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Summertime freshwater fractions in the surface water of the western Arctic Ocean evaluated from total alkalinity

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Abstract As a quasi-conservative tracer, measures of total alkalinity (TA) can be utilized to trace the relative fractions of freshwater and seawater. In this study, based on the TA and related data collected during the third Chinese National Arctic Research Expedition (July—September 2008, 3rd CHINARE-Arctic) and the fourth Chinese National Arctic Research Expedition (July—September 2010, 4th CHINARE-Arctic), fractions of sea-ice meltwater, river runoff, and seawater within the surface water of the western Arctic Ocean were determined using salinity and TA relationships. The largest fraction of sea-ice meltwater was found around 75°N within the Canada Basin during both surveys, which is located at the ice edge. Generally, it was found that the fraction of river runoff was less than that of sea-ice meltwater. The river runoff, composed mainly of contributions from the Yukon River carried by Bering inflow water and the Mackenzie River, was influenced by the currents, leading to two peak areas of its fraction. Our results show that the dilution effect of freshwater carried by Bering inflow water during the 3rd CHINARE-Arctic in 2008 expedition period may be stronger than that during the 4th CHINARE-Arctic in 2010 expedition period. The peak area of sea-ice meltwater fraction during the 4th CHINARE-Arctic was different from that of the 3rd CHINARE-Arctic, corresponding to their sea-ice condition.

Keywords western Arctic Ocean, total alkalinity, freshwater fractions, sea-ice meltwater, river

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0 Introduction

Although the Arctic Ocean accounts for only 1% of the global ocean volume, it receives ~10% of the freshwater supplied globally by rivers[1]. Except for the Bering Strait and the eastern Greenland area, there is no channel connecting the Arctic Ocean with the outside ocean. Input of fresh water including that of river runoff and low salinity Pacific water, obviously lead to relatively fresher surface water within the Arctic Ocean[2-3]. Accordingly, there is a perennial halocline within the upper Arctic Ocean, which is a unique hydrographic structure. The presence of the halocline limits mixing within the water column to within 25—30 m. Therefore, the heat flux transport from warm, intermediate Atlantic water derived from the Arctic basin to the overlying surface water and sea-ice is strongly inhibi-ted[4], which plays a major role in maintaining the low temperature state and the sea-ice coverage within the Arctic surface. Pacific waters from the sub-polar Bering Sea account for 40% of the freshwater flux into the Arctic Ocean[5]. However, in recent years, as global warming continues to accelerate, many changes in water mass properties within the Arctic Ocean have been observed. With the retreat of the cold halocline water, the fresh water content within the Eurasian Basin declined during the 1990s[6]. Schlosser et al.[7] reported the decrease in river runoff content and reduction in sea-ice formation in the upper waters of the Eurasian Basin from 1991 to 1996. In the Canada Basin, Macdonald et al.[8] observed surface freshening during the 1990s. Model studies[9-10] have shown that these observed changes in water mass and freshwater distributions within

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the Arctic Ocean are associated with atmospheric forcing fluctuations, and show a different tendency within the cyclonic and anticyclonic regimes. Recent studies of direct measurements[11-12] found changes in river discharge from major rivers into the Arctic Ocean. Furthermore, inflow of Pacific water and its freshwater content also changed seasonally and inter-annually, and had a strong relationship with sea-ice formation and melting[13]. This study aimed to obtain a clear understanding of driving mechanisms of freshwater distribution in the western Arctic Ocean. Using total alkalinity (*TA*) and related parameters derived from the third Chinese National Arctic Research Expedition (3rd CHINARE-Arctic) and the fourth Chinese National Arctic Research Expedition (4th CHINARE-Arctic), fractions of sea-ice meltwater and river runoff in the surface water of western Arctic Ocean were calculated, and the influencing factors of freshwater distribution were studied.

1 Materials and methods

Data were collected onboard the R/V *XUE LONG* icebreaker during the 3rd CHINARE-Arctic from July—September in 2008 and the 4th CHINARE-Arctic from July—August in 2010. The research cruises passed through the Bering Strait, Chukchi Sea, Chukchi Plateau, Beaufort Sea, Mendeleyev Ridge and Canada Basin, and 86 and 79 hydrocast stations were occupied during the 3rd CHINARE-Arctic and 4th CHINARE-Arctic expeditions, respectively[14-15] (Figure 1). At each CTD/rosette station, conductivity-temperature-depth (CTD) profiles were collected by Seabird SBE911 plus sensors while seawater samples for *TA* were collected from Niskin bottles strictly in accordance with the *Guide to Best Practices for Ocean CO_2 Measurements*[16]. *TA* samples were analyzed by Gran titration using a 25 ml water sample with a precision of ±2 μmol·kg^{-1}. Cer-

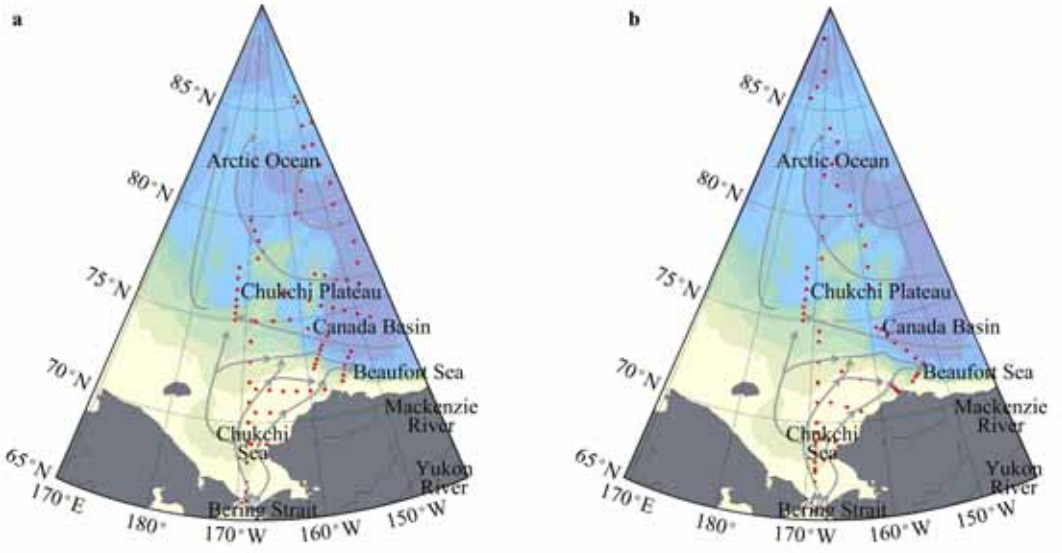

Figure 1 **a**, Location map showing the 3rd CHINARE-Arctic in 2008. **b**, Location map showing the 4th CHINARE-Arctic in 2010. A schematic diagram of the major currents within the Arctic Ocean is illustrated.

tified reference materials from Dickson A G of Scripps Institution of Oceanography were used for calibration.

2 Results and discussion

2.1 End-member *TA* values of the western Arctic surface water

The *TA* (also shortened as A_T) of a sample of sea water is defined as the number of moles of hydrogen ion equivalent to the excess of proton acceptors (bases formed from weak acids with a dissociation constant $K \leqslant 10^{-4.5}$ at 25℃ and zero ionic strength) over proton donors (acids with $K > 10^{-4.5}$) in 1 kilogram of sample. The *TA* represents the charge difference between conservative cations and conservative anions, and can be associated with the difference changes in salinity[17]. Thus the *TA* and salinity often have a relatively constant ratio. CO_2 exchange in the air-sea interface or biological uptake and release of CO_2 will not affect *TA* concentration. Thus, *TA* could be treated as a useful tracer for water mixing research. In actual fact, during the summertime, surface seawater CO_2 is very low because of the strong sea-ice melt and biological uptake of CO_2, and $CaCO_3$ precipitation or dissolution may be negligible[14-15, 18-20]. Therefore, the *TA* value will not vary with temperature and pressure if its unit is mol·kg^{-1}.

In addition, the *TA* concentration formed by mixing of two different water masses can be obtained based on a simple weighted average:

$$M_m \cdot TA_m = M_1 \cdot TA_1 + M_2 \cdot TA_2 \quad (1)$$

Where M_1, M_2, M_m are the quality of water mass one, water mass two and mixed water mass, respectively; TA_1, TA_2, TA_m

are the total alkalinity concentration of water mass one, water mass two and mixed water mass, respectively.

Therefore, *TA* can be used as an appropriate tracer for the freshwater fraction of the western Arctic Ocean.

In order to obtain *TA* for sea-ice meltwater, linear regressions of observed *TA* versus salinity in the surface seawater were constructed (Figure 2). As shown in Figure 2, 3rd CHINARE-Arctic: $TA(\text{sim})=71.2\times S$, $R^2=0.78$, $n=85$; 4th CHINARE-Arctic: $TA(\text{sim})=70.7\times S$, $R^2=0.76$, $n=83$. And R is the correlation coefficient, n is the number of samples.

Assuming that both sea-ice and sea-ice meltwater have a salinity of 5, then the *TA* value of sea-ice meltwater during the 3rd CHINARE-Arctic and 4th CHINARE-Arctic expeditions were are 356 μmol·kg^{-1} and 354 μmol·kg^{-1}, respectively. This is close to the estimated value of 349 μmol·kg^{-1} from Fransson et al.[21]. The mean *TA* value at the summertime temperature minimum (T_{min}) was chosen to represent *TA* of the seawater end-member. During summer, the temperature minimum indicated that the remnant water from the previous winter was at the bottom of the PML. The average salinity of remnant winter water during the 3rd CHINARE-Arctic and 4th CHINARE-Arctic expeditions were 33.1 and 32.9, respectively, with an average *TA* of 2 266 μmol·kg^{-1} and 2 248 μmol·kg^{-1}, respectively, in accordance with previous reports[21-23]. The sources of river runoff in the western Arctic Ocean are the Alaska coastal water influenced by the Yukon River through the Bering Strait, the Mackenzie River water and the East Siberian coastal water. Here the *TA* value of 1 540 μmol·kg^{-1} based on the data of the Mackenzie River from Cooper et al.[24] was used for river runoff source water. Table 1 presents the end-member values used in this study.

2.2 Surface *TA* distribution within the western Arctic Ocean

As can be seen from the surface *TA* distribution during the 3rd CHINARE-Arctic and 4th CHINARE-Arctic expeditions (Figure 3), because of freshwater (especially sea-ice meltwater) dilution, surface *TA* values of the western Arctic Ocean were much lower than that of the Bering Sea. Moreover, an extremely low *TA* area existed to the south of Chukchi Plateau and Canada Basin, located at about 152°W, 75°N. Surface water of the western Arctic Ocean, mainly originating from the Pacific Ocean, is further diluted by sea-ice meltwater and river runoff during summer. Therefore, the lowest *TA* value often directly corresponded to the largest fraction of the surface freshwater areas. Obviously, the *TA* concentrations around 83°N were mainly higher than those around 80°N, indicating that a greater freshwater fraction existed around 83°N.

Two main water masses flow into the western Arctic Ocean through the Bering Strait. The western one characterized by high *TA* concentrations comes from the Bering Slope Current, and the eastern one characterized by relative low *TA* concentrations is carried by the Alaska Coastal Current. The difference of surface *TA* values collected near the Bering Strait between the 3rd CHINARE-Arctic and 4th CHINARE-Arctic expeditions indicates the rapid changes of freshwater input into the western Arctic Ocean (Figure 3). The *TA* concentrations within the Chukchi Sea were influenced by the Bering inflow water during both cruises, but the dilution effect was stronger during the 3rd CHINARE-Arctic expedition.

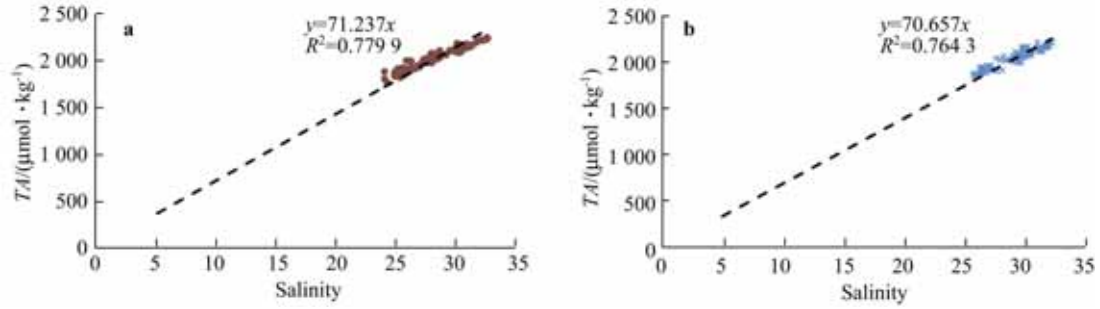

Figure 2 Linear regressions constructed from *TA*-*S* data in the surface seawater collected during the 3rd CHINARE-Arctic in 2008 (**a**) and the 4th CHINARE-Arctic in 2010 (**b**).

Table 1 The salinity and *TA* for the source waters

End-member	Salinity		*TA*/(μmol·kg^{-1})	
	3rd CHINARE-Arctic	4th CHINARE-Arctic	3rd CHINARE-Arctic	4th CHINARE-Arctic
sw	33.1	32.9	2 266	2 248
sim	5	5	356	354
rro	0	0	1 540	1 540

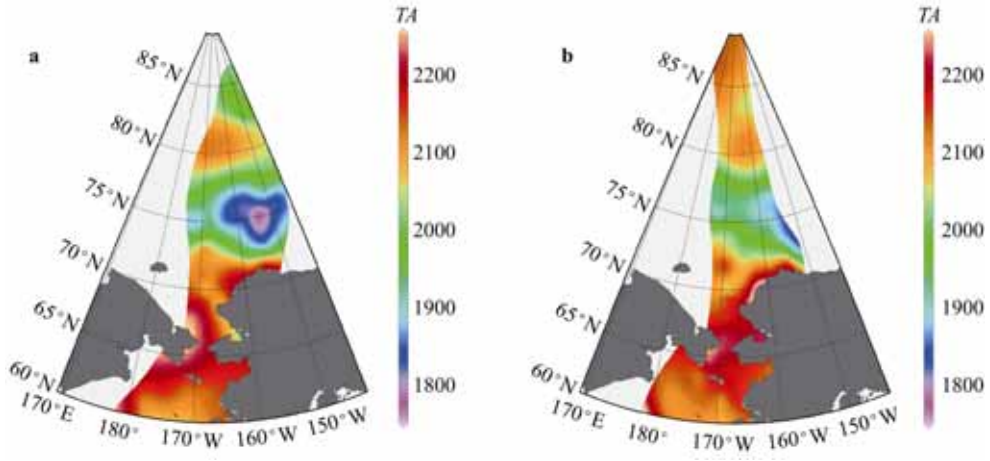

Figure 3 Surface *TA* distribution during the 3rd CHINARE-Arctic (**a**) and 4th CHINARE-Arctic expeditions (**b**).

During the 3rd CHINARE-Arctic and 4th CHINARE-Arctic expeditions, the northernmost station reached 85.5°N and 88.43°N, respectively. Thus, totally new observations that previous studies never observed could be obtained. During the 3rd CHINARE-Arctic expedition, low surface *TA* concentrations were observed to the north of 83°N. Since the river runoff is minor in the high latitudes, the low *TA* may have been mainly owing to the impact of sea-ice meltwater, indicating that sea-ice in this region may undergo more melting than at 80°N. During the 4th CHINARE-Arctic expedition, surface *TA* concentrations to the north of 80°N were relatively low in the 83°N region and high in the northern and southern ends, indicating that ice melting was more prominent in the 83°N region.

2.3 Sea-ice meltwater fractions within the western Arctic surface water

Salinity alone cannot be used to distinguish between river water and sea-ice meltwater. To further study the fractions of river runoff and sea-ice meltwater, the relationships between salinity and total alkalinity and three-end-member mixing (seawater, river runoff and sea-ice melt water) were employed. Compared with the ^{2}H and ^{18}O isotopes as a tracer of freshwater, *TA* has several of its own advantages. The $\delta^{18}O$ (oxygen isotope ratio of water) value of river runoff (-21‰) is significantly different from other end members, but the $\delta^{18}O$ value of sea-ice (-1.9‰) cannot be simply distinguished from the seawater (+0.3‰ of Atlantic water, -1.1‰ of Pacific water)[25]. Contrastingly, *TA* can easily be used to distinguished sea-ice from seawater. The typical *TA* values of seawater, river runoff and ice melt water are 2 300, 1 100, and 400 μmol·kg^{-1}, respectively[24,26]. Therefore, it can be a good tracer of freshwater and brine within the conservative mixing.

Surface seawater within the western Arctic Ocean is mainly mixed by three endmembers, seawater (sw), river runoff (rro) and sea-ice melt water (sim). As mentioned above, freshwater fractions can be evaluated by using the mass balance equations as follows[21]:

$$1 = f_1(\text{sim}) + f_2(\text{rro}) + f_3(\text{sw}) \quad (2)$$

$$A_T(\text{m}) = A_T(\text{sw})\times f_1 + A_T(\text{sim})\times f_2 + A_T(\text{rro})\times f_3 \quad (3)$$

$$S(\text{m}) = S(\text{sw})\times f_1 + S(\text{sim})\times f_2 + S(\text{rro})\times f_3 \quad (4)$$

where f is the relative fraction of seawater, sea-ice-melt or river runoff, and m indicates the measured values.

The relative fractions of sea-ice meltwater calculated from equations (2)–(4) are shown in Figure 4. It is evident that the major source of fresh water in the surface Arctic Ocean was sea-ice meltwater during both cruises, whose fraction is almost twice as much as river runoff. The largest fraction of sea-ice meltwater was found around 155°W, 75°N within the Canada Basin. This special region can also be reflected from the salinity distribution (Figure 5), and the extremely low salinity indicated the strong dilution of sea-ice meltwater.

2.4 The river runoff fractions in the western Arctic surface water

The relative fractions of river runoff during the 3rd CHINARE-Arctic and 4th CHINARE-Arctic expeditions are illustrated in Figure 6. It is obvious that the distribution pattern of river runoff was significantly different from that of sea-ice meltwater. There were two peak areas of river runoff fractions. One was located at about 169°W, 75°N within the Chukchi Sea. The central location was the same during both cruises while the coverage during the 4th CHINARE-Arctic expedition was about three times as much as during the 3rd CHINARE-Arctic expedition. The other was located at Canada Basin, which may have been influenced by the Mackenzie River. However, the central location changed from 152°W, 74°N—158°W, 73°N and the maximum value decreased.

River runoff fractions within the Beaufort, Chukchi Plateau and Canada Basin accounted for about 5%—15%, generally higher than that of the Chukchi Shelf, in which the fractions were below 5%. Within the middle and western

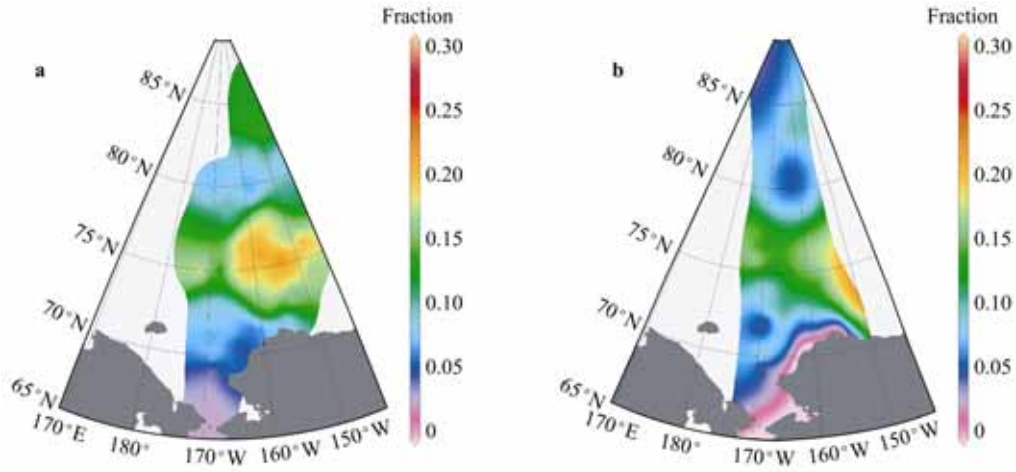

Figure 4 The relative fractions of sea-ice melt water during the 3rd CHINARE-Arctic (**a**) and 4th CHINARE-Arctic expeditions (**b**). The color bar illustrates the scale in decimal fractions.

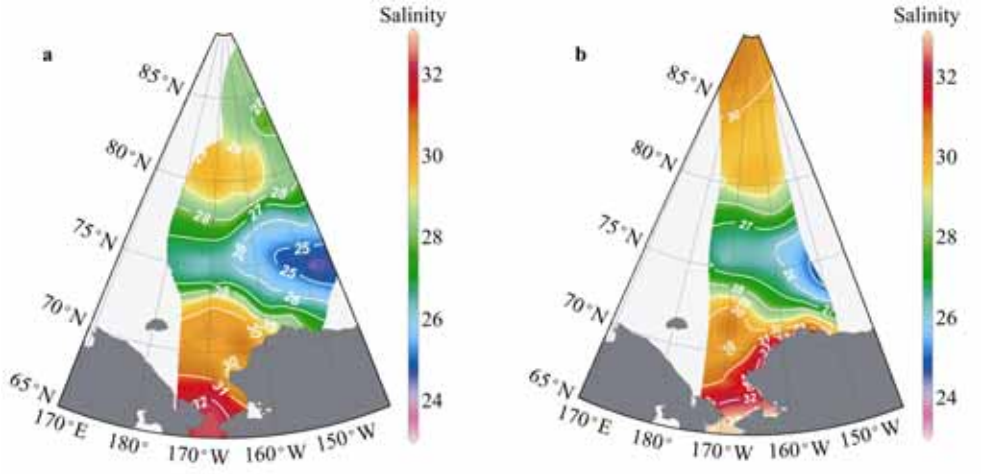

Figure 5 The surface salinity distribution within the western Arctic Ocean during the 3rd CHINARE-Arctic (**a**) and 4th CHINARE-Arctic expeditions (**b**).

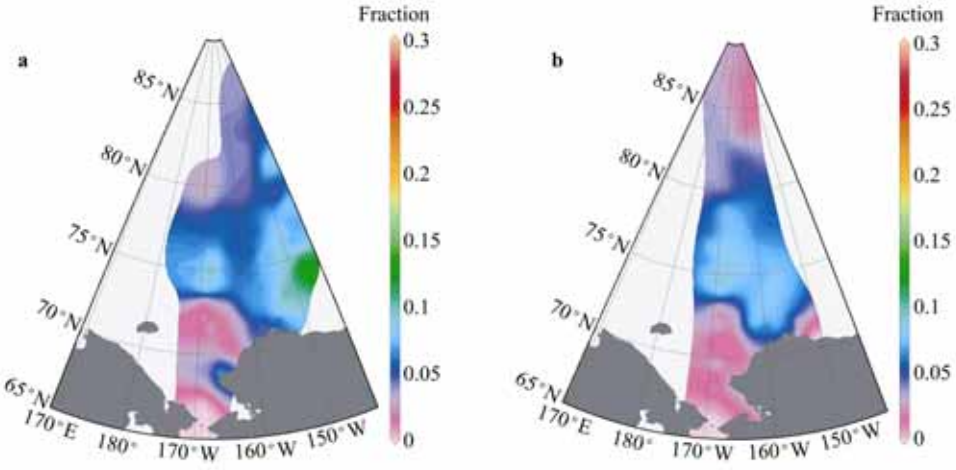

Figure 6 The relative fractions of river runoff during the 3rd CHINARE-Arctic (**a**) and 4th CHINARE-Arctic expeditions (**b**). The color bar illustrates the scale in decimal fraction.

Chukchi Shelf, water masses with a property of Pacific water showed low river runoff fractions. Within the eastern Chukchi Shelf, the river runoff fractions were relatively high because of the input of the Yukon River carried by the Alaska Coastal Current. This is particularly reflected within Figure 6a.

Although the contribution of river runoff was generally lower than that of sea-ice meltwater, the river runoff fraction indeed indicates the distribution pattern impacted by transport of currents and accumulation of riverine freshwater within the Arctic Ocean. The peak area located at the southern Canada Basin was due to the input of the Mackenzie River. The river water was transported from the shelf or the coastal area and accumulated within the Canada basin. Subsequently, it was carried by the Beaufort Gyre, and eventually could be found all over the western Arctic Ocean, even above the high latitude of 85°N (Figure 6).

Compared to the sea-ice meltwater, the river runoff played a minor role in the Arctic Ocean, consistent with Fransson et al.[21]. Yamamoto-Kawai et al.[27] also found that the impact of Mackenzie River was limited, and noted that the accumulation of freshwater within the Canadian Basin was caused by transport of shelf-derived freshwater.

2.5 The difference of river runoff fractions between the 3rd CHINARE-Arctic and 4th CHINARE-Arctic expeditions

Differences of river runoff fractions between the 3rd CHINARE-Arctic and 4th CHINARE-Arctic expeditions were a shift of the peak area. Compared with the data collected during the 3rd CHINARE-Arctic expedition, the peak area located at the Canada Basin during the 4th CHINARE-Arctic expedition shifted southwestward, and connected with the other peak area located at about 169°W, 75°N, forming one larger area. These changes were due to the different influences of Mackenzie River. Contrastingly, because of the different freshwater contents of the Bering inflow water, an area displaying a high river runoff fraction was observed at about 68.5°N，166.5°W during the 4th CHINARE-Arctic expedition rather than during the 3rd CHINARE-Arctic expedition, coinciding with the pathway of Alaska Coastal Current which carried plenty of freshwater (mainly river runoff).

2.6 The changing sea-ice condition

As illustrated in the Figure 7b, during the 4th CHINARE-Arctic expedition, to the east of Chukchi Sea, the temperature was relatively high and sea-ice melted in the early summer season. Subsequently, the sea-ice meltwater was carried by the Alaska Coastal Current and accumulated in the Beaufort Sea (Figure 4b). During the 3rd CHINARE-Arctic expedition, there was a region of high temperature within the Canada Basin, where sea-ice melting was severe and Marginal Ice Zone was located (Figure 8b), leading to a peak area of sea-ice meltwater.

As mentioned above, the sea-ice meltwater fractions during the 4th CHINARE-Arctic expedition was no more than during the 3rd CHINARE-Arctic expedition, which could also be confirmed from the sea-ice distribution (Figure 8). During the 3rd CHINARE-Arctic expedition, almost all the sea-ice melted to the south of 75°N, but heavy ice cover existed in the high-latitude. During the 4th CHINARE-Arctic expedition, sea-ice cover was more than that during the 3rd CHINARE-Arctic expedition, but there were many fractures, leads and sea-ice melt ponds that provided a path to the higher latitudes. For this reason, the R/V *XUE LONG* icebreaker could reach 88°26'N during the 4th CHINARE-Arctic expedition.

3 Conclusion

Because of its conservative characteristics, seawater total alkalinity could be used to evaluate the freshwater fraction of surface water of the western Arctic Ocean. Our observation shows that:

(1) During the summer, the contribution of sea-ice

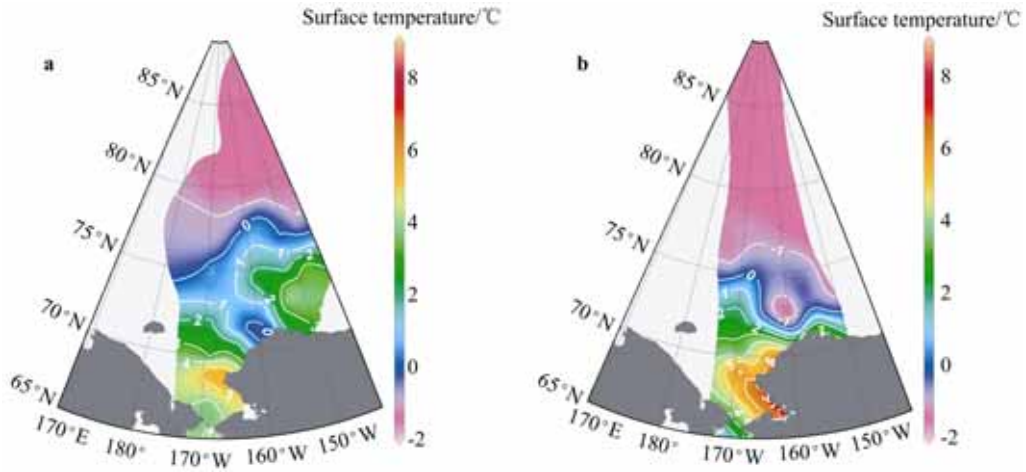

Figure 7 Surface temperature distribution within the western Arctic Ocean during the 3rd CHINARE-Arctic (**a**) and 4th CHINARE-Arctic expeditions (**b**).

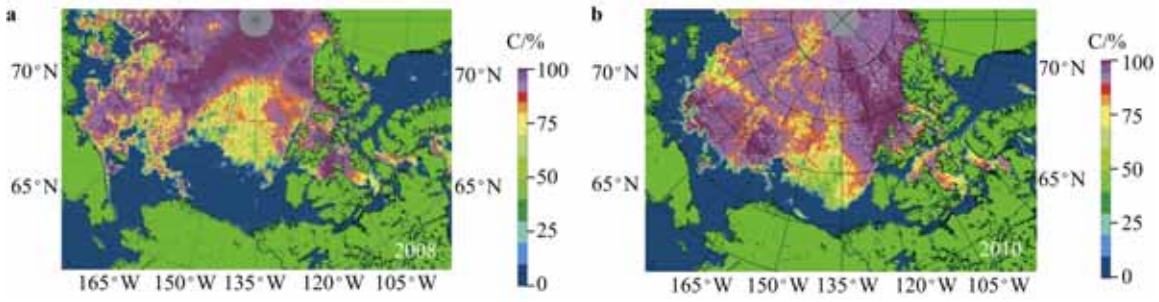

Figure 8 The daily sea-ice concentration within the study area over August during the 3rd CHINARE-Arctic (**a**) and 4th CHINARE-Arctic expeditions (**b**) (http://www.iup.uni-bremen.de:8084/ amsredata/asi_daygrid_swath/l1a/n6250/).

meltwater to the western Arctic Ocean fresh water fraction was larger than that of riverine freshwater because of rapid changes undergone by sea-ice.

(2) The largest fraction of sea-ice meltwater was found around 75°N within the Marginal Ice Zone, with a decreasing fraction at both high and low latitudes, corresponding to the sea-ice condition.

(3) The sea-ice condition during the 3rd CHINARE-Arctic expedition was different from that of the 4th CHINARE-Arctic expedition. There was more sea-ice melt during the 3rd CHINARE-Arctic expedition than the 4th CHINARE-Arctic expedition, especially within the southern Canada Basin. Thus, the sea-ice meltwater fractions were greater during the 3rd CHINARE-Arctic expedition.

(4) The conspicuous increase of sea-ice meltwater fractions occurred at around 83°N during the 4th CHINARE-Arctic expedition in accordance with the sea-ice melt ponds in the sea-ice map.

(5) The distribution of river runoff was obviously associated with the currents that transported and accumulated riverine freshwater along its pathway.

(6) The main difference regarding river runoff fractions between the 3rd CHINARE-Arctic and 4th CHINARE-Arctic expeditions were a shift of peak area.

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