

## Distribution of CFCs and its tracer study in the Chukchi Sea and adjacent areas

Yongzhi Deng, Na Sun, Shulan Zheng, Chuanling Zhuang & Wenquan Li\*

College of Oceanography and Environmental Science, Xiamen University of China, Xiamen, 361005, China

[E-mail: wql@xmu.edu.cn]

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During the second Chinese Arctic Scientific Expedition (CHINARE 2003. 2003.07 ~ 2003.09), chlorofluorocarbons (CFCs) were measured from water samples collected from 26 stations in the Chukchi Sea and adjacent areas. CFCs data indicated that they had not reach saturation in surface waters. The 170°W section distribution of CFCs and the thermohaline characteristics in the Chukchi Sea confirmed that there was an inflow of Pacific Ocean water into the Arctic Ocean via the Central Channel. There are three main new results. The first, there were two sources of freshwater, the Alaskan Coastal Water (ACW) and sea ice melt water, in the shallower than 20 m seawater. The second, the water mass at station BS09A was ACW, and that stations BS06A and BS07A were likely to be a place of confluence for ACW and Bering Sea shelf Water (BSW), or for ACW, BSW and Anadyr Water (AW) water masses. The third, the ACW almost flowed along the coast, and so it had less influence on the more distant offshore stations.

**[Keywords:** Chukchi Sea, CFCs, Distribution, Tracer Study]

### Introduction

The anthropogenic chlorofluorocarbons, such as trichlorofluoromethane (CFC-11), dichlorodifluoromethane (CFC-12), 1,1,2-trichloro-1,2,2-trifluoroethane (CFC-113) and carbon tetrachloride (CCl<sub>4</sub>) have been emitted into the atmosphere as a result of their widespread use as coolants, foaming agents and aerosol propellants in industrial, home and commercial areas since the 1930s. However, CFCs have been well documented as playing an important role in the depletion of the global stratospheric ozone layer and in the augmentation of global warming in the troposphere<sup>1</sup>, and so the 1987 Montreal Protocol endeavored to phase out the release of CFCs<sup>2</sup>. As a result, the levels of CFCs in the atmosphere started to decline<sup>1</sup>.

CFCs in the atmosphere can access the ocean surface through air-sea exchange, and the resulting trace of CFCs in the upper seawater will be redistributed into the lower seawater through vertical convection and currents. CFCs do not have any biological activity in seawater and they are relatively stable<sup>3</sup>, so they can be used as a tracer to study the formation rates<sup>4</sup> and the structure of seawater masses<sup>5,6</sup>. Together with thermohaline data, their interactions can be used to estimate the age of water masses<sup>7</sup>. In addition, they can be used to study air-sea exchange<sup>8,9</sup>. In the present study CFCs is used as

tracers to study the structure of seawater masses in the Chukchi and adjacent areas.

### Materials and Methods

Chukchi Sea is a marginal sea of the Arctic Ocean, and is connected to the Bering Sea of the Pacific Ocean through the Bering Strait in the south, has the Chukchi Plateau and the Canadian Abyssal plain to the north, the East Siberian Sea to the west, and Alaska and the Beaufort Sea to the east. Water of the Pacific Ocean enters the Arctic Ocean basin must pass through the Chukchi Sea<sup>10</sup>, therefore, study the structure of the Chukchi Sea water masses is playing an important role to understand the structure of water masses in the Arctic Ocean.

#### Sample Collection

Water samples were collected at 26 stations during the CHINARE 2003 expedition (2003.07~2003.09) in the Chukchi Sea and its adjacent regions to analyze CFCs. The southernmost moorings (BS06A, BS07A and BS09A) were located in the Bering Strait, R moorings in the 170°W section, S moorings in the slope of the Chukchi Sea and C moorings across the central Chukchi Sea. The locations of the sample stations are shown in Figure 1.

Using a Rosette sampler, 100 mL of seawater was collected into a special long neck borosilicate ampoule bottle, enclosed to prevent air bubbles, conserved at 4°C and then transferred to the on-land laboratory.

\* Corresponding author

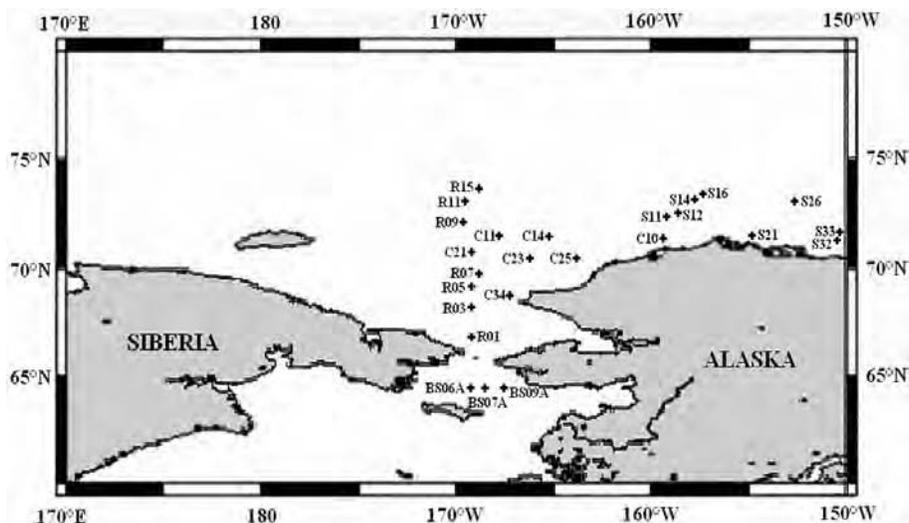


Fig. 1—Location of sample stations in the Chukchi Sea.

#### Instrumentation

A Tekmar 3100 purge and trap concentrator system coupled with a Varian 3800 gas chromatograph (GC) equipped with a micro  $^{63}\text{Ni}$  ECD was used for measurements of CFCs samples. The trap used for preconcentration of CFCs was packed with carboxen1000, carboxen1001 and carbotrap B. Liquid  $\text{CO}_2$  was used to control the vocarb 3000 trap at  $20^\circ\text{C}$ . After 2 minute desorbing, the vocarb 3000 was rapidly heated to  $200^\circ\text{C}$  within seconds and then the preconcentration sample was immediately transferred by the  $\text{N}_2$  gas stream into the Cryofocus. Liquid  $\text{N}_2$  was used to control the Cryofocus trap at  $-150^\circ\text{C}$  in the Cryofocusing Module. The Cryofocus trap was then heated to  $180^\circ\text{C}$ , and released CFCs into the GC column within 1 min. The column used for CFCs separation was a wide-bore DB-624 fused silica capillary column ( $75\text{ m}\times 0.53\text{ mm}\times 3\text{ }\mu\text{m}$ ). For CFCs separation, the temperature was held at  $60^\circ\text{C}$  for 1 min in an oven, slowly increased by  $8^\circ\text{C min}^{-1}$  to  $180^\circ\text{C}$  and then held at this temperature for 3 min. A representative chromatogram for a Chukchi Sea water sample is shown in Figure 2.

The analytical system is calibrated frequently using a standard solution of known CFCs composition. The recovery of the measurements was 100.6% for CFC-11, 99.9% for CFC-113 and 99.8% for  $\text{CCl}_4$ . The precision of the measurements were 1.9% for CFC-11, 3.7% for CFC-113 and 4.1% for  $\text{CCl}_4$ . The detection limit of our device were  $0.0145\text{ pmol kg}^{-1}$  for CFC-11,  $0.0332\text{ pmol kg}^{-1}$  for CFC-113 and  $0.0198\text{ pmol kg}^{-1}$  for  $\text{CCl}_4$ .

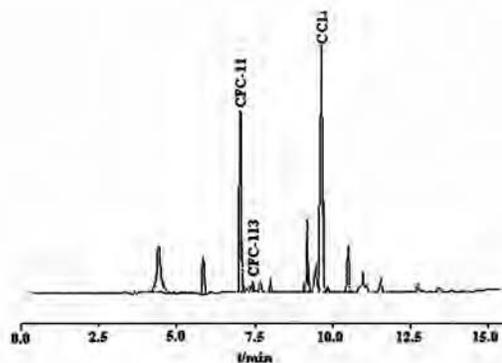


Fig. 2—Gas chromatogram of CFCs in seawater sample.

Temperature and salinity data of seawater were collected using a MARKIII-C-CTD (G O Corporation, USA) and preprocessed and calibrated by the First Institute of Oceanography, State Oceanic Administration of China.

#### Results and Discussions

##### Concentrations of CFCs in the Chukchi Sea surface water

The concentrations of CFC-11 in the Chukchi Sea surface water during the CHINARE 2003 expedition were determined to be  $3.979\sim 7.439\text{ pmol kg}^{-1}$ , or an average of  $5.436\pm 0.998\text{ pmol kg}^{-1}$ . The concentrations of  $\text{CCl}_4$  were  $4.926\sim 9.273\text{ pmol kg}^{-1}$ , or an average of  $6.739\pm 1.485\text{ pmol kg}^{-1}$ , and those of CFC-113 were  $0.380\sim 0.800\text{ pmol kg}^{-1}$ , or an average of  $0.632\pm 0.139\text{ pmol kg}^{-1}$  respectively.

The saturation levels of CFC-11,  $\text{CCl}_4$  and CFC-113 in surface water were 67.10%~97.83%, 67.64%~92.93%, and 61.68%~97.98%, respectively.

During the expedition in the Chukchi Sea (late July and early August 2003), the sea ice at the south of station R11 was almost melted<sup>11</sup>. Refer to previous studies<sup>12,13</sup>, surface seawater takes approximately one month to be saturated with CFCs under the conditions of air-sea balance<sup>12,13</sup>, none of the surface seawater was ever saturated with CFCs during the expedition.

#### Concentrations of CFCs in the Bering Strait

Eight CFCs samples were collected from different depths at stations BS06A, BS07A, and BS09A in the Bering Strait. The results showed that CFCs in surface waters were unsaturated at the stations BS06A and BS07A, with saturation levels ranged from 88.64% to 96.56%, and CFCs in surface water were saturated at the station BS09A, with saturation level ranged from 101.20% to 110.00%. Vertical thermohaline distribution at stations BS06A and BS09A was quite uniform, while it was apparently stratified at station BS09A. A strong vertical mixing of the seawater around station BS06A indicated that it may have been the confluence area of different water masses, and there was no vertical mixing at station BS09A, where the water was stratified.

As shown in Figure 3, high temperature and low salinity appeared to the east of the Bering Strait entrance, whereas low temperature and high salinity appeared to the west of the entrance, and this indicated that different water masses coexisted in the entry to the Bering Strait. Previous reports show that the Pacific inflow water which goes into the Chukchi Sea from the Bering Strait consists of three water masses<sup>14,15</sup>. The water mass along the coast of Alaska, the Alaskan Coastal Water (ACW), comes from the Alaska stream and mixes with the imported flows on the Bering Sea shelf. It has a general salinity less than 32.0, and enters the Bering Strait via the Cabot Strait, which lies to the east of the St. Lawrence Island.

Anadyr Water (AW) is a water mass from the coast of Russia, and which is a branch of the northern Bering continental slope current, enters the Bering Strait via the Anadyr Gulf<sup>16</sup>. The salinity of the AW water mass is between 32.8 and 33.0, the highest salinity among the water masses of the Bering Strait. Another water mass in the Bering Sea shelf to the south of St. Lawrence Island is the Bering Sea shelf Water (BSW). Thus, the ACW, AW and BSW occur to the east, the west and in the middle of the Bering Strait, respectively. However, the various significant properties of these three water masses result in the sharp front and intensive mixing, shown by Piatt *et al.*<sup>17</sup>. In addition, because of the temperature increase caused by solar radiation and runoff inflow in summer, ACW usually appears to have a stable stratified structure with a thermocline at the 10 to 20 m depth. Therefore, in addition to a salinity of less than 32.0, the water mass at the station BS09A with stable stratified structure, was identified to be ACW, and the stations BS06A and BS07A, without stable stratified structure, is likely a confluence place of ACW and BSW, or ACW, BSW and AW water masses.

#### Spatial distribution of CFCs in surface water and at 20 m

Figure 4 presents the dimensional distribution of temperature, salinity, DO and nutrients in surface water and at 20 m depth water in the Bering Strait, the Chukchi Sea and on the northeast slope of the Chukchi Sea. Temperature and salinity decreased from south to north in the research area, and lower temperatures (below 0°C) existed on the northeast slope. The distributional trend of the dissolved oxygen (DO) and nutrients were opposite to those of temperature and salinity. The 20 m depth water showed nearly the same properties as the surface water, indicating that they both belonged to an identical source of freshwater.

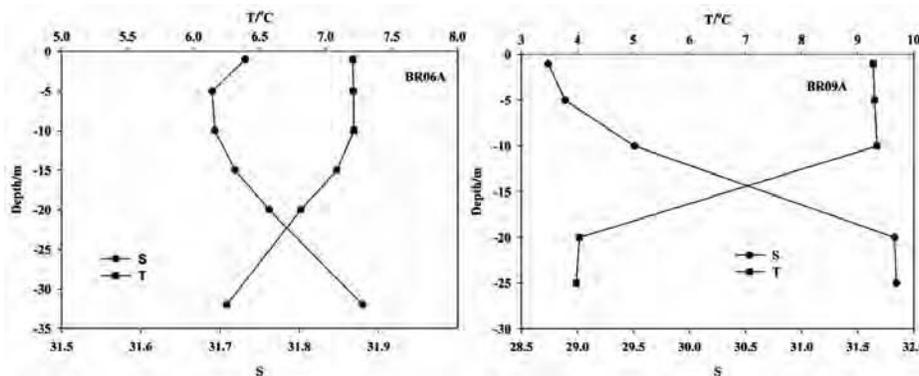


Fig. 3—Temperature and salinity vertical distribution at stations BS06A and BS09A in the Bering Sea Strait.

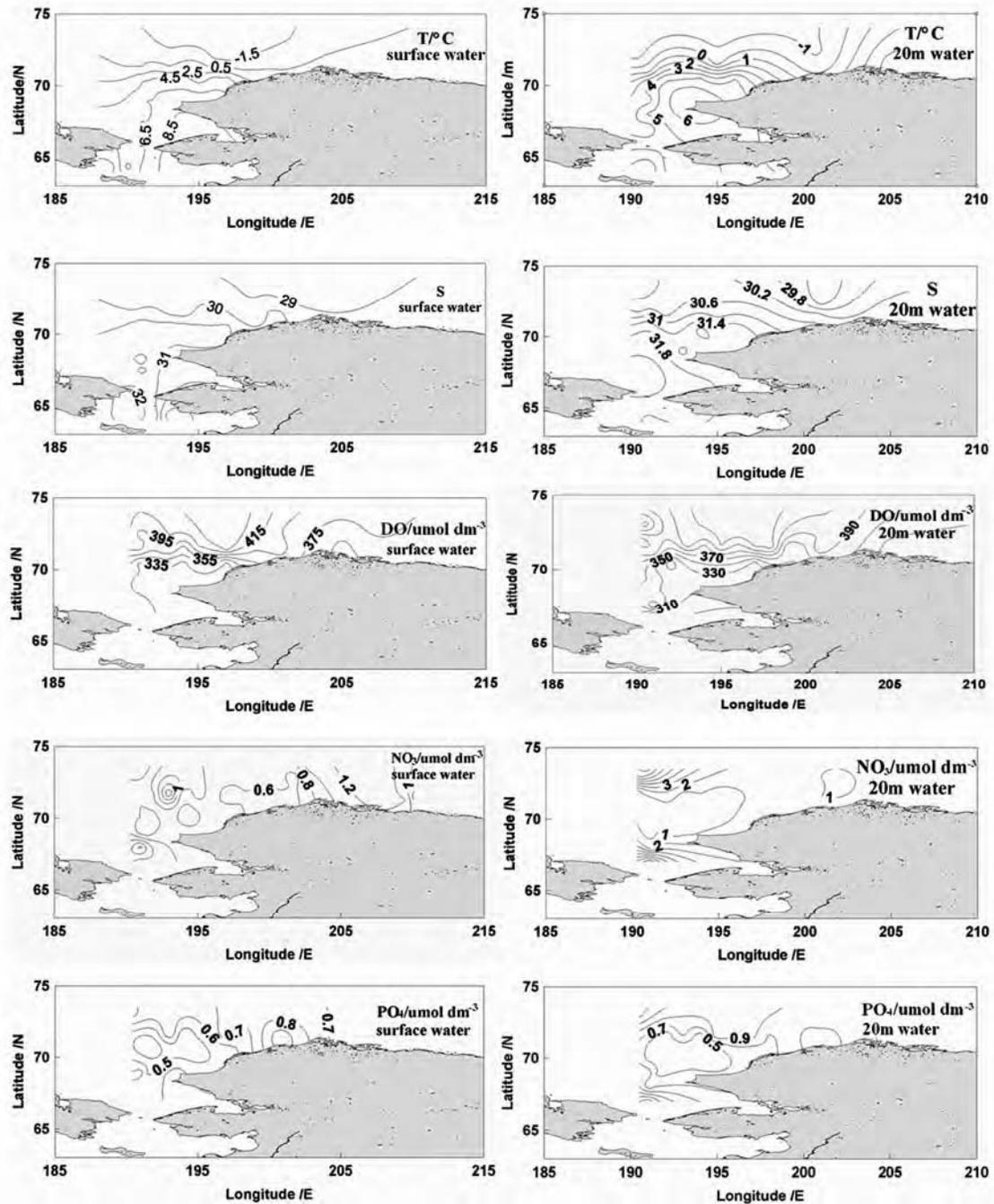


Fig. 4—Spatial distribution of T, S, DO, nutrients in surface water and at 20 m.

As shown in Figure 5, the distribution of CFCs also increased from south to north. The water mass on the northeast slope with high CFCs but low temperature and salinity was different from that on the Chukchi slope. According to the analysis in the last section, ACW generally existed in the eastern Bering Strait, with salinity less than 32.0 and high temperature.

As shown in Figure 4, the temperature of both surface water and 20 m-depth water was above 0°C, and the average salinity was less than 32.0, which implied that the seawater in the research area during CHINARE 2003 was primarily the ACW. According to CFCs dimensional distribution, the ACW corresponded to an area of low CFCs. The fact that

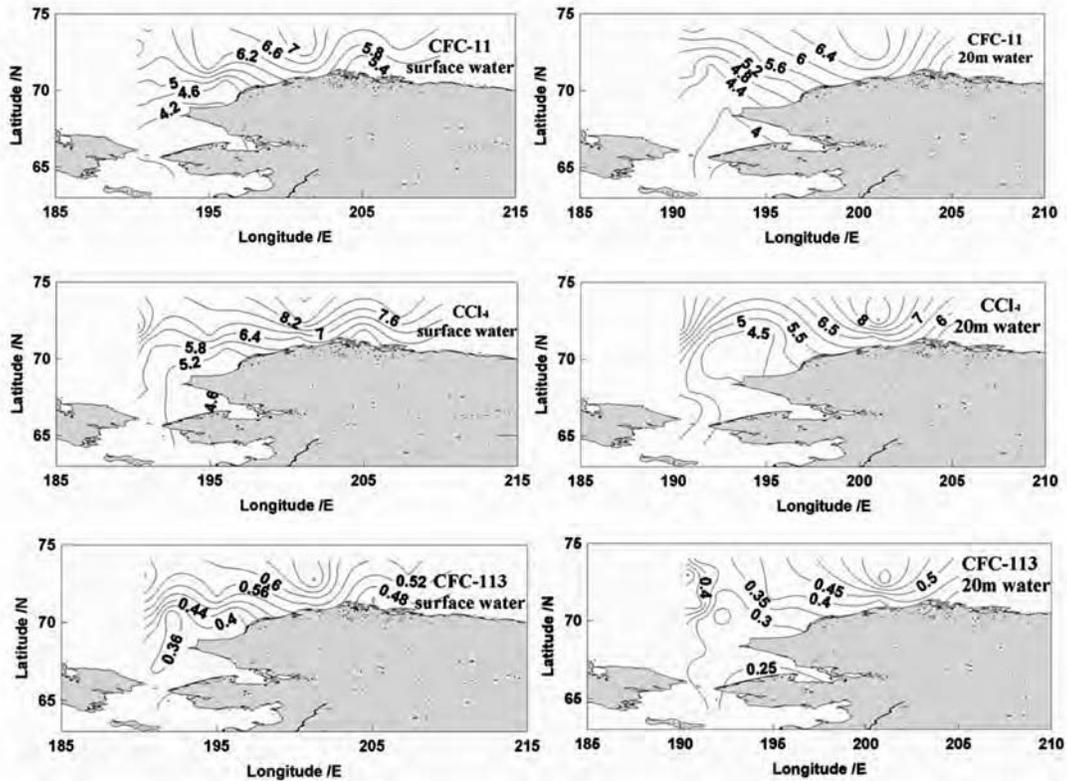


Fig. 5—Spatial distribution of CFCs in surface water and at 20 m.

low CFCs levels extended eastward along the continental margin also suggested that the ACW mainly moved eastward along the continental margin. As found by D'Asaro<sup>18</sup>, the ACW primarily moves eastward along the continental shelf to the northern sea area of the Greenland and only a small part of it goes into the central region of the Arctic Ocean along with the eddy<sup>19</sup>. Figure 4 and Figure 5 also show that high CFCs water on the northeast slope was primarily sea ice meltwater, with low temperature and salinity, and was not affected by entry of the Pacific Ocean water, with higher temperature and low salinity commonly, during the period of the CHINARE 2003. Accordingly, the water with a depth less than 20 m in the research area mainly consisted of the ACW and sea ice meltwater during the period of CHINARE 2003.

#### 170°W Section Distribution

The 170°W cross-section map (Figure 6) shows that there was low CFCs content water, with high temperature and high salinity, at the bottom along the north slope of the Chukchi Sea, and this reached station R10. Therefore, the water should flow into the Pacific Ocean through the Bering Strait. The 170°W section ran through the Central Channel. All these

analyses suggested that Pacific water already reached station R10 (71°29'51"N, 169°0'34"W) during the CHINARE 2003 summer voyage. The distribution of CFCs and the thermohaline at the 170°W section in the Chukchi Sea indicated that an inflow of Pacific water definitely ran into the Arctic Ocean via the Central Channel.

The earliest research of the Chukchi shelf current is that of Coachman *et al.*<sup>14</sup> and Walsh *et al.*<sup>20</sup>. The former authors point out that the Pacific current is divided into two branches after flowing into the Chukchi Sea. The west one flows through a sea valley between the Hope and the Herald, and has high salinity; and the east one flows through the Barrow Valley in the northeast of the Chukchi Sea, and has relatively low salinity. However, recently, on the basis of the distribution of temperature, salinity and Ba, Weingartner *et al.*<sup>21</sup> analyze the situation of the Chukchi shelf current and find a third way, the central waterway, through which the Pacific current flows into the Arctic Ocean via the Chukchi Sea, which is also affected by the terrain similar to the other two ways. This also agrees with the anchored observations by Woodgate *et al.*<sup>22</sup> in the Chukchi Sea during 1990 and 1991.

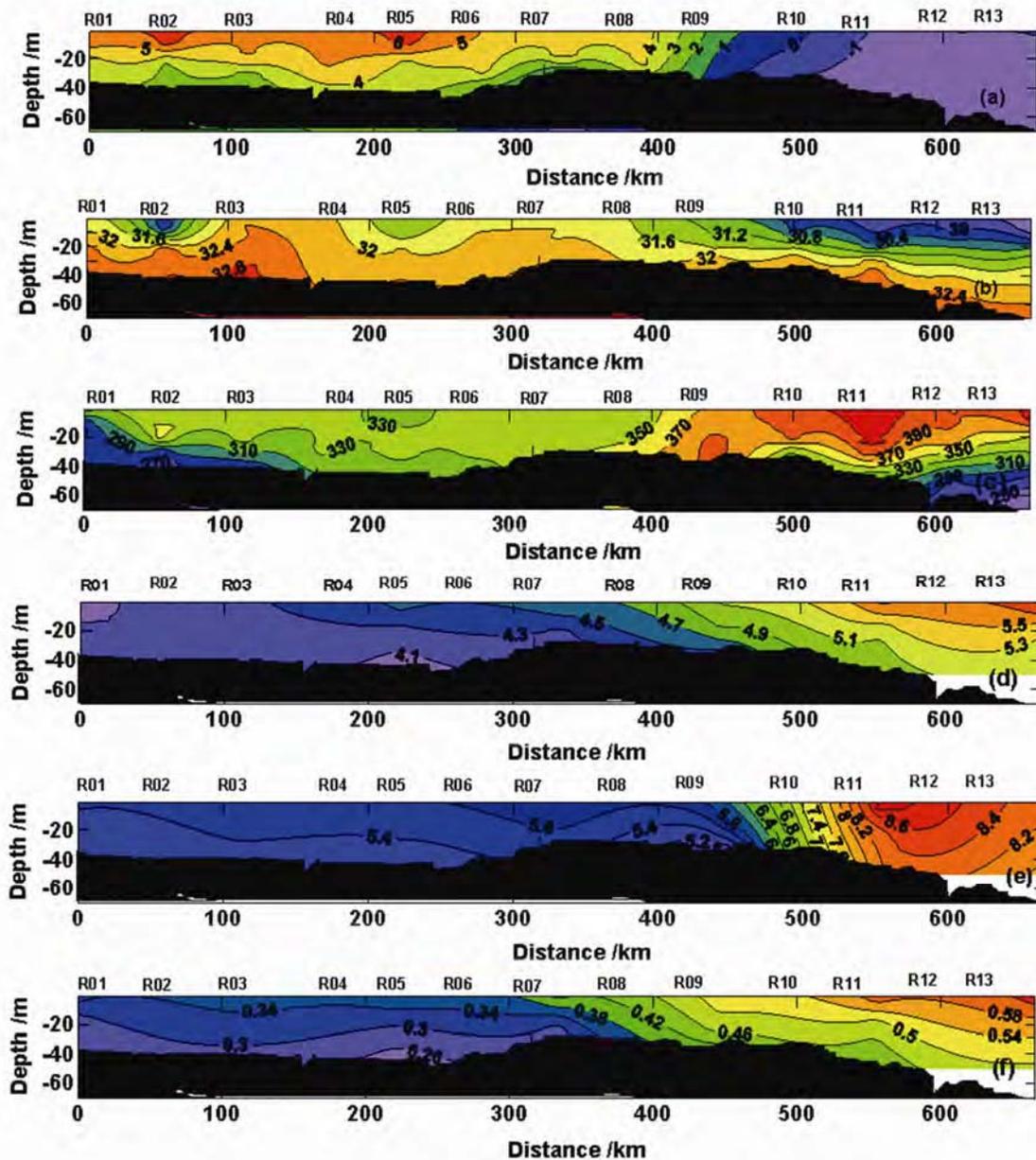


Fig. 6—Vertical distribution of various parameters in 170°W. section in the Chukchi Sea. (a) Temperature (°C) (b) Salinity; DO ( $\mu\text{mol dm}^{-3}$ ) (d) CFC-11 ( $\text{pmol kg}^{-1}$ )

In addition, there were obvious fronts of temperature, salinity, DO and CFCs fronts between stations R09 and R10 (Figure 6), which suggested that this was the confluence area where two different water masses met. As mentioned above, the water mass at the south of the front was a Pacific inflow current, characterized by high temperature, high salinity, low CFCs and low DO. The water mass in the north of this front had obviously different properties, namely lower temperature (below 0°C),

and lower salinity of the surface water (less than 31.0) but somewhat increased in the bottom water. Their CFCs and DO contents were obviously higher than those of the Pacific inflow current. Without enough isotope data, so we suspect that this water mass may be a mixed water mass made up of the melted polar ice water and the winter Pacific inflow current through the water mass data of DO, T, S. 170°W section was made of these different water masses during the CHINARE 2003 voyage,

Weingartner *et al.*<sup>21</sup> suggest that the water masses on the Chukchi Sea shelf have an obvious annual variation, which is consistent with what we found. The transportation time of water masses from the Bering Strait to the northern Chukchi Sea slope changed with season, for example, there was a slower flow in winter. Because the transportation time of these water masses changed seasonally, it was possible that these two different water masses coexisted during the CHINARE 2003 voyage.

Vertical Distribution of CFCs

Our results showed that low concentrations of CFCs and higher temperatures (above 0°C) existed in the surface water at stations S21 and S33. We have not enough data for all stations, so we took S33,

S16, S14 and S26 as example. The vertical distributions of CFCs were similar, so we took CFC-11 as example. The vertical distribution of CFC-11 at the station S33 (Table 1 and Figure 7) clearly showed that the minima of CFCs and DO all occurred at a depth of 50 m. These data indicated that the surface water at station S33 was controlled by ACW. Conversely, the fact that high concentrations of CFCs and lower temperatures (below 0°C) appeared at stations S11, S12 and S14, which were located on the slope and therefore distant from the coast, indicated that these stations were not affected by ACW during the period of CHINARE 2003. In other words, ACW flowed mainly along the coast and had less influence on the sea area away from the coast.

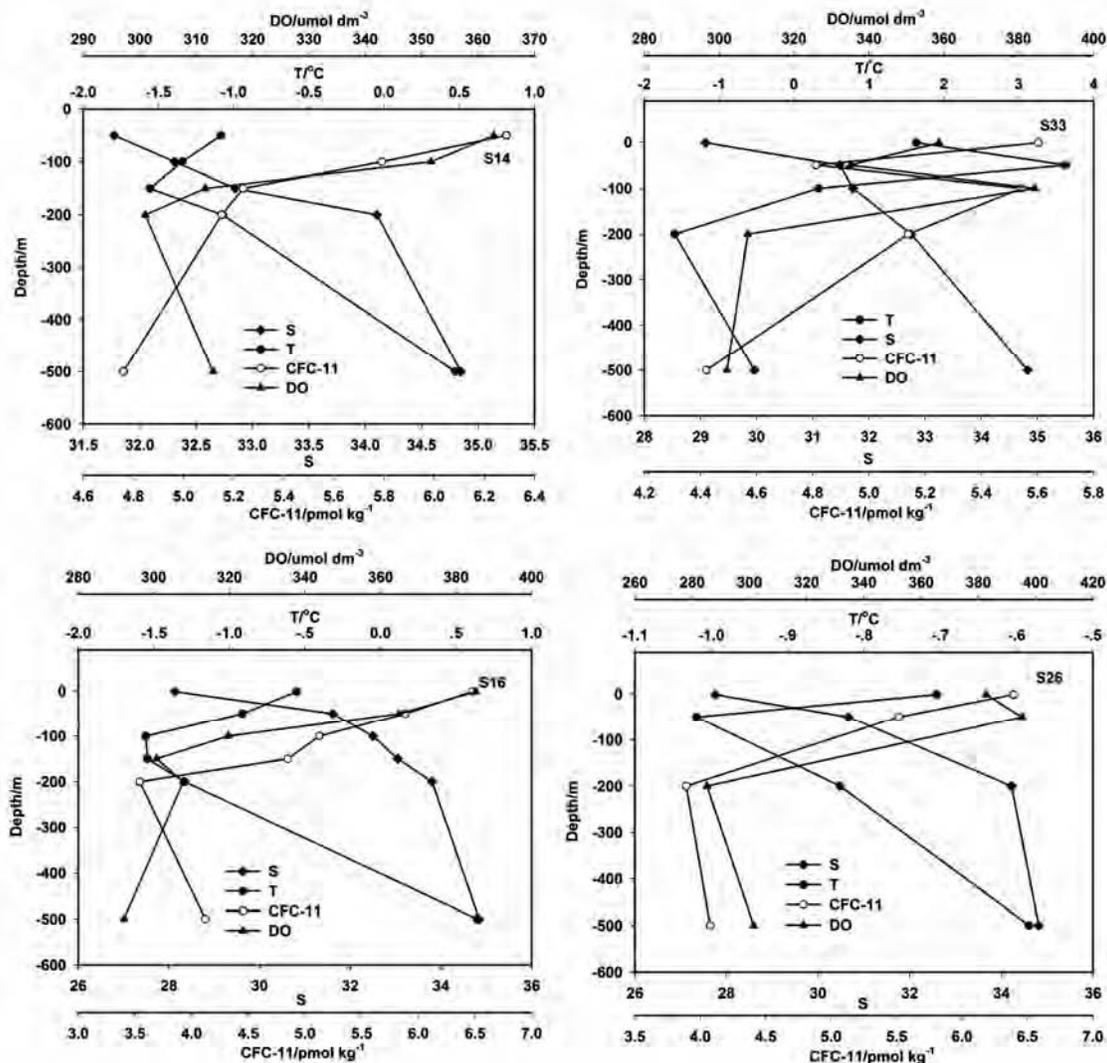


Fig. 7—Vertical distributions of CFCs and other parameters at station S.

Table 1—The concentration of CFCs and other parameters at station S

Stations	Depth/m	Temperature/°C	Salinity	DO umol dm <sup>-3</sup>	CFC-11 pmol kg <sup>-1</sup>	CFC-113 pmol kg <sup>-1</sup>	CCl <sub>4</sub> pmol kg <sup>-1</sup>
S14	50	-1.0848	31.7747	362.8	6.288	0.576	8.195
S14	100	-1.3420	32.3101	351.7	5.791	0.496	7.272
S14	150	-1.5576	32.8487	311.6	5.238	0.415	7.299
S14	200	-1.0725	34.1031	301.0	5.152	0.382	6.489
S14	500	0.4730	34.8466	313.0	4.760	0.352	5.695
S16	1	-0.5553	28.1291	385.2	6.475	0.593	8.729
S16	50	-0.9145	31.6139	364.9	5.884	0.528	7.750
S16	100	-1.5536	32.5002	319.7	5.126	0.470	7.361
S16	150	-1.5431	33.0495	300.7	4.849	0.332	6.829
S16	200	-1.2973	33.8058	307.8	3.541	0.373	4.869
S16	500	0.6388	34.8401	292.1	4.120	0.246	5.156
S26	1	-0.7046	27.7562	382.7	6.393	0.560	8.570
S26	50	-1.0194	30.6600	395.2	5.515	0.493	7.862
S26	200	-0.8313	34.2257	285.2	3.892	0.261	4.769
S26	500	0.5835	34.8180	301.5	4.075	0.291	5.095
S33	1	1.6357	29.0931	358.7	5.603	0.471	6.264
S33	50	3.6287	31.4829	335.1	4.812	0.343	5.392
S33	100	0.3229	31.7191	384.3	5.541	0.413	6.447
S33	200	-1.5950	32.7562	307.6	5.140	0.392	5.922
S33	500	-0.5290	34.8265	302.1	4.421	0.329	5.586

As shown in Figure 7 and Table 1, vertical distributions of CFCs were obviously different at stations S14 and S16, and vertical distributions of DO also showed some differences. The CFCs minimum layer did not exist at station S14, but was clearly observed in the 200 m depth water at station S16. This was probably because station S14 was closer to the slope, where occupied with freezing winter Pacific water, and better ventilation occurred. Vertical distribution results revealed minimum DO in the 200 m depth water at station S14, and thus the main body of water there consisted of winter Pacific water.

### Conclusions

The results of CFCs tracer study in the Chukchi Sea and its adjacent areas in summer 2003 led to the following conclusions: Water mass at station BS09A was the ACW, and stations BS06A and BS07A were likely to be a confluent area for ACW and BSW, or ACW, BSW and AW water masses. During CHINARE 2003, the water above 20 m in the study area was mainly occupied by the ACW and sea ice meltwater. Distributions of CFCs in the 170°W section of the Chukchi Sea indicated that an inflow of Pacific water definitely ran into the

Arctic Ocean via the Central Channel. ACW primarily flowed along the coast, and had less impact on more distant offshore stations.

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