

Methanesulphonic acid in aerosols along a cruise path from China to the Arctic Ocean: Spatial and temporal distributions and link with iodine

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Abstract Methanesulphonic acid (MSA) may play an important role in the climate change occurring in response to the warming of the Arctic Ocean. However, the spatial and temporal distributions of MSA in this region are poorly understood. We report on the MSA content of aerosols over oceans measured during the 3rd Chinese National Arctic Research Expedition (CHINARE2008) from July to September, 2008. Results show that the aerosol MSA content can be influenced by multiple processes in different areas. In coastal regions, airborne pollutants, especially nitric oxide, may strongly influence the oxidation of dimethyl sulfide (DMS) and increase the concentration of aerosol MSA. In remote areas of the Pacific and Arctic oceans, changes in plankton will indirectly influence the airborne MSA concentration. Moreover, we found fairly similar trends in the variation of the concentrations of total iodine (TI) and MSA in the Arctic during CHINARE2008, suggesting that iodine and MSA may come from similar sources in the Arctic. Compared with the findings from other two cruises, CHINARE1999 and CHINARE2012, we found that sea ice is an extremely important factor that influences the aerosol MSA content in the Arctic. In addition, MSA concentrations may increase in the Arctic in the future caused by sea ice melting due to global warming.

Keywords Arctic, MSA, iodine, phytoplankton, sea ice

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1 Introduction

Oceans cover 70% of the earth's surface area and have considerable effects on the earth's climate system. The effects of sulfur on the biogeochemical cycle in the atmosphere have certainly influenced climate change^[1]. In addition to atmospheric sulfur, airborne sulfur at the ocean surface mainly comes from dimethyl sulfide (DMS) produced by

microbes at the sea surface, such as phytoplankton^[2-4]. It has been estimated that half of the total biological sulfur comes from DMS produced by marine phytoplankton^[5]. When DMS is released into the air from the ocean/atmosphere boundary, it is oxidized by OH radicals, generating non-seasalt sulfate (nss-SO₄²⁻) and methanesulphonic acid (MSA)^[6]. Oceanic sulfur emissions containing MSA acting as cloud condensation nuclei (CCN) are believed to play an important role in the earth's radiation balance^[7-8]. This may be caused by a negative feedback for climatic perturbations through the effects of MSA on cloud cover and the earth's albedo^[9]. MSA is considered to be a stable oxidized form of DMS in the

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marine atmosphere. Measures of MSA concentrations have therefore been frequently used to estimate the productivity of marine organisms^[10-11], and serve as a useful tracer to distinguish marine biogenic sources of atmospheric sulfur from other sources^[12-13].

The Arctic and Antarctic are the world's source of cold currents in both the atmosphere and oceans, and play a significant role in global climate change. General atmospheric circulation may transmit anthropogenic pollutants to remote oceans; these could form a thick layer of smog over the Arctic every winter and spring^[14]. Therefore, climatic research in the Arctic must be an important component in the study of global climate change. In the Arctic, the primary productivity of phytoplankton plays an important role in DMS emissions^[15]. Moreover, phytoplankton is a significant source of iodohydrocarbon^[16-18]. We will therefore discuss the potential relationship between iodine and DMS.

In the past several decades, many researchers have attempted to analyze the characteristics of MSA in different oceanic regions, including the northwestern Pacific in different oceanic regions. Saltzman et al. found high concentrations of MSA corresponding to high primary productivity in the vicinity of Shemya of the Aleutian Islands in the northwest Pacific Ocean^[19]. Li et al. reported on seasonal changes in the atmospheric MSA concentration along the west coast of Canada, and also mentioned that the concentration varied depending on seasonal changes with higher values in August^[20]. Gao et al. found that most secondary MSA aerosols were created from the anthropogenic release of SO₂ in the China Sea region in the northwestern Pacific^[21]. Mihalopoulos et al. argued that a high level of air pollution may result in the production of greater amounts of MSA. Based on the above analyses, we can conclude that many factors can influence the atmospheric concentration of MSA, such as phytoplankton, temperature, solar radiation, and air pollutants^[22].

In summary, many types of research related to MSA have been conducted in the Arctic, in both the open ocean and in coastal regions. However, reports related to the spatial and temporal distributions and the interannual variations

of MSA in the Arctic are lacking. To fill these gaps, we conducted a study using R/V *XUE LONG* icebreaker as a monitoring platform, and collected and analyzed samples from the 3rd Chinese National Arctic Research Expedition (CHINARE2008). The new data were compared with those from the 1st and 5th cruises (CHINARE1999 and CHINARE2012, respectively). Furthermore, we compared the spatial and temporal distributions, and the interannual variations of MSA in the Arctic, northwest Pacific Ocean, and offshore China. The overall goal of this study was to gain a thorough understanding of the way in which biogenic sulfur aerosol concentrations respond to global climate change.

2 Experimental methods

2.1 Two cruises

In this study, samples were collected from two different routes. The first and major cruise of CHINARE2008, conducted from July to September 2008 by R/V *XUE LONG* icebreaker, sailed from Shanghai, China, to the Arctic Ocean. The ship returned to Shanghai through the western and northern Pacific Ocean and the Bering and Chukchi seas (31.1°N–85.18°N, 122.48°W–146.18°W; Figure 1).

The second cruise was the 1st China Offshore Research Expedition (CORE2006) organized by the Institute of Oceanology of the Chinese Academy of Sciences. The route was divided into three segments: (1) Qingdao to Zhoushan, (2) Zhoushan to Xiamen, and (3) Xiamen to Sanya. The trip began in September 2006 in Qingdao using Research Vessel *Science III*, and reached Xiamen two weeks later. We collected samples from the first two segments in this study (24.49°N–36.07°N, 118.98°E–123.55°W).

In addition, this present study also employed and compared data from 1999 and 2012 CHINAREs^[23-24]. However, the routes of these expeditions were different. For example, CHINARE2012 started in the Chukchi Sea on 18 July and returned on 8 September by crossing the central Arctic Ocean.

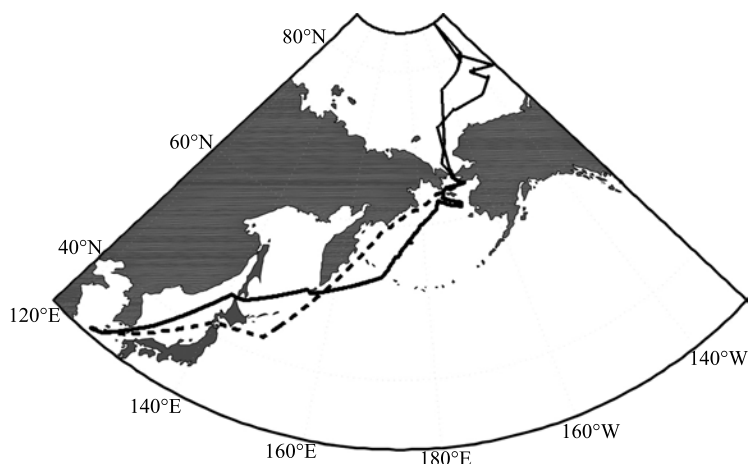


Figure 1 The Arctic Ocean route of the CHINARE2008. The solid and dotted lines represent the departure and return trips, respectively.

2.2 Sampling and experimental methods

We analyzed a total of 22 suspended particle (TSP) samples and four field control samples, which were collected during CHINARE2008. A high volume air sampler (Tianhong Instruments, Wuhan, China) was placed on the uppermost deck of the vessel. Wind direction was monitored to ensure the samples were not influenced by the vessel's own emissions. The TSP samples were collected at a flow rate of $\sim 1.0 \text{ m}^3 \cdot \text{min}^{-1}$ by glass microfiber filters (Whatman epm2000, Maidstone, UK, $20 \times 25 \text{ cm}^2$) for 24 h. The filtered samples were removed from the sampler at the end of the sample period and placed in individual clean plastic bags, which were then sealed and stored at 4°C prior to laboratory analysis.

Eight TSP samples had been collected during CORE2006; four filter samples in the daytime, and four at night. To meet the demands of marine operations, the ship stopped every 3–6 h during the day. When the ship was stationary, sampling also ceased to avoid possible contamination. After the ship-related operations were completed and sailing was again underway, sampling was resumed. Samples were acquired continuously at night.

A $2 \times 2 \text{ cm}^2$ section was taken from each filter and analyzed. Every sample was sonicated twice for 40 min each time with 20 mL ultra-pure water ($\geq 18 \text{ M}\Omega$). Samples were placed in an ice-water bath to control the water temperature. Samples were passed through a clean $0.45 \mu\text{m}$ filter to extract particles from the samples. Then, a Dionex DX-2100 ion chromatograph (IC) system (Sunnyvale, CA, USA) with an AG11-HC guard column and an AS11-HC analytical column was used to analyze MSA from the samples. Four field filter blanks were analyzed as controls; the MSA concentrations were subtracted from the value of the filter blanks to calibrate the measurements.

3 Results and discussion

Figure 2 shows the cruise paths of CHINARE2008 and CORE2006, including the locations where samples had

been collected to observe aerosol MSA concentrations. Detailed information for each sample is listed in Table A1. During CHINARE2008, the MSA concentrations varied considerably from non-detectable to $319 \text{ ng} \cdot \text{m}^{-3}$ (mean, $66 \pm 84 \text{ ng} \cdot \text{m}^{-3}$; median, $35 \text{ ng} \cdot \text{m}^{-3}$). This finding was similar to that of Xie et al. who reported an average MSA concentration of $71 \pm 60 \text{ ng} \cdot \text{m}^{-3}$ over the Arctic Ocean during CHINARE-1999 (69°N – 75°N , 133°W – 165°W)^[23]. During CORE2006, the concentration of MSA in the China Sea and vicinity averaged $28 \pm 14 \text{ ng} \cdot \text{m}^{-3}$ (median, $30 \text{ ng} \cdot \text{m}^{-3}$).

3.1 Regional characteristics

To improve the analysis of the two routes, the sea area was divided into four parts: (1) CORE2006 in offshore China, (2) CHINARE2008 in the northwestern Pacific Ocean including the Bering Sea, (3) the Chukchi Sea, and (4) the Arctic Ocean including the Beaufort Sea. The last three regions belong to the CHINARE study area.

Figures 2 and 3 show that the Arctic Ocean has the highest MSA concentration among the four regions listed above. In addition, the concentration of MSA in the Arctic Ocean exhibited a large magnitude of variation, peaking in the Beaufort Sea region near the edge of the ice shelf ($319 \text{ ng} \cdot \text{m}^{-3}$; Table 1). In this region, the ice would melt in summer creating an ice-free sea. The minimum MSA concentration ($2 \text{ ng} \cdot \text{m}^{-3}$) was observed in an area with pack ice.

The MSA concentration of the northwestern Pacific Ocean was also high and changed dramatically over time (Table 1); the highest two values were observed on the outbound trip and return trip in Japanese waters (Sample A02, 14 July, $208 \text{ ng} \cdot \text{m}^{-3}$; Sample A21, 15 September, $225 \text{ ng} \cdot \text{m}^{-3}$). This shows that the concentration changes in the Sea of Japan over time. MSA was not detected in the middle of the northwestern Pacific at Sample A06 (chlorophyll appears black here) during July. In Figure 3, the black areas indicate that there is no valid Chlorophyll-*a* data. We assumed that the Chlorophyll-*a* in these areas is similar to the value at the edge of black areas. Based on this assumption, the

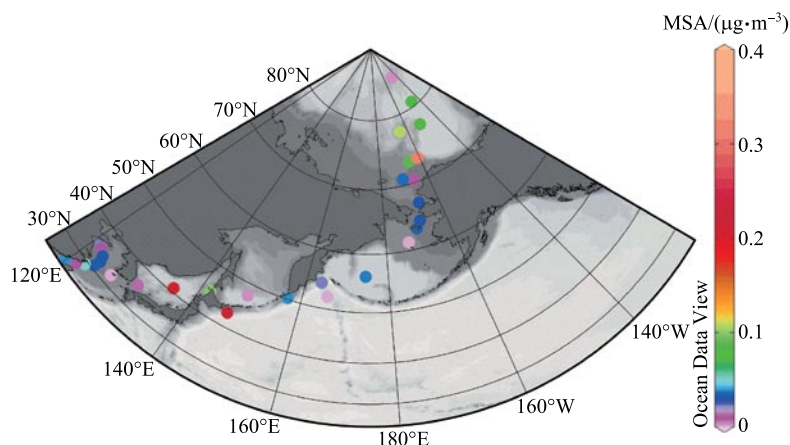


Figure 2 Spatial distribution of aerosol MSA along the two cruises during CHINARE2008 and CORE2006, generated by Ocean Data View 4.0. Include units of the colour scale in this caption.

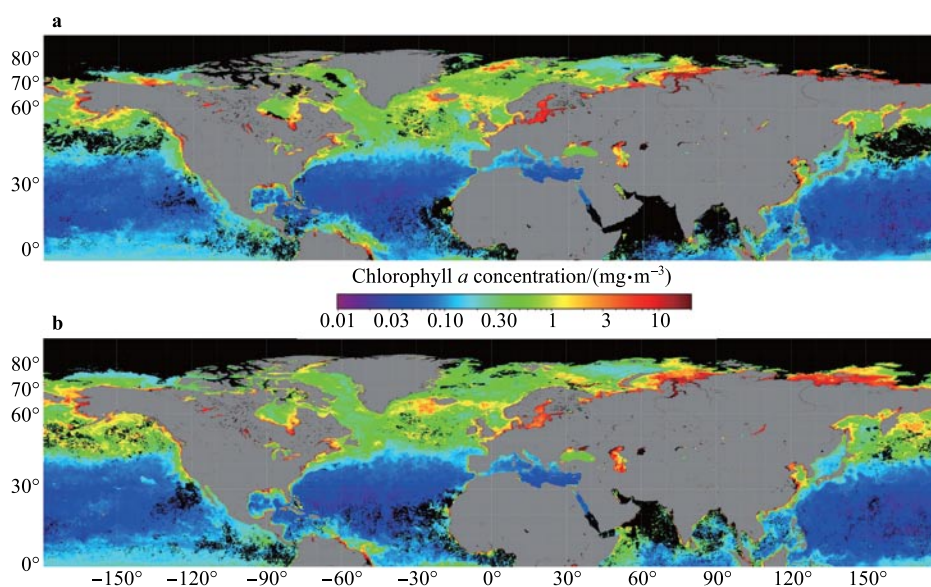


Figure 3 Map of oceanic Chlorophyll-*a* concentrations in the Northern Hemisphere. **a**, Chlorophyll-*a* concentrations for July 2008, and **b** for August 2008. Map from the NASA Ocean color website (<http://oceancolor.gsfc.nasa.gov>).

concentration of Chlorophyll-*a* in July was lower than in August in the middle of the northwestern Pacific Ocean. This may be the reason for the relatively low MSA observed in July in this region.

From Table 1 we can see that the MSA concentration in the Chukchi Sea was similar to the area offshore China and that it remained stable. Changes in the distribution of MSA in offshore China may be affected by terrigenous MSA sources.

Table 1 Comparison of MSA concentrations from different data sources

Location	Sampling time	Average/(ng·m ⁻³)	Range/(ng·m ⁻³)	Reference
Arctic Sea	August, September 2008	114	2–319	This study
Chukchi Sea	August, September 2008	25	10–36	This study
Northwestern Pacific Ocean	July, September 2008	54	ND–225	This study
China Offshore	September 2006	28	9–49	This study
Chukchi Sea	July, September 2012	12	ND–42	[24]
Central Arctic	August 2012	1.2	ND–5	[24]
East Asia	September 1999	10	6–13	[23]
North Pacific Ocean	July, August 1999	263	4–946	[23]
Arctic Ocean	July, August 1999	71	ND–202	[23]
Arctic Ocean	August 1991	134	–	[25]
Arctic Ocean	October 1991	5	–	[25]
Japan	1983–1992	–	5–130	[32]
Shemya(52°N, 174°E)	May–September 1981	170	–	[31]
Shemya(52°N, 174°E)	October 1981–March 1982	14	–	[31]
MaceHead, Ireland	August 1989–August 1990	69	–	[10]
Bermuda	July 1988, 1990	43	–	[10]
East China Sea	September, October 2002	27	ND–68	[49]
Qingdao	April 1992	69	–	[21]
Xiamen	May 1992	29	–	[21]

Note: “ND” indicates that the MSA concentrations were below the detection limit. “–” indicates no information was available.

3.1.1 The Arctic Ocean

The MSA concentration of the Arctic Ocean (mean $114 \text{ ng}\cdot\text{m}^{-3}$) was highest among the values documented for different regions during CHINARE2008. In addition, Xie et al. reported the average MSA concentration over the Arctic Ocean during CHINARE1999 of $71 \text{ ng}\cdot\text{m}^{-3}$, slightly lower than that of the present study^[23]. Leck and Persson reported that the average MSA concentration in the Arctic Ocean was $134 \text{ ng}\cdot\text{m}^{-3}$ in August, and then sharply declined to $5 \text{ ng}\cdot\text{m}^{-3}$ in October^[25]. The MSA data of CHINARE2012, which was much lower than that of CHINARE1999 and CHINARE2008, is discussed below (Section 3.4).

Leck and Persson pointed out that during August the concentration of organic sulfur in ice was always the highest year round at the edge of the Arctic^[25]. As mentioned above, marine phytoplankton produce DMS, which comprise over 90% of the sulfur flux in oceans^[26]. Chlorophyll-*a* is well-known to be a good proxy for the primary productivity of phytoplankton^[5,27]. Chlorophyll-*a* concentrations were much higher in August than in July throughout the route in the Arctic and northwestern Pacific Ocean (Figures 3a and 3b). However, almost all of the CHINARE2008 samples from the Arctic were collected in August, while those of other regions were collected in July.

Sample A14 had the highest MSA concentration found in samples from the Arctic. This was also the highest found over the entire route to the Beaufort Sea ($319 \text{ ng}\cdot\text{m}^{-3}$) in August. Sample A14 was also collected at the highest air temperature among all Arctic samples. In general, air temperature appears to peak in August in the Northern Hemisphere. In the Arctic, high August temperatures could accelerate the melting of sea ice, and greatly enhance the exchange of MSA between the ocean surface and the air^[28]. In addition, all these factors increased the availability of nutrients that would accelerate the growth of phytoplankton. August is more suitable for the growth of phytoplankton than July or any other time (Figure 3). In summary, August may have conditions that lead to the highest MSA concentrations.

Based on satellite data from the National Snow and Ice Data Center, we found that the average ice coverage in the Arctic Ocean in August 2008 was the second lowest on record (based on data from 1979 to 2008). The warm southern

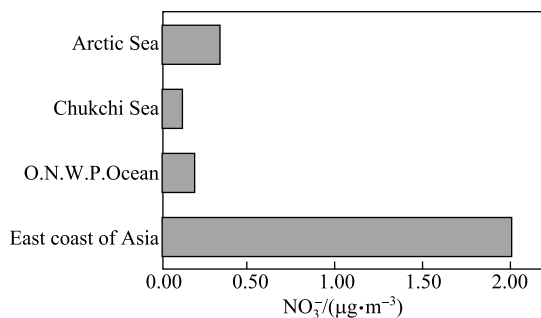


Figure 4 Concentrations of NO_3^- from different sampling areas during CHINARE2008 (O.N.W.P. indicates other areas of the northwestern Pacific).

airflow in August 2008 may have been partially responsible for this major loss of sea ice^[29]. The data from NASA's Ice, Cloud, and land Elevation Satellite revealed a clear trend in the decline in the thickness of Arctic Ocean ice in 2008^[30]. This resulted in a large area of algal growth and additional air-sea exchange^[28]. All the factors listed above may therefore contribute to the high concentration of MSA observed in the Arctic during August 2008.

3.1.2 Chukchi Sea

Chukchi Sea was specifically selected from the Arctic Ocean for further discussion to compare it with the data observations from CHINARE2012. The MSA concentration of the Chukchi Sea ($25 \pm 13 \text{ ng}\cdot\text{m}^{-3}$; median, $29 \text{ ng}\cdot\text{m}^{-3}$) was lower than that of the other regions in this study (Table 1), but was higher than the MSA concentration of CHINARE-2012 ($12 \pm 16 \text{ ng}\cdot\text{m}^{-3}$). The samples of CHINARE2012 were collected in July whereas the samples of CHINARE 2008 were collected in August (peak primary productivity), partially explaining why concentrations of MSA in samples were higher in CHINARE2008 than in CHINARE2012.

3.1.3 Northwestern Pacific Ocean

The average aerosol MSA concentrations in the northwestern Pacific Ocean ($54 \pm 77 \text{ ng}\cdot\text{m}^{-3}$) were the second highest for the entire CHINARE2008 route (Table 1). These values were similar to the average MSA concentrations ($97 \pm 98 \text{ ng}\cdot\text{m}^{-3}$) in northwestern Pacific in the vicinity of Shemya (52°N , 174°E), which were collected from May 1981 to April 1982^[31]. These were also similar to the MSA concentration ($69 \text{ ng}\cdot\text{m}^{-3}$) from Ireland's Mace Head (53.32°N , 9.85°W) in August 1989 to August 1990^[10]. For the present study, the aerosol MSA samples were collected in July (lower primary production from phytoplankton than August) and the MSA values were lower than those of CHINARE1999 ($263 \text{ ng}\cdot\text{m}^{-3}$)^[23].

The northwestern Pacific Ocean region exhibited two extremely high MSA values (Sample A02, $208 \text{ ng}\cdot\text{m}^{-3}$; Sample A21, $225 \text{ ng}\cdot\text{m}^{-3}$), both collected during CHINARE 2008, and both from the Sea of Japan. From Figure A1, it can be seen that samples A02 and A21 were clearly affected by air masses originating from areas near Japan, Korea, and

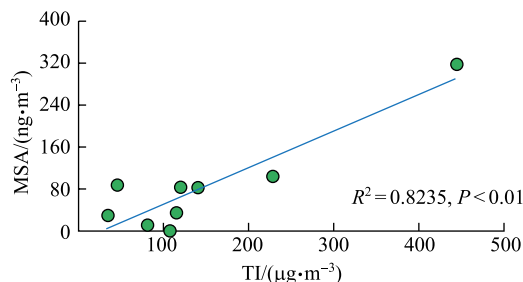


Figure 5 Relationship between MSA and TI over the Arctic Ocean (including Chukchi Sea) during CHINARE2008.

China. Pollutants from inland air may have caused the high MSA values in these two samples. Mukai and Yokouchi had observed similar high MSA concentrations from 1983 to 1992^[32].

The Chlorophyll-*a* concentration in the Bering Sea ($25 \pm 17 \text{ ng}\cdot\text{m}^{-3}$) was higher than that of the Sea of Japan (Figures 2 and 3). However, the MSA concentration was the opposite. Turner et al. pointed out that sometimes the concentration of DMS in seawater would not necessarily be associated with the chlorophyll concentration, since various factors, such as weather conditions (including precipitation), temperature, and algal growth, may have a combined effect^[33].

The concentrations of nitrogen oxides, such as nitrates, peak in the inland areas of Japan during summer^[34]. This, in turn, affects the efficiency of oxidation of DMS and thereby creates significantly higher concentrations of MSA in the atmosphere^[35].

To better analyze the data, we divided the northwestern Pacific Ocean into two parts: the east coast of Asia (based on the Sea of Japan, 33°N – 45°N , 126°E – 147°E) and the other areas of the northwestern Pacific Ocean (46°N – 64°N , 148°E – 168°W). Then, we analyzed the NO_3^- concentrations of these regions during CHINARE2008. The aerosol NO_3^- concentration ($2.01 \mu\text{g}\cdot\text{m}^{-3}$) on the east coast of Asia was far greater than that of other areas (Figure 4). In addition, the mean MSA value ($107.4 \text{ ng}\cdot\text{m}^{-3}$) was also much higher than that of the northwestern Pacific Ocean ($20.3 \text{ ng}\cdot\text{m}^{-3}$) and the Chukchi Sea ($25.3 \text{ ng}\cdot\text{m}^{-3}$). This may have been caused by the long distance transport of pollutants from Japan and other east Asian inland areas^[34]. Furthermore, the high nitrogen oxide content of the pollutants may have improved the oxidation efficiency of DMS.

Yuan et al. reported that MSA was detected from most aerosol samples collected in the Beijing area, and in concentrations that were significantly higher than those in coastal Chinese cities and oceanic areas^[36]. However, no obvious sea-salt source from the aerosol was observed in Beijing. The release of DMS in the inland areas and dimethyl sulfoxide (DMSO) from industrial wastes may be two precursors to MSA. The CHINARE2008 vessel passed through the Sea of Japan, which is near the inland areas of China. Also, anthropogenic pollution on land may play an important role in the formation of MSA in this area.

3.1.4 Offshore China

The MSA concentration over areas offshore China was $28 \pm 14 \text{ ng}\cdot\text{m}^{-3}$ and the distribution of MSA was relatively stable (Table 1). This mean MSA value was comparable to previous studies related to the MSA content of air in coastal areas worldwide, and our findings were similar to results from these areas. Nakamura et al. reported that the MSA content of air in the East China Sea was $27 \pm 20 \text{ ng}\cdot\text{m}^{-3}$ (26°N – 34°N , 122°E – 130°E). Gao et al. found that the average MSA concentrations in Qingdao, Xiamen, and on an East China Sea voyage ranged from 29 to $69 \text{ ng}\cdot\text{m}^{-3}$. These results are

close to the MSA levels in the current study^[21,37].

The route of CORE2006 also documented the spatial distribution of MSA concentrations. The East China Sea, offshore China ($32 \text{ ng}\cdot\text{m}^{-3}$, 25°N – 33°N) had higher MSA concentrations than the other part of China's offshore region ($21 \text{ ng}\cdot\text{m}^{-3}$, 34°N – 36°N). The diverse areas of the main region of China Sea have different levels of marine productivity. The regions near the Yellow and Yangtze rivers, both of which flow into the East China Sea, have higher marine primary productivity. The concentration of atmosphere NO_x , which plays an important role in the process of oxidation of DMS into MSA, also influences the MSA concentrations. High concentrations of NO_x pollutant gases will cause atmospheric concentrations of MSA to become very high^[22,36,38]. The eastern coastal areas of China are industrial with well-developed manufacturing infrastructure. Therefore, a high concentration of anthropogenic NO_x can be transmitted to the East China Sea from the inland areas, causing an increase in the atmospheric concentration of MSA.

3.2 Link with iodine

Marine phytoplankton are well known as producers of DMS, which comprises more than 90% of the sulfur flux in oceans^[2]. Moreover, phytoplankton are a significant source of various halocarbons (including iodocarbons)^[16–18]. In the Arctic, diatoms are the most frequently documented phytoplankton taxa that may produce significant amounts of iodocarbons^[39–40]. By coincidence, diatoms may also produce DMS in the Arctic Ocean^[41–42].

The data from CHINARE2008 show that Sample A14 had the highest MSA content of all samples from the Arctic Ocean and the entire cruise. Similarly, the highest concentration of TI found during this cruise was also found in Sample A14^[43]. Therefore, by combining our data with the TI data from Xu et al.^[43], we analyzed the correlation between MSA and TI in the Arctic Ocean (including the Chukchi Sea).

The concentrations of MSA and TI show a strong correlation ($R^2 = 0.82$, $P < 0.01$, Figure 5). When the same environmental factors are considered, DMS and TI may be derived from similar sources in the Arctic marine boundary.

3.3 Comparing previous cruises in the Arctic Ocean

Previous studies have shown that the highest concentration of organic sulfur was observed at the edge of the Arctic Ocean ice in August^[44] when warm humid weather corresponds with the high concentration of MSA in the atmosphere^[45]. In the Arctic, the highest concentration of atmospheric MSA occurs in summer. In addition, the atmospheric concentration of MSA at the edge of the area between the ocean and sea ice is far higher than that in areas with thick ice. High temperatures accelerate the melting sea ice, which is a significant cause of the high MSA concentrations observed in summer. Ice cover plays an important role in air-sea exchange, and influences the nature of the marine community and climate^[46]. Sea ice

may limit the DMS air-sea exchange and reduce the content of MSA in the atmosphere^[25,44].

The extent of ice coverage in the Arctic Ocean has tended to decrease in recent years, as a result of great changes in the Arctic environment^[47]. In addition, the overall downtrend may be continuing throughout the entire year, during both summer and winter.

Compared with CHINARE1999, the concentration of MSA throughout the Arctic segment in CHINARE2008 (114 ± 107 ng·m⁻³) was slightly higher than that in CHINARE 1999 (71 ± 60 ng·m⁻³). The average ice cover in the Arctic Ocean during August 2008 was much lower than that in 1999^[29]. This maybe the most important cause of the higher MSA concentrations observed during CHINARE2008. However, CHINARE2012 documented much lower MSA concentrations (1.2 ng·m⁻³) than previous research trips in the Arctic, especially when compared to CHINARE2008. The extremely low concentrations may be the result of the specific route. The cruise of CHINARE2012 began in the Chukchi Sea and passed through the entire central Arctic Ocean. Furthermore, a majority of the samples collected during this cruise were from the central Arctic Ocean, which has extensive ice cover.

The distribution of sea ice in the high Arctic (77°N–86°N), measured by helicopter aerial photography from R/V *XUE LONG* icebreaker, the CHINARE2008 vessel^[48], can be divided into three parts: (1) areas with pack ice (83°N–86°N, the pack ice covered more than 70% of the sea), (2) areas with floating sea ice (77°N–83°N), and (3) areas of open sea (<77°N). The samples collected during CHINARE 2008 were nearly all from areas of open sea, and areas with floating sea ice. Only one sample was collected in an area of pack ice (Sample A17, 2 ng·m⁻³). The MSA value here was similar to the samples collected from CHINARE2012, which were collected in areas with pack ice. Thus, the CHINARE2012 samples were mostly collected in areas of pack ice, which may be the primary reason for the much lower MSA values observed during the 2012 cruise.

From the above, we can infer that the MSA concentration is negatively correlated with the spatial extent of sea ice, and a large expansion of sea ice provides an important barrier that limits DMS and MSA concentrations. In the event of continuing loss of sea ice in the future, MSA concentrations will be expected to increase.

4 Summary

We investigated MSA concentrations from aerosol samples collected during CHINARE2008 from July to September. We found that the MSA concentrations varied considerably from non-detectable to 319 ng·m⁻³ (mean, 66 ± 84 ng·m⁻³; median, 35 ng·m⁻³). In coastal regions, such as the Sea of Japan, air pollution (especially nitric oxide) from inland areas could also have strong effects on the concentration of aerosol MSA. In remote areas of the Pacific and Arctic oceans, MSA generated by phytoplankton is the dominant factor

influencing the airborne MSA concentration. Moreover, we found a fairly similar variation trend between TI and MSA in the Arctic during CHINARE2008, indicating that iodine and MSA may come from similar sources in Arctic. High MSA concentrations were always observed during August throughout CHINARE2008, similar to many previous reports from the Northern Hemisphere. The combination of increased warmth and nutrients creates more suitable conditions for the growth of phytoplankton in August than at any other time. Finally, when comparing the CHINARE2008 data with the data from CHINARE1999 and CHINARE2012 cruises, we found that sea ice is an extremely significant factor that influences the aerosol concentration of MSA in the Arctic. Global warming will tend to accelerate the melting of sea ice, leading to higher MSA concentrations in the future.

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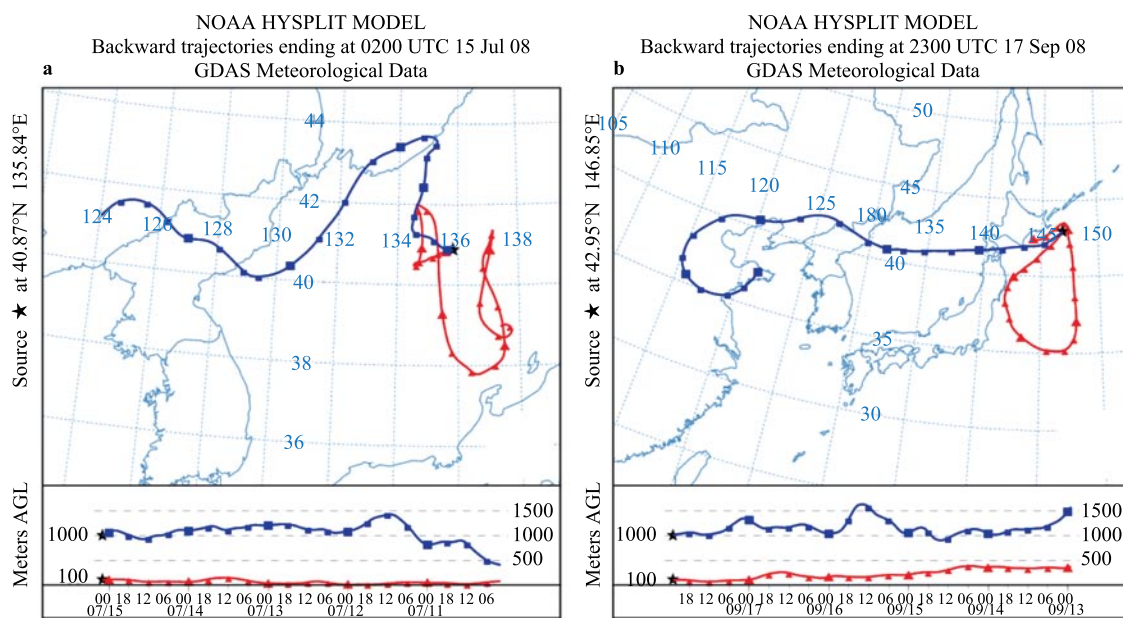
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Supplementary Table A1 Sampling information and concentration of MSA during CHINARE2012 and CORE2006

Sample number	Latitude*	Longitude*	Sampling date	MSA/(ng·m ⁻³)
A01	35.93	130.76	13–14 July 2008	6
A02	40.87	135.84	14–15 July 2008	208
A03	44.89	141.79	15–16 July 2008	98
A04	47.82	148.86	16–17 July 2008	3
A05	50.24	157.00	17–18 July 2008	39
A06	52.18	165.54	18 July 2008	ND
A07	56.30	174.26	19–21 July 2008	36
A08	61.32	-173.27	23–25 July 2008	ND
A09	63.14	-170.00	25–27 July 2008	34
A10	64.22	-168.32	27–29 July 2008	29
A11	66.91	-166.87	31 July–2 August 2008	29
A12	70.45	-166.05	2–4 August 2008	12
A13	73.18	-165.53	4–6 August 2008	89
A14	73.30	-160.87	6–9 August 2008	319
A15	77.39	-150.82	13–15 August 2008	84
A16	80.69	-146.134	15–18 August 2008	83
A17	85.10	-147.08	27–28 August 2008	2
A18	77.71	-165.03	1–5 September 2008	106
A19	70.96	-170.52	5–8 September 2008	36
A20	54.45	163.63	12–14 September 2008	21
A21	42.95	146.85	15–17 September 2008	225
A22	32.70	126.38	20–21 September 2008	ND
C01	35.80	120.73	18 September 2006	21
C02	34.99	121.89	18 September 2006	9
C03	34.13	123.03	19 September 2006	32
C04	32.80	123.52	19–20 September 2006	29
C05	30.92	123.38	20 September 2006	32
C06	29.02	122.28	23 September 2006	49
C07	27.15	121.31	24 September 2006	9
C08	25.36	119.83	24–25 September 2006	38

Note: *The latitude and longitude represent the mean location of the start and end of each sampling episode. Sample sites in latitude south and north are denoted with “-” and “+”, respectively. Sample sites in longitude west and east are denoted with “-” and “+”, respectively. “ND” indicates MSA concentrations under the detection limit. Samples A1–A22 were collected during CHINARE2008, and samples C1–C8 were collected during CORE2006. Samples A1–A10 and A20–A22 were collected from the northwestern Pacific Ocean; samples A11, A12, and A19 were collected from the Chukchi Sea; samples A13–A18 were collected from the Arctic Ocean; and samples C1–C8 from offshore China.



Supplementary Figure A1 Air mass back trajectories (AMBTs) were calculated from the National Oceanic and Atmospheric Administration (NOAA) GDAS meteorology database, using the Hybrid Single-Particle Lagrangian Integrated Trajectories (HY-SPLIT) program. AMBTs were performed at 100 and 1000 m height levels over the sampling locations with backward five days: Sample A02 (a) and Sample A21 (b).