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Response of phytoplankton community to different water types in the western Arctic Ocean surface water based on pigment analysis in summer 2008

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Abstract

Nutrients and photosynthesis pigments were investigated in the western Arctic Ocean during the 3rd Chinese Arctic Research Expedition Cruise in summer 2008. The study area was divided into five provinces using the K-means clustering method based on the physical and chemical characteristics of the sea water, and to discuss the distribution of the phytoplankton community structure in these provinces. CHEMTAX software was performed using HPLC pigments to estimate the contributions of eight algal classes to the total chlorophyll *a* (TChl *a*). The results showed that on the Chukchi Shelf, the Pacific Ocean inflow mainly controlled the Chl *a* biomass and phytoplankton communities by nutrient concentrations. The high nutrient Anadyr Water and Bering Shelf Water (AnW and BSW) controlled region have high Chl *a* levels and the diatom dominated community structure. In contrast, in the region occupied by low-nutrient like Alaska Coastal Water (ACW), the Chl *a* biomass was low, with pico- and nano-phytoplankton as dominated species, such as prasinophytes, chrysophytes and cryptophytes. However, over the off-shelf, the ice cover condition which would affect the physical and nutrient concentrations of the water masses, in consequence had a greater impact on the phytoplankton community structure. Diatom dominated in ice cover region and its contribution to Chl *a* biomass was up to 75%. In the region close to the Mendeleev Abyssal Plain (MAP), controlled by sea-ice melt water with relatively high salinity (MW-HS), higher nutrient and Chl *a* concentrations were found and the phytoplankton was dominated by pico- and nano-algae, while the diatom abundance reduced to 33%. In the southern Canada Basin, an ice-free basin (IfB) with the lowest nutrient concentrations and most freshened surface water, low Chl *a* biomass was a consequence of low nutrients. The ice retreating and a prolonged period of open ocean may not be beneficial to the carbon export efficiency due to reducing the Chl *a* biomass or intriguing smaller size algae growth.

Key words: photosynthetic pigments, phytoplankton community, biological pump, organic carbon, ice retreat, Chukchi Sea and Canada Basin

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1 Introduction

The Arctic has faced rapid and severe changes in recent decades. Global warming has caused temperature increases in the Arctic Ocean, resulting in ice melting, sea ice cover thinning, higher terrestrial river discharge input and Pacific water inflow (Rothrock et al., 1999; Parkinson, 2000; Zhao et al., 2003). The perennial sea ice cover is decreasing at a rate of approximately 10% per decade, and it is reported that the average ice extent in September, 2007–2010 was 40% less than what it was three decades ago (Comiso et al., 2008; Stroeve et al., 2012). In the Arctic Ocean, the duration and extent of the sea ice, the sea ice thickness, and seawater temperature, as well as the water mass characteristics, have critical influence on the primary production and structure of the phytoplankton community and hence alter the carbon biogeochemical cycles and the carbon flux efficiency (Chen et al., 2004; Grebmeier et al., 2006a; Reid et al., 2007; Wassman, 2011).

Mooring observations in the Chukchi Sea indicated that the Pacific inflow from the Bering Strait increased by ~50% in the last ten years and drove the increasing heat and fresh water flux, together with the Arctic ice retreat (Woodgate et al., 2012). Warm fresh Pacific inflow water not only complements nutrients, but

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also provides an under-ice heat source, triggering the sea-ice retreat and freshening the upper water in the western Arctic Ocean (Steele et al., 2008). In consequence, this would promote the biological pump more efficiently than before in the marginal region of the western Arctic Ocean. An increase of annual phytoplankton net primary production (NPP) was observed on the inflow shelf of the Chukchi Sea over the past 15 years (Arrigo and van Dijken, 2015). Additionally, with the increasing of river runoff and the changing pathways of the fresh river water, the Chukchi Sea and Canada Basin have become the region with the greatest ice retreat and water freshening in the Arctic over the last ten years (Rabe et al., 2011; Morison et al., 2012). The increase in fresh water induces intensive stratification and has a remarkable influence on phytoplankton community structures in the upper ocean (Wassman, 2011; Coupel et al., 2012). The smaller phytoplankton cells thrive, but larger cells languish (Li et al., 2009; Doney et al., 2012).

Such shifts within the phytoplankton community may not only affect the traditional "biological pump" and "microbial biological pump" efficiency (Cai et al., 2010; Jiao et al., 2010; Chen et al., 2015), but also influence the structure of the food chain (Grebmeier et al., 2006a). At shallow shelves with high primary production, an ice-algae bloom and subsequent phytoplankton bloom occurs when the ice begins to retreat (Grebmeier et al., 2006a). Also, with the decreasing of the ice extent and the duration of the open water extent, the food chain lengthens, zooplankton grazing and the microbial loop in the water column become more dominant, and the ecosystem shifts from benthic to pelagic (Carroll and Carroll, 2003; Grebmeier et al., 2006b; Grebmeier, 2012). The pelagic ecosystem plays a more and more important role in the Arctic Ocean, not only in the open ocean but also under sea-ice due to continuous Arctic Sea ice retreat (Arrigo et al., 2012; Arrigo, 2015).

The structure of phytoplankton community can be identified by using diagnostic photosynthesis pigments (Jeffrey and Vesk, 1997; Wright and Jeffrey, 1997; Gibb et al., 2001). High-performance liquid chromatography (HPLC) is a fast and reproducible pigment analysis method in researching the response of the phytoplankton community to long-term environmental changes, especially in the rapidly changing Arctic region. A comparison of the phytoplankton community using microscopy and pigment analysis in the Arctic Ocean has underlined that CHEMTAX with pigment analysis is an efficient tool for the description of phytoplankton, especially in smaller phytoplankton-dominated regions (Coupel et al., 2012, 2015). CHEMTAX software was developed by considering the chemical taxonomy relationship among the phytoplankton with pigment signals (Mackey et al., 1996). And it has been widely applied in the global ocean to study the phytoplankton community (Barlow et al., 1993; Andersen et al., 1996), including the Antarctic and Arctic regions (Wright and Van den Enden, 2000; Hill et al., 2005; Kozlowski et al., 2011; Coupel et al., 2012, 2015; Zhuang et al., 2014). Previous studies showed that the response of phytoplankton to environmental changes differs spatially (Carmack and Wassmann, 2006), and the effect of different water types to phytoplankton in these region is still uncertain.

The objective of this study was to survey the phytoplankton community structure in the surface water of the western Arctic Ocean by using pigment signals from samples collected during the third Chinese Arctic Research Expedition in 2008. We focused on the impacts of different water types on the phytoplankton considering the physical and chemical characteristics of these water masses in the Arctic Ocean. And we also tried to give a distribution pattern of the phytoplankton community structure in the western Arctic Ocean as it plays an important role in the "Biological Pump" efficiency.

2 Materials and methods

2.1 *Study site and samples*

A comprehensive investigation cruise was conducted onboard the Chinese icebreaker R/V *Xuelong* in the western Arctic Ocean during the 3rd Chinese Arctic Research Expedition (CHINARE 2008) in summer 2008 from 11 Junly to 24 September. During the cruise, 76 hydrographic stations were sampled for nutrient analysis and 49 stations were sampled for pigment analysis from latitudes 65°N to 86°N, covering the region of the Chukchi Sea, Beaufort Sea and Canadian Basin in late summer from 1 August to 8 September (Fig. 1). Seawater samples were collected in Niskin bottles mounted on a CTD-Rosette sampler system. The hydrological parameters (salinity and temperature) were recorded in situ with CTD (Sea-bird, SBE 911 Plus, Sea-Bird electronics Inc. USA). Horizontal variables of the hydrological and chemical parameters were constructed using VG gridding package in Ocean Data View 4 (Schlitzer, 2012).

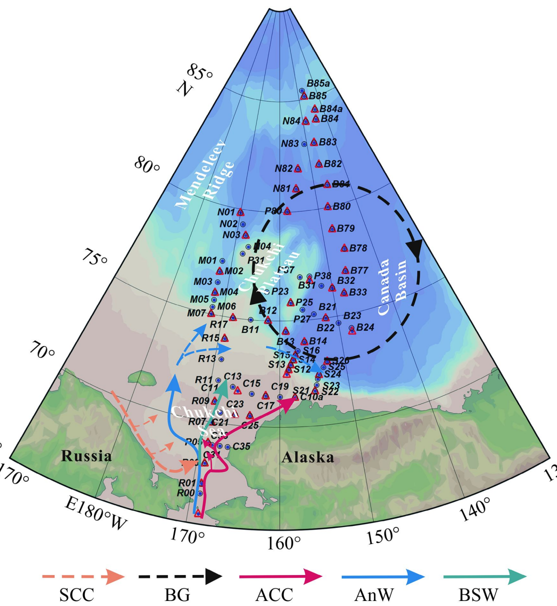

Fig. 1. Map of the study area and the locations of the stations in the western Arctic Ocean. Solid dots represent nutrient stations and red triangles pigment stations. The arrows indicate the different currents and their flow directions. Main surface currents are modified from Hunt et al. (2013) and Woodgate (2013). The water currents are Siberia Coastal Current (SCC), Beaufort Gyre (BG), Alaska Coastal Current (ACC), Anadyr Water (AnW), and Bering Shelf Water (BSW) lies between AnW and ACC.

Water samples were filtered through pre-cleaned cellulose acetate membranes (0.45 μm, 47 mm). The filtrates were collected for nutrient analysis and measured onboard. 250 mL sea water was filtered with GF/F glass fibers (ϕ25 mm, 0.7 μm) for Chl *a* samples, and the filters were freeze-stored at –20°C. 2–4 L sea water was filtered with GF/F glass fibers (ϕ47 mm, 0.7 μm) under gentle vacuum (<0.5 atm) and dim light conditions for pigment analysis, and the filters were stored at –80°C until analysis.

2.2 *Nutrient and Chl a analysis*

Nutrients were measured onboard using a continuous flow analyzer (Skalar San++, Holland). Analysis methods for nutrients were provided in detail in Li et al. (2011) which referred to the Specification for Oceanographic Survey (General Administration of Quality Supervision, Inspection and Quarantine of the People's Republic of China and Standardization Administration of China, 2008) and Grasshoff et al. (1999). The detection limits for nitrate+nitrite (NO_3^--N+NO_2^--N), silicate (SiO_3^{2-}-Si) and phosphate (PO_4^{3-}-P) were 0.1 μmol/dm³, 0.1 μmol/dm³ and 0.03 μmol/dm³, respectively. The Chl *a* samples were extracted with 90% acetone and kept in –20°C in the dark for 24 h. The extracts were analyzed with a Turner design fluorometer (Turner10-AU).

2.3 *Pigment analysis*

Pigment samples were separated using an HPLC system with the reverse phase method, referenced from Van Heukelem and Thomas (2001) and modified by Zhuang et al. (2011). The frozen filters were extracted with 3 mL 100% HPLC-grade methanol at –20°C for 1 h, sonicated (ice-bath) for 30 s and stored at –20°C again for another 1 h. Then, the extracts were pre-filtered through a 0.22 μm microporous membrane and mixed with 28 mmol/dm³ tetrabutyl ammonium acetate (TBAA) (v:v, 1:1) before injection. The analysis work for all the extracted samples was completed within 24 h.

Samples were analyzed using an HPLC system (Waters, USA) consisting of a Waters 600E pump controller, a 2998 photodiode array detector (PAD) and an auto sampler (Waters 717) at the wavelength of 450 nm. An Agilent Eclipse C8 column (150 mm×4.6 mm, 3.5 μm) was used, and the column temperature was set to 45°C. The solvent system consisted of Solvent A (100% HPLC-grade methanol) and Solvent B (methanol and TBAA, 70:30, v/v). The linear gradient program was set as follows (min, A%, B%): (0, 90, 10), (36, 5, 95), (41, 5, 95) at the flow rate of 1 mL/min. The injection volume was 200 μL. The peaks were identified according to the retention time and quantified using pigment standards purchased from DHI Lab (Denmark). The pigments measured here are listed in Table 1.

2.4 *CHEMTAX analysis*

A CHEMTAX program (Version 1.00) proposed by Mackey et al. (1996) was used to estimate the relative contributions of the different phytoplankton communities to the total Chl *a* (TChl *a*) at the class level. Twelve diagnostic pigments were used in CHEMTAX run, and the initial pigment ratios required to run the CHEMTAX are referenced in Wright and van den Enden (2000). The initial ratio was used in the Antarctic marginal ice zone (63°S to 66°S) and produced a reasonable result. The final pigment ratios were derived from a steepest descent algorithm based on CHEMTAX, and it was used to calculate the relative abundance of eight phytoplankton groups with respect to the TChl *a* at the class level (diatoms, chrysophytes, dinoflagellates, prymnesiophytes, chlorophytes, prasinophytes, cryptophytes and cyanobacteria). The whole study region was separated into two parts when we ran the CHEMTAX, one is the Chukchi Shelf and the other is the off-shelf region, including the shelf slope and the deep basin.

3 Results

3.1 *Hydrology and nutrients*

The surface water masses were defined according to the salinity and temperature in the western Arctic Ocean (Fig. 2). In the summer, the hydrology characteristics of surface seawater were significantly influenced by the water masses of the Pacific inflow, freshwater river input and ice melting processes in the western Arctic Ocean. The surface water was freshened, with the salinity ranging from 23.89 to 32.55 and the temperature from –1.6°C to 6.91°C. On the Chukchi Shelf, especially at latitudes lower than 71°N, high temperature and high salinity were observed, with averages of 3.83°C and 30.73 (n=11), respectively. This region was mainly influenced by the Pacific inflow water through the Bering Strait. In general, more saline, nutrient-rich Anadyr Water (AnW) transited northward through the Bering Strait on the western side, while more nutrient-limited, fresher (<31.8) Alaska Coastal Water (ACW) transited through the Bering Strait on the east side along the Alaskan coast. Between these two currents is the Bering Shelf Water (BSW) (Grebmeier et al., 2006a). On the northern Chukchi Shelf, the mixing of Pacific summer water, Pacific winter water and ice melting water in the summer was termed as the Chukchi Shelf Modified Water (CSMW). Stations R00 and R01, located in the southern Chukchi Sea showed high salinity in the surface water, with values of 32.42 and 32.55, respectively. This indicated that this region is controlled by the BSW. In the off-shelf region, including the Chukchi Plateau, shelf break, Mendeleev Abyssal Plain (MAP) and deep Canada Basin, the surface seawater was intensively freshened, not only due to ice melting but also due to freshwater river inputs. The salinity of the station located in MAP (78.8°–82°N, 155°–170°W) was higher than 29, while the salinity of other stations in the off-shelf region was lower than 29. Remarkably low salinities were observed at Stas B21, B22, B23, and B24, located in the Beaufort Sea-Canada Basin (BS-CB). The salinity was approximately 24 with relatively high temperature in this region. BS-CB was termed as an ice-free basin (IfB), with an ice cover lower than 20% (Coupel et al., 2012). The average temperature and salinity of these four stations were

Table 1. Diagnostic pigments and the phytoplankton community (Wright and Jeffery, 1997)

Pigment	Abbreviation	Phytoplankton community
a. Chlorophylls		
Chlorophyll *a*	Chl *a*	all except prochlorophytes
Divinyl chlorophyll *a*	DV Chl *a*	prochlorophytes
Chlorophyll *b*	Chl *b*	chlorophytes, prasinophytes
b. Carotenoids		
Peridinin	Peri	dinoflagellates
19′-Butanoyloxy-fucoxanthin	But-fuco	chrysophytes
Fucoxanthin	Fuco	diatoms, prymnesiophytes, chrysophytes
Neoxanthin	Neo	chlorophytes, prasinophytes
Prasinoxanthin	Pras	prasinophytes
Violaxanthin	Viola	chlorophytes, prasinophytes
19′-Hexanoyloxyfu-xanthin	Hex-fuco	prymnesiophytes
Diadinoxanthin	Diadino	diatoms, dinoflagellates, prymnesiophytes, chrysophytes
Alloxanthin	Allo	cryptophytes
Dinoxanthin	Dino	diatoms, dinoflagellates
Zeaxanthin	Zea	cyanobacteria, prochlorophytes, chlorophytes
Lutein	Lut	chlorophytes, prasinophytes
β,β-carotene	β,β-car	all except cryptophytes

Note: Twelve pigments used in CHEMTAX are highlighted in bold to calculating the contributions of different phytoplankton communities to the total Chl *a* (TChl *a*).

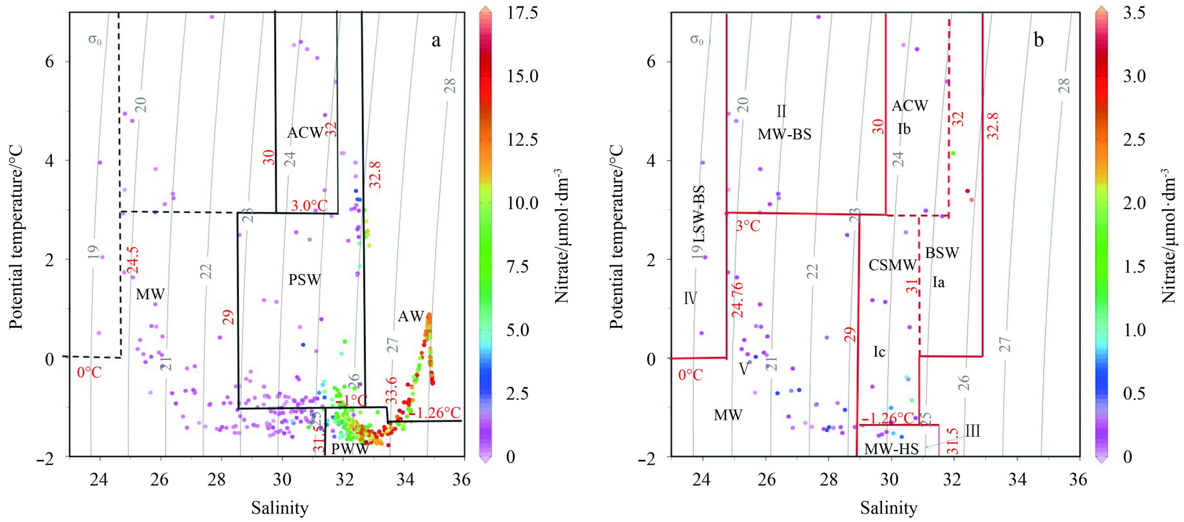

Fig. 2. Temperature/salinity/nitrate plot for the total water column (a) and the surface water (b) in the western Arctic Ocean. The numbers are the corresponding temperature and salinity values of the boundaries according to Itoh et al. (2015) and Gong and Pickart (2015). The details of *T-S* properties of the water masses in the Chukchi Sea were showed in Fig. A1. There are no Atlantic (AW) and PWW signals in the surface water. In Fig. 2b, the red solid lines denote the boundaries of the different provinces/water masses considered in the study, and the dotted lines the boundaries of the different water masses on the Chukchi Shelf (Province I). The Rome number denotes the five provinces in this study which were divided according to environmental conditions. The water masses are Atlantic Water (AW), Pacific Winter Water (PWW), Pacific Summer Water (PSW), Alaskan Coastal Water (ACW), Bering Shelf Water (BSW), Sea-ice Melt Water-Relatively High Salinity (MW-HS), Chukchi Shelf Modified Water (CSMW), Melt Water-Beaufort Sea (MW-BS), and Low Salinity Water-Beaufort Sea (LSW-BS).

(2.36±1.27)°C and 24.20±0.32, respectively.

The horizontal distribution of dissolved inorganic nutrients (NO_3^--N, SiO_3^{2-}-Si and PO_4^{3-}-P) had the same plain distribution profiles as the hydrological parameters in the western Arctic Ocean (Fig. 3). The concentrations of NO_3^--N, SiO_3^{2-}-Si and PO_4^{3-}-P ranged from 0.00–3.41 μmol/dm^3, 0.20–22.99 μmol/dm^3 and 0.35–1.66 μmol/dm^3, respectively. Relatively high concentrations were observed on the Chukchi Shelf due to the warm, salty, nutrient-rich Pacific inflow water controlling over the Chukchi Shelf, while the concentrations were quite low in other regions. On the Chukchi Shelf, the region with the maximum concentration of nitrate was not the same as the region with the maximum silicate concentration. The highest value of NO_3^--N was observed at Sta. R01 at the Bering Strait entrance, with concentrations of 3.41 μmol/dm^3. It then gradually decreased towards the off-shelf and deep basin. However, the highest concentration of SiO_3^{2-}-Si was not observed in the southern Chukchi Sea nearest the Bering Strait but rather in the region of the northern Chukchi Shelf at Sta. R17, with strong signals of a high-nutrient Pacific Winter Water mass with a high silicate concentration of 22.99 μmol/dm^3. It also inferred that a high consumption of the SiO_3^{2-}-Si process occurred on the southern Chukchi Shelf. A high value of PO_4^{3-}-P was observed at Sta. C31 on the shelf.

The concentrations of nitrate in the surface water were quite low over the off-shelf region, indicating the significant nutrient supplementation of BSW, mainly on the Chukchi Shelf, which is hard to supply the deep basin ecosystem. Previous studies showed that the whole Arctic Ocean was a remarkable nitrogen-limited region, and the nitrogen supplementation of BSW on the Chukchi Shelf maintained the growth of primary production and plays an important role in the Arctic ecosystem (Li et al., 2011).

Outside of the Chukchi Shelf, the nutrition level is quite low, with nitrate and phosphate levels lower than 0.8 μmol/dm^3. The lowest value of nutrients was observed in BS-CB, termed the IfB with high temperature. The average concentrations of NO_3^--N, SiO_3^{2-}-Si and PO_4^{3-}-P of the four stations (B21, B22, B23 and B24) in the IfB were (0.18±0.13) μmol/dm^3, (1.63±0.31) μmol/dm^3 and (0.53±0.02) μmol/dm^3, respectively. The nutrient concentration showed a slight elevation at MAP. The distribution of Chl *a* showed the same pattern as the nutrients. In the whole study area, the Chl *a* showed a wide range of concentrations from 0.01 to 19.37 μg/dm^3. The highest value of Chl *a* was observed at Sta. R01, and micro-algae contributed to the TChl *a* (Liu et al., 2011), while the value of Chl *a* in other regions was quite low. The concentrations of Chl *a* were lower than 1 μg/dm^3 at most stations located north of the latitude of 75°N. At MAP, the average concentration of Chl *a* was (0.42±0.29) μg/dm^3 (n=6) .

3.2 *Horizontal distribution of photosynthesis pigments*

The horizontal distribution of photosynthesis pigments was showed in Fig. 4. The pigment assemblage in the surface water was largely dominated by Fuco, which is mainly produced by diatoms in the Western Arctic Ocean. The distribution pattern of Fuco is similar to that of Chl *a*. Relatively high values were observed on the shelf, with concentrations ranging from 32 to 3 223 ng/dm^3. In the other region, away from the shelf, the concentrations of Fuco were lower than 50 ng/dm^3. Peri and Allo, the diagnostic pigments of dinoflagellates and cryptophytes, ranged from 0 to 38 ng/dm^3 and 0 to 12 ng/dm^3, respectively. The horizontal distributions of these two pigments have two high-value patches, the Chukchi Shelf and MAP, but in many stations in the deep basin, these two pigments were under the detection limits. Higher concentrations of Hex-fuco and Lut were observed at MAP. The highest values were observed at Sta. N01, 53 ng/dm^3 for Hex-fuco and 7 ng/dm^3 for Lut. In other regions, the concentrations of these two pigments were quite low. The concentrations of Hex-fuco at other stations were lower than 11 ng/dm^3. But-fuco, the diagnostic pigment of chrysophytes, ranged from 0

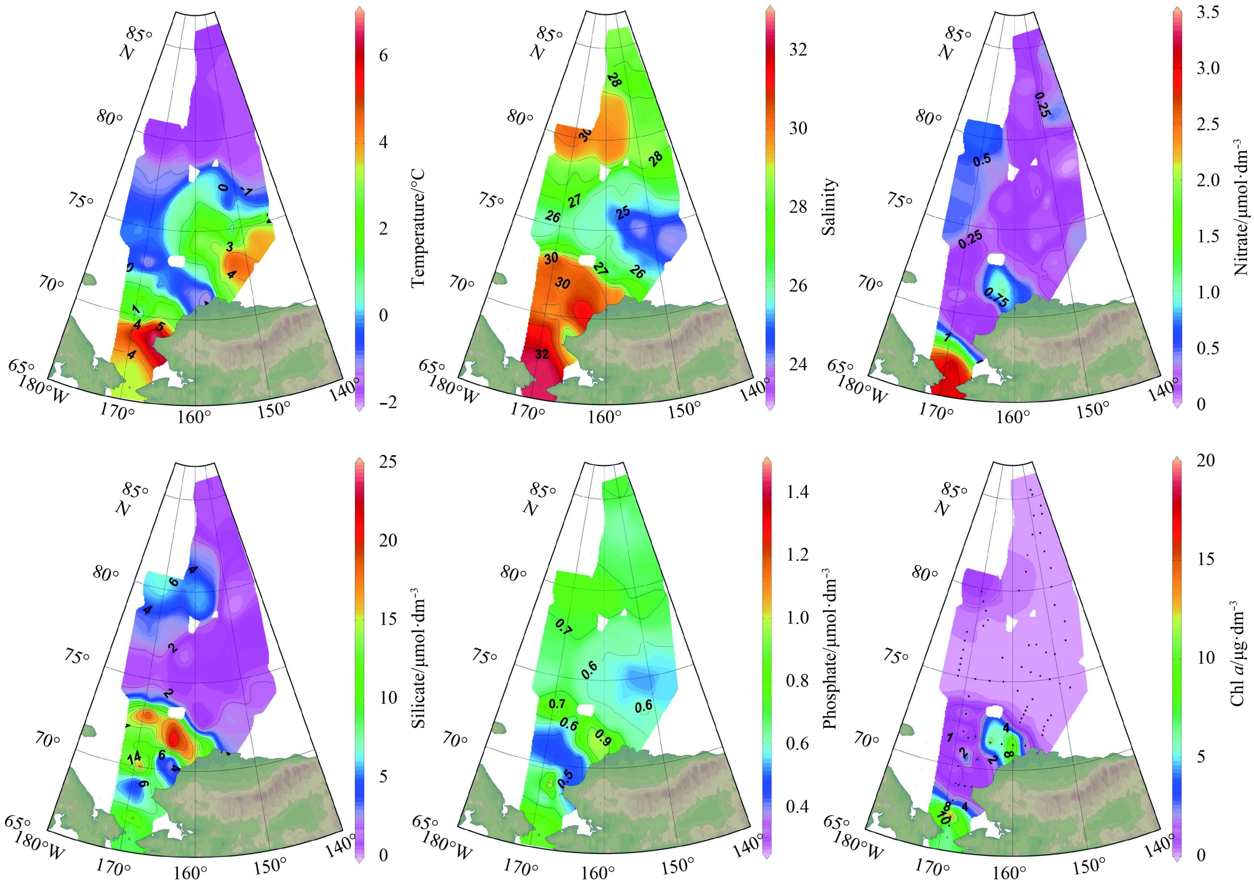

Fig. 3. Distribution of temperature, salinity, nutrients, and Chl *a* in the western Arctic Ocean in summer 2008.

to 51 ng/dm³. Pras, which is mainly produced by pico-size prasinophytes (Coupel et al., 2015), ranged from 0 to 27 ng/dm³. Chl *b*, the pigment dominating in chlorophytes and prasinophytes, ranged from 0 to 19 ng/dm³. The distribution of But-fuco, Pras and Chl *b* were similar to those of Peri and Allo. There are two high-value patches in our study area, Chukchi Shelf and MAP. Compared these two patches, the concentrations of But-fuco, Pras and Chl *b* in MAP were higher than those on the shelf. The results indicate that nano-phytoplankton plays a more active role in MAP than in other regions. Zea, the pigment produced by cyanobacteria, was observed on the Chukchi Shelf and MAP, but in other regions, especially on the shelf slope and the southern Canada Basin, the value was quite low. The concentrations of Zea ranged from 0 to 7 ng/dm³.

3.3 *Relative abundances of phytoplankton classes revealed by CHEMTAX*

The result of CHEMTAX analysis of phytoplankton community in the shelf showed that high abundance of diatoms (exceeding 70%) were detected in most part of the shelf except for the central shelf (Fig. 5). The contribution of diatoms significantly dropped in the central shelf (Stas R05, C31 C23 and C25), with the proportions of prasinophytes, dinoflagellates and chrysophytes increased. Besides, the relative percentage of diatoms in the surface water column of MAP only account for ca 30%, accompanied by increasing contributions of prasinophytes, chrysophytes and chlorophytes. In the basin, diatoms and prasinophytes co-dominated the phytoplankton community in the surface water, and chlorophytes and chrysophytes also contributed to total Chl *a*.

4 Discussion

4.1 *Environmental factors and phytoplankton community structure*

Environmental conditions significantly impact the phytoplankton community in the surface water. Previous study showed that the availability of nutrients ultimately controlled the annual limit of primary production (Carmack et al., 2004). The study region was divided into five provinces using K-means clustering method (SPSS statistical software) based on physical and chemical properties (salinity, temperature, depth, nitrate and phosphate). The phytoplankton Chl *a* biomass and phytoplankton community structure were discussed in these five provinces. First, the stations were classified into two provinces according to the water depth and topography, the Chukchi Shelf (Province I) and the off-shelf region. The off-shelf region was then divided into another four provinces using the K-means clustering method (SPSS statistical software) based on the physical and chemical properties. Thus, the whole study region was divided into five provinces (Table 2) for further discussion. These provinces can be well depicted using a temperature/salinity diagram (*T-S* diagram, Fig. 2).

Diatoms have been found to be distributed throughout the western Arctic Ocean. On the Chukchi Shelf, occupied by the high-salinity, nutrient-rich AnW, BSW and CSMW, the Chl *a* indicating biomass was high and diatoms dominated, with a maximum contribution to Chl *a* higher than 90%. However, in the region controlled by ACW on the Chukchi Shelf, the diatom abundance decreased to 22%, but the pico-and nano-phytoplankton abundances increased with a low Chl *a* concentration of 0.95 μg/dm³.

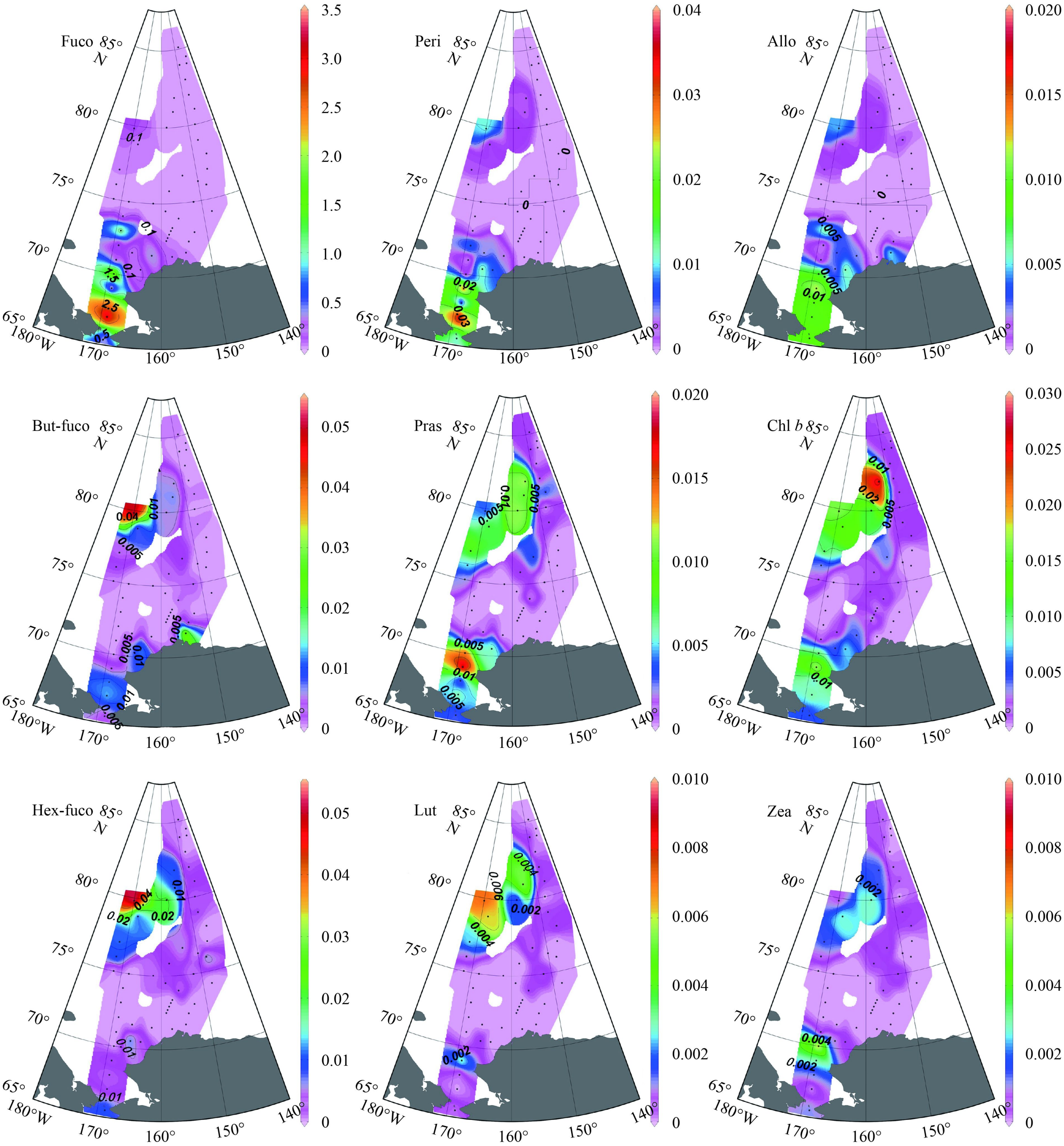

Fig. 4. Distribution of pigments in the western Arctic Ocean in summer 2008 (μg/dm^3).

Phytoplankton community structure and Chl *a* biomass were closely influenced by the physical and chemical characteristics of the upper layer water on the Chukchi Shelf. Nitrogen limitation has been reported in the western Arctic Ocean according to the Redfield ratio (Li et al., 2011). During the cruise, significant nitrogen limitation was observed over the whole study area in terms of the low nitrate concentration, low N/P and low N/Si ratios. That means the Pacific inflow carrying the DIN-rich water through the Bering Strait into the Chukchi Sea was the key factor to support the high primary productivity (PP) on the Chukchi Shelf. With the supply of the nutrients, especially nitrate, carried by the high-salinity, low-temperature AnW, high Chl *a* standing stocks were observed over the south and north-east parts of the Chukchi Shelf, and the phytoplankton was dominated by larger size microalgae (Fig. 6). On the other hand, in the region occupied by the nutrient-poor, high-temperature ACW, the Chl *a* biomass was low and nano- and pico-phytoplankton dominated (Fig. 6). Because of the strong connection between the trophic levels and the phytoplankton community, pigments have also been used to indicate the trophic status in previous studies (Claustre, 1994).

On the northern Chukchi Shelf, the surface water was modified by mixing with the northward AnW, BSW and ice-melting fresh water, formed the CSMW. CSMW shows the features of high nutrients and low temperature. Some of the water from the central shelf flows eastward, presumably carrying nutrients from the Herald Valley and the Central Channel to benefit not only the benthic community, but also its associated upper trophic levels of the north-east of the Chukchi Shelf (Weingartner et al., 2005). Furthermore, this region was the ice-edge area according to the ice cover conditions. Wave ice-edge upwelling may occur within

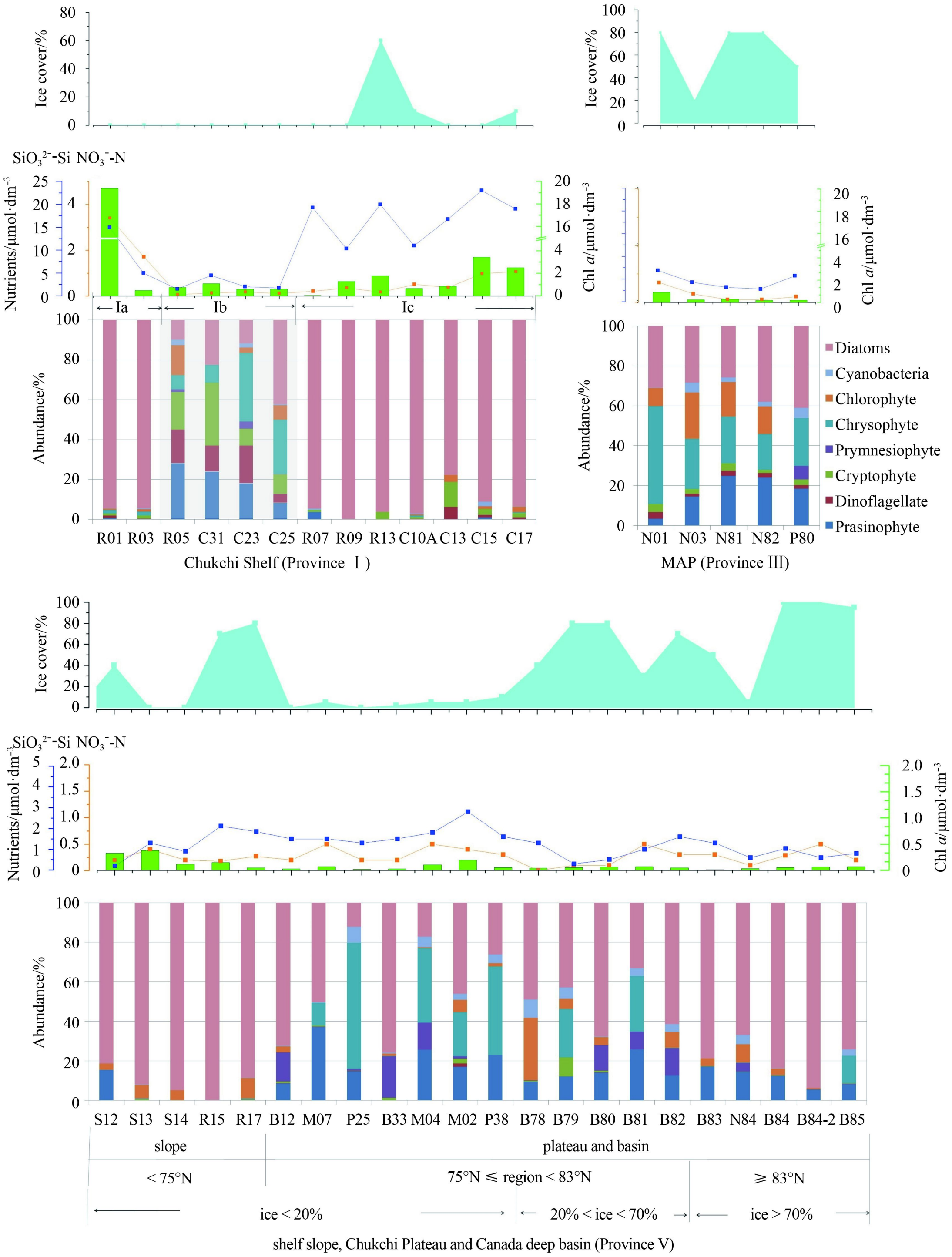

Fig. 5. Relative abundances of different phytoplankton community biomasses to TChl *a* and concentrations of nutrients, Chl *a* in Provinces I, III and IV. The ice cover conditions were showed at the top of each province. In the plot chart of nutrients and Chl *a*, the green columns indicate the concentrations of Chl *a* (μg/dm³). The orange and blue squares indicate the concentrations of NO_3^--N and SiO_3^{2-}-Si, respectively (μmol/dm³).

the embayments (Weingartner et al., 2005) and supply additional nutrients to the euphotic zone. That would enhance and support primary production in the upper layer (Carmack and Wassmann, 2006; Nishino et al., 2015). Extremely high silicate concentrations were observed and diatoms dominated in this region, with a relative abundance higher than 90% (Fig. 6). Our result of the diatom dominance in the shelf region was in agreement with the microscopy result (Joo et al., 2012), while the contribution of diatoms to the TChl *a* biomass was much higher than that of the microscopy result.

On the off-shelf region, including the shelf slope and the deep basin, the ocean trophic status impacted the Chl *a* biomass, and the hydrological characteristics and ice cover condition affected the phytoplankton community structure. Compared to the shelf region (Province I), the TChl *a* biomass was quite low, with a Chl *a* concentration lower than 0.5 μg/dm³ on the slope and deep

Table 2. Mean values of physical and chemical parameters of the surface water in the western Arctic Ocean (±SD)

Province		T/°C	S	PO_4^{3-}-P/ μmol·dm^{-3}	SiO_3^{2-}-Si/ μmol·dm^{-3}	NO_3^--N/ μmol·dm^{-3}	Chl a/ μg·dm^{-3}	Main phytoplankton
Chukchi Shelf (Province I, 66°–73°N)	Province I (n=20)	2.07±2.68	30.62±1.11	0.68±0.65	11.31±6.36	0.68±0.93	2.27±4.15	Ia and Ic: diatoms dominated; Ib: pico- and nano-size algae dominated
	Ia (n=3)	3.58±0.41	32.3±0.25	0.74±0.18	8.83±4.37	2.69±0.72	7.33±8.54	diatom (95%)
	Ib (n=6)	5.16±1.62	30.56±1.37	0.64±0.46	4.45±3.05	0.12±0.06	0.95±0.22	pico and nano-size algae (>62%) diatoms and dinoflagellates (35%)
	Ic (n=11)	0.03±1.17	30.19±0.47	0.68±0.22	15.73±4.05	0.44±0.33	1.60±1.18	diatoms (93%)
Border zone (from shelf to deep basin, Province II, 72°–75°N, n=9)		3.57±0.78	25.99±1.10	0.59±0.03	2.09±0.49	0.21±0.10	0.09±0.06	diatoms dominated (75%)
MAP (Province III, 78.8°–82°N, n=6)		−1.52±0.08	29.77±0.39	0.73±0.04	4.67±1.41	0.37±0.28	0.42±0.29	diatoms (33%), chrysophytes (28%), prasinophytes (17%), chlorophytes (13%)
South Canada Basin (IfB, Province IV, 74°–75.25°N, n=4)		2.36±1.27	24.20±0.32	0.53±0.02	1.63±0.31	0.18±0.13	0.02±0.01	-
Shelf slope-Canada Basin stations mainly>75°N (Province V, n=37)		−0.46±0.91	26.83±1.18	0.64±0.05	1.38±0.67	0.26±0.15	0.09±0.08	diatom (65%), prasinophytes (12%), chrysophytes (11%), prymnesiophytes (4%)

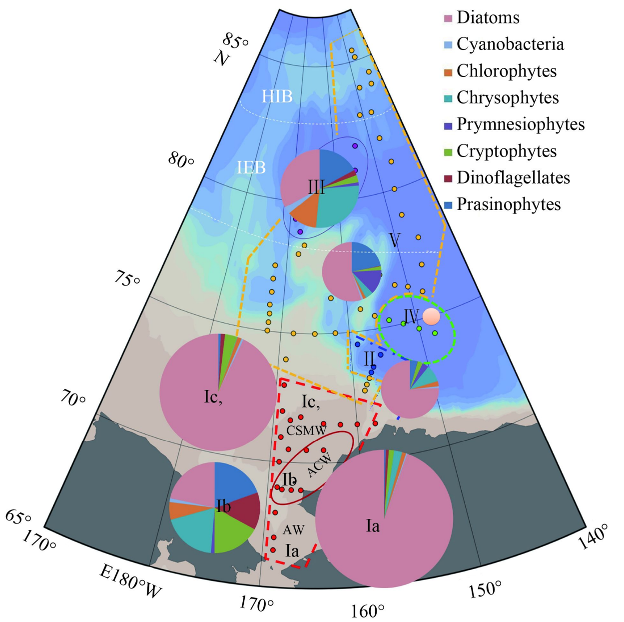

Fig. 6. Phytoplankton communities in the western Arctic Ocean in summer 2008. The five provinces (see Table 2) are shown with their Rome numbers. The pie charts show the mean relative proportions of the phytoplankton community by class level, and the size of the pie charts denotes the Chl a biomass. The white dotted line and characters refer to the ice cover conditions. The dividing lines of heavy ice basin (HIB, ice coverage >70%) and ice edge basin (IEB, 20%<ice<70%) are cited from Coupel et al. (2012).

basin (Provinces II, III, IV, and V). The abundance of diatoms to TChl a biomass decreased. On the other hand, the abundance of other pico- and nano-phytoplankton increased over the shelf slope and deep basin (Fig. 6). On the region of the shelf slope and the deep basin, both the ice conditions and nutrient concentrations profoundly influence the TChl a biomass, as well as the phytoplankton community structure.

The border zone between the Chukchi Shelf and the deep Canada Basin (72°–75°N) is an ice-free region, with relatively high temperatures of (3.57±0.78)°C but low salinity of 25.99±1.10. The salinity significantly decreased compared with the values on the Chukchi Shelf due to the influence of the ice-melt process and fresh water accumulation. Nutrient concentrations were much lower than that on the Chukchi Shelf, especially for SiO_3^{2-}-Si. In agreement with the low nutrient concentration, the TChl a biomass was low. The relative abundance of diatoms decreased outward along the shelf, while the abundances of prasinophytes, chlorophytes, chrysophytes and prymnesiophytes increased (Fig. 6). In previous studies on the shelf slope and the Beaufort Sea (BS), heterotrophic dinoflagellates were reported to play an important role in this province (Sherr and Sherr, 2007; Sherr et al., 2009). However, the pigment analysis in our study showed that peridinin, the diagnostic pigments of dinoflagellates, was under the detection limits in this province. Heterotrophic dinoflagellates and some dinoflagellates do not have peridinin (Zapata et al., 2012), so the contribution of dinoflagellates to TChl a biomass estimated using CHEMTAX analysis may underestimate its importance in this study.

The water mass occupied in MAP (Province III, 78.8°–82°N) was sea-ice melt water-relatively high salinity (MW-HS) with lower temperature ((−1.52±0.08)°C), higher salinity (>29). Higher nutrient concentrations were observed compared with the values at the other deep basin stations (Provinces II, IV and V), probably because nutrients were supplied by sea ice melt water. The result of ice-melting experiment in the central Arctic Ocean showed that concentration of dissolved inorganic nitrogen in the sea ice was about 3–4 times of that in the oligotrophic surface water, indicating melting ice could complement nutrient to the surface water (Zhuang et al., 2011). The phytoplankton community was mainly dominated by nano- and pico-algae, such as prasinophytes, chrysophytes and chlorophytes, which together contributed 58% to TChl a, while the diatom abundance decreased to 33%. Recent studies found that a pan-Arctic prasinophyte called *Micromonas*, which can adapt to cold water masses, constituted a large portion of the pico-algae (Lovejoy et al., 2007). In terms of the ice cover condition, MAP was located in the Marginal Ice Zone defined by Coupel et al. (2012) with ice cover ranging from 20% to 70%.. The ice melting process relieves the optical confinement. If the nutrients have not yet exhausted, the changing light conditions activate the biological activity and induce a higher

TChl *a* biomass in MAP compared to the northern Canada Basin, which is ice-covered year round. Though nano- and pico-algae are hard to detect by microscopy analysis, Coupel et al. (2012) identified prasinophytes (*Micromonas*), cryptophytes (*Cryptomonas* sp.) and chrysophytes (*Dinobryon belgica*) in the high latitude area of the Western Arctic Ocean. This supports our result of the phytoplankton community structure induced by pigment signals using CHEMTAX analysis.

In IfB, water mass was characterised as Low Salinity Water-Beaufourt Sea (LSW-BS). Fuco and Diadino were the main pigments, while most of other diagnostic pigments were under their detection limits. The results indicated that sea ice retreat in the deep Basin could increase the phytoplankton growth and increase the phytoplankton biomass to some extent, but the dominant phytoplankton changes from large-size diatoms to smaller pico- and nano-phytoplankton. With the ice retreating northward, a prolonged period of ice-free open ocean in the south Canada Basin was found, such as IfB. In general, sea ice retreat would increase the primary production due to relieving the light limitation (Arrigo, 2015). However, the depleting nutrients and strengthening stratification impoverish the upper layer and reduce the biomass in the surface water in IfB, causing surface water "desertification".

Province V includes all the other stations and most of the stations located north to 75°N and four stations located at south of the latitude 75°N on the Chukchi Shelf Slope. During the sampling period, a low-temperature low-salinity water mass hovered over this province, with the temperature ranging from –1.53°C to 1.74°C ((–0.46±0.91)°C) and the salinity ranging from 24.80 to 28.84 (26.83±0.94). The Chl *a* concentration was (0.07±0.05) μg/dm^3. The CHEMTAX result indicated that though diatoms dominated at the stations located at the north Canada Basin and Alpha Ridge with latitudes higher than 83°N, where the perennial sea ice was covered, the relative abundance of diatoms was significantly reduced to 55% of the TChl *a* biomass. This is consistent with the microscopy result (Coupel et al., 2012). The contributions of smaller phytoplankton to TChl *a* biomass increased, such as prymnesiophytes, prasinophytes, chlorophytes and cyanobacteria.

4.2 *Relationship between phytoplankton diagnostic pigments and Chl a*

In general, the biomass of phytoplankton can be indicated by the concentration of Chl *a*. The contribution of different phytoplankton communities to total biomass can be calculated by analyzing the correlation between Chl *a* and diagnostic photosynthetic pigments. The K-S test was processed to test the distribution of these photosynthetic pigments and the result showed that test distributions are normal. A binary linear regression analysis between different diagnostic pigments and TChl *a* showed significant correlations between Chl *a* and the pigments of Fuco, Peri, and Allo (Fig. 7). Pearson correlation coefficients were calculated for diagnostic pigments against TChl *a* using Statistical Product and Service Solution software (SPSS). As shown in Table 3, the Pearson correlation coefficients between Chl *a* and diagnostic pigments were Fuco, 0.990; Peri, 0.745; and Allo, 0.513, indicating significant positive correlations. However, there were no significant correlations between Chl *a* and other diagnostic pigments (Table 3, the regression figure of these pigments vs. Chl *a* was not shown here). r^2 between Chl *a* and these pigments were lower than 0.250, showing no significant correlation between them.

The results suggest that micro-algae contributed to the high marine biomass. It coincides with the results of previous research based on Chl *a* fraction analysis and microscopy analysis (Liu et al., 2011). The results of Chl *a* fractionation suggested that micro-algae (size>20 μm) did mainly contribute to the high biomass (Liu et al., 2011). Microscopy identification verified that the contribution of larger micro-size phytoplankton to the total biomass was much larger than that of the smaller sized taxa, while the pico- and nano-phytoplankton largely contributed to the cell abundance over the shelf and the basin (Joo et al., 2012; Coupel et al., 2012)

The highest Chl *a* value (~20 μg/dm^3) was encountered in the southern Chukchi Shelf because of algae bloom. However, in the Canada Basin, the surface water nutrients were extremely exhausted, together with a quite low Chl *a* concentration. This is coincident with the low level of total PP (Honjo et al., 2010; Lee et al., 2012). Considering that the high Chl *a* value in the shelf region would cover up the low pigment signal when performing a binary linear regression analysis between Chl *a* and other photosynthetic diagnostic pigments, the stations off the shelf with concentrations of Chl *a* lower than 1 μg/dm^3 were selected, excluding the effects of high Chl *a* due to the phytoplankton bloom on the Chukchi Shelf. The correlation analysis showed that Fuco and Peri have significant positive correlations with Chl *a* in the offshelf region, shelf slope and deep basin. The linear regression coefficient between Chl *a* and Fuco was 0.922 and between Chl *a* and Peri was 0.878, indicating a significant contribution of microalgae to the total phytoplankton biomass. But-fuco, Hex-fuco, Allo, Chl *b* and Lut also presented significant positive correlations to Chl *a*, with regression coefficients of 0.869, 0.838, 0.875, 0.564, and 0.695, respectively. This suggests that chrysophytes and chrypophytes may also have great contributions to the total biomass. However, Pras and Zea showed poor correlations to Chl *a*. Only considering the Chl *a* concentrations lower than 0.3 μg/dm^3 (another three stations were excluded), the regressions between these pigments and Chl *a* showed high positive correlations. This suggests that the contributions of phytoplankton species represented by these phytoplankton pigments to the total biomass or organic carbon are significant only at low biomass. Pras is the diagnostic pigment of Prasinophytes (Coupel et al., 2015), and Zea and Chl *b* are diagnostic pigments of Prochlorophytes and cyanobacteria. These phytoplankton communities are classified as pico-phytoplankton. Despite their small size, these organisms have been found to play important roles in terms of biomass and primary production in the open ocean, especially in the oligotrophic ocean (Cotner and Biddanda, 2002; Worden et al., 2004; Fouilland et al., 2004). These small size picophytoplanktons are more prone to mineralization and degradation in the upper ocean. The total biomass contributed by these algae groups was low, and it is not conducive to the effective output of organic carbon and sedimentary organic carbon burial efficiency.

The weak correlation between Zea and Chl *a* over the whole study area indicate that the biomass of cyanobacteria does not increase at the pace of the increasing total biomass. At high biomass conditions, the contribution of the cyanobacteria biomass to the total biomass is small. However, in the off-shelf region with a low Chl *a* condition, the contribution of the cyanobacteria biomass to the total Chl *a* biomass cannot be ignored. Previous research reported that nitrogen fixation cannot be ignored where nutrients were dramatically depleted, especially in the nitrogen limited Arctic waters (He et al., 2012). Results of binary linear regression analyses between Pras and both Zea and Chl *b* show high positive correlations with regression coefficients of 0.883

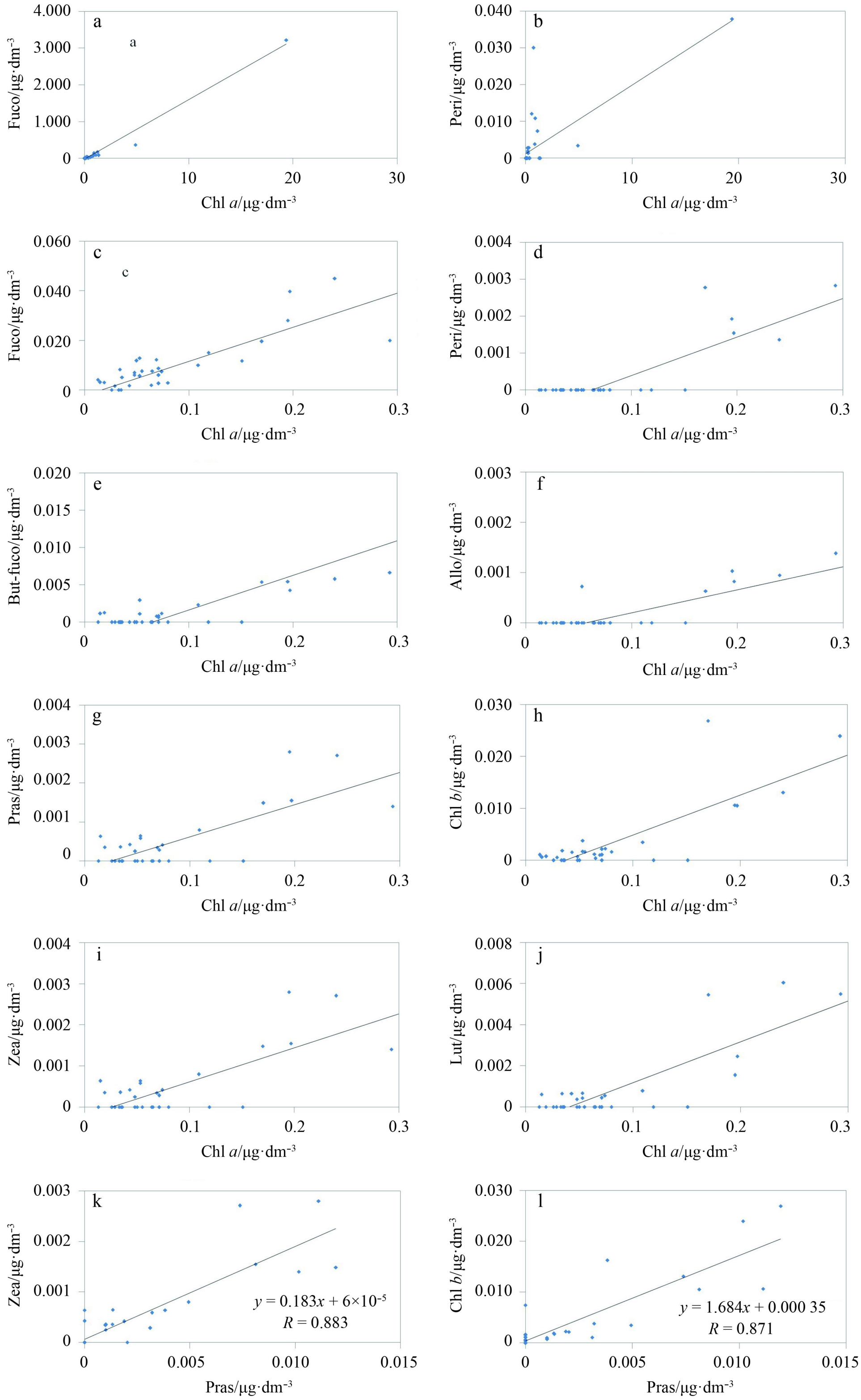

Fig. 7. Scatter diagrams of diagnostic pigments and these pigments to total Chl *a*. a and b. Data of the whole study region, and c–l. stations with Chl *a* concentrations lower than 0.3 μg/dm³.

and 0.871, respectively. Chl *b* exists in both Prasinophytes and Chlorophytes. The positive correlation between Chl *b* and Pras suggests that pico-prasinophytes are the major contributor to Chl *b*. If Zea is mainly extracted from cyanobacteria, the significant relationship between Pras and Zea indicates that these two picophytoplanktons have similar adaptabilities to the environment, and their co-existence promotes algae growth. Nitrogen fixation during the process of cyanobacteria growth may feed the growth of other pico-algae. While there is another possibility that most of the Zea comes from prasinophytes since the Zea/Pras ratio is 0.1 and consistent with the ratio observed in Micromonas pusilla by Latasa et al. (2004).

Table 3. Pearson correlation coefficients (r^2) (SPSS statistical analysis) between Chl *a* (μg/dm³) and other photosynthetic diagnostic pigments

	Fuco	Peri	But-fuco	Allo	Pra	Chl *b*	Zea	Lut	Hex-fuco
Total area (*n*=43)	0.990*	0.745*	0.213	0.513*	0.134	0.138	–0.099	–0.067	0.024
Off shelf (*n*=35)	0.922*	0.878*	0.869*	0.875*	0.342	0.564**	0.275	0.695*	0.838*
Off shelf, Chl *a*<0.3 (*n*=32)	0.826*	0.840*	0.845*	0.844*	0.826*	0.802*	0.761*	0.818*	0.740*

Note: * Correlation is significant at the 0.01 level; ** correlation is significant at the 0.001 level.

5 Conclusions

The characteristics of water masses significantly influence the phytoplankton communities and Chl *a* biomass in the western Arctic Ocean. Large phytoplankton species are associated with high nutrients Pacific inflow water controlled shelf regions and contribute to high Chl *a* standing stocks, whereas the relative abundances of smaller phytoplankton increased off shelf of the oligotrophic provinces that present low Chl *a* standing stocks, and its proportion was impacted by the ice cover conditions. Furthermore, a prolonged period of ice-free ocean will also reduce the biomass due to nutrient depletion and surface water freshening.

Compared to previous research on the phytoplankton community using microscopy and flow cytometry, using pigment signals to estimate the phytoplankton community may lost a portion of heterotrophic dinoflagellates, but the contribution of the autotrophic phytoplankton community to TChl *a* induced from pigments is consistent with the microscopy result. Its stability and repeatability make it useful for the long term study of the ecosystem response to sea ice retreat, especially in deep basin and ACW controlled regions where nano- and pico-phytoplankton have high proportions.

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Appendix:

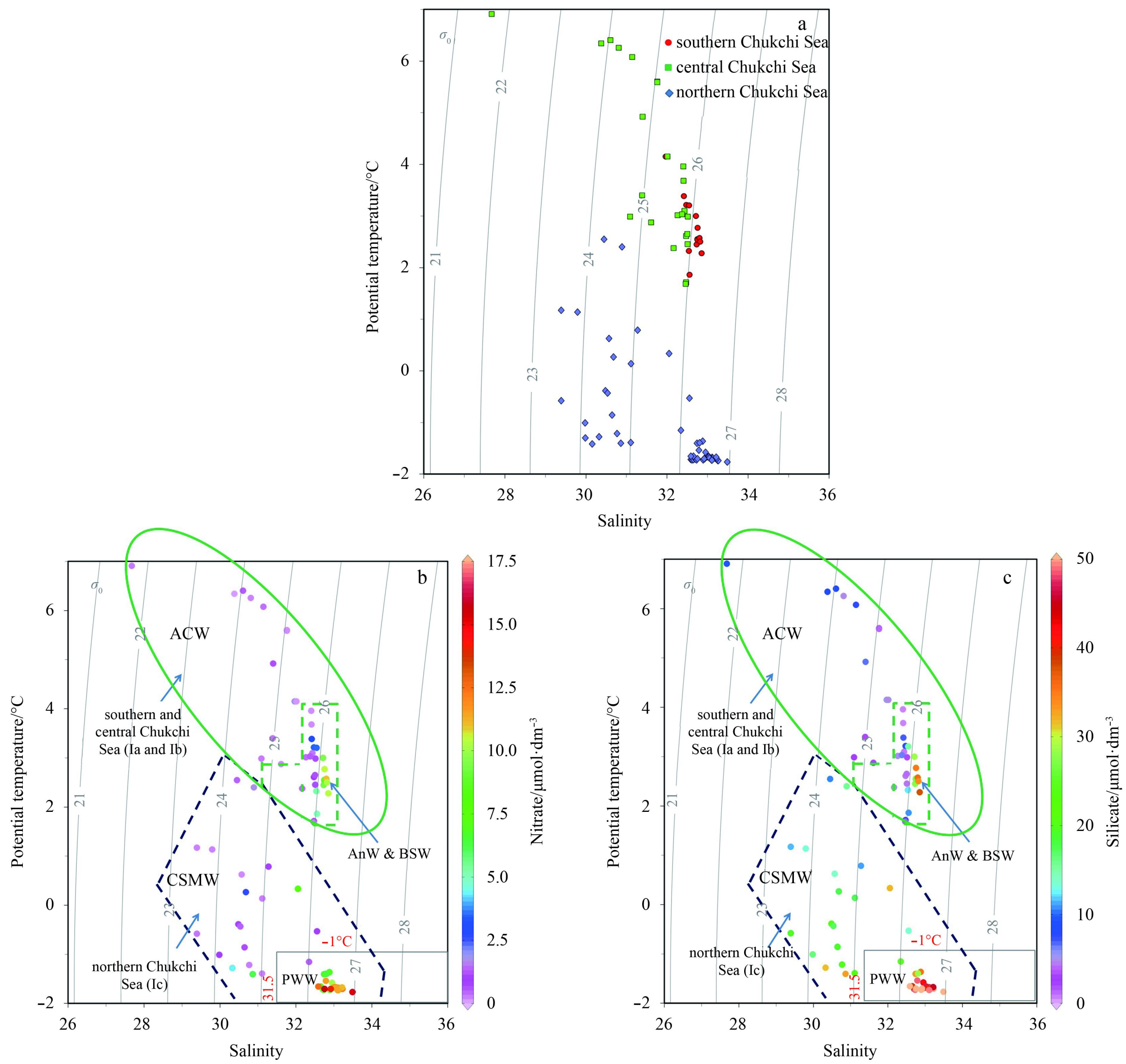

Fig. A1. Temperature/salinity/nutrient plot of water masses in the Chukchi Sea. Stations in the southern, central and northern Chukchi Sea with salinity and temperature features (a); concentrations of nitrate in different water masses (b) and concentrations of silicate in different water masses (c). The water masses are Pacific Winter water (PWW), Alaskan Coastal Water (ACW), Bering Shelf water (BSW), Anadyr Water (AnW), and Chukchi Shelf Modified Water (CSMW).