

Seasonal changes in quantity and composition of suspended particulate organic matter in lagoons of the Alaskan Beaufort Sea

Tara L. Connelly^{1,*}, James W. McClelland¹, Byron C. Crump²,
Colleen T. E. Kellogg^{2,3}, Kenneth H. Dunton¹

¹Marine Science Institute, University of Texas at Austin, 750 Channel View Dr., Port Aransas, TX 78373, USA

²College of Earth, Ocean and Atmospheric Sciences, Oregon State University, Corvallis, OR 97331, USA

³Present address: Department of Microbiology and Immunology, Life Sciences Institute, University of British Columbia, Vancouver, BC V6T 1Z3, Canada

ABSTRACT: Estuarine ecosystems in the Arctic are subject to extreme seasonal changes in the physico-chemical environment, but multi-season studies of these near-shore systems are relatively scarce. We measured bulk concentrations, fatty acids, pigments, and bulk $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ of suspended particulate organic matter (POM) collected from lagoons along the Alaskan Beaufort Sea coast during full-ice cover (April), ice break-up (June), and open water (August) and found that the quantity, composition and sources of suspended POM vary widely among seasons. We saw a shift across all lagoons from (1) low concentrations ($80 \mu\text{g C l}^{-1}$) and predominantly refractory material in April to (2) high concentrations ($>500 \mu\text{g C l}^{-1}$) with new inputs of organic matter from diatom production and river sources in June to (3) a consumer-, dinoflagellate- and/or green algae-influenced system in August. Relatively low $\delta^{13}\text{C}$ values in all seasons ($\leq -25\text{‰}$) suggest that terrestrial material was a major component to the POM pool throughout the year. Concurrently, fatty acid and pigment profiles show varying inputs of primary producers among seasons, with higher diatom relative to dinoflagellate contributions in June and vice versa in August. Elevated 22:6 ω 3/20:5 ω 3 (docosahexaenoic acid/eicosapentaenoic acid) ratios and polyunsaturated fatty acid proportions in the lagoons during August indicate that POM from lagoons provides animals with essential nutrients. These results demonstrate that the compositions and sources of organic matter available to consumers are a product of the dynamic seasonality of these ice-dominated, yet productive Arctic estuarine ecosystems.

KEY WORDS: Particulate organic matter · Fatty acids · Bulk stable isotopes · Pigments · Food webs · Nutritional quality · Biomarkers · Polar waters

—Resale or republication not permitted without written consent of the publisher—

INTRODUCTION

Coastal environments in the Arctic are characterized by extreme seasonality in day length, runoff, ice-coverage, solar radiation, and temperature. In turn, these variables influence stratification, salinity, inputs of terrestrial-sourced matter, nutrient concentrations, and biological production in coastal waters.

Shifts in the timing of sea ice melt and runoff from snowmelt due to climate forcing have the potential to produce significant changes in the timing, magnitude, and distribution of primary production in Arctic coastal waters (Carmack & Wassmann 2006). Improved knowledge of seasonal dynamics in these waters is needed to anticipate future changes. In aquatic ecosystems, conditions during winter are im-

portant regulators and predictors for food web structure and function later in the year (e.g. Schroeder et al. 2013, Saba et al. 2014). Thus, a better grasp of winter and spring conditions is needed to understand the physical, chemical, and biological controls on estuarine Arctic ecosystem function and to better predict future change.

The roles of terrestrial versus marine organic matter as resources supporting food webs within estuarine systems vary widely among seasons and geographic regions. Terrestrial inputs may exert a particularly strong influence in the Arctic, because the Arctic Ocean is relatively small compared to the land area that drains into it. Rivers entering the Arctic Ocean supply enormous quantities of organic matter (Dittmar & Kattner 2003, Holmes et al. 2012) and changes in the timing or composition of these inputs affects biological production and pan-Arctic carbon budgets. Over the last decade there have been increased efforts to understand the seasonality of terrestrial inputs of organic matter into the Arctic Ocean (e.g. Guo et al. 2012, Holmes et al. 2012), yet these studies are primarily focused on the largest river systems, whose watersheds are not wholly within the Arctic. In contrast, much less attention has been given to the cycling of organic matter occurring in coastal systems that are fed by smaller rivers. One exception is the recent work by Schreiner et al. (2013) looking at the composition of organic carbon in sediments of Simpson's Lagoon near the Colville River delta of the Alaskan Beaufort Sea.

Riverine input to the Beaufort Sea is dominated by the Mackenzie River, but numerous smaller rivers are also locally important (McClelland et al. 2014). Much of the Alaskan Beaufort Sea coast is characterized by barrier islands that frame numerous shallow lagoons, which are fed by many small rivers and streams. These coastal systems support abundant and diverse marine communities consisting of migratory birds, fish and mammals (Craig 1984, Brown et al. 2012). Likewise, the marine life found in these lagoons is an important source of subsistence and cultural identity for the indigenous human population (Pedersen & Linn 2005). Recent work in lagoons of the eastern Alaskan Beaufort Sea during summer indicates that terrestrial organic matter is a notable carbon subsidy for lagoon food webs (Dunton et al. 2012). However, little work has been done to quantify seasonal variations in terrestrial versus marine organic matter within these lagoons.

Our main objective was to investigate seasonal patterns in the quantity and composition of suspended particulate organic matter (POM; i.e. C and N con-

centrations and ratios, bulk $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$, fatty acids and pigments) in lagoon ecosystems along the eastern Alaskan Beaufort Sea during full ice cover (April), ice break-up (June), and open water (August). This work was part of a larger effort aimed at evaluating the importance of terrestrial organic matter to the seasonal dynamics of food webs along the northern Alaska coastline. We anticipated that seasonality of environment conditions would be accompanied by marked differences in the quantity and composition of POM within the lagoons.

MATERIALS AND METHODS

Sample collection

Several sites inside and outside barrier islands along the coastal Alaskan Beaufort Sea were sampled for suspended POM in August 2011, and April, June, and August 2012 and 2013 (Table 1). Four lagoons, Kaktovik (KA), Jago (JA), Angun (AN) and Nuvagapak (NU), and 1 site outside the barrier islands near Barter Island (BP) were sampled in all 3 seasons (Fig. 1). Two additional lagoons, Tapkaurak (TA) and Demarcation Bay (DE), and 3 sites outside the barrier islands, near the Hulahula River (HU), Bernard Spit (BE) and Demarcation Point (DP), were also sampled in August (Fig. 1). In August 2013, we were only able to sample at KA, JA, AN, BP and BE due to severe weather. The 4 lagoons sampled in all 3 seasons (KA, JA, AN and NU) represent the core of our study and are the only sites included in statistical analysis testing difference among seasons (see 'Statistical analysis' below). In August, samples were col-

Table 1. Number of sites sampled inside barrier islands (lagoons, bold) or outside barrier islands (italics) along the Alaskan Beaufort Sea coast during ice cover (April), ice break-up (June) and open water (August) in 2011, 2012 and 2013. See Fig. 1 for details

Month	Ice/water conditions	Year		
		2011	2012	2013
April	Full ice cover	—	4, 1^b	4, 1^b
June	Ice break-up	—	4, 1^b	4, 1^b
August	Open water	6, 3^a	6, 4^c	3, 1^d

^aAll sites, except Bernard Point (BP); results from 2011 are presented in Table S1 in the Supplement
^bThe 5 sites sampled in all 3 seasons: Kaktovik (KA), Jago (JA), Angun (AN), Nuvagapak (NU) and BP
^cAll sites
^dThe 5 sites sampled in all 3 seasons, except NU

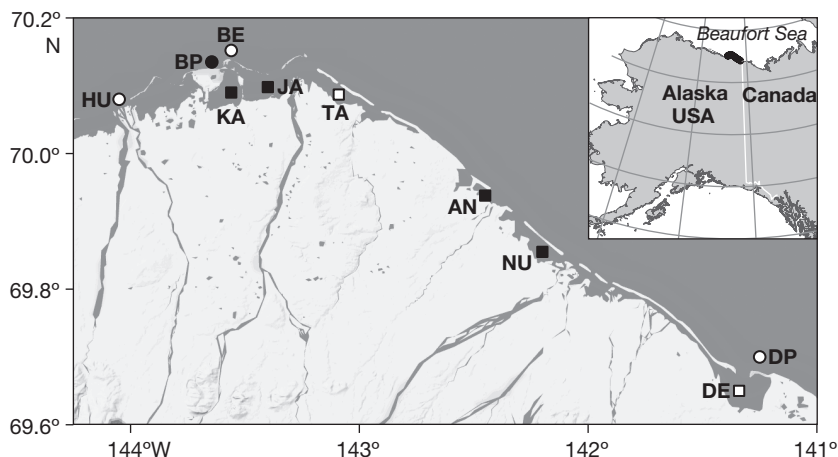


Fig. 1. Locations of sites sampled for suspended particulate organic matter during ice-cover (April), ice break-up (June) and open water (August). Filled points indicate sites sampled in all 3 seasons, whereas open points are those only sampled during open water. ■□ Sites within lagoons; ●○ sites outside the barrier islands. HU: Hulahula, BP: Bernard Point, BE: Bernard Spit, KA: Kaktovik, JA: Jago, TA: Tapkaurak, AN: Angun, NU: Nuvagapak, DE: Demarcation Bay, DP: Demarcation Point

lected from 2 to 3 stations within each site, while in June and April, generally, 1 or 2 stations were occupied. BP has only 1 station in all seasons. Most sites were <4 m deep, except BE and DP, where water depths were ~9 to 10 m.

Water samples were taken for particulate organic carbon and nitrogen (POC and PON) concentration, $\delta^{13}\text{C}$, $\delta^{15}\text{N}$, pigment and fatty acid analyses. Samples for fatty acid analysis were not taken in August 2011 and pigments other than chlorophyll *a* were only analyzed in August 2012, and April and June 2013. All other measurements were taken during all sampling efforts. Our seasonality analysis focuses on data from 2012 and 2013. However, POC and PON concentration and stable isotope values from August 2011 are provided in Table S1 in the Supplement at www.int-res.com/articles/suppl/m527p031_supp.pdf. Samples in April and June were collected from 2 m below the top of the ice or water surface with a peristaltic pump. A depth of 2 m below the top of the ice surface corresponds to ~0.5 m from the ice-water interface. August samples were collected from approximately 0.5 m by submerging carboys into the water. Additional samples were occasionally taken from deeper depths when higher chlorophyll *a* concentrations were present. Chlorophyll *a* was initially assessed with a YSI sonde, but data presented here are from analytical measurements done in the laboratory (see 'Pigments' below). The YSI sonde was also used to read temperature, salinity, and dissolved oxygen from discrete depths throughout the water column.

POC and PON concentrations and isotopes

Within hours of sample collection, samples for POC and PON concentration and isotope analyses were filtered in duplicate onto combusted 25 mm GF/F filters (except for August 2011, as described below) and immediately dried at ~60°C. One set of filters was used for PON analysis and the other for POC. Those for POC were triple acidified by wetting with sulfurous acid (6%) prior to analysis to remove any inorganic carbon. Samples were run on a Finnigan MAT Delta Plus isotope ratio mass spectrometer coupled to a Carlo Erba 1500 elemental analyzer at the Marine Science Institute of the University of Texas at Austin, USA. In August 2011 only, samples for POC and PON were filtered onto pre-weighed 47 mm GF/F filters. After weigh-

ing the entire filter to determine total suspended sediment, a filter wedge was weighed and analyzed at the Marine Biological Laboratories, USA. Isotope values are expressed in δ notation:

$$\delta^{13}\text{C} \text{ or } \delta^{15}\text{N} (\text{‰}) = [(R_{\text{sample}} / R_{\text{standard}}) - 1] \times 1000$$

where R is $^{13}\text{C}/^{12}\text{C}$ or $^{15}\text{N}/^{14}\text{N}$ and the standard reference material is Vienna Pee Dee Belemnite and atmospheric nitrogen N_2 , respectively. Molar ratios were used to calculate C/N ratios.

Fatty acids

Water for fatty acid analysis was poured through a 300 μm mesh and then filtered through combusted 47 mm GF/F filters. Filters were immediately frozen in Kaktovik, AK, USA. As soon as the samples were brought to Texas, USA (usually within 10 d of sampling), filters were put into glass centrifuge tubes (15 ml) and covered with chloroform (~2 ml). The headspace in the tube was purged with N_2 gas. Samples were stored frozen this way until lipid extraction, typically within 1 mo. Total lipids were extracted following a modified method of Folch et al. (1957) using a 2/1/0.5 chloroform/methanol/water ratio (Parrish 1999). Whole lipid extracts were derivatized for fatty acid methyl esters (FAME) using BF_3 . FAMES were run on a Shimadzu GC-FID with a Phenomenex ZB-WAX plus column (30 m, 0.53 mm i.d., 1.0 μm film thickness). Peaks were identified using external commercial standards or comparing retention

times from samples with known peaks. An internal standard 23:0 was used to quantify fatty acid peaks.

The diatom fatty acid biomarker used here is the sum of C₁₆ monounsaturates divided by C₁₆ saturates ($\Sigma 16:1/16:0$; Claustre et al. 1988). Bacterial fatty acid biomarkers were calculated by summing odd-carbon numbered and branched-chain fatty acids (OBFA; Sargent et al. 1987, Kaneda 1991), while the sum of 22:1 and 20:1 was used as a copepod marker (Falk-Petersen et al. 1987). Terrestrial plant fatty acid biomarkers were calculated as the sum of 18:3 ω 3 and 18:2 ω 6 (Budge & Parrish 1998). These fatty acids are dominant fatty acids of sedge and willow genera (Hietala et al. 1998, Ayaz & Olgun 2000) that are dominant in the North Slope of Alaska (Spetzman 1959). This marker has previously been used in the Beaufort Sea, where Connelly et al. (2012a) found a gradient of values that decreased towards the shelf break from the mouth of the Mackenzie River. The C₁₆ PUFA (polyunsaturated fatty acid) index, used as an indicator of nutrient status of diatoms, is the ratio of (16:2 ω 4 + 16:3 ω 4 + 16:4 ω 3 + 16:4 ω 1) to (16:0 + 16:1 ω 7 + 16:1 ω 5 + 16:2 ω 4 + 16:3 ω 4 + 16:4 ω 3 + 16:4 ω 1) (Parrish et al. 2005), reported here as a percent. Sources and characteristics of fatty acids and fatty acids

biomarker are summarized in Table 2. Additional source interpretations are possible, but our primary interpretations (Table 2) are in line with the review of Dalsgaard et al. (2003).

Pigments

Water for pigment analysis was filtered through 25 mm GF/F filters in duplicate and immediately frozen. Extracts from August 2012, and April and June 2013 were analyzed for multiple pigments using HPLC and for chlorophyll *a* by measuring absorbance at wavelengths 750, 664, 647, 630, and 600 nm on a Shimadzu UV-2401 PC spectrophotometer. Chlorophyll *a* concentrations were not significantly different between methods (data not shown), so only HPLC data is presented for these seasons. For all other seasons, only chlorophyll *a* was quantified using the spectrophotometer. All samples beginning in August 2012 were extracted by placing filters into centrifuge tubes with 3 ml 100 % acetone. The tubes containing the filters were sonicated in an ice bath for 15 min and then centrifuged for 5 min. After decanting the extract, the process was repeated and

Table 2. Character and source of fatty acids (FA) and fatty acid biomarkers, and regions where FA markers have been previously applied or described; most character and source attributions after Dalsgaard (2003)

FA and biomarkers	Character or source	Regions of application/description
Polyunsaturated FA (PUFA)	Labile; high nutritional quality	
Saturated FA (SFA)	Refractory; low nutritional quality	
ω -3 (PUFA)	Autotrophs; high nutritional quality	
ω -3/ ω -6	High nutritional quality	
$\Sigma 16:1/16:0$	Diatom	Mediterranean Sea (Claustre et al. 1988); Svalbard Fjord (Mayzaud et al. 2013)
DHA/EPA (22:6 ω 3/20:5 ω 3)	Dinoflagellate versus diatom Nutritional index	Newfoundland coast (Budge & Parrish 1998); Bering Sea (Wang et al. 2014)
C ₁₆ PUFA (e.g. 16:4 ω 1)	Diatom	North Sea (Kattner et al. 1983); Alaskan Arctic coast (Budge et al. 2008)
C ₁₆ PUFA index	Nutritional status of diatoms	Hokkaido waters (Shin et al. 2000); Newfoundland coast (Parrish et al. 2005)
C ₁₈ PUFA/C ₁₆ PUFA	Dinoflagellate versus diatom	North Sea (Kattner et al. 1983); Svalbard Fjord (Mayzaud et al. 2013)
18:3 ω 3 + 18:2 ω 6	Terrestrial plants, when >2.5% of total FA Green algae; macroalgae	Newfoundland coast (Budge & Parrish 1998); Beaufort Sea (Connelly et al. 2012a) California coast (Khotimchenko et al. 2002); Svalbard Fjord (Graeve et al. 2002)
$\Sigma 20:1 + \Sigma 22:1$	Copepod	Norwegian fjord (Falk-Petersen et al. 1987)
18:1 ω 9	Animal detritus; animal tissue	Barents and Greenland Seas (Graeve et al. 1997); freshwater (Napolitano 1999); Fram Strait and central Arctic Ocean (Auel et al. 2002)
Σ odd-carbon numbered + Σ branched-chain FA	Bacteria	North Water Polynya (Stevens et al. 2004); Canada Basin (Shah et al. 2013)

the two 3 ml extracts were combined. Previous to August 2012, chlorophyll *a* was extracted overnight in 5 ml 90% acetone and measured on the spectrophotometer as described above. All extractions were done in the dark. Concentrations for a given season did not significantly differ between years that used different extraction methods (data not shown).

Before running the HPLC samples, extracts were concentrated by drying them in the dark under a stream of N₂ in an ice bath and then reconstituted in 0.5 ml 100% acetone. All samples were run on a Shimadzu Prominence HPLC system within 24 h of extraction using a C₈ Agilent Eclipse XDB column (150 mm, 4.6 mm i.d., 3.5 μm film thickness). The mobile phase consisted of a binary gradient with (1) tetrabutyl ammonium acetate (28 nM) in methanol and (2) methanol. Pigments were monitored by visible UV light (UV_{vis}) absorbance (450 nm wavelength), and commercial standards (DHI, VWR, and Sigma-Aldrich) were used to identify and quantify peaks. Pigment standards included chlorophyll *a*, the pheopigments pheophytin *a*, pheophorbide *a* and pyropheophorbide *a*, and accessory pigments chlorophyll *b*, chlorophyll *c*, fucoxanthin, peridinin, prasinoxanthin, 19-but-fucoxanthin and 19-hex-fucoxanthin.

Statistical analysis

Principal component analysis (PCA) was used on stable isotope, C/N ratio, fatty acid, fatty acid marker and chlorophyll *a* data from all sites in all 3 seasons in 2012 and 2013 (6 sampling periods, $n = 71$). Other pigment data were not included because they are only available for 3 sampling periods. Prior to analysis, fatty acid and chlorophyll *a* data was transformed using the centered log-ratio (R package: 'compositions'), whereas stable isotope data was not transformed (Tolosana-Delgado et al. 2005). Correlations among variables were evaluated. Only those fatty acids that were >0.5% of total fatty acids in >60% of samples were included in the analysis. In addition, those fatty acids that were included in calculating the copepod, bacterial or terrestrial fatty acid markers (i.e. fatty acid markers composed solely of sums) were not included in the PCA as a separate factor. Seasonal attributions (color coding) in the PCA plot were done ad hoc.

Statistical analyses were done with the general linear model (GLM, e.g. ANOVA) to test for differences (1) among seasons and (2) between inside and outside the barrier islands ($\alpha = 0.05$). Only data from the 4 lagoons that were sampled in all 3 seasons (KA, JA,

AN, and NU) were used for analyses evaluating differences among seasons. Other sites sampled during August or outside the barrier islands were not used in the analysis of seasonal difference (i.e. HU, BP, BE, TA, DP, and DE). A pairwise *t*-test with a Holm-Bonferroni correction was used to determine which season had the highest or lowest values. Any mention of statistical significance among seasons in the following paragraphs refers to the analyses with only the 4 lagoons. For comparisons between inside and outside the barrier islands, we use data from all sites collected during August. April and June are not included in this analysis because we only have 1 site outside the barrier islands during these 2 seasons. Residuals were visually inspected to ensure they met assumptions of homoscedasticity, independence and normality. A Pearson product-moment correlation coefficient was calculated to assess the relationship between $\delta^{13}\text{C}$ and the terrestrial fatty acid marker. Errors are reported as standard deviation unless stated otherwise. All statistical analyses were done using R statistical software (v 3.0.0).

RESULTS

Conditions in April were characterized by full ice cover (ca. 1.5 to 1.8 m thick), salinities of 31 to 42, variable dissolved oxygen (26 to >100%) and low temperatures (ca. -2°C) inside and outside the lagoons. As sea ice began to break up, ice coverage in June became very dynamic from day to day with ice conditions varying among and within lagoons. The water that we sampled at 2 m in June inside and outside the lagoons was typically much fresher (<5) and warmer (1 to 4°C) than in April. However, the few samples taken deeper than 2 m in June with higher chlorophyll *a* levels were often from saltier waters (up to 42) with temperatures generally <0°C. By August, the water was completely open and surface temperatures in lagoons had increased to between 7 and 13°C, although marine sites remained colder (0 to 7°C). Overall, surface salinities in August were generally brackish (mean 23.2 ± 6.7). Dissolved oxygen in June and August was $\geq 85\%$.

Quantity of organic matter

POM concentrations were greatest after the spring freshet in June, both inside and outside the barrier islands (Fig. 2). Overall, the concentrations of POC and PON for a given site were 4 to 5× and 2 to 3×

greater, respectively, in June than in August and April. These seasonal differences in POM concentrations in the lagoons were statistically significant (Table 3). Mean POM concentrations were significantly higher inside the lagoons than outside the barrier islands in August 2012 and 2013 (Table 4), and generally higher inside the lagoons during other sampling periods, except in August 2011 and June 2012 (Fig. 2, Table S1 in the Supplement).

Overall, there was no significant difference in C/N ratios among seasons, but there were differences in the C/N ratios among seasons within a given year ($p < 0.05$, Table 3). In 2012, the C/N ratios decreased from April (8.9 ± 0.9) to June and August (~ 7.5), while in 2013, June (9.6 ± 1.0) had the highest C/N ratios and April (6.8 ± 1.6) the lowest for all lagoon sites (Fig. 2).

Seasonal changes in the concentration of total fatty acids were similar to those of bulk POM (Fig. 3A). Concentrations of fatty acids in April and June were significantly lower and higher, respectively, than in the other seasons (Table 3). Mean values ranged from $1.6 \mu\text{g l}^{-1}$ in April to $13.5 \mu\text{g l}^{-1}$ in June (Table 3). These fatty acid concentrations correspond to approximately 2 to 3% of POC by weight depending on season, but there was no statistical difference among the seasons (Table 3).

Composition of organic matter

Principal component analysis

A total of 27 variables were included in the final PCA analysis. The first 2 axes of the PCA accounted for 38 and 21% of the variability in POM composition. Principal component 1 (PC1) generally separated April (positive scores) from June and to a lesser extent August (negative scores), whereas PC2 separated June (negative scores) from August (positive scores) (Fig. 4). Factors important for positive scores on PC1 (April) include saturated fatty acids (i.e. 18:0, 16:0, and 20:0), bacterial fatty acid markers, C/N ratios, and 18:1 ω 9, while phytoplankton-derived compounds and markers (18:4 ω 3, 16:4 ω 3, the C₁₆ PUFA index and chl *a*) were important drivers of negative scores on PC1 (June and August). For PC2, 16-carbon PUFA and the diatom fatty acid marker were important for negative scores (June), and the DHA/EPA (docosahexaenoic acid/eicosapentaenoic acid; 22:6 ω 3/20:5 ω 3) ratio, DHA, the copepod fatty acid marker, and the C₁₈ PUFA/C₁₆ PUFA ratio were important for positive scores (August).

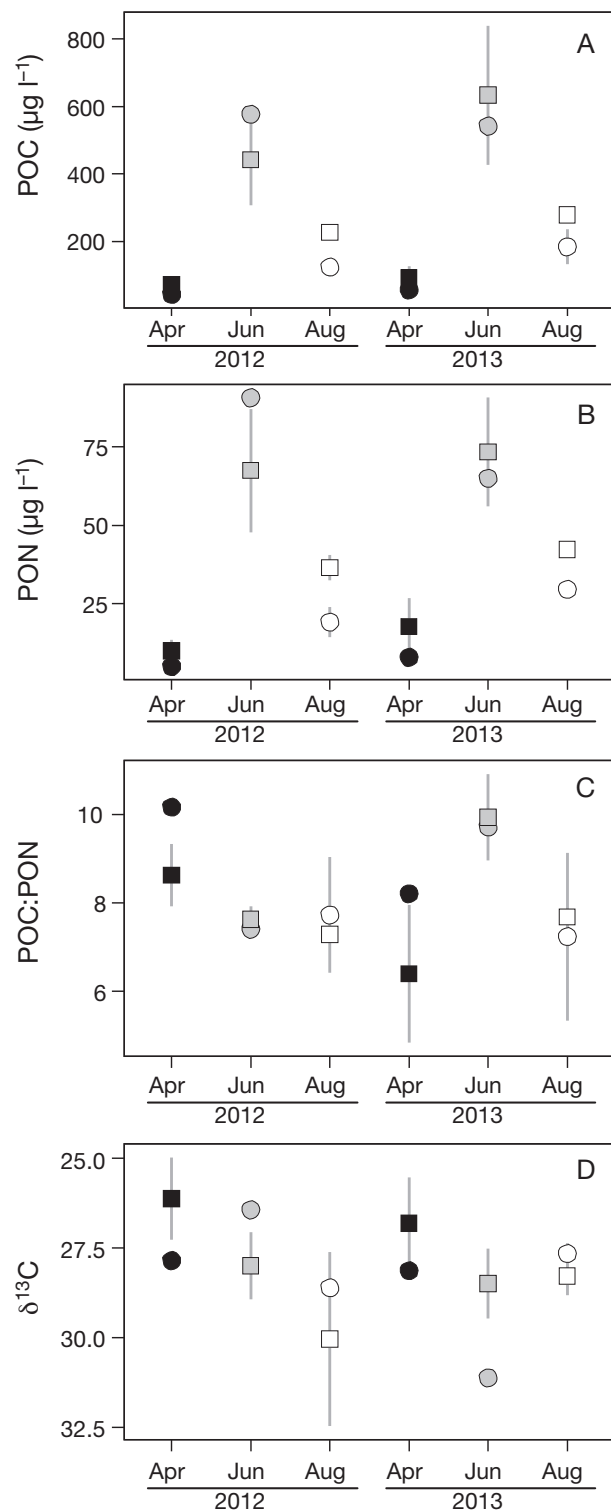


Fig. 2. Mean (\pm SD) concentrations of (A) particulate organic carbon (POC) and (B) particulate organic nitrogen (PON), (C) POC/PON ratio, and (D) $\delta^{13}\text{C}$ of POC in suspended matter collected within lagoons (■) and outside the barrier islands (●) along the eastern Alaskan Beaufort Sea coast. $n = 3$ to 6, except for sites outside the barrier islands in April and June, where $n = 1$

Table 3. Temperature, salinity, and the quantity and composition (i.e. C/N, fatty acid [FA] composition and markers) of suspended particulate matter collected during ice cover (April), ice break-up (June) and open water (August) from 4 lagoons (Kaktovik, Jago, Angun, and Nuvagapak) of the Alaskan Beaufort Sea coast. Samples were collected from ≤ 2 m in April, June and August 2012 and 2013. Diatom, Terrestrial, Bacteria and Copepod are FA markers. DO: dissolved oxygen; POC and PON: particulate organic carbon and particulate organic nitrogen; DHA: 22:6 ω 3; EPA: 20:5 ω 3; SFA: saturated FA; MUFA: monounsaturated FA; PUFA: polyunsaturated FA. Only values that were significantly higher (bold) or lower (underlined) than values from both of the other 2 seasons are identified, based on a pairwise comparison with an adjusted p-value. Standard deviations of the mean are in parentheses. *Significant difference among seasons based on ANOVA. #Variation among seasons differs between years (i.e. there was an interaction between season and year)

	April (n = 8) ^a	June (n = 8) ^a	August (n = 7) ^a
Temperature (°C) ^{*#}	<u>-2.1</u> (0.2)	2.5 (1.2)	11.1 (2.0)
Salinity [*]	36.4 (4.3)	<u>2.4</u> (1.3)	18.6 (7.0)
DO (%)	93.2 (17.2)	100.4 (8.1)	103.4 (5.5)
POC ($\mu\text{g l}^{-1}$) [*]	<u>82.3</u> (29.1)	537 (191)	250 (31.2)
PON ($\mu\text{g l}^{-1}$) [*]	<u>13.8</u> (7.6)	70.4 (17.4)	39.6 (3.8)
C/N [#]	7.5 (1.6)	8.8 (1.4)	7.4 (0.3)
FA ($\mu\text{g l}^{-1}$) ^{* #}	<u>1.6</u> (0.8)	13.5 (4.9)	6.1 (3.2)
FA (% POC)	2.1 (0.0)	2.9 (0.2)	2.4 (0.1)
$\delta^{13}\text{C}$ (‰) [*]	<u>-26.5</u> (1.2)	-28.2 (0.9)	-28.7 (0.9)
$\delta^{15}\text{N}$ (‰)	5.2 (2.1)	4.0 (1.0)	6.1 (1.7)
chl a ($\mu\text{g l}^{-1}$) [*]	0.04 (0.04)	2.1 (2.9)	0.5 (0.4)
ΣSFA (%) ^{*#}	65.3 (7.1)	36.4 (7.1)	40.3 (3.2)
ΣMUFA (%) [*]	23.3 (4.1)	40 (4.8)	25.8 (1.9)
ΣPUFA (%) [*]	<u>10.1</u> (3.7)	23.5 (9.0)	33.5 (3.6)
$\Sigma\omega$ -3 (%) [*]	<u>5.5</u> (3.1)	16.2 (7.7)	26.1 (4.4)
$\Sigma\omega$ -6 (%)	3.9 (0.9)	4.4 (1.3)	5.3 (0.9)
ω -3/ ω -6 [*]	<u>1.4</u> (0.6)	3.6 (1.4)	5.0 (0.9)
EPA (%) [*]	<u>2.7</u> (1.9)	4.9 (1.7)	6.2 (1.5)
DHA (%) [*]	1.1 (0.8)	2.2 (1.1)	7.1 (1.9)
DHA/EPA [*]	0.4 (0.1)	0.4 (0.2)	1.1 (0.1)
Diatom ^{*#}	<u>0.3</u> (0.1)	1.4 (0.3)	0.6 (0.2)
Terrestrial (%) [*]	<u>3.4</u> (0.9)	6.9 (3.9)	8.6 (1.3)
Bacteria (%) [#]	5.8 (1.4)	4.9 (2.2)	6.3 (1.3)
Copepod (%) [*]	2.1 (0.7)	2.7 (1.0)	4.4 (0.9)
18:1 ω 9 (%) ^{*#}	9.5 (1.8)	8.7 (2.2)	<u>6.2</u> (1.0)
C ₁₆ PUFA index [*]	<u>4.3</u> (1.1)	9.7 (4.0)	12.6 (3.7)
ΣC_{16} [*]	37.5 (2.5)	47.7 (5.5)	<u>32.6</u> (3.3)
ΣC_{18} ^{*#}	42.7 (4.9)	27.6 (4.9)	31.5 (2.2)
ΣC_{16} PUFA (%) [*]	<u>1.5</u> (0.3)	4.6 (1.7)	4.1 (1.6)
ΣC_{18} PUFA (%) [*]	<u>4.6</u> (1.3)	11.2 (5.8)	14.8 (1.8)
C ₁₈ PUFA/C ₁₆ PUFA	3.1 (1.1)	2.6 (1.1)	4.0 (1.2)

^an = 4 for each season within a single year, except August 2013 where n = 3

Composition of fatty acids

Saturated fatty acids were significantly different among seasons, accounting for >60% of fatty acids in April and <50% of fatty acids in June and August (Table 3). In contrast, monounsaturated fatty acids

Table 4. Temperature, salinity, and the quantity and composition of suspended particulate organic matter collected from sites inside and outside barrier islands along the coast of the Alaskan Beaufort Sea in August 2012 and 2013. POC and PON: particulate organic carbon and particulate organic nitrogen; DHA: 22:6 ω 3; EPA: 20:5 ω 3; SFA: saturated fatty acids (FA); MUFA: monounsaturated FA; PUFA: polyunsaturated FA; Terrestrial is a FA marker (18:3 ω 3 + 18:2 ω 6). Standard deviations of the mean are in parentheses. *Significant difference between sites inside and outside the barrier islands based on ANOVA

	Inside barrier islands (n = 9)	Outside barrier islands (n = 6)
Temperature (°C) [*]	10.9 (1.7)	5.9 (3.4)
Salinity	17.7 (6.3)	24.0 (4.5)
POC ($\mu\text{g l}^{-1}$) [*]	243.8 (32.5)	143.8 (44.1)
PON ($\mu\text{g l}^{-1}$) [*]	38.4 (4.4)	22.5 (6.6)
C/N	7.4 (0.3)	7.6 (1.3)
FA ($\mu\text{g l}^{-1}$)	5.5 (3.0)	2.8 (2.0)
$\delta^{13}\text{C}$ (‰)	-29.5 (0.9)	-28.3 (0.6)
Chl a ($\mu\text{g l}^{-1}$) [*]	0.5 (0.4)	0.1 (0.1)
ΣSFA (%)	40.7 (2.9)	47.5 (10.1)
ΣMUFA (%) [*]	25.7 (1.8)	29.5 (2.8)
ΣPUFA (%) [*]	33.3 (3.3)	22.6 (7.8)
$\Sigma\omega$ -3 (%) [*]	26.4 (3.9)	16.5 (8.0)
$\Sigma\omega$ -6 (%)	5.0 (1.0)	5.0 (0.8)
ω -3/ ω -6 [*]	5.4 (1.1)	3.4 (1.9)
EPA (%)	6.0 (1.5)	4.8 (3.0)
DHA (%) [*]	7.0 (1.9)	3.2 (3.2)
DHA/EPA [*]	1.2 (0.1)	0.6 (0.3)
Terrestrial (%) [*]	8.6 (1.1)	6.8 (1.6)
18:1 ω 9 (%) [*]	6.0 (1.0)	8.8 (1.5)
C ₁₆ PUFA index [*]	12.5 (3.4)	7.1 (1.8)

were highest in June (Table 3, Fig. 3B), and PUFA was significantly highest in August (Table 3). Consistent with April having the lowest proportions of total PUFA, C₁₆ and C₁₈ PUFA and the C₁₆ PUFA index were also significantly lower in April than in the other 2 seasons (Table 3). (See Table S2 in the Supplement at www.int-res.com/articles/suppl/m527p031_supp.pdf for greater detail of fatty acid profiles.)

Fatty acid markers and $\delta^{13}\text{C}$

Results for fatty acid markers were consistent with the source designations listed in Table 2, although other interpretations could be possible because individual fatty acids can have multiple sources. The diatom fatty acid marker was highest in June and lowest in April (Fig. 5A, Table 3). In contrast, DHA/EPA ratios and the copepod fatty acid marker were highest in August and similar in April and June (Figs. 3D & 5C). These differences were statistically significant for the 4 lagoons sampled in all seasons (Table 3). Further, in August, the DHA/EPA ratios in

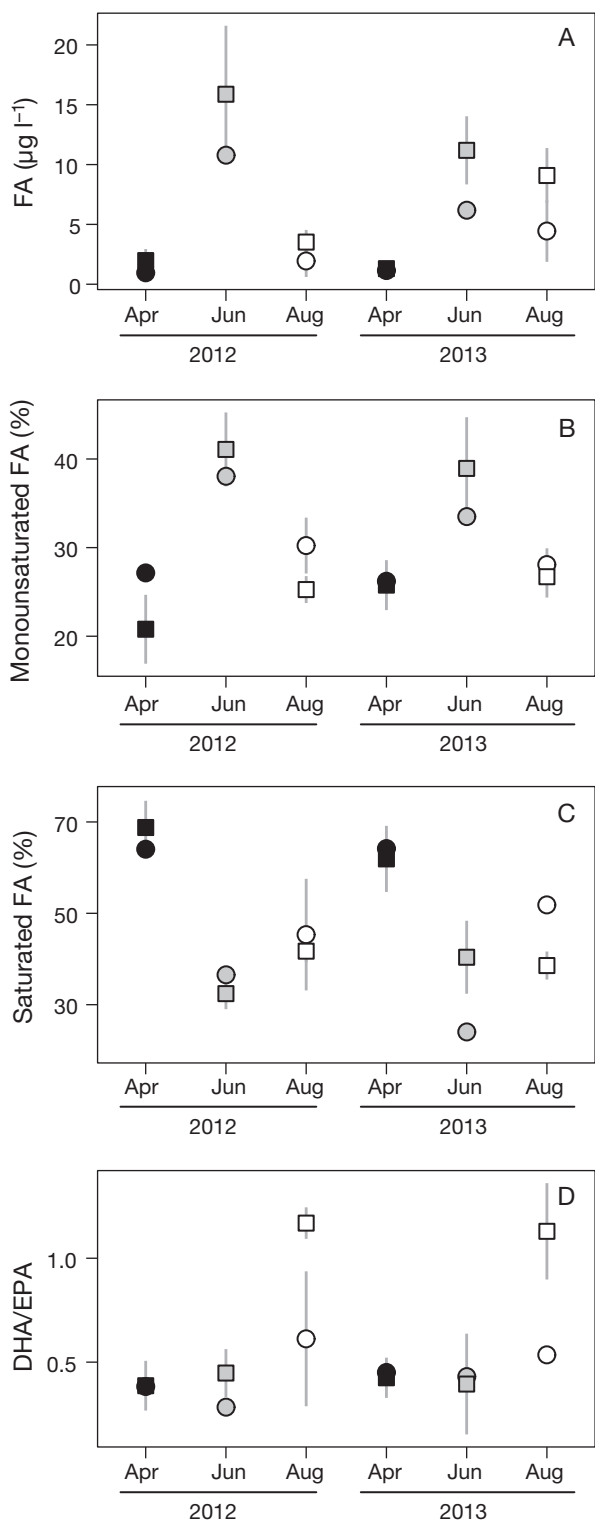


Fig. 3. Mean (\pm SD) (A) concentration of fatty acids (FA), proportions of (B) monounsaturated and (C) saturated FA, and (D) DHA/EPA ratios (22:6 ω 3/20:5 ω 3) in suspended particulate matter collected from sites within lagoons (■) and outside the barrier islands (●). $n = 3$ to 6, except for sites outside the barrier islands in April and June where $n = 1$

lagoons were higher than the ratios found outside the barrier islands (mean 0.6 ± 0.3 , Fig. 3D, Table 4). The C_{18} PUFA/ C_{16} PUFA ratio was also higher in August, but this difference was not significant for the 4 lagoons based on the pairwise t -test (Table 3). The bacterial fatty acid marker was generally between 3 and 7% of total fatty acids and varied among seasons depending on the year. Specifically, in 2012, this marker was highest in August and lowest in June, but in 2013, the marker was higher in April and June than it was in August (Fig. 5). Values for $\delta^{13}C$ were $< -25\text{‰}$ in all seasons (Fig. 2, Table 3) except in August 2011 (Table S1 in the Supplement) and were significantly correlated with the terrestrial fatty acid marker ($r = -0.54$, $n = 69$, $p < 0.001$), which was lowest in April (Table 3). It was expected that this terrestrial marker would be low in April, regardless of the relative contribution of terrestrial organic matter, because total PUFA proportions were very low in April ($\sim 10\%$ or $0.2 \mu\text{g l}^{-1}$) and this marker is the sum of 2 PUFA (18:3 ω 3 + 18:2 ω 6). However, normalizing for PUFA concentration, these 2 fatty acids contributed 32% of PUFA in April, compared to 26% and 28% found in June and August, respectively.

Pigments

The concentrations of all pigments were very low in April (Fig. 6A–C). Total phaeopigments (pheophytin a + pheophorbide a + pyropheophorbide a) contributed $>50\%$ of the detected pigments at lagoon sites (Fig. 6D). These phaeopigments also comprised $\sim 50\%$ of identified pigments in August, but the concentrations in lagoons in August were higher at $\sim 1.0 \mu\text{g l}^{-1}$ (compared with $\sim 0.06 \mu\text{g l}^{-1}$ for April, Fig. 6A,D). In contrast, chlorophyll a represented $\sim 50\%$ of identified pigments in June, whereas it only contributed $\sim 25\%$ in April and August (Fig. 6E). Accordingly, the chlorophyll a /phaeopigment ratio was highest in June (mean 2.6 ± 1.1), when all lagoons had ratios of ≥ 1 (Fig. 6F). Concentrations of fucoxanthin were also highest in June, especially at the site outside the barrier islands (Fig. 6B). Note, however, that this data point is based on duplicate samples from 1 sampling trip to the same location. In addition to phaeopigments, there was also an increase in the concentration of chlorophyll b in August. Proportions and concentrations for chlorophyll c , peridinin, prasinoxanthin, 19-but-fucoxanthin and 19-hex-fucoxanthin were on average $< 2\%$ of total pigments and $\leq 0.1 \mu\text{g l}^{-1}$ across all seasons.

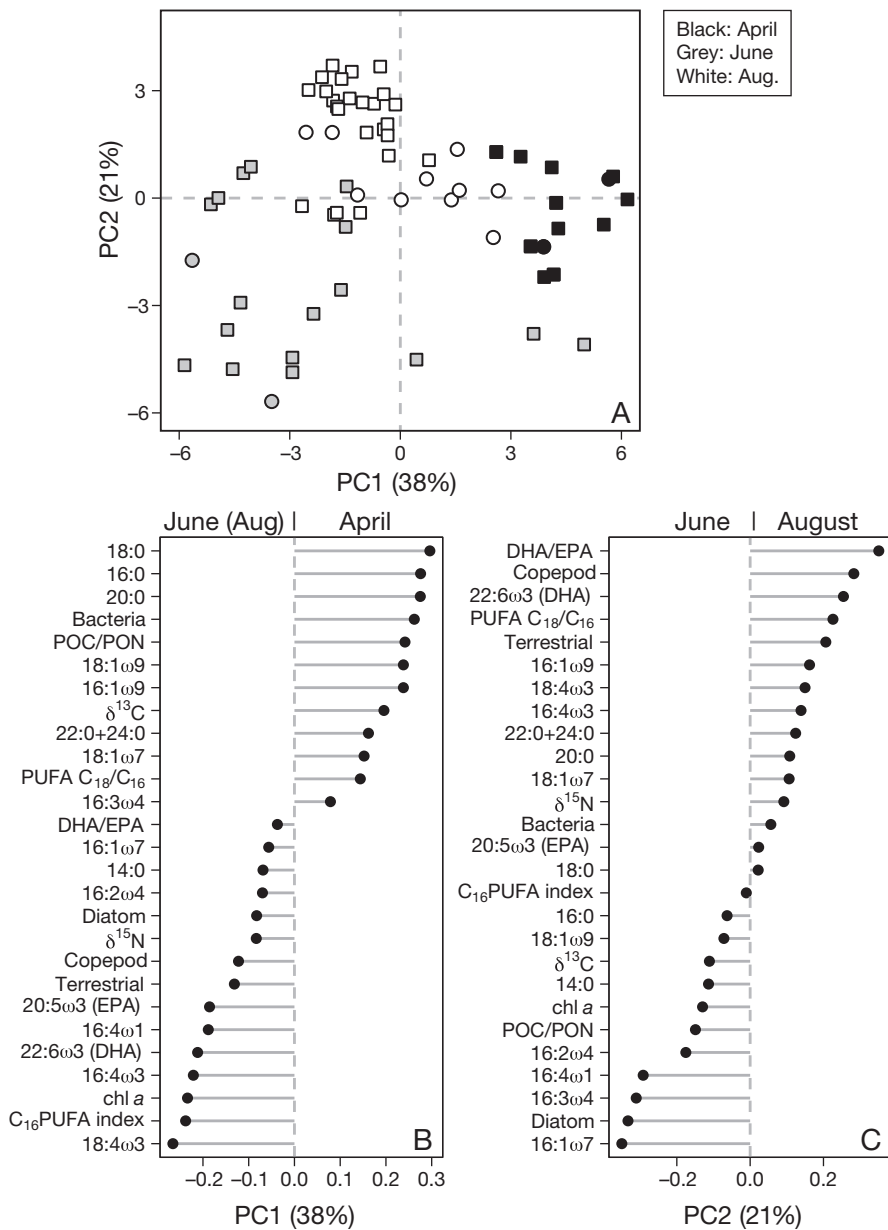


Fig. 4. (A) Scores for the first 2 principal components (PC1 and PC2) from analysis of the composition of suspended particulate matter in samples collected within lagoons (■) and outside the barrier islands (●), and loadings of variables on (B) PC1 and (C) PC2. See Table 3 for abbreviations

DISCUSSION

April

POM in April was characterized by (1) low bulk and fatty acid concentrations, (2) high proportions of saturated fatty acids, (3) low proportions of poly- and mono-unsaturated fatty acids, (4) low levels of photosynthetic pigments, and (5) generally higher proportions of pigment degradation products. These results

indicate that the POM pool after winter was refractory and highly processed, having little contemporary input from photosynthesis. These April results are in stark contrast to those taken approximately 8 wk later, in June, when there was clear evidence of organic matter inputs from algae (see next section).

For our study area, complete darkness occurs for about 2 mo from late November to January. By mid-March there is >12 h daylight, but snow-covered sea ice continues to obstruct light penetration even when the sun does return (Nicolaus et al. 2013). In the coastal Alaskan Arctic, first-year sea ice is still growing in April, thickening until May or June (Nicolaus et al. 2013). The lack of daylight in winter, extensive sea ice coverage in early spring, and persistent sub-zero temperatures combine to limit photosynthesis and phytoplankton cell abundance (Harrison et al. 1982) throughout this time period, thus establishing an environment with low inputs of fresh phytoplankton production (Horner & Schrader 1982). River inputs to the Alaskan Beaufort Sea are also negligible during the November to April timeframe (McClelland et al. 2014). Our results are consistent with those of Horner & Schrader (1982), who found that both primary production and chlorophyll *a* levels in water collected just below the ice in Stefansson Sound were very low throughout March and April, and did not increase until May and June. Likewise, in deeper coastal water (~230 m, 20 km offshore) of the Canadian Beaufort Sea, surface chlorophyll *a* values have been shown to remain low (<0.05 $\mu\text{g l}^{-1}$) throughout winter and

only begin increasing slightly in April (Forest et al. 2008). Further, the refractory nature of POM in April with low levels of photosynthetic pigments and PUFA indicate that contributions from ice-algae or benthic algae into the water column were insignificant.

Heterotrophic processes most likely dominated the lagoons during April. Despite low temperatures and negligible inputs from primary production in winter and early spring, Arctic waters contain viable and metabolically active heterotrophs throughout the

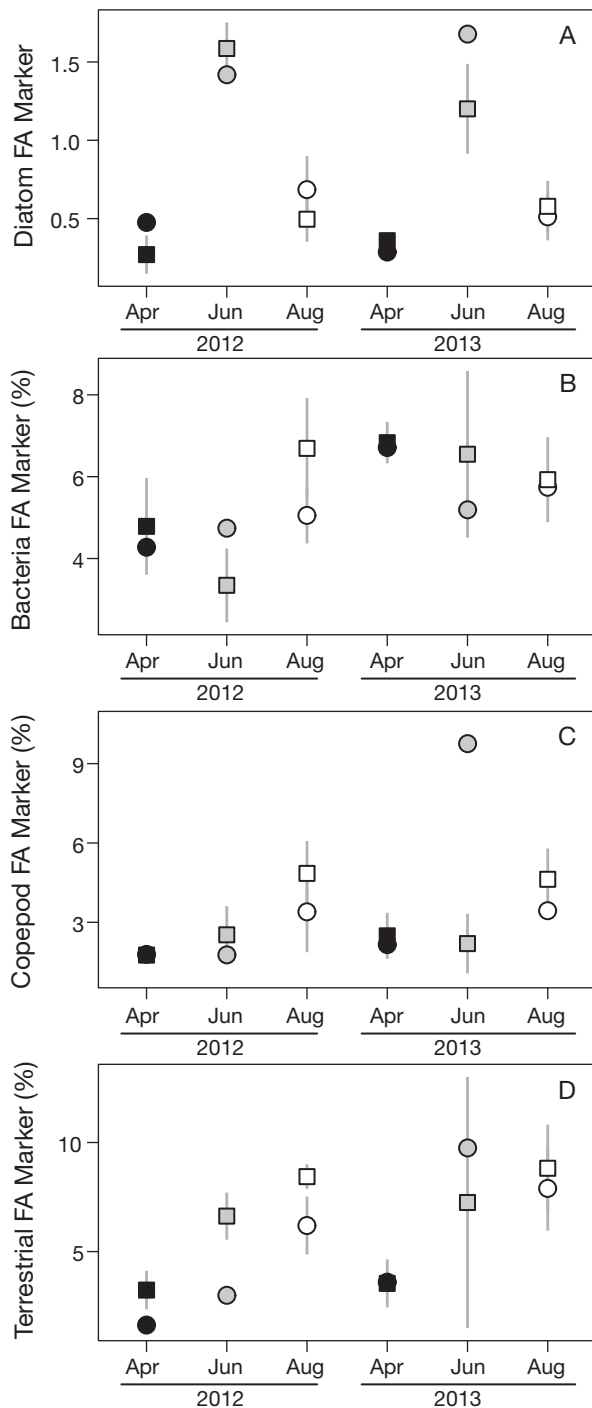


Fig. 5. Seasonal variation in the mean (\pm SD) fatty acid (FA) markers of suspended particulate matter collected from sites within lagoons (■) and outside the barrier islands (●) along the eastern Alaskan Beaufort Sea coast. Samples were collected from ≤ 2 m during full ice cover (April, black), ice break-up (June, grey), and open water (August, white) in 2012 and 2013. $n = 3$ to 6, except for sites outside the barrier islands in April and June where $n = 1$. (A) Diatom FA marker: $\Sigma 16:1/16:0$; (B) Bacterial FA marker: Σ odd-carbon numbered and branched chain FA; (C) Copepod FA marker: $\Sigma 20:1 + \Sigma 22:2$; (D) Terrestrial FA marker: $18:3\omega 3 + 18:2\omega 6$

year (Renaud et al. 2007, Darnis & Fortier 2012, Nguyen et al. 2012). The energy and organic matter sources that support consumers during the Arctic winter are poorly resolved and need further attention. Possible sources of organic matter used by heterotrophic communities (metazoan and microbial) during this time could be reworked autochthonous material produced during the prior light season (including dead crustacean carcasses and coprophagy, Sampei et al. 2009, 2012), terrestrial organic matter supplied during previous periods of runoff, or even chemoautotrophic production during winter (Alonso-Sáez et al. 2010, Connelly et al. 2014a). Some animal consumers may subsist off energy stores built during the previous growing season (Lee et al. 2006, Connelly et al. 2012b), while some researchers have proposed that some consumers may use heterotrophic microbial production to a greater extent than they do in summer (Rivkin & Anderson 1999, McClelland et al. 2014).

Based on the lack of primary production in winter and on our fatty acid and pigment data, we hypothesize that consumers likely contributed to the character of POM observed in April. Overall, POM in April appeared to be material remaining after consumers used or transformed what was available to them throughout winter. For example, bacterial fatty acid markers and $18:1\omega 9$ had strong positive loadings on PC1, where April scores were exclusively positive on PC1. Our bacterial fatty acid marker is an estimate of the relative contribution of fatty acids of bacterial origin (Stevens et al. 2004, Connelly et al. 2012a, Shah et al. 2013) and $18:1\omega 9$ indicates possible animal detritus inputs into the POM pool (Napolitano 1999) because it is a dominant fatty acid in many marine animals (e.g. Graeve et al. 1997, Auel et al. 2002), including those found in the Beaufort Sea (Connelly et al. 2014b). Moreover, phaeopigments in lagoons were the most dominant pigment in April, contributing $>50\%$ of identified pigments. Relative increases in phaeopigments reveal increased biological breakdown of chlorophyll *a* relative to new production because the phaeopigments used here are the products of biological degradation of chlorophyll *a* (Bianchi & Canual 2011). Low dissolved oxygen levels present in some lagoons in April further support the importance of respiration and heterotrophic processes to biogeochemical cycling in winter and early spring. Additionally, low PUFA ($\sim 10\%$) and elevated saturated fatty acid ($\sim 65\%$) proportions suggest that the organic matter available to animal consumers in April was refractory and of low nutritional quality. These observed proportions likely resulted from the greater stability of

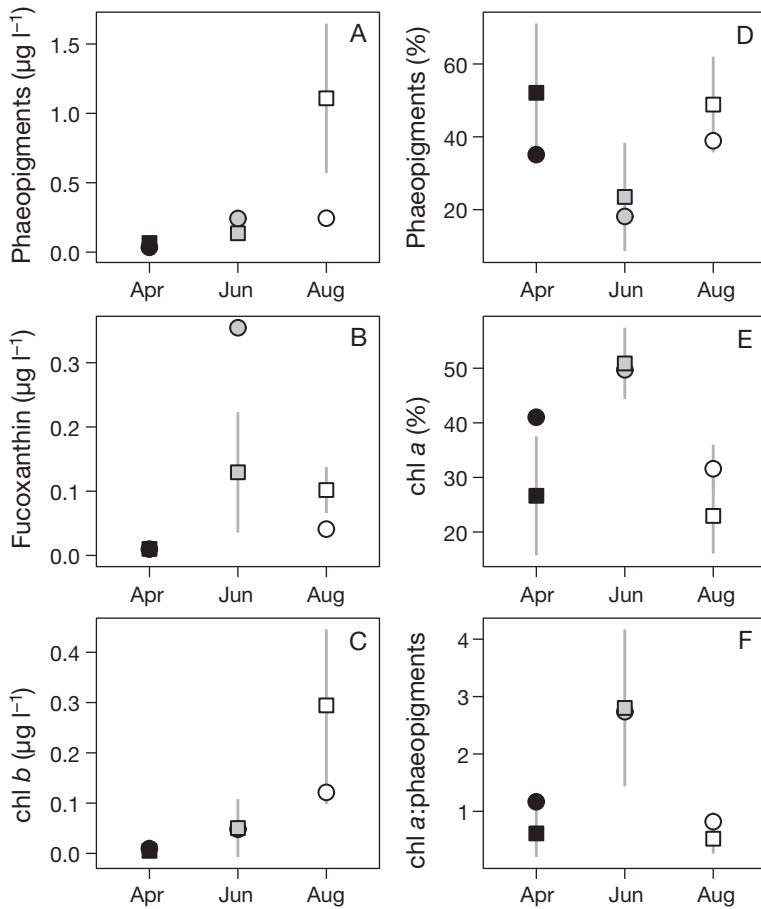


Fig. 6. Seasonal variation in the mean (\pm SD) concentration of (A) total phaeopigments, (B) fucoxanthin and (C) chl b, proportions of (D) phaeopigments and (E) chl a of total identified pigments, and (F) the chl a to phaeopigment ratio in suspended particulate matter collected from sites within lagoons (■) and outside the barrier islands (●) along the eastern Alaskan Beaufort Sea coast. Samples were collected from ≤ 2 m during full ice cover (April 2013, black), ice break-up (June 2013, grey), and open water (August 2012, white). $n = 4$ to 6, except for sites outside the barrier islands in April and June where $n = 1$. Data for chl c, peridinin, prasinoxanthin, 19-but-fucoxanthin and 19-hex-fucoxanthin are not shown as they were on average $< 2\%$ of total pigments and $\leq 0.1 \mu\text{g l}^{-1}$ across all seasons

statured fatty acids compared with PUFA (which are more reactive) and reflect enhanced heterotrophic processing of POM compared to primary production and other inputs during winter.

In addition to the compositional changes, the concentration of POM was significantly less in April than in the previous August (by 40 to 80% depending on lagoon). This change in bulk concentration was also associated with interannual variation in compositional changes in the bulk organic matter pool between these 2 seasons. For example, the percent decrease in PON from August 2012 to April 2013 was less than the decrease in POC (~12% versus 65%). In the absence

of any new inputs of POM between these sampling periods, this pattern suggests preferential retention of PON, microbial uptake of dissolved nitrogen, or loss of carbon to respiration. In contrast, from August 2011 to April 2012 the percent decrease in PON was similar or greater than that of POC. This inter-annual variability in POC and PON loss is reflected in the C/N ratios, which were lower in April 2013 (6.8) than in 2012 (8.9). Since we did not sample in fall, these August to April comparisons should be viewed with caution: Any fall phytoplankton blooms (Forest et al. 2008) could influence the C/N ratios. April POM chemistry would not reflect a direct compositional change due to diagenesis from August through winter if new inputs of POM occurred between the sampling periods. However, in this case, the universal percent decrease would be a conservative estimate of bulk changes in the concentration of POM through winter.

The $\delta^{13}\text{C}$ values of terrestrial material are generally lower (-30 to -23‰) than those from marine material (-25 to -18‰), and therefore $\delta^{13}\text{C}$ can be useful for understanding the importance of terrestrial or marine organic matter to coastal environments (Fry & Sherr 1984, Parsons et al. 1989). The $\delta^{13}\text{C}$ values for POM in April (-28 to -25‰) overlapped directly with assumed terrestrial sources, suggesting that most POM in April was of terrestrial origin. However, on average, these April values were more enriched in ^{13}C than those from June or August (except August 2011), suggesting greater proportional contributions of marine-sourced POM in April as compared to the other time periods. Since there is little other evidence for autochthonous inputs from fatty acid or pigment

analyses in April, this trend could also result from the kinetic advantage of respiring ^{12}C , resulting in ^{13}C -enriched POM. This same mechanism has been proposed to account for small enrichments in ^{13}C in the sediment compared to water directly overlying these sediments in other Arctic systems (Tamelander et al. 2006, Connelly et al. 2012a).

June

Sea ice was present in all of the lagoons during sampling trips in late June, but coverage varied sub-

stantially over space and time. Despite this variability in sea ice conditions and associated physical attributes of the environment, several generalities about the quantity and composition of POM in the lagoons were apparent. POM in June was characterized by (1) high bulk and fatty acid concentrations, (2) low $\delta^{13}\text{C}$ values, (3) high fatty acid and pigment markers indicative of diatom inputs, (i.e. fucoxanthin, and the diatom and C_{16} PUFA/ C_{18} PUFA fatty acid markers), (4) high proportions of monounsaturated fatty acids, (5) high chlorophyll *a*/pheopigments ratios, and (6) high, but variable terrestrial fatty acid markers. These results indicate that both terrestrial inputs and autochthonous production contributed to the POM pool during June.

June is a period of rapid change in the coastal Arctic and therefore studies during this time period are crucial for full understanding of coastal Arctic processes. However, it is precisely the dynamic nature of the environment in June that makes sampling a challenge, limiting our current understand of processes occurring at this time. In June, under 24 h of sunlight, rivers are flowing (although past peak flow) and sea ice is melting. The spring freshet occurs before ice break-up in coastal waters, and introduces warmer water that enhances sea ice melt (Dean et al. 1994) and drastically reduces salinity. While this brings tremendous amounts of terrestrial organic matter into the system, it also stimulates an increase in phytoplankton production. Overall, we saw POC and PON concentrations increase by 8-fold in ~2 mo from April to June.

In addition to phytoplankton, ice algae and benthic algae are 2 other sources of autochthonous production in the coastal Alaskan Arctic (Horner & Schrader 1982). The most complete study looking at the inputs of these sources in a coastal Alaskan lagoon was done in Stefansson Sound (Horner & Schrader 1982). Throughout May and June, concentrations of chlorophyll *a* in Stefansson Sound were an order of magnitude higher in sea ice than in the water column, reaching a maximum of $>25 \mu\text{g l}^{-1}$ in the first week of June (Horner & Schrader 1982). Yet, chlorophyll *a* levels in sea ice were an order of magnitude lower at coastal Alaskan sites, including Stefansson Sound, compared to other regions of the Arctic as predicted from water column NO_3^- concentrations (Rózanska et al. 2009). Rózanska et al. (2009) suggest several reasons for this pattern, including higher light attenuation due to sediments entrapped in the sea ice, which is also probably true for our study area. We did not measure chlorophyll *a* in sea ice and therefore are unable to determine the extent of ice algae inputs.

However, the highest chlorophyll *a* levels were often found in saltier waters just above the sediments, and not in the top meters with lower salinity water. This suggests that the higher chlorophyll *a* levels in bottom waters were not directly associated with ice algae inputs, but instead reflect active growth of phytoplankton or resuspension of benthic algae. In the Stefansson Sound study, benthic chlorophyll *a* levels, like those in sea ice, were an order of magnitude greater than water column levels in June (Horner & Schrader 1982), suggesting that benthic algae could have contributed to the elevated chlorophyll *a* levels in bottom waters.

The elevated diatom fatty acid marker ($\Sigma 16:1/16:0$), C_{16} PUFA/ C_{18} PUFA fatty acid ratios, fucoxanthin concentrations, and C_{16} PUFA index in June suggest that any autochthonous production was predominantly from diatom growth. Results from the PCA analysis is consistent with this interpretation where C_{16} PUFA (i.e. 16:4 ω 1 and 16:3 ω 4) and the diatom fatty acid marker were important factors for the negative PC2 scores for June samples. C_{16} PUFA are reported to be the most dominant fatty acids during diatom blooms (Kattner et al. 1983, Claustre et al. 1988), fucoxanthin is a photosynthetic pigment commonly synthesized by diatoms (Stauber & Jeffrey 1988), and 16:4 ω 1 is diagnostic of diatoms (Budge et al. 2001) because it is found in most diatoms but rarely in other microalgae groups (Volkman et al. 1989, Viso & Marty 1993). Also, diatoms generally have higher proportions of PUFA with 16 carbons relative to dinoflagellates, which have higher proportions of C_{18} PUFA (Dalsgaard et al. 2003). The combination of these biomarkers identifies diatoms as substantially contributing to autochthonous production during ice break-up in June. Further, the C_{16} PUFA index at 3 m in June was higher than at 2 m. Specifically, the highest C_{16} PUFA index (21–24 %) in June was found in saltier waters collected from 3 m in Kaktovik Lagoon, which also had the highest chlorophyll *a* concentrations (6 to $8 \mu\text{g l}^{-1}$, data not shown). This concurrence suggests that chlorophyll *a* in deeper, saltier waters in June was from actively growing diatom cells under nutrient-replete concentrations (Shin et al. 2000).

August

By August, sea ice has completely melted and freshwater inputs from rivers into the Alaskan Beaufort Sea have greatly diminished (McClelland et al. 2014). Our data indicate that POM in August was

characterized by (1) generally low $\delta^{13}\text{C}$ values and high proportions of terrestrial fatty acid markers, (2) elevated proportions of PUFA, (3) fatty acids or markers indicative of dinoflagellates (e.g. C_{18} PUFA/ C_{16} PUFA, DHA/EPA, and proportions of DHA), (4) elevated phaeopigment and chlorophyll *b* concentrations, and (5) greater proportions of copepod fatty acid markers. These results suggest that a combination of terrestrial sources, dinoflagellate and/or green algae input, and transformations by consumers contributed to the POM pool after sea ice melt.

A shift in the relative contributions of diatoms versus dinoflagellates to the POM pool between June and August is evident in the proportions of C_{16} to C_{18} PUFA, total C_{16} and C_{18} fatty acids, and the ω -3 fatty acids EPA and DHA in these 2 time periods. Like the comparison between C_{16} and C_{18} fatty acids for determining diatom and dinoflagellate inputs, diatoms generally have greater proportions of EPA and dinoflagellates have greater proportions of DHA (Dalsgaard et al. 2003), and DHA/EPA ratios of ≥ 1 have been used to indicate the dominance of dinoflagellates (Budge & Parrish 1998, Dalsgaard et al. 2003). DHA in lagoons increased from $\sim 2\%$ in June to $\sim 7\%$ in August, whereas EPA was ~ 5 to 6% in both seasons, resulting in DHA/EPA ratios of > 1 in August. This successional shift in autotrophs in our study area has also been observed using other analytical approaches (i.e. microbial eukaryotic amplicon sequencing, C. T. E. Kellogg unpubl.).

Certain microzooplankton are capable of synthesizing DHA resulting in higher DHA/EPA ratios than their food (Klein Breteler et al. 1999). Therefore, microzooplankton, which include heterotrophic dinoflagellates, could have contributed to the composition of POM in our study. Additional evidence for consumer-mediated organic matter transformations in August compared with June include higher concentrations of phaeopigments, lower chlorophyll *a*/phaeopigment ratios, and higher proportions of copepod fatty acid marker, which is a sum of fatty acids typical of wax ester-storing zooplankton (Lee 1975).

The nutritional quality of POM in the lagoons in August with higher PUFA, especially ω -3 fatty acids, and DHA/EPA ratios suggest that lagoons (rather than marine sites) may supply animal consumers with food that meets their nutritional needs. ω -3 and ω -6 PUFA, which cannot be synthesized *de novo* by most metazoans, are vital for proper marine invertebrate and fish reproduction, growth and development (see review by Parrish 2009), and certain ω -3 fatty acids have been implicated in controlling sec-

ondary production (Jónasdóttir et al. 1995, Müller-Navarra et al. 2000). Moreover, higher DHA/EPA ratios have been connected with better quality eggs and larval development in copepods and fish (see review by Parrish 2009). Thus, the greater availability of PUFA during summer and the higher DHA/EPA ratio found only in the lagoons in summer highlights the importance of lagoons during open water to aquatic food webs along the Alaskan Beaufort Sea coast.

As in April and June, low $\delta^{13}\text{C}$ values in August ($< -27\%$) signal the dominance of terrestrial matter to POM. High terrestrial fatty acid markers during August are seemingly consistent with the stable isotope data. However, interpretations of these fatty acids could be confounded by contributions from green algae. Elevated chlorophyll *b* levels in August are consistent with inputs of green algae to the POM pool (Jeffrey 1976), and fatty acid profiles of green algae are also characterized by high proportions of the 2 fatty acids used in calculating the terrestrial fatty acid marker (Dalsgaard et al. 2003). Since chlorophyll *b* is found in both terrestrial plants and green algae, it is difficult to discern between terrestrial plants and green algae using these markers. Overall, however, $\delta^{13}\text{C}$ values underscore the strong influence of terrestrial contributions of POM during all 3 seasons, consistent with surface sediment data from other near shore locations along the Alaskan Beaufort Sea coast (Schreiner et al. 2013) and the apparent significance of terrestrial matter to these coastal food webs (Dunton et al. 2012).

Acknowledgements. We thank R. Thompson, S. Linn, S. Smith, C. Harris, T. Dunton, and J. Dunton for their help in the field, C. Faulk and L. Fuiman for being generous with their support of the GC-FID, P. Garlough for running sampling on the CF-IRMS, and Z. Liu, S. Liu, and C. Ren for help with HPLC analysis. We also thank the US Fish and Wildlife Service, especially D. Payer, CH2M Hill Polar Services (CPS) and the Kaktovik Inuviat Corporation for their support. This paper benefited from input by 3 anonymous reviewers. This project was funded by NSF award #1023582.

LITERATURE CITED

- Alonso-Sáez L, Galand PE, Casamayor EO, Pedrós-Alió C, Bertilsson S (2010) High bicarbonate assimilation in the dark by Arctic bacteria. *ISME J* 4:1581–1590
- Auel H, Harjes M, da Rocha R, Stübing D, Hagen W (2002) Lipid biomarkers indicate different ecological niches and trophic relationships of the Arctic hyperiid amphipods *Themisto abyssorum* and *T. libellula*. *Polar Biol* 25: 374–383
- Ayaz FA, Olgun A (2000) Fatty acid composition of leaf lipids of some *Carex* L. (Cyperaceae) species from North-

- east Anatolia (Turkey). *Grasas Aceites* 51:307–310
- Bianchi TS, Canual EA (2011) *Chemical biomarkers in aquatic ecosystems*. Princeton University Press, NJ
- Brown S, Kendall S, Churchwell R, Taylor A, Benson AM (2012) Relative shorebird densities at coastal sites in the Arctic National Wildlife Refuge. *Waterbirds* 35:546–554
- Budge SM, Parrish CC (1998) Lipid biogeochemistry of plankton, settling matter and sediments in Trinity Bay, Newfoundland. II. Fatty acids. *Org Geochem* 29:1547–1559
- Budge SM, Parrish CC, McKenzie CH (2001) Fatty acid composition of phytoplankton, settling particulate matter and sediments at a sheltered bivalve aquaculture site. *Mar Chem* 76:285–303
- Budge SM, Wooller MJ, Springer AM, Iverson SJ, McRoy CP, Divoky GJ (2008) Tracing carbon flow in an arctic marine food web using fatty acid-stable isotope analysis. *Oecologia* 157:117–129
- Carmack E, Wassmann P (2006) Food webs and physical-biological coupling on pan-Arctic shelves: Unifying concepts and comprehensive perspectives. *Prog Oceanogr* 71:446–477
- Claustre H, Marty DG, Cassiani L, Dagaut J (1988) Fatty acid dynamics in phytoplankton and microzooplankton communities during a spring bloom in the coastal Ligurian sea: ecological implications. *Mar Microb Food Webs* 3:51–66
- Connelly TL, Deibel D, Parrish CC (2012a) Biogeochemistry of near-bottom suspended particulate matter of the Beaufort Sea shelf (Arctic Ocean): C, N, P, $\delta^{13}\text{C}$ and fatty acids. *Cont Shelf Res* 43:120–132
- Connelly TL, Deibel D, Parrish CC (2012b) Elemental composition, total lipid content, and lipid class proportions in zooplankton from the benthic boundary layer of the Beaufort Sea shelf (Canadian Arctic). *Polar Biol* 35:941–957
- Connelly TL, Baer SE, Cooper J, Bronk DA, Wawrik B (2014a) Urea uptake and carbon fixation by marine pelagic bacteria and archaea during the Arctic summer and winter seasons. *Appl Environ Microbiol* 80:6013–6022
- Connelly TL, Deibel D, Parrish CC (2014b) Trophic interactions in the benthic boundary layer of the Beaufort Sea shelf, Arctic Ocean: combining bulk stable isotope and fatty acid signatures. *Prog Oceanogr* 120:79–92
- Craig PC (1984) Fish use of coastal waters of the Alaskan Beaufort Sea: a review. *Trans Am Fish Soc* 113:265–282
- Dalsgaard J, St John M, Kattner G, Muller-Navarra D, Hagen W (2003) Fatty acid trophic markers in the pelagic marine environment. *Adv Mar Biol* 46:225–340
- Darnis G, Fortier L (2012) Zooplankton respiration and the export of carbon at depth in the Amundsen Gulf (Arctic Ocean). *J Geophys Res* 117:C04013, doi:10.1029/2011-JC007374
- Dean KG, Stringer WJ, Ahlnäs K, Searcy C, Weingartner T (1994) The influence of river discharge on the thawing of sea ice, Mackenzie River Delta: albedo and temperature analyses. *Polar Res* 13:83–94
- Dittmar T, Kattner G (2003) The biogeochemistry of the river and shelf ecosystem of the Arctic Ocean: a review. *Mar Chem* 83:103–120
- Dunton KH, Schonberg SV, Cooper LW (2012) Food web structure of the Alaskan nearshore shelf and estuarine lagoons of the Beaufort Sea. *Estuaries Coasts* 35:416–435
- Falk-Petersen S, Sargent JR, Tande KS (1987) Lipid composition of zooplankton in relation to the sub-Arctic food web. *Polar Biol* 8:115–120
- Folch J, Lees M, Sloane Stanley GH (1957) A simple method for the isolation and purification of total lipids from animal tissues. *J Biol Chem* 226:497–509
- Forest A, Sampei M, Makabe R, Sasaki H, Barber DG, Gratton Y, Wassmann P, Fortier L (2008) The annual cycle of particulate organic carbon export in Franklin Bay (Canadian Arctic): Environmental control and food web implications. *J Geophys Res* 113:C03S05, doi:10.1029/2007-JC004262
- Fry B, Sherr EB (1984) $\delta^{13}\text{C}$ measurements as indicators of carbon flow in marine and freshwater ecosystems. *Contrib Mar Sci* 27:13–47
- Graeve M, Kattner G, Piepenburg D (1997) Lipids in Arctic benthos: does the fatty acid and alcohol composition reflect feeding and trophic interactions? *Polar Biol* 18:53–61
- Graeve M, Kattner G, Wiencke C, Karsten U (2002) Fatty acid composition of Arctic and Antarctic macroalgae: indicator of phylogenetic and trophic relationships. *Mar Ecol Prog Ser* 231:67–74
- Guo L, Cai Y, Belzile C, Macdonald RW (2012) Sources and export fluxes of inorganic and organic carbon and nutrient species from the seasonally ice-covered Yukon River. *Biogeochemistry* 107:187–206
- Harrison WG, Platt T, Irwin B (1982) Primary production and nutrient assimilation by natural phytoplankton populations of the eastern Canadian Arctic. *Can J Fish Aquat Sci* 39:335–345
- Hietala T, Hiikkala P, Rosenqvist H, Laakso S, Tahvanainen L, Repo T (1998) Fatty acid and alkane change in willow during frost-hardening. *Phytochemistry* 47:1501–1507
- Holmes RM, McClelland JW, Peterson BJ, Tank SE and others (2012) Seasonal and annual fluxes of nutrients and organic matter from large rivers to the Arctic Ocean and surrounding seas. *Estuaries Coasts* 35:369–382
- Horner RA, Schrader GC (1982) Relative contributions of ice algae, phytoplankton, and benthic microalgae to primary production in nearshore regions of the Beaufort Sea. *Arctic* 35:485–503
- Jeffrey SW (1976) A report of green algal pigments in the Central North Pacific Ocean. *Mar Biol* 37:33–37
- Jónasdóttir SH, Fields D, Pantoja S (1995) Copepod egg production in Long Island Sound, USA, as a function of the chemical composition of seston. *Mar Ecol Prog Ser* 119:87–98
- Kaneda T (1991) Iso- and anteiso-fatty acids in bacteria: biosynthesis, function, and taxonomic significance. *Microbiol Rev* 55:288–302
- Kattner G, Gercken G, Eberlein KH (1983) Development of lipids during a spring plankton bloom in the northern North Sea: I. Particulate fatty acids. *Mar Chem* 14:149–162
- Khotimchenko SV, Vaskovsky VE, Titlyanova TV (2002) Fatty acids of marine algae from the Pacific coast of north California. *Bot Mar* 45:17–22
- Klein Breteler WCM, Schogt N, Baas M, Schouten S, Kraay GW (1999) Trophic upgrading of food quality by protozoans enhancing copepod growth: role of essential lipids. *Mar Biol* 135:191–198
- Lee RF (1975) Lipids of Arctic zooplankton. *Comp Biochem Physiol B* 51:263–266
- Lee RF, Hagen W, Kattner G (2006) Lipid storage in marine zooplankton. *Mar Ecol Prog Ser* 307:273–306

- Mayzaud P, Boutoute M, Gasparini S (2013) Differential response of fatty acid composition in the different lipid classes from particulate matter in a high arctic fjord (Kongsfjorden, Svalbard). *Mar Chem* 151:23–34
- McClelland JW, Townsend-Small A, Holmes RM, Pan F, Stieglitz M, Khosh M, Peterson BJ (2014) River export of nutrients and organic matter from the North Slope of Alaska to the Beaufort Sea. *Water Resour Res* 50: 1823–1839
- Müller-Navarra DC, Brett MT, Liston AM, Goldman CR (2000) A highly unsaturated fatty acid predicts carbon transfer between primary producers and consumers. *Nature* 403:74–77
- Napolitano GE (1999) Fatty acids as trophic and chemical markers in freshwater ecosystems. In: Arts MT, Wainman BC (eds) *Lipids in freshwater ecosystems*. Springer, New York, p 21–44
- Nguyen D, Maranger R, Tremblay JÉ, Gosselin M (2012) Respiration and bacterial carbon dynamics in the Amundsen Gulf, western Canadian Arctic. *J Geophys Res* 117:C00G16, doi:10.1029/2011JC007343
- Nicolaus M, Petrich C, Hudson SR, Granskog MA (2013) Variability of light transmission through Arctic land-fast sea ice during spring. *Cryosphere* 7:977–986
- Parrish CC (1999) Determination of total lipid, lipid classes, and fatty acids in aquatic samples. In: Arts MT, Wainman BC (eds) *Lipids in freshwater systems*. Springer, New York, p 4–20
- Parrish CC (2009) Essential fatty acids in aquatic food webs. In: Arts MT, Brett MT, Kainz MJ (eds) *Lipids in aquatic ecosystems*. Springer, New York, p 309–326
- Parrish CC, Thompson RJ, Deibel D (2005) Lipid classes and fatty acids in plankton and settling matter during the spring bloom in a cold ocean coastal environment. *Mar Ecol Prog Ser* 286:57–68
- Parsons TR, Webb DG, Rokeby BE, Lawrence M, Hopky GE, Chiperek DB (1989) Autotrophic and heterotrophic production in the Mackenzie River/Beaufort Sea estuary. *Polar Biol* 9:261–266
- Pedersen S, Linn A Jr (2005) Kaktovik 2000–2002 subsistence fishery harvest assessment. Final Project Report FIS 01-101. US Fish Wildlife, Office Subsistence Management, Fishery Information Services Division, Federal Subsistence Fishery Monitoring Program, Anchorage AK
- Renaud PE, Riedel A, Michel C, Morata N, Gosselin M, Juul-Pedersen T, Chiuchiolo A (2007) Seasonal variation in benthic community oxygen demand: a response to an ice algal bloom in the Beaufort Sea, Canadian Arctic? *J Mar Syst* 67:1–12
- Rivkin RB, Anderson MR (1999) Microbial dynamics in polar oceans: a bipolar comparison. In: Bell CR, Brylinsky M, Johnson-Green P (eds) *Microbial biosystems: new frontiers*. Proc 8th Int Symp Microb Ecol. Atlantic Canada Society for Microbial Ecology, Halifax, Nova Scotia, p 307–316
- Rózanska M, Gosselin M, Poulin M, Wiktor JM, Michel C (2009) Influence of environmental factors on the development of bottom ice protist communities during the winter–spring transition. *Mar Ecol Prog Ser* 386:43–59
- Saba GK, Fraser WR, Saba VS, Iannuzzi RA and others (2014) Winter and spring controls on the summer food web of the coastal West Antarctic Peninsula. *Nat Commun* 5:4318
- Sampei M, Forest A, Sasaki H, Hattori H, Makabe R, Fukuchi M, Fortier L (2009) Attenuation of the vertical flux of copepod fecal pellets under Arctic sea ice: evidence for an active detrital food web in winter. *Polar Biol* 32:225–232
- Sampei M, Sasaki H, Forest A, Fortier L (2012) A substantial export flux of particulate organic carbon linked to sinking dead copepods during winter 2007–2008 in the Amundsen Gulf (southeastern Beaufort Sea, Arctic Ocean). *Limnol Oceanogr* 57:90–96
- Sargent JR, Parkes RJ, Mueller-Harvey I, Henderson RJ (1987) Lipid biomarkers in marine ecology. In: Sleigh MA (ed) *Microbes in the sea*. Ellis Horwood, Chichester, p 119–138
- Schreiner KM, Bianchi TS, Eglinton TI, Allison MA, Hanna AJM (2013) Sources of terrigenous inputs to surface sediments of the Colville River Delta and Simpson's Lagoon, Beaufort Sea, Alaska. *J Geophys Res Biogeosci* 118: 808–824
- Schroeder ID, Black BA, Sydeman WJ, Bograd SJ, Hazen EL, Santora JA, Wells BK (2013) The North Pacific High and wintertime pre-conditioning of California current productivity. *Geophys Res Lett* 40:541–546
- Shah SR, Griffith DR, Galy V, McNichol AP, Eglinton TI (2013) Prominent bacterial heterotrophy and sources of ¹³C-depleted fatty acids to the interior Canada Basin. *Biogeosciences* 10:7065–7080
- Shin KH, Hama T, Yoshie N, Noriki S, Tsunogai S (2000) Dynamics of fatty acids in newly biosynthesized phytoplankton cells and seston during a spring bloom off the west coast of Hokkaido Island, Japan. *Mar Chem* 70: 243–256
- Spetzman LA (1959) Vegetation of the Arctic Slope of Alaska. USGS Professional Paper 302-B, Washington US Govt Print Off, p 19–58
- Stauber JL, Jeffrey SW (1988) Photosynthetic pigments in fifty one species of marine diatoms. *J Phycol* 24:158–172
- Stevens CJ, Deibel D, Parrish CC (2004) Copepod omnivory in the North Water Polynya (Baffin Bay) during autumn: spatial patterns in lipid composition. *Deep-Sea Res I* 51: 1637–1658
- Tamelander T, Renaud PE, Hop H, Carroll ML, Ambrose WG Jr, Hobson KA (2006) Trophic relationships and pelagic–benthic coupling during summer in the Barents Sea Marginal Ice Zone, revealed by stable carbon and nitrogen isotope measurements. *Mar Ecol Prog Ser* 310: 33–46
- Tolosana-Delgado R, Otero N, Soler A (2005) A compositional approach to stable isotope data analysis. In: Mateau-Figueres G, Barceló-Vidal C (eds) 2nd International Workshop on Compositional Data Analysis (CoDa-Work'05), October 19–21, 2005, University of Girona
- Viso AC, Marty JC (1993) Fatty acids from 28 marine microalgae. *Phytochemistry* 34:1521–1533
- Volkman JK, Jeffrey SW, Nichols PD, Rogers GI, Garland CD (1989) Fatty acid and lipid composition of 10 species of microalgae used in mariculture. *J Exp Mar Biol Ecol* 128:219–240
- Wang SW, Budge SM, Gradinger RR, Iken K, Wooller MJ (2014) Fatty acid and stable isotope characteristics of sea ice and pelagic particulate organic matter in the Bering Sea: tools for estimating sea ice algal contribution to Arctic food web production. *Oecologia* 174:699–712