

The composition and origination of particles from surface water in the Chukchi Sea, Arctic Ocean

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Abstract Suspended particle samples were collected at 11 stations on the shelf and slope regions of the Chukchi Sea and the central Arctic Ocean during the fifth Chinese National Arctic Research Expedition (summer 2012). The particle concentration, total organic carbon (TOC), total nitrogen (TN) and the isotopic composition of the samples were analyzed. The suspended particle concentration varied between 0.56 and 4.01 mg·L⁻¹; the samples collected from the sea ice margin have higher concentrations. The organic matter content is higher in the shelf area (TOC: 9.78%–20.24%; TN: 0.91%–2.31%), and exhibits heavier isotopic compositions ($\delta^{13}\text{C}$: –23.29‰ to –26.33‰ PDB; $\delta^{15}\text{N}$: 6.14‰–7.78‰), indicating that the organic matter is mostly marine in origin with some terrigenous input. In the slope and the central Arctic Ocean, the organic matter content is lower (TOC: 8.06%–8.96%; TN: 0.46%–0.72%), except for one sample (SR15), and has lighter isotopic compositions ($\delta^{13}\text{C}$: –26.93‰ to –27.78‰ PDB; $\delta^{15}\text{N}$: 4.13‰–4.84‰). This indicates that the organic matter is mostly terrestrially-derived in these regions. The extremely high amount of terrigenous organic matter (TOC: 27.94%; TN: 1.16%; $\delta^{13}\text{C}$: –27.43‰ PDB; $\delta^{15}\text{N}$: 3.81‰) implies that it was carried by transpolar currents from the East Siberian Sea. Material, including sea ice algae, carried by sea ice are the primary source for particles in the sea ice margins. Sea ice melting released a substantial amount of biomass into the shelf, but a large amount of detrital and clay minerals in the slope and the central Arctic Ocean.

Keywords Chukchi Sea, particles, organic matter, stable isotopes

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1 Introduction

The Arctic Ocean is almost completely surrounded by the Eurasian and the North American continents. It is connected to the Pacific Ocean via the Bering Strait and to the Atlantic Ocean through the Fram Strait. Shallow continental shelf regions account for ~50% of the total surface area of the Arctic Ocean, which makes it unique among the world's oceans. The Chukchi Sea is a marginal sea of the Arctic Ocean. It is bounded on the west by the East Siberian Sea, to the east by Alaska and the Beaufort Sea, and to the north by the Chukchi Plateau and Canadian Abyssal Plain. The Bering Strait is its southernmost limit and connects it to the Bering Sea and the Pacific Ocean. Its surface currents include the warm and relatively saline water originating from the

narrow Bering Strait between Alaska and Siberia, and the Transpolar Current that inputs large volumes of fresh water and terrigenous material from the East Siberian, Laptev and Kara Seas. The sea ice cover in the Arctic Ocean reaches its maximum in March, and minimum in September^[1]. Sea ice in the Chukchi Sea is seasonal with melting starting in July; it is covered completely in December^[2].

Global warming in the Arctic is decreasing the extent and thickness of sea ice cover, increasing the ice free season in the Arctic Ocean. The changing climate is also altering the timing and magnitude of river discharge and coastal erosion, and the delivery of terrigenous organic carbon to the Arctic Ocean. Recently, many scientists (funded by different countries) investigated global changes in the Arctic Ocean. For example, the US National Science Foundation (NSF)-funded Shelf–Basin Interaction (SBI) Studies project aimed to provide a thorough understanding of the current status of the Chukchi/Beaufort ecosystems with a regional focus on

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the outer shelves and slopes. Additional projects included the Russian–American Long-term Census of Marine Life (RUSALCA) and Bering Strait Environmental Observatory (BSEO). The Chinese National Arctic Research Expedition also has sponsored five expeditions since 1999. Suspended particle sources and composition could therefore be of great interest to scientists because it aids in the understanding of depositional processes, primary production and carbon cycling.

In the Chukchi Sea, organic matter mainly derives from the marine environment, but contains contributions from the Yenisei, Ob and Yukon rivers^[3-4]. Primary production from sea ice contributes significantly to biogeochemical cycles in Arctic waters and the stable isotopic composition of the ice-derived material differs from pelagic-derived material. This difference can be used to assess cryopelagic–benthic coupling^[5-11]. The influence of sea ice contribution on the biochemical cycles and depositional processes has been a topic of interest over the last decade^[9-11].

In the western Arctic Ocean, research on marine biology, chemical oceanography and marine geology has been carried out by Chinese scientists since the late 1990s. Some of the publication topics included: the short-term flux and composition of particulate organic matter^[12]; phytoplankton spatial variation^[13]; chlorophyll-*a* and primary productivity^[14]; characteristics of the water chemistry^[15]; organic carbon burial efficiency^[16]; organic isotopic composition in surface sediments; sedimentary environmental changes^[17] and paleoceanography^[18].

The primary objectives of our study were to understand the composition and origin of surface particles and evaluate the sea ice contribution to these particles. To this end, we analyzed particle concentration, viewed the composition, and traced the organic matter origin based on its elemental (TOC and TN) and stable isotope ($\delta^{13}\text{C}$ and $\delta^{15}\text{N}$) composition.

2 Materials and methods

2.1 Samples

Suspended particle samples were collected at 11 stations on the shelf and slope regions of the Chukchi Sea and the central Arctic Ocean during the 5th Chinese National Arctic Research Expedition (July–September 2012; Table 1). Samples were collected from stations R02, CC2, CC5, CC7, R04 and R05 in July. The station R05 is located on the sea ice margin, while the others are located in the open sea. Samples were collected from stations ICE01, ICE05, SR18, SR15 and M01 in late August–September. Station M01 is located in the open sea, while the others are located on the sea ice margin (Figure 1).

The surface (<1 m) water samples were filtered on board the ship through a pre-weighed and pre-combusted (400°C, 4 h) Whatman glass fiber filter (GF/F; 0.7 μm). After filtration, the filters were washed 3 times with 20 mL of deionized water to remove salt and then stored (-20°C). After the expedition, the filter samples were freeze-dried and re-weighed to determine the particle concentration.

The filters were exposed for 24 h to concentrated HCl fumes, then washed with deionized water to remove inorganic carbon, and finally analyzed for total organic carbon (TOC), total nitrogen (TN), $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$.

2.2 Organic matter elemental and stable isotopic compositions

TOC, TN, stable carbon and nitrogen isotopic compositions were measured on a Thermal-Finnigan Delta plus AD mass spectrometer ConFlo III interfaced with an elemental analyzer (EA112). Organic standards (USGS-24, GBW4408 and IAEA N1) had a precision of $\pm 0.2\%$ for $\delta^{13}\text{C}$ and $\pm 0.3\%$ for $\delta^{15}\text{N}$ and the relative analytical reproducibility was 20%. For abnormal results, parallel samples were analyzed to confirm the data.

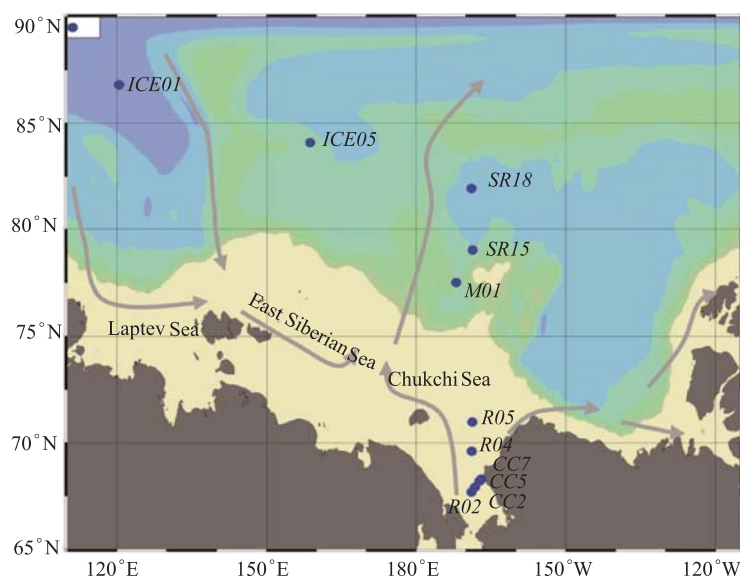


Figure 1 Location of sampled stations and distribution of surface currents (gray line^[19]). The arrows indicate current directionality.

2.3 SEM-EDS

Scanning electron microscopy (SEM) was performed with a Zeiss Ultra 55 coupled to energy dispersive X-ray spectroscopy (EDS; OXFORD X-MAX 20); Emission voltage: 15 kV; Pt film.

3 Results

3.1 Surface water particle concentration

The surface water particle concentrations varied between 0.56 and 4.01 mg·L⁻¹ with an average value of 1.54 mg·L⁻¹. Samples collected from the sea ice margin have higher concentrations, and the samples collected from onshore are higher than those offshore. In the shelf area, the particle concentrations nearer the coast (stations R02, CC2, CC5 and CC7) are clearly different than further offshore (station R04). Additionally, the particle concentration is 2.5 times higher at the sea ice margin (station R05) than in open water (station R04). On the slope and in the central Arctic Ocean, most of the stations located at sea ice margins exhibit higher particle concentrations, except for station M01, which is located in the open sea (Table 1 and Figure 1). The particle concentration distribution suggests that terrigenous material carried by sea ice is the main particle source.

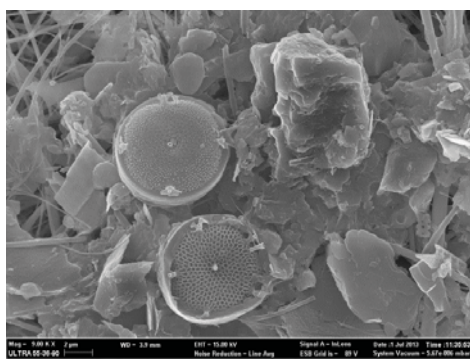
3.2 Particle composition

The samples collected from stations R02, CC7, R05, M01,

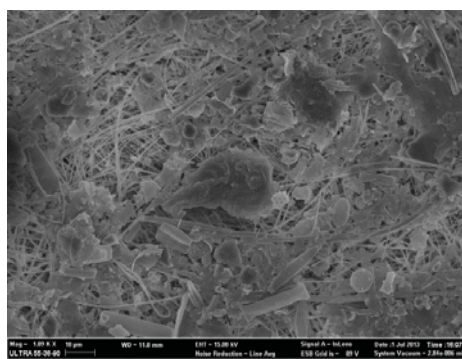
Table 1 The suspended particle concentration of the Chukchi Sea and the central Arctic Ocean

No.	Stations	Depth/m	Concentration/ (mg·L ⁻¹)	Regions	Sampling date
1	R02	43.5	1.05		20120718
2	CC2	51.1	1.24		20120718
3	CC5	40.8	1.05		20120719
4	CC7	28.9	0.83	Chukchi Shelf	20120719
5	R04	45.3	0.56		20120719
6	R05	36.9	1.41		20120720
7	M01	2277	0.68		20120906
8	SR15	3090	1.67	Chukchi Slope	20120905
9	SR18	3393	1.71		20120904
10	ICE05	3180	4.01	the central	20120902
11	ICE01	4385	2.78	Arctic Ocean	20120829

SR15 and ICE05 were examined by scanning electron microscopy (SEM) to determine the particle composition. In general, the particles were composed of well-preserved biomass (algae), bio-debris, detrital and clay minerals. Spatial variations were observed in the particle composition because higher biomass content and fewer detrital and clay minerals were found in the shelf stations (R02, CC7 and R05). Biomass included disco, bally, rosary and leaf-like algae with sizes generally <20 µm, and preserved microstructures formed *in situ* (Figures 2a–2h).



a Algae and detrital minerals (station CC5)



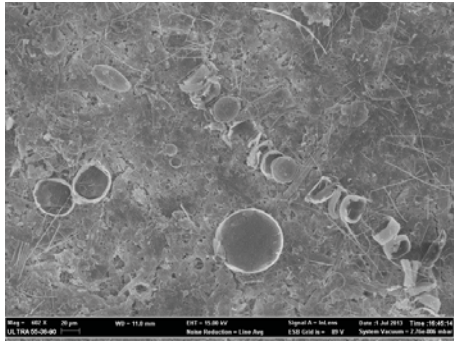
b Detrital minerals and alga (station CC5)



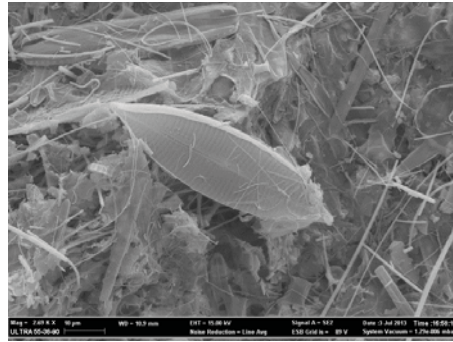
c Algae (station R02)



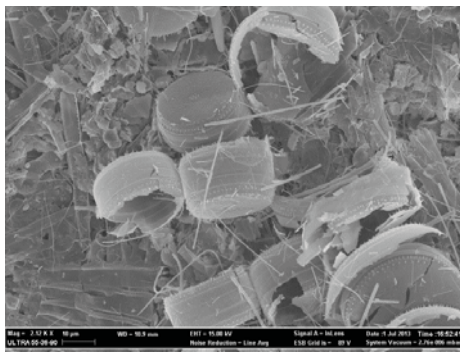
d Algae (station R05)



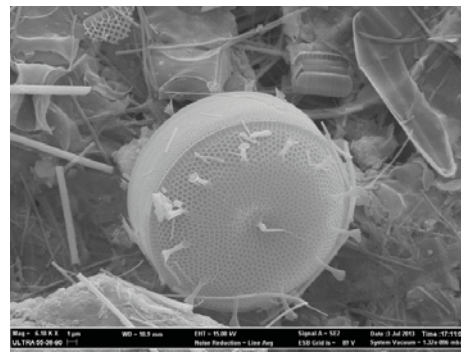
e Algae and detrital minerals (station R05)



f Algae (station R05)



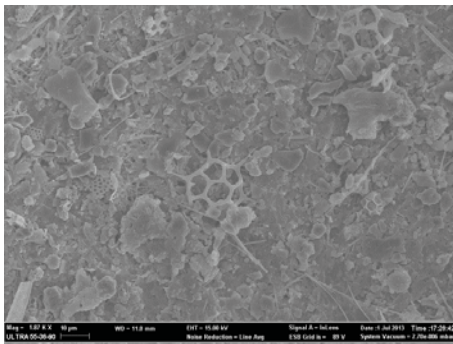
g Algae (station R05)



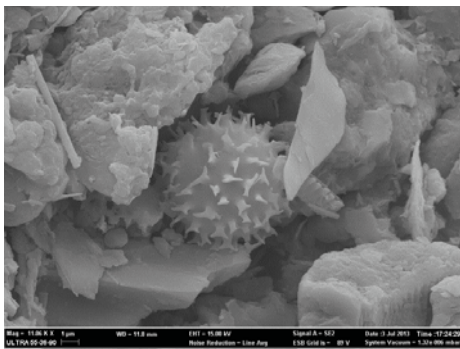
h Algae (station R05)



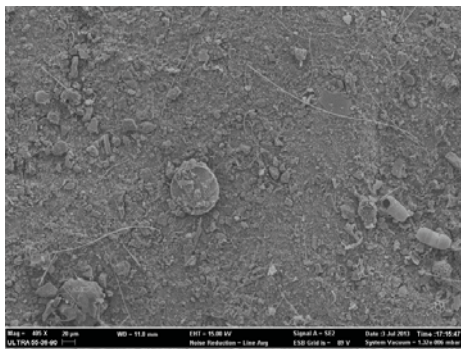
i Detrital minerals and algae (station ICE05)



j Silicoflagellate (station ICE05)



k Algae (station ICE05)



l Detrital minerals and algae (station ICE05)

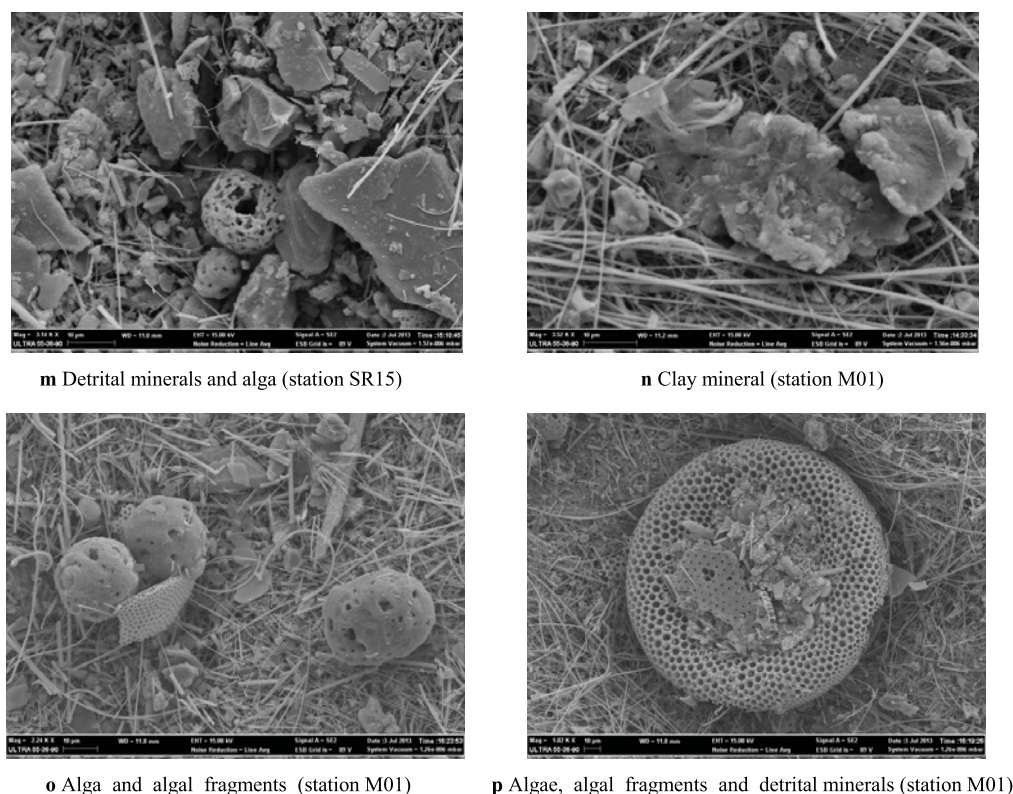


Figure 2 SEM image of suspended particles (a–h, shelf; i–p, slope and central Arctic Ocean).

Terrigenous detrital minerals, some clays and little biomass were observed at the sea ice margin stations (ICE05 and SR15) on the slope and in the central Arctic Ocean. Sea ice carried the less rounded, mixed-size detrital minerals. There is little well-preserved biomass (algae). The biomass consisted of predominantly two types, slightly pigmented ones $>40\ \mu\text{m}$ and transparent ones with microstructures $<5\ \mu\text{m}$. In addition, pigmented radiolarians were found. The well-preserved biomass content is higher in the open water station M01 (Figures 2i–2p).

3.3 Organic matter elemental and stable isotopic compositions

The TOC values varied from 8.06% to 27.99% and 73% of samples fell within 8%–14%. The TN values ranged from 0.63% to 2.3% and most of the samples fell within either 0.5%–1.0% or 1.5%–2.0%. The C/N ratio ranged from 6.9 (Station CC5) to 24.1 (Station SR15). Most samples fell within two ranges: 8–10 and >15 . Except for station R05 at the sea ice margin, the C/N ratio is <9 in the shelf area and with the exception of station M01 in open water, it is >15 on the slope and in the central Arctic Ocean (Table 2).

The isotopic composition is characterized by enriched ^{13}C and ^{15}N in the samples collected from areas without sea ice. The $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ values ranged from -23.29% to -26.33% PDB and 6.14% – 7.78% , respectively. The ^{12}C and ^{14}N is enriched in the samples from the sea ice margin. The $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ values ranged from -26.93% to -27.78% PDB

Table 2 TOC, TN, C/N ratio and isotopic composition of suspended particles

No.	Stations	TOC/%	TN/%	C/N/(wt%)	$\delta^{13}\text{C}/$ (‰ PDB)	$\delta^{15}\text{N}/$ ‰
1	R02	20.24	2.31	8.8	-23.96	7.55
2	CC2	11.21	1.42	7.9	-24.94	6.96
3	CC5	12.29	1.79	6.9	-24.92	6.7
4	CC7	14.82	1.78	8.3	-26.04	6.14
5	R04	13.02	1.58	8.2	-26.33	6.66
6	R05	9.78	0.91	10.8	-23.29	7.78
7	M01	8.96	0.72	12.4	-27.78	4.84
8	SR15	27.94	1.16	24.1	-27.43	3.81
9	SR18	8.69	0.46	18.9	-27.68	4.21
10	ICE05	8.06	0.51	15.8	-26.93	4.13
11	ICE01	8.86	0.53	16.7	-27.06	4.77

and 3.65% – 4.84% , respectively. These data agree well with previously reported values from this area^[3,20–22].

There was a significant correlation between TOC and TN, and $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ (Figures 3a, 3b). The coefficient of correlation, R , is 0.928 between $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ and 0.926 for TOC and TN. The only exception is the sample from station SR15. These correlation coefficient values suggested that these parameters were controlled by the same factors, so that TN represents organic nitrogen, while inorganic nitrogen is negligible or was removed with inorganic carbon during sample pre-processing. This result is inconsistent with particle

data from the Kara Sea and the Canadian Arctic Ocean^[3-4], but not with surface sediments from the Yermak Plateau^[23] and Chukchi Sea^[16].

The sample collected from station SR15 contained extremely high TOC and TN content compared with the others on the slope and in the central Arctic Ocean. Parallel analyses were carried out to dismiss the errors caused by analysis and heterogeneous distribution. The analyses showed the range of TOC (26.2%–28.9%, mean 27.9%) and $\delta^{13}\text{C}$ values (–27.6‰ to –27.9‰ PDB, mean –27.8‰ PDB), as well as TN (1.15%–1.21%) and $\delta^{15}\text{N}$ (3.6‰–3.8‰; Table 3). The analytical error fell within the allowable range and

indicated the particles were distributed uniformly on the filter.

Table 3 Parallel analyses of TOC, TN and their isotopic composition in the suspended particles of station SR15

Parallel analysis	$\delta^{13}\text{C}/(\text{‰ PDB})$	TOC/%	TN/%	$\delta^{15}\text{N}/\text{‰}$
1	–27.64	26.20	1.11	3.56
2	–27.76	28.85	1.21	3.75
3	–27.82	28.11		
4	–27.83	28.55		
5	–27.78	27.99		

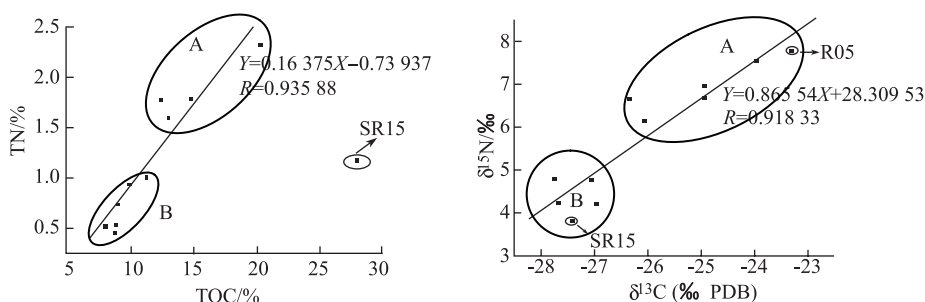


Figure 3 Relationship between TOC and TN and their isotopic composition.

4 Discussion

The isotopic composition of C and N and the ratio of C/N are often used to determine the relative contribution of terrigenous and marine organic matter in suspended particulates as well as environmental fluctuations. Marine phytoplankton have $\delta^{13}\text{C}$ values between –19‰ and –25‰ PDB, $\delta^{15}\text{N}$ values between 4‰–6‰ and C/N ratios from 7 to 10. The $\delta^{13}\text{C}$ values of lacustrine algae are between –25‰ and –30‰ PDB. The $\delta^{13}\text{C}$ value of C3 plants is about –27‰ PDB, while C4 plants average –14‰ PDB. Vascular plant material has significantly higher C/N ratios (20–>50), while bacterioplankton are nitrogen-rich and therefore have C/N ratios from 2–5. In general, the range of $\delta^{15}\text{N}$ is broader with marine organisms exhibiting heavier $\delta^{15}\text{N}$ values than those on land.

The Arctic Ocean has a special geography because it is separated from the other oceans and covered by sea ice for long periods of time. Therefore, fluvial terrigenous input and sea ice algae are very important organic sources. In addition, the differences found among the C/N ratios, $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ values of particles from the Laptev, Kara and Beaufort Seas resulted from terrestrial vegetation and nutrient input^[3-4].

In the Arctic Ocean, light availability and nutrient supply are the most important factors controlling primary production, including sea ice algae^[6,9]. It was shown that the $^{15}\text{N}/^{14}\text{N}$ ratio of particulate organic matter has a close relationship with nutrient (NO_3) utilization in the overlying surface waters. In the photic zone there is preferential uptake of $^{14}\text{NO}_3$ by phytoplankton producing photosynthetic products

enriched in the light isotope and isotopic enrichment under low nutrient (or nutrient limited) conditions^[9,16,18,23-24].

4.1 Particle sources in surface water

In general, the $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ values of particulate organic matter are influenced by the isotopic values of nutrients in the surface water. In the Arctic Ocean, the $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ values of particulate organic matter ranged from –26‰ to –21‰ PDB and 3.5‰–10.6‰, respectively^[9,23]. According to the data obtained from the RUSALCA Second Expedition, the average $\delta^{13}\text{C}$ value of particulate organic matter is –24.5‰ PDB in the East Siberian Sea and between –22.2‰ and 23.4‰ PDB in the Chukchi Sea^[21].

Based on the relationship of TOC and TN and of $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ values, particles can be divided into two groups: Group A (shelf samples) and Group B (slope and the central Arctic Ocean; Figure 3). Group A contains higher TOC and TN content and heavier C and N isotopic compositions, which indicates that organic matter predominantly originated from the marine realm with a small contribution from the terrestrial realm. In contrast, Group B exhibits lower TOC and TN content, lighter C and N isotopic compositions, and the organic matter is mainly composed of terrigenous material. These data agree well with the SEM observations.

It is interesting to note the differences in TOC, TN, $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ from the stations R05 and SR15. In R05, the isotopic compositions are characteristic for Group A, but its TOC and TN content belong to Group B. This sample was collected at the sea ice margin during the melting period (sampling date: 20 July 2012), so the lower organic matter content may be

a result of the plankton not blooming at that time coupled with depleted nutrient content from the Bering Strait current owing to plankton growing in the southern area^[15,25]. The nutrient conditions limited plankton growth, which resulted in lower organism content and heavier isotopic composition in the sample. Additionally, these may reflect sea ice algae contributions to the particulate material (see details below). In SR15, the C/N ratio has an abnormally high value and the correlation of TOC and TN departed from the main trend, but the isotopic composition is characteristic for Group B (Figure 3). Station SR15 is located at the Chukchi slope, where the Transpolar Current carries large volumes of fresh water and terrigenous material from the East Siberian, Kara and Laptev Seas (Figure 1). Particulate organic matter in the surface water showed lighter $\delta^{13}\text{C}$ values (-25.2‰ to -31.0‰ PDB), and there was a positive correlation of salinity with $\delta^{13}\text{C}$ ^[4]. The C/N ratios are between 11.7 and 29.2 (Laptev Sea) and 11.7 and 17.5 (Kara Sea)^[3]. These organic matter properties are consistent with our results. The extra source of terrigenous organic material in station SR15 is thus thought to originate from the Transpolar Current.

4.2 Sea ice contribution to particulate material

In the study area, the surface water particle sources include: terrigenous material carried by rivers; airborne particulates in areas free of sea ice; biogenic matter carried by sea ice along with algae living in the sea ice. Recent research suggested that interactions between sea ice, the water column and benthos are strongly enhanced during ice melt. Ice melt leads to a freshening of the ocean surface layer and an initiation of the spring phytoplankton bloom, and also to a biomass release, which is an important early food source for pelagic and benthic herbivores^[10]. The sea ice melting in the Chukchi region releases a substantial amount of organic material from the ice, which contributes both to phytoplankton seeding and the nutrition of zooplankton and benthos^[6].

In the shelf area, the particle concentration is higher at station R05, which is located at the sea ice margin. The algae content is higher and contains well-preserved microstructures (Figures 2c–2h), which implies the origin was biomass released from the ice. However on the slope and in the central Arctic Ocean, the particles are mainly detrital and clay minerals and algae fragments, and the living biomass is much less (Figures 2i–2p). A similar result was also shown in the high latitude (75°N – 80°N) Kann Basin, where sea ice algae contributed little to the pelagic biomass^[9].

The particle carbon isotopic composition also reflects the contribution of sea ice algae to the particulate organic carbon. The sea ice algae that live under nutrient limitation have heavier carbon isotopic compositions than those living in the water^[9]. In the shelf-basin interaction region, the stable isotopic signatures for ice and water samples did not differ significantly for $\delta^{15}\text{N}$ (ice: 6.1‰ – 13.5‰ ; water: 5.2‰ – 12.6‰), but they did for $\delta^{13}\text{C}$ (ice: -25.1‰ to -14.2‰ PDB; water: -26.1‰ to -22.4‰ PDB)^[6].

The particulate $\delta^{13}\text{C}$ is $\sim 3\text{‰}$ is heavier in the sea ice margin station (R05) than in the adjacent open water station (R04) on the shelf. The difference is less than 0.9‰ on the slope and in the central Arctic Ocean. These results also suggested that sea ice algae contribute significantly to particles on the shelf, but not on the slope and in the central Arctic Ocean.

5 Conclusions

The surface water particle concentration is higher on the shelf and the sea ice margin. In samples collected from the shelf area, the organism content is higher and algae microstructures were *in situ* properties. Samples collected from the slope and the central Arctic Ocean contain mainly detrital and clay minerals and biomass fragments carried by sea ice with a lower organism content.

The organic matter sources were mixed in the study area. The organic matter is mostly marine with some terrigenous input in the shelf area and mostly terrigenous on the slope and in the central Arctic Ocean.

Material carried by sea ice contribute significantly to particles in the surface water. The melting of sea ice released a substantial amount of biomass on the shelf, but a large amount of detrital and clay minerals and little biomass on the slope and in the central Arctic Ocean.

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