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Response of nutrients and the surface phytoplankton community to ice melting in the central Arctic Ocean

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Abstract During the fourth Chinese National Arctic Research Expedition cruise in summer 2010, a time-series observation was carried out to examine the response of nutrients and phytoplankton community in the ice-water interface to the ice melting ice in the central Arctic Ocean. Phosphate and silicate in the ice-water interface were rich relative to dissolved inorganic nitrogen (DIN), based on the Redfield ratio (16N:1P:16Si), suggesting that DIN was the potential limiting nutrient. DIN concentrations in the sea ice were about 3–4 times that in the surface seawater, indicating that melting ice delivered DIN to the surface water. Pigment analysis showed that fucoxanthin and chlorophyll *a* contribute to carotenoids and chlorophylls in particles. The mean concentrations of chlorophyll *c*, diatoxanthin, diadinoxanthin and fucoxanthin from 15 August to 18 August were 6 μ g·m⁻³, 22 μ g·m⁻³, 73 μ g·m⁻³ and 922 μ g·m⁻³, respectively, suggesting that diatoms dominated in the phytoplankton community composition. Furthermore, a notable enhancement in fucoxanthin and chlorophyll *a* during a large-scale ice melting was likely attributed to senescent diatoms released from the bottom sea-ice as well as phytoplankton diatoms growth in the water column due to the input of nutrients (i.e., DIN) and reducing light limitation from melting ice. Temporal distribution patterns of prasinoxanthin and lutein differed from fucoxanthin, indicating that the response of green algae and diatoms to ice melting were different.

Keywords Ice melting, photosynthetic pigments, nutrient limitation, Arctic

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0 Introduction

Seasonal ice retreat and melting in polar regions are important factors in regulating food web structure and primary production regimes by modulating salinity-based stratification and light availability^[1-2]. As sea-ice melts, an ice-algal dominated ecosystem is being gradually replaced by the dominance of pelagic algae. In marginal ice zones and polynya, a rapid onset of salinity stratification driven by less saline meltwater is a key factor triggering phytoplankton blooms^[3]. Sea-ice primary production^[4] and nutrient concentrations in the sea ice are inconsistent with that seen in surface seawater^[5]. This could have considerable influence on algal blooms by seeding the bloom and changing the nutrient balance in the icewater interface^[6-7]. Sea-ice disappearance has a large impact on marine ecosystems in the Arctic in terms of phytoplankton community structure, ecological function and organic carbon accumulation^[8-9].

Primary production and phytoplankton communities in the Arctic Ocean are primarily controlled by the

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extent of ice cover^[10]. Arctic sea-ice coverage has undergone dramatic changes over the last few decades^[11], leading to significant changes in the ecosystem $environment^{[12-13]}$. However, little is known about the mechanisms by which sea-ice melting affects ecosystems and nutrient dynamics in the water column in the Arctic. During the fourth Chinese National Arctic Research Expedition cruise in summer 2010, a time-series experiment was conducted at a ice station in the central Arctic where fast ice melting was occurring. Nutrients (nitrate+nitrite, phosphate and silicate) and particle pigments in ice cores and the ice-water interface were determined to track time-series changes in nutrient status and photosynthetic pigments in the ice-water interface. This will help us to better understand the impact of ice melting on nutrient status, phytoplankton biomass and community composition in the ice-water interface.

1 Materials and methods

1.1 Study sites and sampling

From 9 August to 18 August 2010, a time-series observation was carried out at a floating ice station in the Canada Basin (drift speed of about 8 km·d⁻¹, estimated from daily changes in latitude and longitude) (Figure 1a, 1b). A 1 m-diameter ice-hole was dug in order to collect surface seawater at an interval of 1–2 d. Ice cores were taken at the same site using a Mark II ice auger on 15 August and 17 August. The ice cores were sectioned at 20 cm intervals to analyze the vertical profile of nutrients. The hydrological parameters (i.e., salinity and tempera-

ture) were determined by an RBR marine CTD XR-620 (Canada). Salinity from 9 August and 10 August was estimated from ship-based surface sensor since the RBR data was missing for these dates. Nutrient samples (nitrate, nitrite, silicate, phosphate) for ice cores and seawater were filtered through cellulose acetate membranes (0.45 μ m) and measured immediately using a continuous flow analyzer (Skarlar, Holland, Breda). The detection limits were 0.1 μ mol·L⁻¹ for NO₃⁻+NO₂⁻, 0.1 μ mol·L⁻¹ for SiO₃²⁻ and 0.03 μ mol·L⁻¹ for PO₄³⁻, respectively.

1.2 Pigments

4 L of water were filtered through GF/F filters under gentle vacuum pressure (<0.5 MPa) and dim light conditions, and then stored at -80° C until pigment analysis. Filtered samples were extracted with 3 mL of 100% HPLC-grade methanol at -20° C for 1 h, sonicated in an ice-bath for 30 s and extracted again for 1 h. The extracts were filtered through 0.22 μ m microporous membrane and were premixed with 28 mmol·L⁻¹ tetrabutyl ammonium acetate (TBAA) (1:1 v/v) before injection. 200 μ L mixing extract was injected into the HPLC system for pigments analysis.

Pigment was analyzed by an HPLC (Waters 600) system equipped with an Eclipse SDB C8 column (150 mm×4.6 mm, 3.5 μ m) and photodiode array detector (Waters 2998) using a solvent system proposed by Van Heukelem and Thomas^[14] consisting of solvent A (methanol) and solvent B (methanol and TBAA, 70:30 v/v), at a flow rate of 1 mL·min⁻¹ and a column temperature of 45°C. The gradient systems used (min, A%,



Figure 1 (a) Sampling sites in the high-latitude Arctic and (b) drift route of sea-ice (dates separated by solid and dashed lines).

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B%) was as follows: (0, 90, 10), (36, 5, 95), (41, 5, 95), (45, 90, 10), (60, 90, 10).

Pigments were qualified and quantified by absorption wavelengths at 450 nm for chlorophylls and

carotenoids. The peaks were identified by comparing their retention time and spectra with those of pigment standards (DHI water and environment, Demark). Pigments measured were listed in Table 1.

Table 1 Major pigments in algal groups and abbreviation recommended by SCOR^[15]

Pigments	Abbreviation	Algal group
A. Chlorophylls		
Chlorophyll a	Chl a	Allo photosynthetic microalgae (except prochlorophytes)
Divinyl chlorophyll a	DV Chl a	Prochlorophytes
Chlorophyll b	Chl b	Green algae: chlorophytes, prasinophytes
B. Carotenoids		
Alloxanthin	Allo	Cryptophytes
19-Butanoyloxyfucoxanthin	But-fuco	Premnesiophytes & chrysophytes
β, β -carotene	β, β -car	All algae except cryptophytes
Diadinoxanthin	Diadino	Diatoms, dinoflagellates, prymnesiophytes, chrysophytes
Neoxanthin	Neo	Green algae: chlorophytes, prasinophytes
Fucoxanthin	Fuco	Diatoms, prymnesiophytes, chrysophytes
19'-Hexanoyloxyfucoxanthin	Hex-fuco	Premnesiophytes
Lutein	Lut	Green algae: chlorophytes, prasinophytes
Peridinin	Perid	Dinoflagellagtes
Prasinoxanthin	Prasino	Prasinophytes
Diatoxanthin	Diato	Diatoms, dinoflagellates, prymnesiophytes, chrysophytes
Violaxanthin	Viola	Green algae: chlorophytes, prasinophytes
Zeaxanthin	Zea	Cyanophytes & Prochlorophytes

1.3 Relative contributions of different size classes of algae to chlorophyll a

A method proposed by Claustre^[16] and further developed by Uitz et al.^[17] by using 7 diagnostic pigments to reveal phytoplankton taxa, was used to estimate the relative contributions of three size classes of phytoplankton (micro 20–200 μ m; nano 2–20 μ m; pico 0.2–2 μ m) to total chlorophyll *a*. The empirical equations were as follows:

 $F_{\text{micro}} = (1.41 \text{ Fuco}+1.41 \text{ Peri})/\text{wDP}$ $F_{\text{nano}} = (0.60 \text{ Allo}+0.35 \text{ But-fuco}+1.27 \text{ Hex-fuco})/\text{wDP}$ $F_{\text{pico}} = (0.86 \text{ Zea}+1.01 \text{ T Chl } b)/\text{wDP}$

Where the wDP is the sum of these concentrations:

wDP= 1.41 Fuco+1.41 Peri+0.60 Allo+0.35 Butfuco+1.27 Hex-fuco+0.86 Zea+1.01 T Chlb

This method was often used to study phytoplankton community structure and estimate the contributions of phytoplankton to particulate organic carbon (POC) in the water column.

2 Results and discussions

2.1 Nutrient status in sea-ice

Previous studies suggested nutrient concentrations in sea

ice fluctuate over time. Nutrient concentrations in firstyear ice in many cases corresponded to those in surface seawater, but differed in multi-year ice^[5,18]. Our research was focused on the central Arctic Ocean with perennial ice, where sea ice was characterized by oligotrophic conditions. The vertical profiles of nutrient concentrations in the ice cores collected on 15 August and 17 August were presented in Figure 2. The mean concentrations of $NO_3^- + NO_2^-$, PO_4^{3-} and SiO_3^{2-} in the ice core on 8/15 were 0.46±0.22 μ mol·L⁻¹, undetectable (<0.03 μ mol·L⁻¹) and 0.51±0.15 μ mol·L⁻¹ respectively, and on 8/17 the concentrations were 0.77±0.39 μ mol·L⁻¹, undetectable and 0.45±0.16 μ mol·L⁻¹.

2.2 Time-series changes in nutrients and pigments in the surface seawater beneath ice floes

2.2.1 Hydrological conditions

Major processes influencing surface seawater salinity beneath ice floes included the input of less saline meltwater and exchange with the external water mass. The changes in temperatures and salinities in the surface seawater during the study period are presented in Figure 3. From 11 August to 12 August, a slight decrease in temperature and increase in salinity were observed.

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Figure 2 Vertical profiles in nutrient concentrations in sea-ice cores collected on 15 and 17 August.

The average salinity of 30.1 both on 9 August and 10 August was recorded by ship-based surface sensor (data not shown), suggesting that high salinity water invaded the study area between 9 August and 12 August Surface salinity significantly decreased by 0.2 from 14 August to 17 August, due to ice melting. Subsequently, salinity slowly rose from 17 August to 18 August, but decreased from 18 August to 19 August.



Figure 3 Changes in temperature and salinity measured with RBR at 3 m from 11 to 19 August.

2.2.2 Nutrient distribution

As in the other oceans in the world, nitrogen limitation constrains primary production in the Arctic Ocean^[19].

Surface seawater beneath the ice-water interface was considered to be the most nitrogen limited in the Arctic Ocean with minimum nutrients in the stratified water $column^{[20]}$. The mean concentrations of nitrate + nitrite, phosphate and silicate during 10 d study period were 0.18 μ mol·L⁻¹, 0.69 μ mol·L⁻¹ and 4.78 μ mol·L⁻¹, respectively (Figure 4). Phosphate and silicate were relatively high compared to DIN. The average Si/N ratio was 27:1 and the mean concentration of nitrate + nitrite was lower than 0.2 μ mol·L⁻¹, suggesting that DIN was the potential limiting nutrient in the surface water. DIN concentration in the sea ice was about 3-4 times greater than that measured in the surface water, suggesting that melting ice delivered DIN to the surface water. Since sea ice was relatively deficient in phosphate and silicate, the meltwater input diluted the concentrations of these two nutrients in the ice-water interface.

All nutrients displayed a decreasing gradient from 11 August to 13 August and phosphate in the ice-water interface declined at a rate that was about 2 times higher than that of inorganic nitrogen, which deviated from the Redfield ratio of 16N:1P. A reduction in nutrient concentrations in the surface water was primarily caused by three processes: (i) Biological utilization; (ii) dilution by melting ice; (iii) exchange with the low-nutrient water mass. Low chlorophyll a levels measured during 9 August to 13 August could not account for such a high consumption of nutrients. During this period, salinity did not decrease, so dilution by meltwater made only a minor contribution to the decrease in nutrient concentrations. Therefore, dilution by an external low-nutrient water mass was the most likely cause for a reduction in nutrient concentrations. From 14 August to 16 August, a rapid decrease in salinity, accompanied by a reduction in silicate, indicated that a dramatic ice melting event occurred. As a result, meltwater carried DIN into the seawater, resulting in a significant increase in DIN on 14 August and also diluted silicate in the water column. The input of DIN from meltwater triggered an algal bloom, as indicated by a significant increase in fu
coxanthin and chlorophyll a concentrations on
 $15~{\rm Au}\textsc{-}$ gust Nutrients considerably decreased because of algal utilization from 14 August to 15 August, with a reduction of 0.17 $\mu \mathrm{mol}\cdot\mathrm{L}^{-1}$ for $\mathrm{NO}_3^-\mathrm{+}\mathrm{NO}_2^-,\,0.10\;\mu\mathrm{mol}\cdot\mathrm{L}^{-1}$ for PO_4^{3-} and 0.42 μ mol·L⁻¹ for SiO₃²⁻. Subsequently, phosphate increased during 15 August to 17 August probably due to its faster regeneration. In contrast, during this period, DIN decreased continuously. DIN regenerated slower than phosphate and since it was the limiting nutrient, DIN was utilized by phytoplankton and bacteria as soon as it was released. During this period, if the nutrients in surface water were entirely contributed by melting ice, silicate and phosphate in seawater should be significantly reduced, coupled with a slight increase in



Figure 4 Changes in nutrient concentrations and the photosynthetic pigments fucoxanthin and chlorophyll *a* during 9 August to 18 August.

nitrate. However, the results turned out to be the opposite, indicating there were some extra nutrient inputs. A major factor leading to the elevated phosphate might be nutrient mineralization, while increasing silicate and decreasing nitrate mainly resulted from the slowed ice melting and increasing proportion of seawater. During 17 to 18 August, a rise in DIN and a decrease in salinity reflected the input of the ice melting.

2.2.3 Pigments distribution and phytoplankton community composition

Pigment analysis revealed that fucoxanthin and chlorophyll *a* were the main contributors of carotenoids and chlorophylls in algal particles. Time-series changes in fucoxanthin and chlorophyll *a* were shown in Figure 4. In the first phase (9 to 13 August), these two pigments were low, with an average value of 12 μ g·m⁻³. In the second phase (15 to 18 August), the mean concentration of chlorophyll *c*, diatoxanthin, diadinoxanthin and fucoxanthin were up to 6 μ g·m⁻³, 22 μ g·m⁻³, 73 μ g·m⁻³ and 922 μ g·m⁻³, respectively, indicating diatom dominance in the phytoplankton community.

A notable enhancement of fucoxanthin was observed in the second phase (15 to 18, August), however, chlorophyll *a* increased disproportionately with fucoxanthin. The chromatogram of pigment extract on 15 August is shown in Figure 5. The low concentrations of ambient DIN (as the limiting nutrient) and silicate could not support a diatom bloom in the oligotrophic ice-water interface, although ice melting resulted in an increase in nutrients (i.e., DIN), which triggered diatom growth. Hence, such high fucoxanthin concentration was more likely due to diatoms released from melting sea-ice rather than diatom blooms. It is known that ice algae primarily inhabit brine channels at the bottom of the sea-ice, reach



Figure 5 Chromatogram analysis of pigments on 15 August (X-axis represents retention time; Y-axis represents absorption intensity, λ =405 nm).

a biomass peak in spring due to accumulation^[21-22] and are released as aggregates during melting^[23]. Furthermore, yellow crumb-like materials were frequently found in the water column, which were speculated to be icealgae aggregates.

2.3 Phytoplankton communities beneath the icewater interface

Some diagnostic pigments displayed a significant trend in spite of low concentrations (Figure 6). Prasinoxanthin, an indicator of green algae, and lutein, exhibited different temporal patterns from fucoxanthin (Figure 4 and Figure 6), indicating that green algae (including prasinophyta and chlorophyta, which were abundant in under-ice melting $ponds^{[24]}$), differed from diatoms in response to ice melting. Green algae declined due to dilution by meltwater. In contrast, the mean abundance of peridinin during 15 August to 18 August was 5 times that measured during 9 August to 13 August, suggesting dinoflagellates abundance increased in response to ice melting, since dinophyta were released from sea ice. The other diagnostic pigments, such as But-fuco, Hex-fuco, Allo and zea, were low ($<1 \,\mu g \cdot m^{-3}$), indicating a minor contribution of golden-brown flagellates (including prymnesiophytes and chrysophytes), cryptophyta and cyanobacteria. Divinyl chlorophyll a was undetectable in all samples, implying an absence of prochlorophytes in the study area.



Figure 6 Time series changes in the concentrations of diagnostic pigments.

The relative contribution of three size classes of algae revealed that the largest phytoplankton (microphytoplankton) dominated the phytoplankton community, with the contribution of $F_{\rm micro}$ between 64% and nearly 100% (Figure 7). Previous studies also concluded that large algae contributed 77%–91% of total pigment biomass beneath the sea-water interface^[25]. Picophytoplankton, which mainly consisted of green algae, accounted for 1%–30% of total pigment biomass and was more abundant than nanophytoplankton during 9 August to 13 August.



Figure 7 The relative contribution of three size classes of phytoplantkon to total chlorophyll *a* biomass.

3 Conclusions

During the sampling period, in the ice-water interface, DIN was the potential limiting nutrient as indicated by low concentrations of DIN and low N:P and N:Si ratios. In the sea ice, DIN was 3–4 times that in the surface water, hence, large-scale ice melting led to an increase in DIN concentration in the water column.

Fucoxanthin (Fuco) and chlorophyll a (Chl a) contributed to carotenoids and chlorophylls in algal particles, suggesting that diatoms dominated the phytoplankton community composition. A remarkable increase in fucoxanthin during the second phase after ice melting resulted from releasing the senescent diatoms inhabiting the bottom of sea ice and the diatoms growing in the surface seawater. Prasinoxanthin and lutein exhibited different temporal pattern from fucoxanthin.

A large input of organic matter and ice algae from melting ice altered the highly sensitive ecosystem at the sea-ice interface either directly or indirectly. Microphytoplankton (diatoms) dominated in the surface seawater at the beginning of the ice melting, with the contribution of Fmicro between 64% and 100%. Picophytoplankton, which mainly consisted of green algae, accounted for 12%-30% of total pigment biomass. Acknowledgments This study was supported by the National Natural Science Foundation of China (Grant nos. 41076135, 41003036), the Scientific Research Fund of the Second Institute of Oceanography, SOA (Grant no. JG200820), the Marine Scientific Research Projects (Grant no. 200805095) and the project "Fourth Chinese National Arctic Expedition". We greatly appreciate the help from all crews of the R/V *XUE LONG* icebreaker. Thanks to Kang Jianhua at Third Institute of Oceanography, SOA for providing ice cores samples.

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