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Relationship Between Carbon- and Oxygen-Based Primary Productivity in the Arctic Ocean, Svalbard Archipelago

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Phytoplankton contribute half of the primary production (PP) in the biosphere and are the major source of energy for the Arctic Ocean ecosystem. While PP measurements are therefore fundamental to our understanding of marine biogeochemical cycling, the extent to which current methods provide a definitive estimate of this process remains uncertain given differences in their underlying approaches, and assumptions. This is especially the case in the Arctic Ocean, a region of the planet undergoing rapid evolution as a result of climate change, yet where PP measurements are sparse. In this study, we compared three common methods for estimating PP in the European Arctic Ocean: (1) production of ^{18}O-labeled oxygen (GPP-^{18}O), (2) changes in dissolved oxygen (GPP-DO), and (3) incorporation rates of ^{14}C-labeled carbon into particulate organic carbon (^{14}C-POC) and into total organic carbon (^{14}C-TOC, the sum of dissolved and particulate organic carbon). Results show that PP rates derived using oxygen methods showed good agreement across season and were strongly positively correlated. While also strongly correlated, higher scatter associated with seasonal changes was observed between ^{14}C-POC and ^{14}C-TOC. The ^{14}C-TOC-derived rates were, on average, approximately 50% of the oxygen-based estimates. However, the relationship between these estimates changed seasonally. In May, during a spring bloom of *Phaeocystis* sp., ^{14}C-TOC was 52% and 50% of GPP-DO, and GPP-^{18}O, respectively, while in August, during post-bloom conditions dominated by flagellates, ^{14}C-TOC was 125% of GPP-DO, and ^{14}C-TOC was 175% of GPP-^{18}O. Varying relationship between C and O rates may be the result of varying importance of respiration, where C-based rates estimate net primary production (NPP) and O-based rates estimate gross primary production (GPP). However, uncertainty remains in this comparison, given differing assumptions of the methods and the photosynthetic quotients. The median O:C ratio of

4.75 in May is within the range of that observed for other regions of the world's ocean. However, the median O:C ratio for August is <1, lower than in any other reported region. Our results suggest further research is needed to estimate O:C in Arctic waters, and at different times of the seasonal cycle.

Keywords: primary production, Arctic Ocean, oxygen method, carbon methodology, Svalbard (Arctic) and plankton

INTRODUCTION

Plankton photosynthesis contributes half of the primary production (PP) in the biosphere (Field et al., 1998) and is the main source of carbon for the Arctic Ocean food web (Matrai et al., 2013). Because photosynthesis is a fundamental process affecting, either directly or indirectly, the functioning of marine ecosystems, from their capacity to take up atmospheric CO_2 to the distribution and breeding success of higher trophic levels, quantification of PP has long been a core measurement in biological oceanography (Robinson et al., 2009; Regaudie-de-Gioux et al., 2014). Measurements of PP over the last decades, both remote and *in situ*, have provided critical insight into the spatial and temporal variability of phytoplankton growth in the Arctic. Although the Arctic Ocean is strongly seasonal, some of its regions rank among the most productive in the oceans (Gosselin et al., 1997; Tremblay et al., 2002; Vaquer-Sunyer et al., 2013), which results in high pelagic and benthic secondary production (Grebmeier and Mcroy, 1989; Grebmeier et al., 2006, 2013). While recent modeling and remote sensing studies have also suggested climate-driven changes in the rates of PP in the Arctic (Pabi et al., 2008; Slagstad et al., 2015; Kahru, 2017), methodological differences in PP measurements nevertheless introduce uncertainty in these future projections. To evaluate PP responses, appropriate estimations and evaluations of PP based on comparable methods are fundamental (Robinson et al., 2009; Regaudie-de-Gioux et al., 2014). Until a consensus is reached or an unambiguous method is developed, comparisons between measurements originating from different methods can provide insight on the ecological and physiological processes involved as well as help constrain the uncertainties (Robinson et al., 2009; Regaudie-de-Gioux et al., 2014).

Three primary methods have historically been used to estimate planktonic PP, each with different underlying assumptions. Gross photosynthesis (or gross primary production rate, GPP) estimates the total photosynthetic rate before any losses, like phytoplankton respiration. GPP has been quantified using two oxygen-based methods as the photosynthetic production of ^{18}O from ^{18}O-labeled water additions (GPP-^{18}O) as well as using the Dissolved Oxygen method. The determination of GPP-^{18}O through mass spectrometry, which measures the O_2 produced during a 24-h incubation (Bender et al., 1987), has previously been identified as the best approach to estimate GPP (Regaudie-de-Gioux et al., 2014). However, not all the oxygen-producing metabolic processes measured with the ^{18}O method are directly related to carbon assimilation (Bender et al., 1999; Laws et al., 2000; Dickson et al., 2001; Marra, 2002). The Dissolved Oxygen method (Carpenter, 1995), on the other hand, measures the change in dissolved oxygen in light/dark incubations over 24 h. In this case, GPP, (hereafter GPP-DO) is derived by summing the rate of change of oxygen in dark bottles (an estimate of community respiration, CR) and that in clear bottles (an estimate of net community production, NCP) (Carritt and Carpenter, 1966; Duarte et al., 2011). This procedure assumes that respiration in the dark is the same as that in the light. Recent studies have shown that this assumption may not hold in the Arctic Ocean during spring and summer, where 24-h daylight lead to increased respiration rates (Mesa et al., 2017).

The third and most widely used method to resolve plankton PP is the ^{14}C method (Steemann-Nielsen, 1952), which traces the incorporation of inorganic carbon into live phytoplankton cells, or particulate organic carbon (^{14}C-POC). This method can also be used to track the release of recently incorporated ^{14}C as dissolved organic carbon (^{14}C-DOC). The total carbon incorporation by the ^{14}C method is ^{14}C-TOC, the sum of ^{14}C-POC and ^{14}C-DOC. High variability in incubation times has resulted in significant uncertainty as to how to interpret ^{14}C rate measurements. In daily incubations, ^{14}C-POC is expected to reflect net primary production (^{14}C-NPP) (Marra, 2002, 2009). NPP rates may account for a minimum of ~35% of GPP-^{18}O in 24-h incubations (Bender et al., 1996; Duarte and Cebrián, 1996) and about 48% of GPP-DO in short incubations, as a consequence of losses attributed to algal respiration, and DOC production (Del Giorgio and Duarte, 2002).

Comparison of estimates derived from these various methods have led to a wide range of carbon uptake estimates across spatial scales (Robinson et al., 2009; Regaudie-de-Gioux et al., 2014). While in previous studies in the North Pacific, the Dissolved Oxygen and the ^{18}O methods provided similar estimates of GPP (Grande et al., 1989b), in global comparisons (Robinson et al., 2009; Regaudie-de-Gioux et al., 2014), as well as in the Arctic Ocean (Mesa et al., 2017), the GPP-^{18}O estimates were higher than GPP-DO. In contrast, ^{18}O values can be significantly lower than GPP-DO rates in nutrient-rich areas with low dissolved oxygen concentrations (Gazeau et al., 2007). This large variability indicates that the ability of methods to estimate PP is dependent on environmental conditions, and the use of multiple methods has been recommended as a regional solution (Robinson et al., 2009).

Comparisons between the C-based method and the O_2-based methods have indicated lower rates of ^{14}C incorporation than O_2 production (Robinson et al., 2009; Regaudie-de-Gioux et al., 2014). These discrepancies are likely due to variability in the assumed photosynthetic quotient (PQ), a critical parameter quantifying the amount of oxygen evolved per unit of photosynthetically fixed carbon into organic matter. PQ values range widely, from 1.0 to 1.8, with values 1.0 to 1.4 in non-polar oceanic areas (e.g., Bender et al., 1987; Grande et al., 1989b; Laws et al., 2000; Dickson et al., 2001) and from 1.1 to 1.8 in the Southern Ocean (i.e., Williams et al., 1979; Aristegui et al., 1996; Robinson et al., 1999). Although no PQ value has been derived for the Arctic Ocean, a value of 1.25, proposed by Williams et al. (1979), has been widely applied in this region to convert O_2 molar stoichiometry units into C (i.e., Vaquer-Sunyer et al., 2013; Duarte and Agustí, 1998). However, PQ = 1 is also frequently considered when comparing C and O_2-based PP rates (Duarte et al., 2011; Regaudie-de-Gioux et al., 2014).

Historically, ^{14}C-POC measurements have primarily been collected across the Arctic Ocean, with O_2-based rates collected only in select regions (Matrai et al., 2013). Average ^{14}C-POC rates in Arctic surface waters, compiled over 50 years (1954–2007), are 70 and 21 mg C m^{-3} d^{-1} in spring and summer, respectively (Matrai et al., 2013). By comparison, O_2-based GPP-DO productivity rates of surface waters, collected in the European sector of the Arctic between 2007 and 2011, average 168 and 55 mg C m^{-3} d^{-1} in spring and summer, respectively (Vaquer-Sunyer et al., 2013), twofold higher than those derived for ^{14}C-POC rates. Whether these differences are due to spatial gradients or temporal changes in the system, or a result of bias in the methods of measurement remains unknown due to a lack of comparison between concurrent C-based and O_2-based measurements of PP in Arctic waters.

In this study, we report on rates of PP derived using ^{14}C, Dissolved Oxygen, and ^{18}O methods in the northwestern Svalbard Archipelago in the European Arctic and focus on comparing these rates. We also consider the pathways of carbon and oxygen within the plankton and provide an assessment of the ecological and physiological processes underlying the methods' assumptions. We aim to facilitate future PP studies in the region and to highlight improvements needed in order to interpret results from the various methods in the Arctic Ocean ecosystems.

MATERIALS AND METHODS

Sampling

Two cruises were conducted in the north and northwestern Svalbard region during May and August 2014 aboard R/V Helmer Hanssen (**Figure 1**). Our aim was to analyze the underlying assumptions of primary productivity rate measurements through two different pathways: the carbon assimilation and the oxygen production. In order to achieve this, we measured PP rates in 24-h incubations using three different methods (the ^{14}C method, the Dissolved Oxygen method, and the ^{18}O method). Although the cruise sampled six "P" stations, P6 was not included in this study as GPP-DO measurements are not available. Similarly, no sampling is available from P2 as this station was aborted due to loss of the mooring with the ^{14}C incubations. Five remaining stations were occupied during the May cruise (P1, P3, P4, D1, and D6) and four remaining stations in the August cruise (P5, P7, D1, and D6), with sampling including hydrographic profiling with a calibrated Seabird 911plus CTD (conductivity, temperature, and depth). Discrete water samples for PP incubations were collected from CTD casts, for ^{14}C rate measurement and oxygen measurements (DO and ^{18}O). Seawater for PP analysis was sampled from the same cast at four stations (D1 and D6 in both May and August), while logistical constraints on hydrographic deployments forced collection of water from separate CTD casts at three stations (P1, P3, and P4) in May and two stations (P5 and P7) in August, with time lag between casts ranging from minutes to 32 h (see section "Sampling Time Lag" below). Seawater for all O_2-based PP and for ^{14}C at the D stations was sampled at the surface (1 or 3 m), the deep chlorophyll maximum layer (DCM) depth (20–30 m depending on stations), and an intermediate depth (10 or 15 m). Seawater for ^{14}C–based PP determination at the P stations was sampled at 1–3, 5, 10, 15–20, and 25–30 m, with exact sampling depths varying depending on the presence and depth of the DCM. Rate measurements at a given station were matched by closest depths, with depth differences reaching a maximum of 3 m.

Primary Production Incubations

Primary production rates were measured using three methods: the ^{18}O method (Bender et al., 1987), the Dissolved Oxygen method (Carpenter, 1995), and the ^{14}C method (Steemann-Nielsen, 1952). Samples measured with O_2 methods were incubated on deck with running seawater from the ship's seawater intake (**Supplementary Figure S1**), following the incubation protocols used in previous studies (Regaudie-de-Gioux and Duarte, 2010; Vaquer-Sunyer et al., 2013; Holding et al., 2015; Garcia-Corral et al., 2016; Mesa et al., 2017). The seawater intake was at ∼6 m depth, within the mixed layer. Depending on the station, the mixed layer reached depths between 9 and 15 m (Randelhoff et al., 2018). For deep samples collected below the mixed layer, temperature differences between circulated water and *in situ* temperature ranged from 0.03°C to 4.5°C (**Supplementary Figures S2**, **S3**). Samples measured with the ^{14}C method were incubated both on deck (D stations, **Supplementary Figure S1**), using the incubation system of the O_2 samples, and *in situ* (P stations, see below for additional details).

The ^{18}O Method

GPP-^{18}O was measured as the photosynthetic production of $^{18}O_2$ following the addition of $H_2{}^{18}O$ after 24 h incubations (Bender et al., 1987; **Table 1**). Samples were distributed into eight 12-ml vials, allowing them to overflow to avoid contamination with atmospheric O_2. Borosilicate vials were ultraviolet A and B (UVA/B) opaque. Four replicate vials were immediately preserved with 100 µl of saturated mercury chloride ($HgCl_2$) solution for further determination of natural $\delta^{18}O$ in seawater and the vials stored inverted, in darkness. The other four replicate vials, containing glass beads, were labeled with 80 µl of 98% $H_2{}^{18}O$ and shaken to ensure mixing. The labeled samples were incubated for 24 h on deck in transparent methacrylate tubes that are also UVA/B opaque with flow-through surface seawater. To simulate light attenuation in the water column, methacrylate tubes were wrapped with screen. Screening resulted in an attenuation of 60, 33, and 25% of surface PAR for these

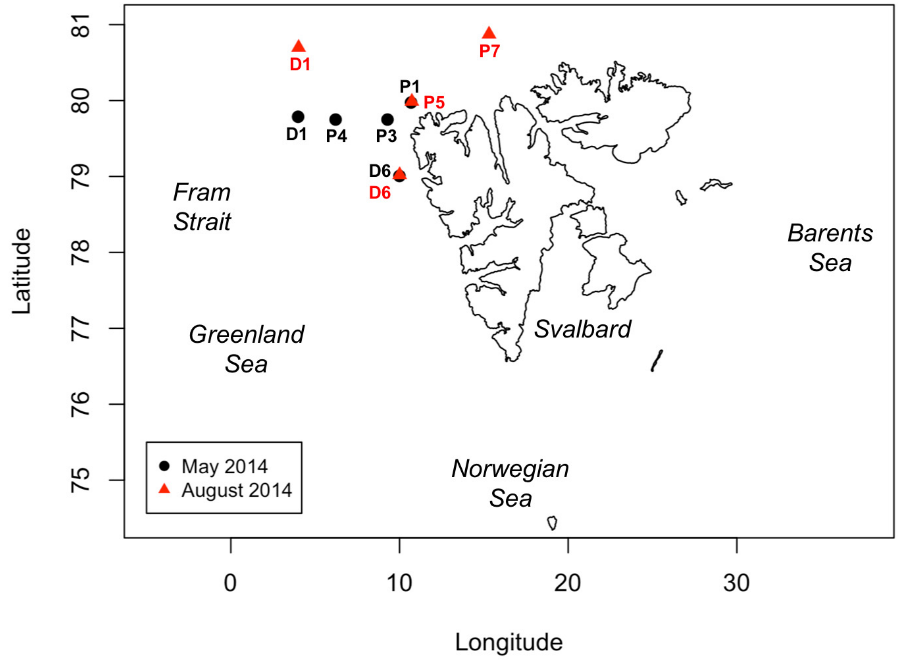

FIGURE 1 | Map of the Svalbard Archipelago, showing the locations of sampling stations occupied in May (stations D1, D6, P1, P3, and P4, black dots) and August 2014 (stations D1, D6, P5 and P7, red triangles). Note that stations P2 and P6 are not included as no data was available for the analysis (see section "Materials and Methods").

bottles (as measured with a portable photosynthetically available radiation (PAR) radiometer, Biospherical Instruments Inc. QSL-101), equivalent to light levels at 1, 10, and 20–30 m depth (Randelhoff et al., 2018). After 24 h, incubation vials were spiked with 100 µl of saturated $HgCl_2$ solution and stored for further analysis.

Samples were analyzed 2 weeks later at the Stable-Isotope Laboratory in IACT-CSIC, Armilla, Spain. A 4-mL headspace with 100% Helium was generated in each vial and left for 24 h at room temperature, letting the dissolved gases in water equilibrate with the headspace. After 24 h, the $\delta^{18}O$ of dissolved oxygen in the headspace was measured in a Finnigan GasBench II attached to a Finnigan DeltaPlusXP isotope ratio mass spectrometer. We used a gas bottle of oxygen as our internal standard and atmospheric air injected in helium vials as an external standard. The analysis of the $\delta^{18}O$ of oxygen from the gas bottle had a standard deviation of 0.05%. Atmospheric air, which was measured following the same route as the samples, had a standard deviation of 0.2%. The flow was passed through a liquid nitrogen trap to remove water vapor before entering into the GasBench II. Molecules of O_2 and N_2 were separated in a Molecular Sieve 5Å chromatographic column. Corrected data with atmospheric air was reported as $\delta^{18}O$ value (‰) relative to V-SMOW (Vienna Standard Mean Ocean Water) standard.

TABLE 1 | Acronyms for primary production variables used in this study, including their definition and source.

Acronyms	Significance	References
GPP-^{18}O	Gross primary production measured with the ^{18}O method adding $H_2{}^{18}O$	Bender et al., 1987
GPP-DO	Gross primary production measured with O_2 mass blance method (GPP-DO = NCP + CR)	Carritt and Carpenter, 1966
NCP	Net community production measured with O_2 mass blance method in light bottles	Carpenter, 1995
CR	Community respiration with O_2 mass blance method in dark bottles	
^{14}C-TOC	Primary production of total organic carbon measured with the ^{14}C method (^{14}C-TOC = ^{14}C-POC + ^{14}C-POC)	Steemann-Nielsen, 1952
^{14}C-POC	Primary production of particulate organic carbon measured with the ^{14}C method	
^{14}C-DOC	Primary production of dissolved organic carbon measured with the ^{14}C method	

The $\delta^{18}O$ (H_2O) composition of labeled samples was measured in a liquid water isotope analyzer (Los Gatos Research), with precision of 0.2%. In order to avoid contamination of the analyzer with highly ^{18}O-enriched H_2O (≈ 3000‰), the labeled sample was diluted (approximately 1:20) with a laboratory standard of known isotopic composition. GPP-^{18}O was calculated using the Eq. (1) from Bender et al. (1999):

$$GPP - {}^{18}O = \left[\left(\delta^{18}O_{final} - \delta^{18}O_{initial}\right) / \left(\delta^{18}O_{water} - \delta^{18}O_{initial}\right)\right] \times [O_2]_{initial} \times (1/\delta t) \quad (1)$$

Where GPP-^{18}O, in units of mmol O_2 m^{-3} d^{-1}, is the gross PP measured with the ^{18}O method, $\delta^{18}O_{initial}$ and $\delta^{18}O_{final}$ are the initial and final $\delta^{18}O$ of dissolved O_2 (‰), respectively,

$\delta^{18}O_{water}$ is the $\delta^{18}O$ of the labeled seawater (‰), $[O_2]_{initial}$ is the initial O_2 concentration (μmol O_2 L^{-1}) measured by high-precision Winkler titration (see below) and δt is the incubation time in days (d).

The Dissolved Oxygen Method

GPP-DO, an acronym previously applied for GPP evaluated with this method (i.e., Regaudie-de-Gioux et al., 2014), also called GP(O_2), (i.e., Robinson et al., 2009) was calculated by solving the daily change in dissolved oxygen in equation GPP-DO = NCP + CR_{dark} where NCP is net primary production and CR_{dark} is community respiration in darkness, in units of mmol O_2 m^{-3} d^{-1}. NCP and CR_{dark} were calculated by subtracting initial dissolved oxygen concentrations from the dissolved oxygen concentrations measured after 24-h incubation in light and dark conditions, respectively (Carritt and Carpenter, 1966; Carpenter, 1995; **Table 1**). For this incubation, water samples were distributed into 21 UVA/B opaque 100 mL narrow-mouth borosilicate Winkler bottles. Seven replicates were used to determine the initial oxygen concentration, and seven replicates were incubated in dark and seven in light for 24 h on deck. O_2 concentrations were determined using an automatic titrator (808 Tritando, Metrohm) (Carritt and Carpenter, 1966; Carpenter, 1995), a potentiometric electrode and automated endpoint detection (Oudot et al., 1988). Values that reported O_2 production in darkness (Pamatmat, 1997) were flagged as unreliable and discarded (Holding et al., 2013).

The ^{14}C Method

Primary production using ^{14}C method included estimates of particulate (^{14}C-POC) and total (^{14}C-TOC) organic carbon production in 24 h incubations (Steemann-Nielsen, 1952; Vernet et al., 1998; **Table 1**). Water samples were distributed in four UVA/B opaque 150-mL polycarbonate bottles. Treatments included 2 light bottles, 1 dark, and one Time Zero. Ten μCi of ^{14}C-labeled bicarbonate was dispensed into each bottle, and the Time Zero filtered immediately. In addition, for each depth, a 100 μL aliquot was sampled into a 6-mL scintillation vial containing 0.1 mL 6N NaOH in order to estimate the initial ^{14}C-bicarbonate concentration, or Specific Activity. In the P stations (**Figure 1**), samples were incubated *in situ*: light and dark bottles were hung from a line anchored to an ice floe and deployed for approximately 22 h. In D stations (**Figure 1**), samples were incubated on deck for 24 h, in UVA/B opaque methacrylate tubes (Plexiglas®), with surface water temperatures maintained with running seawater from the ship's intake. To simulate light attenuation in the water column, screens covered the methacrylate tubes placed inside the incubator (**Supplementary Figure S1**). Light attenuation was simulated using screens as a % of the on-deck photosynthetically available irradiance (PAR), simulating 100, 50, 25, and 12% of surface PAR, respectively. Attenuation within the methacrylate tubes was quantified with a Biospherical Instruments Inc QSL-101. After 22–24 h, bottles for *in situ* or on deck incubations were recovered and sampled, keeping the bottles refrigerated. 200 μL of 20% HCl was dispensed into each 6-mL scintillation vial containing either a Whatman GF/F filter (for particulate, ^{14}C-POC) or 2 mL of seawater (for total production, ^{14}C-TOC) in order to release any inorganic ^{14}C remaining in the sample. After 24 h, 5 ml of Ultima Gold (Perkin Elmer, United States) was added and the samples stored in the dark for further analysis. One week later, each vial was shaken and the ^{14}C activity measured in a Perkin Elmer scintillation counter at the University of Tromsø. PP was calculated as ^{14}C incorporation into the sample, measured in units of disintegrations per minute (DPM). The intensity of the signal is proportional to the beta particle emission from the ^{14}C incorporated into the cells. The total C-based production rates were then calculated as:

$$^{14}C - TOC = \frac{(DPM_L - DPM_D)/Vol \times DIC \times 1.05 \times \left(\frac{1}{\delta t}\right)}{\frac{DPM\ Sp\ Act}{Vol}} \tag{2}$$

where ^{14}C-TOC is production or mg C m^{-3} d^{-1}, DPM_L is disintegration per minute in the samples incubated in the light, DPM_D is disintegration per minute for the samples incubated in the dark, Vol refers to the sample volume (100 ml filtered for POC, 2 ml seawater for TOC and 0.1 ml for determination of Specific Activity) and δt the incubation time in days (d). DIC or dissolved inorganic carbon was measured in every sample (see section "Dissolved Inorganic Carbon"). The value of 1.05 is the discrimination factor between incorporation of ^{14}C and ^{12}C. The ^{14}C incorporation in the light bottle is thought to account both for biotic (i.e., photosynthesis and $CaCO_3$ incorporation) and for abiotic (i.e., adsorption) processes (Banse, 1993). Adsorption processes were accounted for by the Time Zero bottle. The incorporation of ^{14}C into $CaCO_3$ is corrected by conversion to CO_2 following 24-h acidification. Thus, ^{14}C incorporation rates are corrected by subtracting the ^{14}C incorporation in the dark bottle, accounting for biological ^{14}C uptake that can occur outside photosynthesis, and yielding carbon uptake by photosynthesis. The C-based rates were obtained in weight units, mg C m^{-3} d^{-1}, and divided by the molar mass of C (12 g/mol) to obtain final units of mmol C m^{-3} d^{-1}.

Dissolved Inorganic Carbon

Samples for dissolved inorganic carbon (DIC) were measured at the Norwegian Polar Institute (M. Chierici, PI). Seawater for DIC analysis was collected from the same CTD casts as the water for C-based estimates. Seawater was sampled and distributed into 100-mL borosilicate bottles, which were then preserved with 20 μL of $HgCl_2$ and stored in dark and cold until analysis. DIC was determined using gas extraction of the acidified sample followed by coulometric titration and photometric detection using a Versatile Instrument for the Determination of Titration carbonate (VINDTA 3C, Marianda, Germany) following the standard operating procedures from Dickson et al. (2007). Certified reference material provided by Dr. Andrew Dickson (Scripps Institution of Oceanography, University of California San Diego, La Jolla, CA, United States) was used to control accuracy of the analyses. The limit of detection is estimated at approximately 1.0 mg C m^{-3} d^{-1}.

Volumetric and Integrated Primary Production Rates

Volumetric ^{14}C and O_2-based rates were estimated for each depth at every station, yielding a total of 21 volumetric rates for each method (data available in **Supplementary Table S1**). Units of volumetric rates are mmol C or O_2 m^{-3} d^{-1}. Integrated ^{14}C and O_2-based rates, integrated to a depth equal to the 90% of accumulated ^{14}C-POC (which was significantly correlated with the euphotic depth; *p*-value < 0.05 and $R^2 = 0.85$) were calculated from the volumetric rates by the quadratic method, where the volumetric value of PP at two consecutive depths were averaged and multiplied by the depth differential. The resulting units for integrated rates are in mmol C or O_2 m^{-2} d^{-1}. Details of euphotic zone depth calculations are described in Randelhoff et al. (2018).

Data Analysis

Primary production rates for each method were $\log_{10}$-transformed to meet the assumption of normality. Normality of data was tested using the Shapiro-Wilk test, appropriate for small sample size (Shapiro and Wilk, 1965), with $p > 0.05$ for volumetric and integrated rates within each method for the full dataset (i.e., aggregating both cruises; **Supplementary Table S2**). Despite the non-normal nature of the untransformed data, we present PP rates as scatterplots in both untransformed and transformed (i.e., log) space in order to facilitate comparison with results from previous studies (see section "Discussion" below).

Comparison between the ^{14}C- and O_2-based methods were performed for samples collected at similar depths (maximum difference of ∼3 m). Seawater for ^{14}C and O_2-based analysis was sampled with time lags between casts ranging from 4 to 32 h for stations P, and no time lag for stations D (i.e., they were sampled from the same CTD cast, **Supplementary Figures S4, S5**). Similarity in sampled water masses, considering time lag between casts, was examined by comparing cast temperature-salinity characteristics (**Supplementary Figures S6, S7**), with water masses as defined in Randelhoff et al. (2018) and references therein. While sampling at the majority of P stations indeed occurred within the same water mass, samples collected in P1 originated from different water masses (**Supplementary Figure S6A**). This station was subsequently omitted from the comparison analysis, resulting in a total of 19 rates ensembles across 8 stations (i.e., $n = 19$).

Relative contributions of factors (method, cruise, depth and casts) to variability in PP rates were assessed using ANOVA. Examination of scatterplots of log-transformed PP rates (see section "Results" below) suggested wider variance in May than in August within the factor "cruise" (i.e., season, May and August). Levene's test within the factor season (using differences between observations and group median) rejected the null hypothesis of homoscedasticity between log-transformed PP rates in May and August [i.e., homogeneity of variances; $F(1,74) = 9.76$, $p < 0.01$]. By comparison, the assumption of homoscedasticity of log-transformed PP data held for methods, casts and depths (values not shown). To account for inhomogeneity of variances, relative contribution of factors to variability in PP rates was therefore assessed using a 4-way ANOVA (type II) using a heteroscedasticity-corrected coefficient covariance matrix, omitting interactions after insuring they were not significant (not shown). The analysis was run using the "car" package (Fox and Weisberg, 2011), implemented in R software version 1.0.44 (R Core Team, 2014). Given an assumption that neither time differences between cast nor depth were significant in explaining variability in the productivity data, we also ran a 2-way ANOVA analysis focusing on method and cruise (or season) alone, omitting casts and depth, using the same "car" package and in the same way as the 4-way ANOVA. This analysis was performed to independently confirm the results obtained by the 4-way ANOVA relative to differences between seasons.

Regression was applied to $\log_{10}$-transformed data, with a regression equation of the form:

$$\log_{10} PP_1 = a + b \log_{10} PP_2 \tag{3}$$

Where PP_1 and PP_2 correspond to rates from two different PP methods (e.g., GPP-DO and ^{14}C-TOC) and *a* and *b* are fitted intercept and slope parameters. Note that fitting this linear regression in log space is equivalent to fitting a power function in untransformed space:

$$PP_1 = 10^a PP_2^b \tag{4}$$

Multivariate normality of the input data was assessed with the MVN package in R (Korkmaz et al., 2014). Assuming symmetry in the relationship between PP rates derived by the methods under consideration, reduced major axis regression (RMA) was employed to examine relationships between productivity rates (Legendre and Legendre, 1998) Statistical analyses were completed using the lmodel2 R package (Legendre, 2014). Estimates from the pooled data presented in this study were then compared to previous regressions derived from a global PP synthesis aimed at predicting O rates from C rates (Regaudie-de-Gioux et al., 2014).

RESULTS

During May, PP rates based on GPP-^{18}O and GPP-DO averaged 21.0 mmol O_2 m^{-3} d^{-1} while the ^{14}C-TOC averaged 10.7 mmol C m^{-3} d^{-1} (combined ^{14}C uptake in particulate and dissolved carbon) (**Figure 2** and **Table 2**). In August, PP rates based on GPP-^{18}O and GPP-DO averaged 2.4 mmol O_2 m^{-3} d^{-1} while the ^{14}C-TOC was 3.5 mmol C m^{-3} d^{-1}. Seasonally, the O_2-based rates decreased ∼90% from May to August, while the ^{14}C-based rates decreased ∼60% (**Figure 2** and **Table 2**). Particularly in August, the ^{14}C-TOC decreased 68% while ^{14}C-POC decreased 48% from May. As a result, volumetric PP rates in May were approximately six times higher than in August while integrated rates were on average three times higher in May than in August, with variability among specific methods.

For all data combined, our results indicate that volumetric ^{14}C-TOC estimates were 40% of the oxygen-based GPP rates in the study region (calculated as the ratio of averages shown in **Table 2**). However, this relationship also varied seasonally.

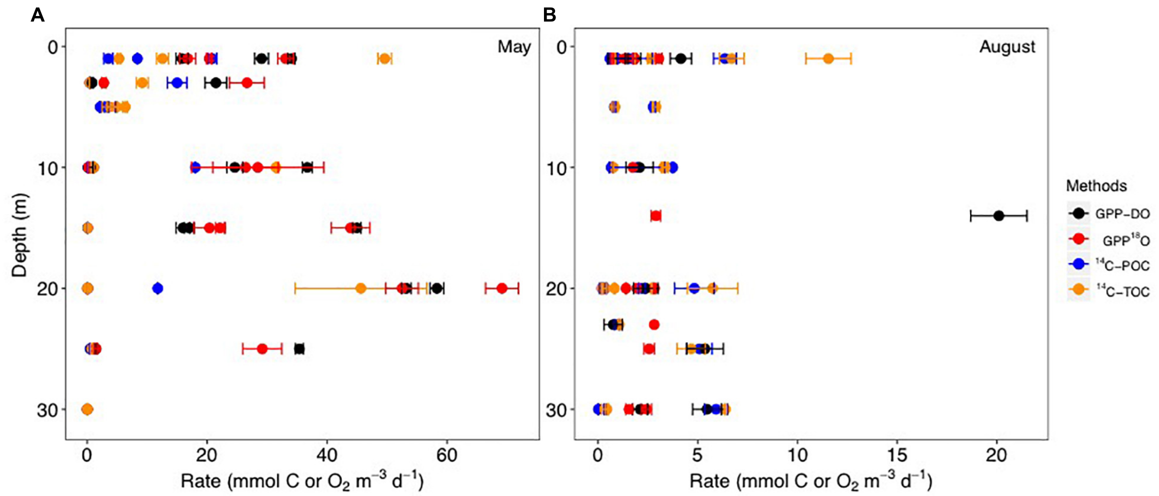

FIGURE 2 | Volumetric primary production (PP) rates compared in this study during the May **(A)** and August **(B)** 2014 cruises for the GPP-DO (in black), GPP-^{18}O (in red), ^{14}C-POC (in blue), ^{14}C-TOC methods (in orange) in mmol C, or O_2 m^{-3} d^{-1}. Locations shown in **Figure 1**. Symbols and error bars indicate average ± SE. Note change of rate scale.

In May, ^{14}C-TOC volumetric rates were on average 51% of the O_2-based rates (**Table 2**). In August, ^{14}C-TOC rates were on average 125% of the GPP-DO rates and 175% of the GPP-^{18}O volumetric estimates. This relationship was also evident when examining scatterplots of the untransformed data (**Figure 3**) and O:C ratios (**Figure 4**), with O:C ratios in the spring generally higher than 1.25:1 and in some cases higher than 3:1, yet below 1:1 in the summer (see section "Photosynthetic Quotient" discussion below). On average for each season, the variability in O:C was larger in May than in August.

Considering all factors in a 4-way ANOVA, differences between rates of PP were statistically significant for cruise (i.e., season; F = 4.25, $p < 0.05$; **Table 3** and **Supplementary Figure S8**). Considering only factors method and cruise in a 2-way ANOVA yielded a similar result, with differences between PP rates proving significant only for the latter, confirming results from 4-way ANOVA [$F(3,71) = 0.17$ and $F(1,71) = 5.49$, $p < 0.05$, respectively]. These results are consistent with those

TABLE 2 | Mean and standard error of the mean for volumetric and integrated rates of GPP-DO, GPP-^{18}O, ^{14}C-TOC, and ^{14}C-POC in units mmol C or O_2 m^{-3} d^{-1} for the volumetric rates and mmol C or O_2 m^{-2} d^{-1} for the integrated rates.

		GPP-DO	GPP-^{18}O	^{14}C-TOC	^{14}C-POC
Volumetric	May	20.5 ± 5.7	21.4 ± 6.3	10.7 ± 4.9	5.9 ± 2.2
	Aug	2.8 ± 0.6	2.0 ± 0.2	3.5 ± 0.8	3.2 ± 0.8
	Total	12.1 ± 3.6	12.2 ± 4.0	7.3 ± 2.7	4.6 ± 1.2
Integrated	May	288.9 ± 124.2	293.6 ± 121.9	146.3 ± 106.3	81.8 ± 56.8
	Aug	26.6 ± 14.2	47.3 ± 4.0	94.2 ± 25.8	81.5 ± 22.1
	Total	176.5 ± 85.1	188.1 ± 82.0	124.0 ± 58.6	81.7 ± 31.5

Values shown indicate rates separated by season (May, August) as well as the aggregate of all data (Total). ^{14}C-DOC production is calculated by subtracting ^{14}C-POC from ^{14}C-TOC (data in ***Supplementary Table S1****).*

presented in **Figures 3**, **4**, as well as **Table 2**, given the large variability within a particular method but larger seasonal differences in productivity rates. In summary, most of the variability in O:C ratios originates from the seasonal evolution of the phytoplankton community and to a lesser extent, the methods employed in measuring PP. However, examination of **Table 2**, where in some cases the distribution of the volumetric (and integrated) rates for different methods do not overlap, suggests that differences among methods cannot be discounted. Specifically, these observations, alongside difference in median O:C ratios presented in **Figure 4** and regressions analyses (see below), suggest that an interaction between Method x Season is likely, and may not have been detected in ANOVA as a result of limitations of both dataset and statistical method.

f) GPP-DO vs 14C-TOC."

Regression of log-transformed PP rates serves to further highlight differences in the relationship between O and C rate estimates in aggregate, but also as a function of season, as well as differences between this Arctic dataset and previous global syntheses. While rates within a particular method class (i.e., C or O) fell approximately along the 1:1 line in log-log space ($0.82 < r^2 < 0.85$, $p < 0.01$, **Figures 5A,B** and **Supplementary Table S3**), far more scatter was apparent when considering relationships across methods (**Figures 5C–F**), with O:C ratios amongst estimates for a particular sampling location sometimes exceeding a factor of 100 (identified as outliers in **Figure 4**). As observed in the untransformed data (**Figure 3**), higher variability was apparent during the spring bloom (May cruise) compared to summer (August cruise). While positive linear relationships between log O and log C rates were apparent, the relationships were sometimes weak (**Figures 5C–F** and **Supplementary Table S3**). Significant correlations were found for linear relationships between log-transformed oxygen and

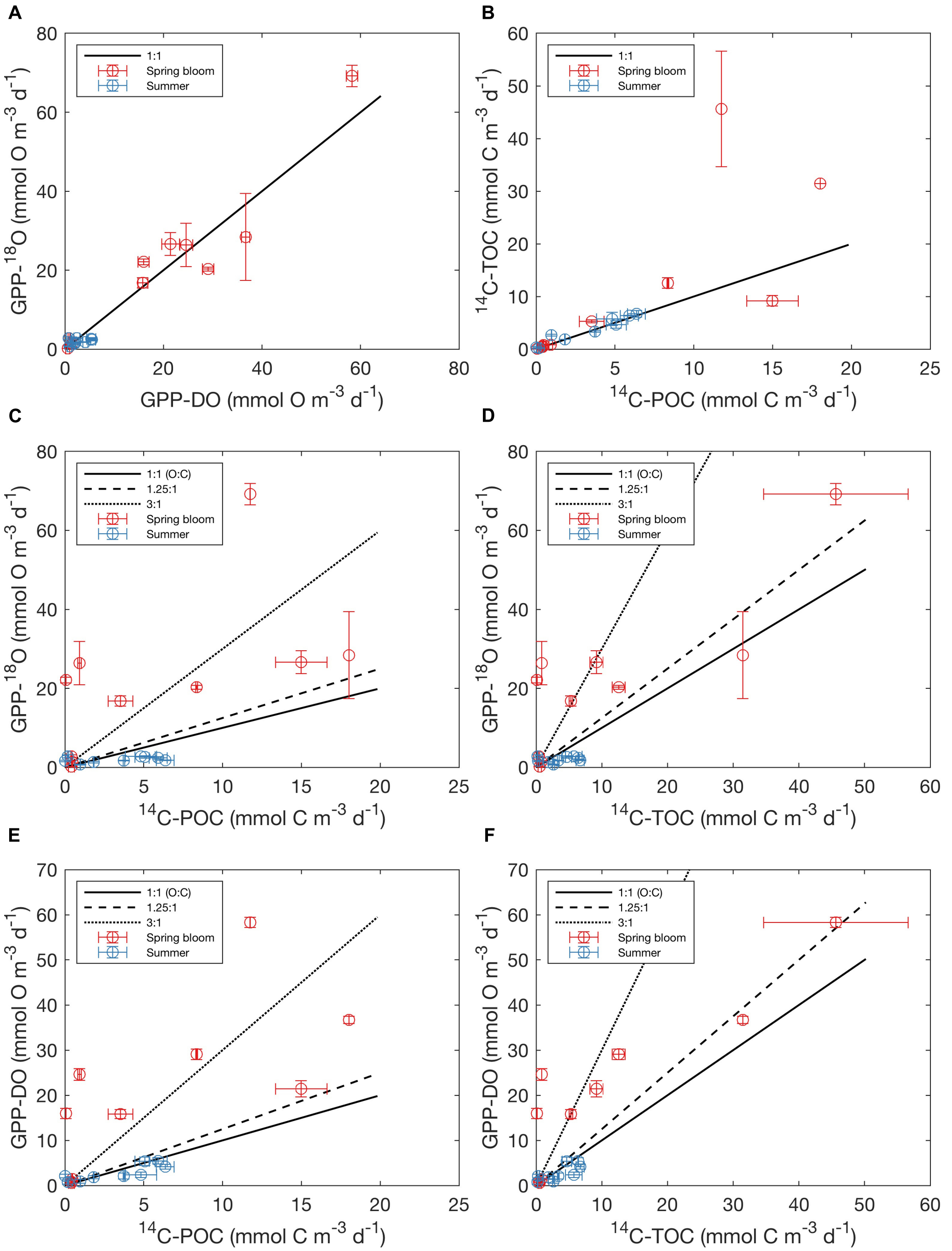

FIGURE 3 | Relationship amongst O- and C-based primary production rates reported in this study, showing mean values (circles) and standard errors on both *x* and *y* (error bars). **(A)** GPP-^{18}O vs. GPP-DO, **(B)** ^{14}C-TOC vs. ^{14}C-POC, **(C)** GPP-^{18}O vs. ^{14}C-POC, **(D)** GPP-^{18}O vs. ^{14}C-TOC, **(E)** GPP-DO vs. ^{14}C-POC and **(F)** GPP-DO vs. ^{14}C-TOC. Colors indicate sampling season (the spring bloom in May and summertime in August), with the solid black line indicating a 1:1 relationship, the dashed line 1.25:1, and the dotted line 3:1 (O:C). Note that the rates are untransformed and reported in native units (mmol O m^{-3} d^{-1} for oxygen and mmol C m^{-3} d^{-1} for carbon).

carbon rates (r = 0.92, p < 0.001 and r = 0.91, p < 0.001, respectively), as well as between C-based productivity rates and GPP-DO (r = 0.50, p < 0.05 and r = 0.58, p < 0.01 for ^{14}C-POC and ^{14}C-TOC, respectively). Confidence intervals on the slope in log-log regressions (i.e., the power slope "b" in Eqs 3 and 4) included 1 (one) in all cases (**Supplementary Table S3**). While this suggests an isometric relationship in untransformed (i.e., O:C) space, this result may also be a consequence of the tendency

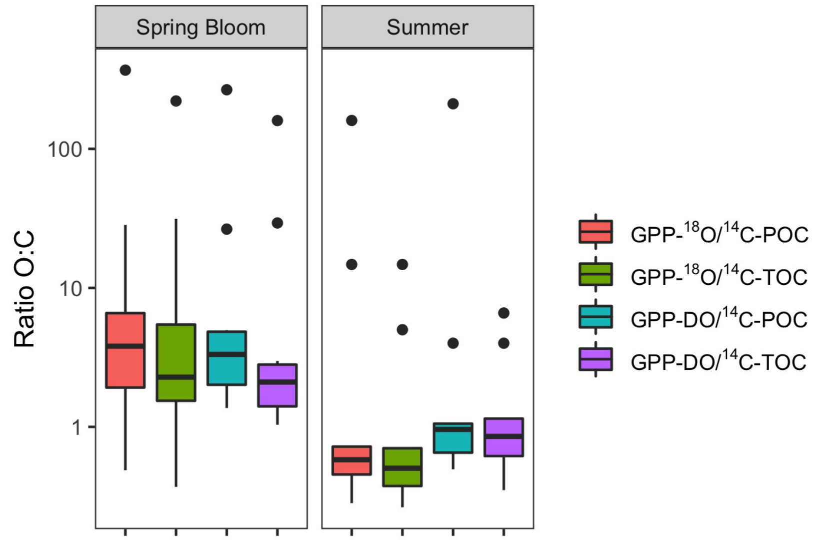

FIGURE 4 | Box plots of O:C ratios of PP estimates, by season (May – spring bloom n = 10; August – summer n = 9). Box plot showing the median (horizontal line), as well as the 25 and 75th percentiles, with vertical lines going to extremes, and outliers denoted by points.

of RMA slopes to tend to 1 for weak linear relationships (Legendre and Legendre, 1998). In several cases, fitted intercepts "a" were however significantly different from 0 (i.e., for ^{14}C-POC vs. ^{14}C-TOC, ^{14}C-POC vs. GPP-^{18}O, ^{14}C-POC vs. GPP-DO, and ^{14}C-TOC vs. GPP-DO; **Supplementary Table S3**). Linear relationships derived for log O and log C PP rates from a previous global data synthesis (Regaudie-de-Gioux et al., 2014), while reasonable within O and C methods (**Figures 5A,B**), also proved a poor fit to the data when comparing methods. In summary, the data demonstrate that there is a large source of variability in these relationships as a function of season, further confirmed when PP methods are compared by cruise (**Supplementary Figure S9**) and that a global conversion equation likely is a poor fit to specific regions in the ocean, including in this case the Arctic.

DISCUSSION

In the spring of 2014, the waters NW and N of Svalbard Archipelago were dominated by a bloom of large chain-forming diatoms and the colonial form of *Phaeocystis* sp. [M. Reigstad, pers. comm.]. Average integrated chlorophyll concentration was 236.7 ± 88.8 mg chlorophyll *a* m^{-2}. By August, toward the end of the growth season, phytoplankton abundance was low and small flagellates dominated the community. Integrated chlorophyll *a* had decreased to 57 ± 22.6 mg m^{-2}. The phytoplankton community was dominated by cryptomonads, coccolithophorids, dinoflagellates, and few' small diatoms. These two scenarios correspond to periods of nitrate-based new production in May, followed by a period of recycled, or ammonium-based, production in August (Randelhoff et al., 2018; Svensen et al., 2019). The C-based and O-based techniques all noted a sharp decrease in primary productivity estimates between May and August, representative of the change in phytoplankton abundance and composition (**Table 2**). The high C-based and O_2-based rates of PP in May corresponded to the boreal spring bloom, at the ice edge, where high rates of productivity are expected (Vaquer-Sunyer et al., 2013).

TABLE 3 | Results of the 4-way (type II) ANOVA testing for significance of treatment by method, cruise (or season), cast, and depth for log10-transformed.

Source	Df	F	Pr (>F)	Significance
Method	3	1.68	0.18	
Cruise	1	4.25	0.04	*
Cast	1	0.69	0.41	
Depth	1	1.01	0.32	
Residuals	69			

*Significance is indicated for *p < 0.05. Df is degrees of freedom, F is the F statistic, Pr (>F) is the significance probability associated with the statistic F and Sig denotes significance.*

Our results indicate that the average volumetric O-based PP, as measured by ^{18}O method (12.2 ± 4.0 mmol O_2 m^{-3} d^{-1}) is ~1.7 higher than the C-based estimates such as ^{14}C-TOC (7.3 ± 2.7 mmol C m^{-3} d^{-1}), which includes particulate and dissolved carbon uptake (**Table 2**). This difference is consistent with other measurements on open ocean phytoplankton, where GPP-^{18}O was ~1.5 higher than ^{14}C-POC (Juranek and Quay, 2005). Based on similar productivity methods as in this study, Regaudie-de-Gioux et al. (2014) showed that GPP-^{18}O > GPP-DO > ^{14}C-TOC > ^{14}C-POC. In our case, the average GPP-^{18}O ≈ GPP-DO > ^{14}C-TOC > ^{14}C-POC as previously reported by Grande et al. (1989b) for the North Pacific. It is only in May that our results agree with those of Regaudie-de-Gioux et al. (2014), with GPP-^{18}O > GPP-DO > ^{14}C-TOC > ^{14}C-POC (**Table 2**).

Seasonal dynamics of the pelagic ecosystem's metabolism could play a key role in the difference between C- and O-based

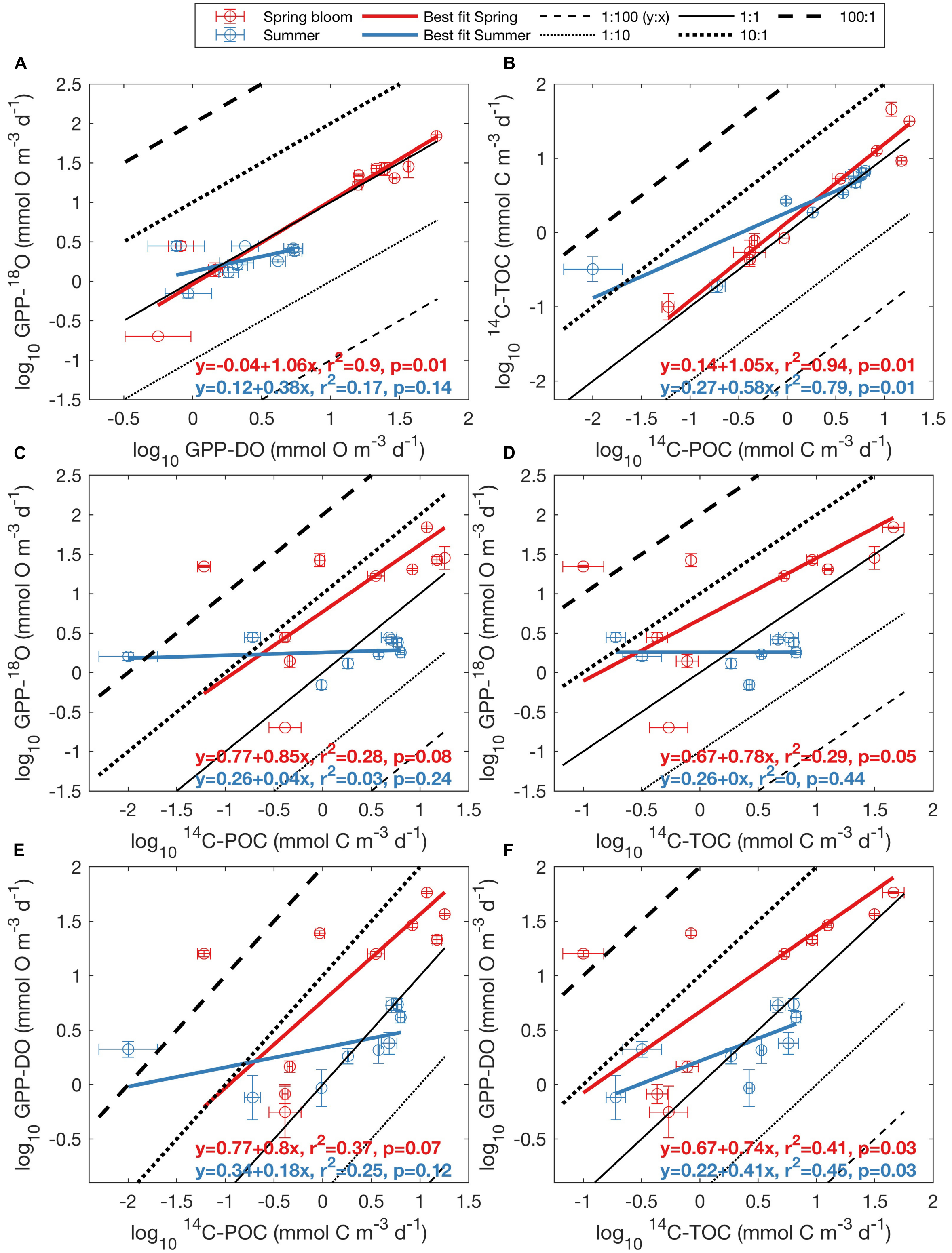

FIGURE 5 | Log-log relationship between oxygen- and carbon-based methods for May (red dots) and August (blue dots), presented as average ± standard error for each depth (**Figure 2**). **(A)** GPP-1^{18}O vs. GPP-DO, **(B)** ^{14}C-TOC vs. ^{14}C-POC, **(C)** GPP-^{18}O vs. ^{14}C-POC, **(D)** GPP-^{18}O vs. ^{14}C-TOC, **(E)** GPP-DO vs. ^{14}C-POC, and **(F)** GPP-DO vs. ^{14}C-TOC. All rates are volumetric in units of mmol O m^{-3} d^{-1} for oxygen and mmol C m^{-3} d^{-1} for carbon. Black lines represent ratios of y to x ranging from 1:100 to 100:1, with the solid line indicating a 1:1 relationship. The bold teal line represents the best linear fit to the aggregate dataset (i.e., including both seasons), while the orange line, if present, represents the best fit line calculated by Regaudie-de-Gioux et al. (2014), based on a global synthesis of PP observations.

rates of primary productivity. In spring, during the ice-edge phytoplankton bloom, ^{14}C-TOC rates equalled 52% and 50% of GPP-DO and GPP-^{18}O estimates, respectively (**Table 2**). A similar difference is observed in the integrated productivity estimates, where ^{14}C-TOC (146.3 ± 106.3 mmol C m^{-3} d^{-1}) were 50% of the average GPP estimates from ^{18}O method (293.6 ± 121.9 mmol O_2 m^{-3} d^{-1}; **Table 2**). In August, when overall rates were low, integrated ^{14}C-TOC was 125% and 175% of DO-GPP and GPP-^{18}O estimates, respectively (**Table 2**). Hence, in low productive waters with low abundance of large phytoplankton and when recycling processes dominate (Olli et al., 2019), the relationship between volumetric C- and O-estimates was reversed, ^{14}C-TOC > ^{14}C-POC > GPP-DO > GPP-^{18}O (**Table 2**). In this way, seasonality not only affected overall PP rates and the absolute amount of the difference between methods, but the sign as well. Possible sources of observed variability in productivity estimates by the various methods are discussed below.

Cellular Processes Affecting Primary Production Estimates

O_2-based GPP rates are higher than ^{14}C- based estimates as the latter excludes respiration (Bender et al., 1987). In this way, our results confirm that similar to lower latitude estimates, the C-based techniques in the Arctic better approximate net primary production (NPP) (Marra, 2002; Robinson et al., 2009; Regaudie-de-Gioux et al., 2014). As ^{14}C-TOC includes both particulate and dissolved C uptake, it is expected to be higher than ^{14}C-POC which only includes the ^{14}C retained in phytoplankton, concentrated on a filter after incubation (see section "Materials and Methods") (Juranek and Quay, 2005; Matrai et al., 2013). ^{14}C-POC is the most common productivity technique when using radioactive carbon (Steemann-Nielsen, 1952). However, the difference between ^{14}C-TOC and ^{14}C-POC can be substantial. ^{14}C-DOC, calculated as the difference between ^{14}C-TOC and ^{14}C-POC (**Table 2** and **Supplementary Table S1**), was higher in May than in August due to high PP rates in spring, accounting for 4.8 ± 3.6 mmol C m^{-3} d^{-1} or approximately 45% of the ^{14}C-TOC and 0.3 ± 0.2 mmol C m^{-3} d^{-1} or 9% of the ^{14}C-TOC in August, similar to rates previously observed in the Barents Sea (**Table 2**; Vernet et al., 1998) and productive areas of the Nansen Basin, Arctic Ocean (Gosselin et al., 1997).

For the North Atlantic, Robinson et al. (2009) highlighted that the difference between the techniques depended on the magnitude of basal (or dark) respiration. Hence, the significant difference between GPP-^{18}O and ^{14}C-POC rates found in this study (**Tables 2**, **3**) could be explained by losses resulting from respiration by autotrophs (Grande et al., 1989b). In May, the basal respiratory losses accounted for 2.52 ± 0.31 mmol O_2 or C m^{-3} d^{-1} (Table 1 in Mesa et al., 2017) or ∼10% of the GPP (**Table 2**), in agreement with the expectation that basal respiration rates in European Arctic communities are characteristically low (i.e., Vaquer-Sunyer et al., 2013). However, the 24-h photoperiod that helps support rapid growth and high rates of photosynthesis may impose higher daily respiratory losses than in temperate regions. Higher respiration rates in the light might be due to the contribution of autotrophic metabolic processes, such as photo-enhanced mitochondrial respiration, chlororespiration, photorespiration, and/or the Mehler reaction (Bender et al., 1999). For example, phytoplankton exposure to higher light irradiances in the shallow mixed layers created by sea ice melt, combined with low temperatures, might lead to the increase of the Mehler reaction, a defense mechanisms to overcome photoinhibition (Laws et al., 2000; Beer et al., 2014). Indeed, high respiration rates have been reported for the Beaufort Sea, in the summer, during periods of high-light exposure (Nguyen et al., 2012).

For the European Arctic, phytoplankton respiration rates during summer, characteristic of continuous daylight, are higher in the light than in the dark (Mesa et al., 2017). These authors found that community respiration rates evaluated in the light increased with increasing GPP-^{18}O rates, establishing a threshold of 10 mmol O_2 m^{-3} d^{-1} beyond which the light compared with the dark process prevail. Respiration in the light was on average 1.37 higher than in the dark and at maximum respiration rates, the light respiration was 17.56 higher. This non-linearity of respiration in relation to productivity rates is expected to underlie the non-linearity of the O:C relationship (**Figure 5**). For the area around Svalbard, the average respiration in the light is 5.2 ± 0.52 mmol O_2 m^{-3} d^{-1} (Table 1 in Mesa et al., 2017). Combining these light respiration rates with a GPP of 21.4 ± 6.3 mmol O_2 m^{-3} d^{-1} (**Table 2**) we can predict an O_2-based net production of ∼16.2 mmol O_2 m^{-3} d^{-1}, while the ^{14}C-TOC is 10.7 ± 4.9 mmol C m^{-3} d^{-1}, with a difference of ∼5.5 mmol O_2 or C m^{-3} d^{-1} after accounting for respiratory losses.

Remaining differences between O- and C-based measurements after correcting for respiration suggests other processes are at play in Arctic plankton communities. The ^{14}C method can underestimate C assimilated due to release $^{14}CO_2$ by photorespiration that results when O_2 binds ribulose-1,5-bisphosphate carboxylase/oxygenase (Rubisco) leading to the excretion of glycolate, though photorespiration is apparently low in many phytoplankton (Peterson, 1980; Laws et al., 2000). In the case where PP is estimated with ^{14}C-POC, it differed by 17.7 mmol C or O_2 m^{-3} d^{-1} from GPP-DO (**Table 2**). Processes that affect the release of ^{14}C-DOC will diminish the ^{14}C-POC estimate. "Sloppy" feeding and photorespiration might release ^{14}C-DOC as well (Laws et al., 2000). Microzooplankton grazers impact the estimation of ^{14}C-POC to the extent that grazed carbon is not only respired but also excreted (Laws et al., 2000). During our study period, average microzooplankton grazing rate was 0.23 d^{-1} (Lavrentyev et al., 2019). On the other hand, consumption by heterotrophic prokaryotes leads to a loss in ^{14}C-DOC, decreasing ^{14}C-TOC estimates (Steemann-Nielsen, 1952; Marra, 2002). Short incubation times (<4 h) are recommended to minimize this loss.

The GPP-^{18}O and triple oxygen isotope method are considered the most accurate measurements of gross photosynthesis available (Laws et al., 2000; Regaudie-de-Gioux et al., 2014) since GPP is best defined on the basis of oxygen evolution rather than carbon fixation (Falkowski and Raven, 1997). However,

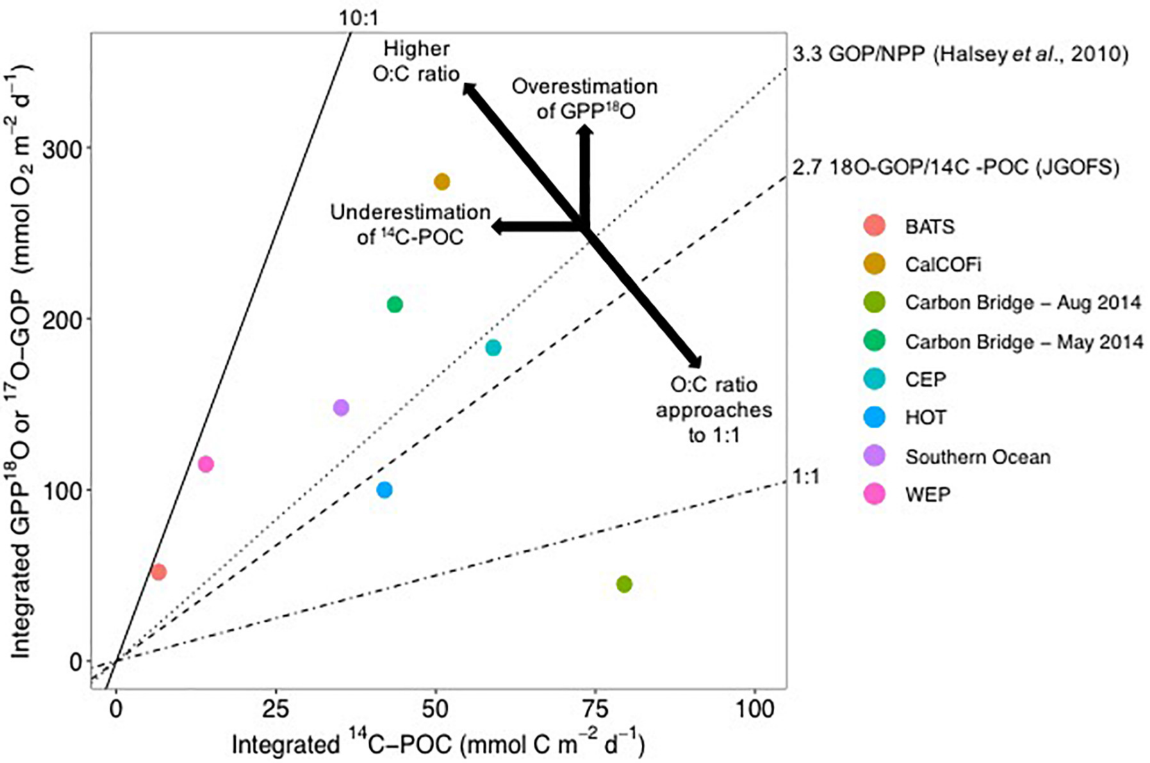

FIGURE 6 | Average O:C ratios from ^{14}C-POC and mixed-layer Gross oxygen production (GOP), equivalent to GPP-^{18}O in this study (Carbon Bridge – May and August 2014), estimated from incubations of ^{18}O and DO. All rates are integrated, with units of mmol m^{-2} d^{-1}. BATS correspond to the Bermuda Atlantic Time Series, CalCOFI to the California Cooperative Fisheries Investigations, Carbon Bridge 2014 (this study), CEP to the Central Equatorial Pacific, HOT to the Hawaii Ocean Time Series, and WEP to the Western Equatorial Pacific. ^{14}C-POC corresponds to ^{14}C-PP in the literature. For the Arctic, a median of 4.75 for May, with 25 and 75% percentiles of 2.6 and 7.6, respectively, and for August, a median of 0.56 with 25 and 75% percentiles of 0.5 and 0.8, respectively. Factors overestimating GPP-^{18}O include photo-enhanced mitochondrial respiration, chloro-respiration, photo-respiration, and Mehler reaction, which increase oxygen consumption not related to carbon uptake. ^{14}C-POC can be underestimated by grazing and DOC excretion as well as photo-respiration where ^{14}C is consumed within the incubation vessel (see text for more details). Graph redrawn from Juranek and Quay (2013).

this technique also has inherent errors where GPP-^{18}O can be overestimated, increasing the difference with DO and ^{14}C techniques. GPP-^{18}O rates are thought to overestimate GPP due to the decoupling of O_2-production and C-assimilation through the Mehler reaction and photorespiration (Grande et al., 1989b; Laws et al., 2000). In the Mehler reaction, a molecule of labeled O_2 is produced and a molecule of unlabelled O_2 is consumed, accounting for an estimated 10% increase in GPP-^{18}O rates (Falkowski and Raven, 1997; Laws et al., 2000). Photorespiration leads to the excretion of glycolate, also increasing GPP-^{18}O estimates by 10% (Falkowski and Raven, 1997; Beardall et al., 2009). Higher C than O_2-based rates during August may also be due to the presence of *Synechococcus* spp. (Paulsen et al., 2016). Indeed, Grande et al. (1989a) demonstrated elevated rates of respiration in light conditions due to photorespiration in *Synechococcus* spp. cultures from the Arabian Sea. Accounting for these sources of gains and losses, the combined effect of the Mehler reaction and photorespiration, increasing GPP-^{18}O by 20%, and the impact of grazing on ^{14}C-assimilation, contributing to differences of 15% after 24 h (Laws et al., 2000), could account for ∼35% of the 51% difference observed in our GPP-^{18}O and ^{14}C-TOC estimates in May (**Table 2**). The rest is accounted for by a minimum of ∼10% respiration losses.

Oxygen: Carbon Ratios in Arctic Phytoplankton

For the Arctic, median O:C ratios of 4.75 and 0.56 can be estimated for May and August, respectively, based on integrated GPP-^{18}O and ^{14}C-POC rates (calculated as the median of the ratios of the integrated C and O productivity estimates for each station, data in **Supplementary Table S1**). The 25 and 75% percentiles for May and August are 2.6 and 7.6, and 0.5 and 0.8, respectively. The May ratio in the Arctic is higher than the average 2.7 of a multidisciplinary study (JGOFS, Joint Global Ocean Flux Study in the Arabian Sea, North Atlantic, Equatorial Pacific, and Southern Ocean), an O:C ratio also based on ^{18}O-GOP, or gross oxygen production, and 24-h ^{14}C incubations of the particulate matter (labeled ^{14}C-PP in JGOFS studies) (**Figure 6**; Juranek and Quay, 2013). This ratio is within the range of other oceanic regions where the ratio of O-based to C-based productivity estimates range from 3.1 to

8.2 (**Figure 6**; data obtained from Table 1 in Juranek and Quay, 2013). In the Southern Ocean a similar ratio of 4.2 ± 2.5 was observed (**Figure 6**; Hamme et al., 2012). These measurements were obtained at the Polar Front, at ∼50°S, during late summer (March), a time of the year more comparable to the August Arctic cruise of 2014 albeit with a difference of 30° in latitude. In all these studies, ^{18}O-GOP is incubation-independent, based on ^{18}O:^{17}O ratio in surface waters and modeling of physical properties of the mixed layer and mixing processes (Bender et al., 1999, 2000; Laws et al., 2000) while ^{14}C estimates are from incubations, as in this study. Nevertheless, Marra (2002) and Marra and Barber (2004) found a robust relationship between these ^{18}O and ^{14}C measurements, where ^{14}C-POC estimations were ∼50% lower than ^{18}O-GOP, as found for the Arctic (**Table 2**). These field O:C ratios were confirmed by laboratory experiments where Halsey et al. (2010) found a consistent O:C of 3.3 for the green microalga *Dunaliella tertiolecta* (**Figure 6**).

The low O:C ratio observed in August (median 0.56) does not have corresponding values in the literature. O:C ratios < 1 could be characteristic of high latitudes, not found in the tropics where most of the available measurements originate (e.g., Juranek and Quay, 2013). Assuming C uptake or loss do not change substantially from spring to summer (e.g., Lavrentyev et al., 2019), what decreases O_2 production with respect to carbon uptake? Possible processes decreasing O_2 production have been mentioned above, such as higher photorespiration by the abundant *Synechococcus* and higher Mehler reaction under conditions of high light (Nguyen et al., 2012; Paulsen et al., 2016). It is possible that coccolithophorids and dinoflagellates, together with *Synechococcus*, have higher basal respiration than the bloom-forming large diatoms or the colonial *Phaeocystis* sp., either due to their smaller cell size or other physiological response. The drastic change in phytoplankton composition from spring to summer suggests that phytoplankton community structure could be an important factor determining the O:C ratio. However, additional experiments are needed to substantiate this hypothesis.

High inter- and intra-seasonal variability characterizes Arctic primary productivity rates (**Figures 2**, **3**). Part of the seasonal variability could originate from a variable proportion of light- and dark respiration, discussed above, as during productive periods of high phytoplankton biomass the proportion of light to dark respiration could be as high as ∼18 (Mesa et al., 2017). This large variability in respiration, potentially affecting the O:C ratio in polar phytoplankton, could explain in part the differences we observed between May and August. As the days shorten the respiration in the light decreases, decreasing O_2- based GPP estimates, such that in the Arctic the O:C ratio in August was <1 (**Figures 4**, **6**). These large discrepancies in O:C ratios between seasons and with the global dataset suggest that more experiments are needed before large-scale regional and seasonal patterns can be determined.

Conclusion

The O_2-based methods and the ^{14}C method provide understanding of different processes critical to describe ecosystem function such as *gross and NPP* and *respiration* at the plankton community level. The choice of either method should be guided by the specific question being addressed. In this way, the methods are complementary. For example, the combination of ^{14}C-TOC and ^{14}C-POC provides information of food supply (as DOC) for the microbial food web, not available from the oxygen methods. Furthermore, ^{14}C-POC represents the phytoplankton carbon production needed when quantifying the food available for higher trophic levels. The DO methods provide independent estimates of community respiration (CR) and net community production (NCP) (Carritt and Carpenter, 1966; Carpenter, 1995). The main difference among methods is the inclusion of respiration in GPP estimates, that in the Svalbard region seems to account for ∼20% of the primary production (Mesa et al., 2017).

In this study we emphasize that (1) the relationship between O and C in the Arctic are relatively weak, with seemingly variable relationship; (2) there is evidence for seasonality in this relationship, mediated in part by rates of productivity; and (3) that this relationship differs from previous ones derived from an aggregation of global datasets. In demonstrating seasonal variability in the O to C relationship, as well as variability between types of O and C methods, our study contributes significantly to the state of the art, while doing so raising a number of interesting questions. One of these is this notion of PQ which relates moles of O released and moles of C produced. This relationship appears variable temporally and perhaps spatially, while the state of the art has been to apply a single number, often with no regional parametrization let alone temporal component. Further exploration of O:C ratios in Arctic and global phytoplankton, and the impact of respiration on rate estimates, will provide valuable insight to better constrain primary production, and ultimately provide a means to track long-term change in the evolving Arctic environment.

DATA AVAILABILITY

All datasets generated for this study are included in the manuscript and/or the **Supplementary Files**.

AUTHOR CONTRIBUTIONS

CD, MS-M, MV, and MR designed the fieldwork. MS-M, MV, EM, and MC carried out the fieldwork and the laboratory analysis. MS-M, CD, MV, and MC analyzed the data. All authors contributed to the writing and editing of the manuscript.

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SUPPLEMENTARY MATERIAL

The Supplementary Material for this article can be found online at: https://www.frontiersin.org/articles/10.3389/fmars.2019.00468/full#supplementary-material

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