth
318 (calculated from the underside of the ice) for PAR from 100 to 40 m. In absolute terms, energy
319 absorption was most strongly impacted in simulations with a melt ponded surface (Fig. 3A).
320 CDOM absorption had the greatest influence on the energy budget of the top several meters of
321 the water column, where its presence potentially increased the temperature by over 20% above
322 that resulting from absorption by optically pure seawater alone (Fig. 3B). Greater light
323 penetration through melt ponds covering the ice surface increased the potential CDOM driven
324 heating to $3.99 \times 10^{-4} \text{ }^\circ\text{C d}^{-1}$ over the top 8 m compared to $9.89 \times 10^{-5} \text{ }^\circ\text{C d}^{-1}$ under bare ice and
325 $4.79 \times 10^{-6} \text{ }^\circ\text{C d}^{-1}$ under snow covered ice (Fig. 3B).

326 *3.3 CDOM within ice cores* – The mean properties of melted ice core sections are
327 represented in Figure 4. Ice core temperatures decreased from the ice surface to the ice bottom
328 (Fig. 4A), whereas salinity followed the classic C-shape with the minimum values observed ~ 20
329 cm from the ice bottom (Fig. 4B). The brine fraction (% of volume) was greatest at the ice-water

interface ($14.5 \% \pm 2.3 \%$) and lowest at the top of the ice ($2.7 \% \pm 0.2 \%$; Fig. 4C), due to vertical temperature and salinity differences that affect the size and number of brine channels within the ice. Bulk CDOM absorption [$a_{gi}(374)$] was highest in sections cut from the bottom of the ice cores (Fig. 4D), and decreased upward away from the seawater interface. When corrected for the brine volume, $a_{gb}(374)$ was highest at the top of the ice where brine volume was lowest (Fig. 4E), decreased to a minimum that coincided with the salinity minimum and then increased again to the ice bottom. Chl *a* concentrations were higher at the bottom of the ice ($1.67 \pm 0.3 \text{ mg m}^{-3}$, Fig. 4F), decreasing to less than 0.2 mg m^{-3} in the top 50% of the cores. Consequently, the functional relationship between Chl *a* and $a_{gb}(374)$ was not statistically significant ($r^2=0.014$, ANOVA $p = 0.38$).

$a_{gb}(374)$ increased four-fold from 0.6 to 2.4 m^{-1} in the bottom 5 cm of the ice over the 18 day period when the ice surface was kept snow free (Fig. 5A, slope = $0.104 \pm 0.0002 \text{ m}^{-1} \text{ day}^{-1}$), and was accompanied by a four-fold increase in Chl *a* (Fig. 5B, slope = $1.155 \text{ m}^2 \text{ mg}^{-1} \text{ Chl } a$). In contrast, $a_{gb}(374)$ did not change in the snow covered ice cores over the same time period (Fig. 5A, slope = $0.011 \pm 0.015 \text{ m}^{-1} \text{ day}^{-1}$). Chl *a* reached the same concentrations in the snow covered cores as in the snow-free cores, but was not accompanied by an increase in $a_{gb}(374)$ (Fig. 5B). The spectral characteristics of CDOM changed over the course of the snow-removal experiment, with broad peaks centered at 275 nm emerging in the bottom and middle sections of the snow free ice cores by Day 18 (Fig. 6A & B). In contrast, $a_{gb}(\lambda)$ in the top of the ice decreased by 85% from 2.14 to 0.32 m^{-1} in the snow free area (Fig. 6B). The spectral characteristics of CDOM in snow covered cores was unchanged over the time course of the experiment (Fig. 6C). $a_{gb}(\lambda)$ was an order of magnitude higher in the ice compared to the water

column (Fig. 6D). There was evidence of small broad peaks at 270 nm in the water column a_{gw} , but these were not as prominent as in the ice cores.

3.4 Excitation-emission matrix spectroscopy – A four component PARAFAC model was developed and validated using the ice core and water column excitation-emission spectra. All four PARAFAC components had signals that were similar to those identified in earlier studies (Fig 7, Table 2). The narrow emission spectra with maxima below 375 nm for components 1 (C1), 2 (C2) and 4 (C4) were indicative of aromatic amino acid like fluorescence (Coble, 1996, Yamashita and Tanoue, 2003). C2, was a good match to fluorescence observed in Antarctic sea ice brine (Norman et al., 2011) and Baltic surface waters (Stedmon et al., 2007b). The broad emission spectrum centered on 425 nm for component 3 (C3) was characteristic of humic-like DOM (Figure 7C, Table 2).

Amino acid-like components (C1, C2, C4) accounted for 95% and 79% of the total fluorescence in sea ice and water column samples respectively (Table 3). There was no statistically significant difference in the fractional distribution of fluorescence assigned to C1, C2 and C4 between ice core and water samples (Table 4, ANOVA, $p > 0.05$). However, the humic-like C3 component was twice as high in the water column as in the ice core samples (Table 3, Table 4, ANOVA $p < 0.01$).

3.5 Photooxidation experiment - The daily integrated irradiance incident on the samples was on average $13.1 \text{ mol photons m}^{-2} \text{ d}^{-1}$ during uncovered days, but was $< 0.5 \text{ mol photons m}^{-2} \text{ d}^{-1}$ between 24 and 26 April when the storm necessitated covering the experimental hole (Fig. 8A). A significant change was observed in $a_{gi}(374)$ in both light (decreased) and dark (increased) incubated samples (Figure 8B, Table 5, ANOVA $p < 0.05$). The $a_{gi}(374)$ of light-incubated samples decreased by 41% over 120 hours (Fig. 8B), and $a_{gi}(374)$ of the dark-

incubated samples increased by 65% between the initial samples and those measured at 120 hours (Fig. 8B). Overall $S_{gi}(300-450)$ increased significantly in both light and dark incubated samples over the course of the experiment (Fig. 8C, Table 6, ANOVA, $p < 0.05$). The $S_{gi}(300-450)$ of dark incubated samples increased 40% over the last 24 hours of the incubation.

The relationship between $a_{gi}(374)$ and cumulative photon flux (300 to 700 nm) absorbed (E_a) by the samples provides a model to explain the photo-oxidation of CDOM (Fig. 8D). There was a net reduction in $a_{gi}(374)$ of $0.1 \text{ m}^{-1} \text{ mol}^{-1}$ photons absorbed, and a gross photo-degradation (taking into account dark bottle production) of $0.5 \text{ m}^{-1} \text{ mol}^{-1}$ photons absorbed. At this rate of photo-oxidation, under bare ice, 200 days would be required to remove the CDOM produced in the snow removal experiment (Figure 4), this is reduced to 61 days under melt-ponded ice, and 30 days in open water (Fig 8E).

4 Discussion

The absorption properties of the late winter/early spring water column in the Canadian Arctic under pre-bloom conditions were dominated by CDOM, significantly increasing the absorption of solar energy into the top 8 meters of the water column. This absorption makes a fundamental contribution to warming the surface layer of the water column beneath the ice. The high contribution of CDOM to non-water absorption observed in this study is common to Arctic waters in the winter and spring (Scully and Miller, 2000; Reynolds et al., 2001; Pegau, 2002; Matsuoka et al., 2011). The source of CDOM in the PML determined through DOM fluorescence characteristics was dominated by autochthonous material, possibly from sea ice, with a smaller humic-like allochthonous component, probably a residue of ocean productivity from the previous year. Circulation through the study region is driven by eastward flow from the

Canada basin and southward flow from the Arctic Ocean (Jones, 2001; Michel et al., 2006). The CDOM composition is therefore consistent with surface Canada Basin water which has a small riverine signal (Guay et al., 2009; Stedmon et al., 2011a), overwhelmed by the high autochthonous production sourced from the shelf seas (Chukchi and Beaufort Seas). The resulting late winter signal is that of refractory components remaining from summertime *in situ* production and riverine inputs that were subjected to photooxidation (Nelson and Siegel, 2013) and bacterial degradation (Junge et al., 2006), with additional more labile marine aromatics possibly freshly sourced from ice algae production. CDOM below the pycnocline reflected an older water mass containing a pool of CDOM that accumulated over time through deep ocean remineralization (Swan et al., 2012; Nelson and Siegel, 2013) and may have been slowly mixed upward into the PML during the latter part of our study as a result of processes that also increased salinity and density of the PML after 9 April.

One mechanism for CDOM input into the PML during the spring is through ice algae production and the release of CDOM into the underlying water column. Increases in Chl *a* were linked to amplification of CDOM absorption, the appearance of large absorption peaks centered at 275 nm which are likely due to mycosporine-like amino acids (Xie et al., 2014b), and the presence of strong proteinaceous fluorescence peaks. This evidence indicates that ice algae were the source of the CDOM found in the sea ice, as has been reported previously in both Arctic (Belzile et al., 2000; Scully and Miller, 2000; Xie et al., 2014a; Jorgensen et al., 2015) and Antarctic sea ice (Norman et al., 2011; Stedmon et al., 2011b). The disconnect between [Chl *a*] and CDOM in the low light environments (snow covered) observed here is attributed to a delay of drivers such as lysis, grazing and microbial action that are linked to the production of CDOM (Thomas et al., 1995; Xie et al., 2014a). Our data represent the early season low algal

productivity end member to the strong relationship between [Chl *a*] and a_{gi325} observed in the Amundsen Gulf sea ice which was conducted from March through July 2008 (Xie et al., 2014a). Now that ice is known to act as a reservoir of highly labile marine CDOM from ice algae, the anticipated impact on water column solar absorption needs to be quantified.

The flux of CDOM from the sea ice initially occurs through brine drainage and then from both surface melt pond drainage and bulk ice melt. The classic C-profile of salinity in the ice indicated that surface melt had not yet been initiated and brine exchange would have been the dominant mechanism for CDOM flux to the underlying water column. Brine volume in the bottom 20 cm of the ice ranged from 7 to 15% during our study, well above the critical volume fraction of 5% that defines impermeable ice (Golden et al., 1998). The release of carbon from sea ice in the late winter and early spring can reasonably be assumed to remain close to the underside of the ice as the volume of brine released is not enough to initiate sinking and convection in the mixed layer (Miller et al., 2011). Although we observed no significant change in a_{gw} during this study, our sampling protocol did not have the spatial resolution to detect very thin layers of high CDOM absorption within a few centimeters of the bottom of the ice. The impact of CDOM flux from the bottom 5 cm of a 1 m² area of ice can be estimated by assuming a 14% brine volume which would contain on average 0.0048 m³ of brine (based on a 220 ml melted volume for sampled 5 cm thick core sections). Complete exchange and mixing with a 5 cm thick layer of the underlying water column will dilute the brine 10.3 fold. Using the mean observed a_{gw374} values of 0.27 m⁻¹, and a_{gb374} of 2.5 m⁻¹ (from the snow free experiment) the resulting brine exchange would produce a doubling of $a_{gw}(374)$ within a thin layer (5 cm deep) close to the ice bottom. As ice algal production increases over the season so will the impact of the CDOM flux. An increase in $a_{gb}(374)$ to 30 m⁻¹ consistent with higher [Chl *a*] later in the

growth season (Xie et al., 2014a) would lead to an order of magnitude increase in $a_{\text{gw}}(374)$ in the first 5 cm. The impact of CDOM sourced from sea ice on the underlying water column across the Arctic will of course be variable depending on the growth of ice algae and the background magnitude of CDOM absorption in the underlying water column.

CDOM produced within the bottom of the ice cores was highly vulnerable to photooxidation, leading to a loss of absorbing material from the system. Photooxidation losses were observed in the top most section of the ice during the snow free experiment. Production in the bottom of the ice, however, outpaced these losses, leading to accumulation of CDOM. The rate of production in the ice also exceeded the photooxidative loss that would occur once the material was released to the water column, allowing for the seasonal accumulation of CDOM both in the brine and under the ice. Photooxidative loss dramatically increases the removal of ice derived CDOM once the system transitions to high light intensity open water conditions, reducing the impact of CDOM on water column absorption. The increase in both $a_{\text{gi}}(374)$ and $S_{\text{gi}}(300-450)$ in dark incubated samples indicates that microbial activity is an active pathway in the production of CDOM from DOM, although these chorophores are short-lived (time scale of days) (Nelson et al., 2004).

The allochthonous CDOM at our study site originated from the Canada Basin/Beaufort Gyre system and was derived from Pacific origin water which picked up humics from the Chukchi sea sediment, autochthonous CDOM production on the Western Arctic shelves, and Eurasian river runoff (Guay et al., 2009, Gueguen et al., 2012). Ongoing climate change impacts can alter the magnitude of these sources through increasing riverine discharge (Peterson et al., 2002), thawing of permafrost (Fichot et al., 2013) and changes in annual marine primary productivity (Arrigo et al., 2008). The influence of increasing CDOM input on solar energy absorption will vary

geographically across the Arctic Ocean. Increased riverine loading of CDOM from North American and Eurasian rivers may impact water column absorption in the Eastern Arctic shelf seas, and the Southern Canadian Archipelago, but its impact on CDOM related heating in the Northern Canadian Archipelago or in the Canada Basin will be small because the majority of terrestrial material is remineralized within Beaufort gyre surface waters before the water enters the northern Canadian Archipelago (Stedmon et al., 2011a).

Future changes in ice algae CDOM production will be determined by the balance between thinning of the Arctic ice pack that permits greater light penetration (Light et al., 2008; Richter-Menge and Farrell, 2013; Renner et al., 2014), and shortening of the window of ice algae production due to faster and earlier ice melt. A new phenomenon of “ice holes” - open melt ponds that refreeze in the late summer - have been identified as new ice algae habitat and could hold CDOM over until the next spring (Lee et al., 2011). Ultimately the impact of climate change on the production of CDOM from ice algae is undetermined, but from this study it is possible to conclude that ice algae CDOM will potentially impact under ice warming in areas where ice algal growth is present and existing water column CDOM is low.

Conclusion

This study established that ice algae are the primary source of CDOM in early spring landfast ice in the Canadian Archipelago, that production of CDOM exceeds photooxidative losses under ice cover and that the presence of CDOM increases energy absorption and the resulting heating impact by 30% relative to CDOM-free water. All of these findings suggest that CDOM represents a critical, although geographically variable factor in the heat budget of the Arctic Ocean. Improving our understanding of the impacts of increasing light penetration and

CDOM production on water column heating and ice melt will require further quantification of the relationships between algal and microbial growth and CDOM production as well as flux rates of CDOM from the ice. The measurement of a_g , irradiance and temperature at fine vertical resolution near the underside of the ice will also be necessary to quantify the heating impact within the ice-ocean boundary layer. The future impact of CDOM on the absorption of solar energy and water column heating will be driven by a balance between increased riverine transport (Fichot et al., 2013), amplified light transmission (Renner et al., 2014; Stroeve et al., 2014) stimulating algal based CDOM production and faster losses through photochemical pathways (Logvinova et al., 2015).

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743 Table 1 Mean (standard error) S_{gw} (300-450) for water column sampling depths 0, 3, 5, 10, 50,
 744 100 and 200m, over the course of the study and ANOVA results for the comparison among
 745 sampling depths.

Depth (m)	0	3	10	50	100	200
S_{gw} (300-450)	0.0225 (0.00035)	0.0229 (0.00017)	0.0229 (0.00032)	0.0217 (0.00024)	0.0193 (0.00067)	0.0198 (0.00053)
Source	SS	DF	MS	F	<i>p</i>	
Groups	0.00005	5	1.06e-05	13.43	< 0.01	
Error	0.000029	37	7.9e-07			
Total	0.0000083	42				

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Table 2. Fluorescence characteristics of PARAFAC model components , excitation (λ_{ex}) and emission (λ_{em}) maxima, compared with previously classified spectral matches from OpenFluor (Murphy et al., 2014)

Catlin	$\lambda_{ex} / \lambda_{em}$	Description and probable source
Model		
C1	278/332	Amino acids, bound in protein Component 6 (Stedmon and Markager, 2005)
C2	298/340	Amino acids (polar studies) Component 1 (Stedmon et al., 2011b) Component 4 (Stedmon et al., 2007b)
C3	250-350/436	Terrestrial and Marine humic-like Did not match well in OpenFluor, characteristic of M peak (Coble, 2007)
C4	266/312	Amino acids, free or bound in proteins Component P2 (Murphy et al., 2008)

Table 3. Mean (standard error) percent contribution of each PARAFAC component to total fluorescence intensity for the bottom 20 cm of ice cores combined and the water column.

Sample type	C1	C2	C3	C4
Ice	50.4 (2.5)	22.2 (1.6)	4.8 (0.5)	22.6 (1.6)
Water	44.9 (3.4)	11.4 (2.1)	20.8 (1.0)	22.8 (1.5)

Table 4. ANOVA results for the comparison of percent contribution of PARAFAC component 1, through 4 between ice and water column samples. * designates a significant difference ($p \leq 0.05$).

Component	Source	SS	DF	MS	F	<i>p</i>
1	Groups	367	4	92	0.62	0.65
	Error	5796	39	148		
	Total	6163	43			
2	Groups	408	4	102	1.87	0.1351
	Error	2128	39	55		
	Total	2536	43			
3	Groups	2555	4	639	56	<0.01*
	Error	444	39	11		
	Total	2999	43			
4	Groups	1436	4	359	2.17	0.09
	Error	6446	39	165		
	Total	7881	43			

Table 5. ANOVA results for the comparison of $a_{gi}(374)$ over the course of both light and dark incubations. * designates a significant difference ($p \leq 0.05$).

Incubation type	Source	SS	DF	MS	F	<i>p</i>
Light	Groups	0.00225	4	0.00056	6.52	<0.05*
	Error	0.00078	9	0.00009		
	Total	0.00303	13			
Dark	Groups	0.03805	4	0.0095	4.74	<0.05*
	Error	0.01807	10	0.00201		
	Total	0.05612	14			

Table 6. ANOVA results for the comparison of S_{gi} over the course of both light and dark incubations. * designates a significant difference ($p \leq 0.05$).

Incubation type	Source	SS	DF	MS	F	<i>p</i>
Light	Groups	4.24E-05	4	1.06E-05	5.77	<0.05*
	Error	1.83E-05	10	1.84E-05		
	Total	6.08E-05	14			
Dark	Groups	0.00065	4	0.00016	32.29	<0.05*
	Error	0.00005	10	0.00001		
	Total	0.0007	14			

Figure Legends

Figure 1. Map showing the location of the Catlin Ice Base 2011 (star) near Ellef Ringnes Island in the Canadian Archipelago. Also shown is the direction of water mass movement from the Canada Basin into the study area, after Jones (2001) and Michel et al., (2006). Inset shows the wider geographic setting of the Canadian Archipelago.

Figure 2. Vertical profiles of water column properties, all profiles (grey), mean (black), first cast 22 March 2011 (red), last cast 21 April 2011 (blue). A. Temperature ($^{\circ}\text{C}$). B. Salinity (PSS). C. $\sigma\text{-t}$. D. Mean ($\pm$ standard error) Chl a (mg m^{-3}). E. Particulate and CDOM absorption $a_{\text{pg}440}$ (m^{-1}). F. Mean ($\pm$ standard error) CDOM absorption $a_{\text{gw}440}$ (m^{-1}). G. Particulate and CDOM attenuation $c_{\text{pg}440}$ (m^{-1}). H. Particulate scattering $b_{\text{p}440}$ (m^{-1}).

Figure 3. A. Depth integrated daily energy absorption in the Polar Mixed Layer (PML) for pure water (solid line) and water plus CDOM (dashed line) under snow covered (blue), bare ice (red) and melt pond covered ice (black). B. Potential daily water column temperature increase in the Polar Mixed Layer (PML) for pure water (solid line) and water plus CDOM (dashed line) under snow covered (blue), bare ice (red) and melt pond covered ice (black).

Figure 4. Mean ($\pm$ standard error) vertical distribution of ice core properties from a total of 10 cores that were collected from 19 March to 26 April at an interval of 4 days. A. Temperature ($^{\circ}\text{C}$). B. Salinity (PSU). C. Percent brine by volume calculated using the equations of Cox and Weeks, 1983. D. $a_{\text{gi}}(374)$ (m^{-1}). E. $a_{\text{gb}}(374)$ (m^{-1}). F. Chl a concentration (mg m^{-3}).

Figure 5. A. $a_{\text{gb}}(374)$ in the bottom 5 cm of ice cores collected from the experimental patch and snow-covered locations as a function of time. B. $a_{\text{gb}}(374)$ versus Chl a in the bottom 5

cm of ice cores collected from the experimental patch and snow-covered locations at the same time steps as Figure 5A.

Figure 6. Spectral absorption of a_{gb} within ice core sections from the snow free experiment, snow covered area and water column. A. Day 0, snow free experiment, B. Day 18 snow free. C. Day 18 snow covered. Lines indicate the position of each spectrum within the ice core, with 100% representing the base of the core at the ice-seawater interface. D. average and standard deviation of all water column a_g spectra from 0 to 50 m and 100 and 200 m.

Figure 7. Contour plots of the spectral characteristics of the four components derived from PARAFAC modeling. A. Component 1. B. Component 2. C. Component 3. D. Component 4.

Figure 8. A. Downwelling plane irradiance (PAR) measured above the ice and on the incubation box during the photooxidation experiment from 23 to 28 April 2011. B. Mean ($\pm$ standard error) values of $a_{gi}(374)$ over the course of the experiment in light and dark incubated samples. C. Mean ($\pm$ standard error) spectral slopes $S_{gi}(300-450)$ of a_{gi} over the course of the experiment in light and dark incubated samples. D. $a_{gi}(374)$ in light samples, and light minus dark samples plotted against cumulative radiant energy absorbed during the photo-oxidation experiment. E. Timescale of modeled $a_{gi}(374)$ reduction through photooxidation, for simulated light fields under bare ice, melt ponded ice and open water. Grey line represents the level at which photooxidation exceeds the $1.8 \text{ m}^{-1} a_{gi}(374)$ that was produced in the snow removal experiment.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8