

Chemical composition of marine aerosols of the 26th Chinese National Antarctic Research Expedition

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Abstract The ionic compositions of aerosol samples collected during the 26th Chinese National Antarctic Research Expedition were analyzed and the sources of ions were distinguished. Cl^- , Na^+ , SO_4^{2-} , NO_3^- , and Mg^{2+} were the most abundant ionic components in the marine aerosols. Cl^- and Na^+ contributed over 70% in the total ionic composition, indicating the sea salt is still the primary composition in marine aerosols, followed by the sulfate as the secondary ionic component existed as NH_4NO_3 , NH_4HSO_4 , $(\text{NH}_4)_2\text{SO}_4$. The maximal sea salt concentrations were found at around 40°S and could be attributed to greater winds. The concentrations of methane sulfonic acid (MSA) appeared increasing trend from the low to high latitudes, possibly caused by lower temperature in air and higher marine biological processes in the marginal waters in Antarctica. The correlation and factor analyzes were used to investigate possible sources of these ions. Cl^- , Br^- , Na^+ , K^+ , Mg^{2+} and Ca^{2+} had predominantly marine sources; while F^- , NO_3^- and NH_4^+ had mostly anthropogenic sources; MSA had marine biogenic sources. The concentrations of SO_4^{2-} were influenced by both marine and anthropogenic sources.

Keywords Soluble ions, MSA, Southern Ocean, 26th Chinese National Antarctic Research Expedition

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0 Introduction

Marine aerosol is the major component of the global atmospheric aerosol, and the specific physical and chemical properties of aerosols have a key role in atmospheric processes and processing^[1]. Aerosol is the main route of transferring marine species onto land, and a major channel through which terrestrial species are transported to the oceans^[2]. So an understanding of the composition and provenance of marine aerosol is important to evaluate the relative impact of anthropogenic and biogenic processes on the global biogeosphere and climate.

There were many studies of the composition of ma-

rine aerosols in polar areas^[3–5]. During the first Chinese National Antarctic Research Expedition (CHINARE), from November 1984 to March 1985, 31 marine aerosol samples from around the Pacific Ocean and Antarctic Peninsula area were analyzed by Ion Chromatography (IC)^[3]. The results showed that the concentration of non-sea-salt sulfate (nss-SO_4^{2-}) in the marine aerosol rapidly decreased from the North Pacific Ocean to the South Pacific Ocean. The sea-air flux of sulfur was calculated in the waters of the Antarctic Peninsula. To understand the latitudinal distribution of marine aerosols, several aerosol samples were collected during the first

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Chinese National Arctic Research Expedition (CHINARE-Arctic, between July 1 and September 9, 1999)^[4], Na^+ , NH_4^+ , K^+ , Mg^{2+} , Ca^{2+} , Cl^- , NO_3^- and SO_4^{2-} were determined using IC. During the 2nd CHINARE-Arctic (between July 15 and September 28, 2003), aerosol samples were also collected^[5], and the concentrations of Na^+ , NH_4^+ , K^+ , Mg^{2+} , Ca^{2+} , Cl^- , MSA, SO_4^{2-} , NO_3^- , $\text{C}_2\text{O}_4^{2-}$ and CH_3COO^- were determined and the distribution and potential sources were discussed. The results showed that sodium and chloride ions were the dominant species in marine aerosols, accounted for 60.2% of the total aerosol loading, followed by sulfate.

To understand the global sulfur cycle, and better quantify the atmospheric sulfur fluxes, the effects of the main marine and terrestrial sources of sulfur (dimethyl sulfide (DMS) and hydrogen sulfide (H_2S) respectively) on the aerosol have been a matter of keen interest. In particular, methane sulfonic acid (MSA) and DMS precursors have been the subject of many measurements, because MSA is found in precipitation and in aerosol samples. DMS is formed in the oceans by the photochemical and enzymic cleavage of Dimethyl sulfonium propionate (DMSP), a phytoplanktonic metabolite, into DMS and acrylic acid. DMS is very insoluble in seawater, and is released quickly from the sea surface to form atmospheric DMS. This DMS subsists in the atmosphere for about 24 h before it is oxidized by either the OH or IO radical to form MSA and SO_2 (the ratio being dependent on temperature, and degree of anthropogenic influence). Because MSA is one of the most water soluble compounds in the atmosphere, it is quickly scavenged onto aerosol particles. The final proportions in remote non-polar areas is about 85% MSA and 15% sulfate^[6].

MSA was first measured using IC by Saltzman et al.^[7] in marine aerosol. According to many observations, MSA was ubiquitous in Marine Boundary Layer (MBL) and even in coastal cities^[8]. Some research showed that MSA concentrations were closely related to acidic precipitation, and global climate change^[9-10]. The flux of marine sulfur into the atmosphere has a great impact on acid precipitation formation processes and the oxidizing ability of the atmosphere^[11]. SO_4^{2-} particles produced by the oxidation of reduced sulfur compounds are the main source of the cloud condensation nuclei (CCN) in the remote marine atmosphere. These parti-

cles determine the cloud albedo, which can influence the global climate greatly^[12]. Precipitation samples from the 12th CHINARE cruise showed that MSA exhibited an increasing trend from Tropic Ocean to Sub-Antarctic Ocean, with two abruptly increasing areas corresponding to around 15°S and 60°S-65°S, respectively^[13]. These coincided with areas of upwelling MSA/nss SO_4^{2-} ratio was found to be sensitive to the temperature change, which is shown by δD values of the samples and the simultaneous temperature records. Generally speaking, the MSA research in the atmosphere of remote open Oceans and Antarctic area is relatively sparse in China.

This work discusses the composition and provenance of ionic components of high volume (hi-vol) marine aerosol samples along the cruise track of the 26th CHINARE, from October, 2009 to April, 2010. There is a focus on MSA and nss- SO_4^{2-} .

1 Sampling and methods

The 26th CHINARE started from Shanghai on October 11, 2009, and returned to Shanghai on April 15, 2010. The cruise was approximately through Christchurch to Great Wall Station, to Ushuaia-Zhongshan Station to Casey Station to Melbourne to Zhongshan Station to Fremantle to Shanghai, the detailed cruise track and sampling points are presented in Figure 1.

48 aerosol samples were collected by using a high-volume sampler M400 (made in USA), and Whatman 41 filters (20.3 cm×25.4 cm, Whatman International Ltd, England), see Table 1. The filters were placed on the upper deck of M/V Xuelong about 25 m above the sea surface. The sampling head was also covered by a cylindrical polyethylene hood to protect from sea surf or rainfall. During the cruise, most of major samples were collected in 3 d. The sampling date, latitude and longitude, air temperature, pressure and other meteorological parameters were recorded at the start and end of the sampling periods. After sampling, filters were removed from the filter holder with disposable gloves and stored in cleaned airtight plastic containers. After labeling, the samples were stored in the refrigerator at 4°C aboard the M/V Xuelong. To avoid contamination by the products of fuel combustion from the vessel's generator set etc, the sampling system was controlled with a wind speed and direction system which only allowed sampling when the

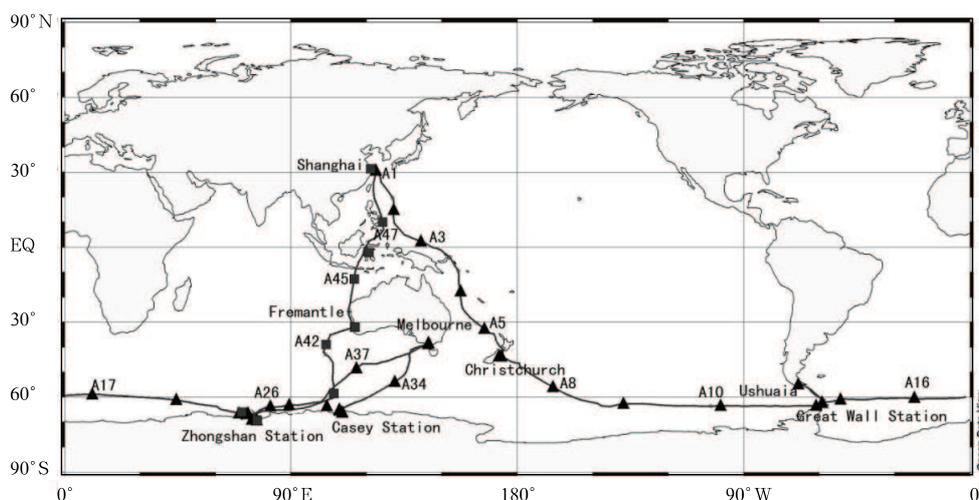


Figure 1 Cruise track of the 26th CHINARE with sampling points. The solid line represents the cruise track. Symbols represent the start of sampling periods; the triangles on the outbound journey and the squares on the inbound journey.

wind was from a sector between left and right 90° down the middle line of the ship's head and at wind velocities $>0.2 \text{ m}\cdot\text{s}^{-1}$. Each filter sampled about $5\,000 \text{ m}^3$ of air at a flow rate about $1 \text{ m}^3\cdot\text{min}^{-1}$.

A Dionex ICS-2500 ion chromatograph was used to analyze the soluble aerosol ions. The cations were analyzed with a CS12A analytical column and a CG12A guard column, and the anions were analyzed with an AS18 analytical column and an AG18 guard column.

Experimental methods were as follows: One eighth of each filter was rinsed with 25 mL of deionized water, ultrasonicated for about 40 min and leached overnight. Then samples were injected into the IC system via $0.45 \mu\text{m}$ filters. The time sequence for the elution of the cations was Na^+ , NH_4^+ , K^+ , Mg^{2+} , Ca^{2+} , and that for anions was F^- , MSA, Cl^- , Br^- , NO_3^- , SO_4^{2-} . The detection limits for above ions were Na^+ $0.015 \text{ mg}\cdot\text{m}^{-3}$, NH_4^+ $0.009 \text{ mg}\cdot\text{L}^{-1}$, K^+ $0.017 \text{ mg}\cdot\text{L}^{-1}$, Mg^{2+} $0.020 \text{ mg}\cdot\text{L}^{-1}$, Ca^{2+} $0.046 \text{ mg}\cdot\text{L}^{-1}$, F^- $0.000\,9 \text{ mg}\cdot\text{L}^{-1}$, MSA $0.000\,4 \text{ mg}\cdot\text{L}^{-1}$, Cl^- $0.009\,5 \text{ mg}\cdot\text{L}^{-1}$, Br^- $0.000\,5 \text{ mg}\cdot\text{L}^{-1}$, NO_3^- $0.006\,9 \text{ mg}\cdot\text{L}^{-1}$, SO_4^{2-} $0.003\,2 \text{ mg}\cdot\text{L}^{-1}$. To consider the Whatman 41 blank, ion concentrations from 7 blank filters were determined, and the average blank was (unit: $\text{mg}\cdot\text{L}^{-1}$): Na^+ 330, NH_4^+ 330, K^+ 40, Mg^{2+} 50, Ca^{2+} 100, F^- 10, MSA 30, Cl^- 690, Br^- 30, NO_3^- 350, SO_4^{2-} 190. These blank values have been subtracted from all aerosol results.

2 Results and discussions

2.1 Major ions constituents and formation

Concentrations and percentages of major water soluble

ions of aerosol samples are presented in Figures 2 and 3. The concentration sequences for various ions were: $\text{Cl}^- > \text{Na}^+ > \text{SO}_4^{2-} > \text{Mg}^{2+} > \text{NO}_3^- > \text{NH}_4^+ > \text{Ca}^{2+} > \text{K}^+ > \text{MSA} > \text{Br}^- > \text{F}^-$. The average concentrations for major water soluble ions were: Na^+ $1\,136.37 \text{ ng}\cdot\text{m}^{-3}$, Mg^{2+} $148.32 \text{ ng}\cdot\text{m}^{-3}$, NH_4^+ $91.33 \text{ ng}\cdot\text{m}^{-3}$, Ca^{2+} $75.34 \text{ ng}\cdot\text{m}^{-3}$, K^+ $45.44 \text{ ng}\cdot\text{m}^{-3}$, Cl^- $1\,999.36 \text{ ng}\cdot\text{m}^{-3}$, SO_4^{2-} $587.76 \text{ ng}\cdot\text{m}^{-3}$, NO_3^- $94.31 \text{ ng}\cdot\text{m}^{-3}$, MSA $23.10 \text{ ng}\cdot\text{m}^{-3}$, Br^- $4.83 \text{ ng}\cdot\text{m}^{-3}$, F^- $1.56 \text{ ng}\cdot\text{m}^{-3}$. The major water soluble ion constituents (Cl^- , Na^+ , SO_4^{2-} , Mg^{2+} , NO_3^-) accounted for the 94.3% of the total aerosol loading. Sea salt particles were the primary marine aerosol constituents, followed by sulfate.

The charge balance was calculated using equivalent concentrations. The usual method was used, i.e., equivalent concentration ($\text{neq}\cdot\text{m}^{-3}$) = chemical valence mass concentration ($\text{ng}\cdot\text{m}^{-3}$)/molecular weight. Strong linear correlations existed between the two electrically charged groups of anions and cations with a slope of 1.04, tending to 1 ($R^2=0.992$), see Figure 4. This suggests that a good charge balance existed between the two groups. Therefore the sampling and measurement methods in the study were reliable^[14].

From the results, it can be seen that sulfate was an important aerosol component of the marine atmosphere^[15]. Previous work suggested that the sulfate aerosol had both direct and indirect impacts on solar radiation. It also acted as the CCN source, which had greatly affected the radiation balance and hence climate change. For these reasons, scientists of atmospheric chemistry have focused on sulfate aerosol. Generally sulfate in tropospheric aerosol can be divided into two parts.

Table 1 Sampling dates of aerosol samples of the 26th CHINARE cruise

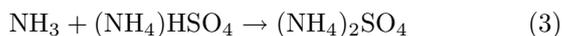
Sample number	Sampling time	Sample number	Sampling time
A1	2009/10/12 02:23–10/15 01:37	A25	2009/12/25 22:08–12/28 14:10
A2	2009/10/15 01:42–10/18 02:05	A26	2009/12/28 14:18–12/31 05:12
A3	2009/10/18 02:09–10/23 01:51	A27	2009/12/31 05:18–2010/01/04 13:15
A4	2009/10/23 01:56–10/26 01:57	A28	2010/01/04 13:20–01/07 16:45
A5	2009/10/26 02:03–10/28 10:58	A29	2010/01/07 16:50–01/10 11:16
A6	2009/10/28 11:02–10/30 21:06	A30	2010/01/10 11:16–01/12 04:50
A7	2009/10/30 21:11–11/02 22:02	A31	2010/01/12 04:50–01/15 04:38
A8	2009/11/02 22:07–11/05 23:23	A32	2010/01/15 04:43–01/17 13:10
A9	2009/11/05 23:30–11/09 00:55	A33	2010/01/17 13:17–01/20 11:10
A10	2009/11/09 01:00–11/11 23:35	A34	2010/01/20 11:16–01/24 04:09
A11	2009/11/11 23:40–11/15 09:57	A35	2010/01/24 04:13–01/27 18:55
A12	2009/11/15 10:01–11/17 02:50	A36	2010/02/03 07:00–02/07 10:50
A13	2009/11/17 02:55–11/20 22:40	A37	2010/02/07 10:55–02/11 06:43
A14	2009/11/20 22:45–11/23 22:33	A38	2010/02/11 06:48–02/14 07:30
A15	2009/11/23 22:46–11/26 18:42	A39	2010/02/14 07:34–02/19 08:45
A16	2009/11/26 18:45–11/29 18:08	A40	2010/03/06 03:14–03/09 07:15
A17	2009/11/29 18:12–12/02 18:12	A41	2010/03/09 07:15–03/13 01:33
A18	2009/12/02 18:16–12/05 11:35	A42	2010/03/13 01:33–03/16 01:45
A19	2009/12/05 11:40–12/08 14:08	A43	2010/03/16 01:45–03/24 04:12
A20	2009/12/08 14:12–12/11 18:34	A44	2010/03/24 04:12–03/27 08:15
A21	2009/12/11 18:50–12/15 08:30	A45	2010/03/27 08:15–03/30 02:30
A22	2009/12/15 08:33–12/19 03:26	A46	2010/03/30 02:35–04/02 09:55
A23	2009/12/19 03:31–12/22 05:10	A47	2010/04/02 10:00–04/05 10:20
A24	2009/12/22 05:15–12/25 22:02	A48	2010/04/05 10:20–04/07 06:15

One part sourced from sea salt, namely sea-salt SO_4^{2-} (ss- SO_4^{2-}), and the other part sourced from the emissions of anthropogenic and biogenic activities, called non-sea-salt SO_4^{2-} (nss- SO_4^{2-}). Based on assumptions of the composition of seawater,

$$\text{nss-SO}_4^{2-} = [\text{SO}_4^{2-}]_{\text{Total}} - [\text{Na}^+] \times 0.2516$$

where 0.2516 is the value of $\text{SO}_4^{2-}/\text{Na}^+$ in seawater.

According to the correlations between various water soluble ions (see Table 3), the secondary aerosol ions: NO_3^- , NH_4^+ and nss- SO_4^{2-} had a significant positive correlation each other (Pearson Correlation Coefficient > 0.5, and $p < 0.01$), which accounted for the NH_4^+ existing as NH_4NO_3 , NH_4HSO_4 and $\text{NH}_4(\text{SO}_4)_2$. Several studies have shown that the likely chemical scheme of reactions to produce NH_4^+ is as follows^[16–17]:



NO_3^- is mostly produced by the chemical equation (1), and the reaction (4) occurs on the sea salt surface and can absorb additional NO_3^- . NH_4^+ is produced by reactions (1), (2), (3).

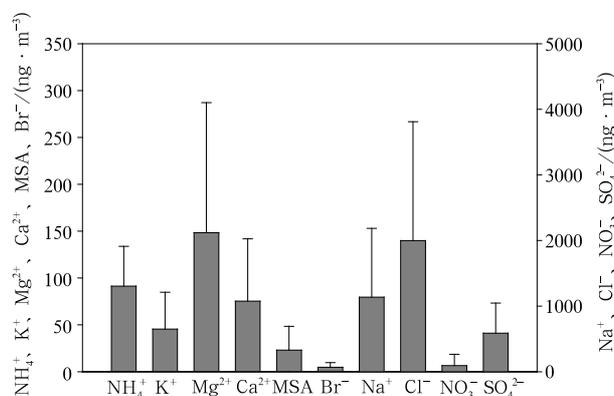


Figure 2 Major ions in marine aerosol along the Xuelong's route during the 26th CHINARE.

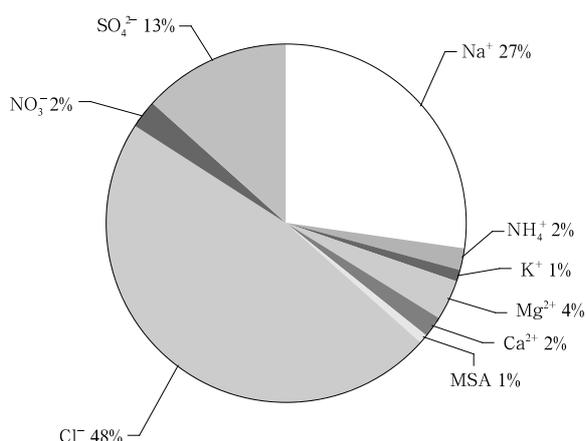


Figure 3 The pie map for major soluble ions in TSP during the 26th CHINARE cruise.

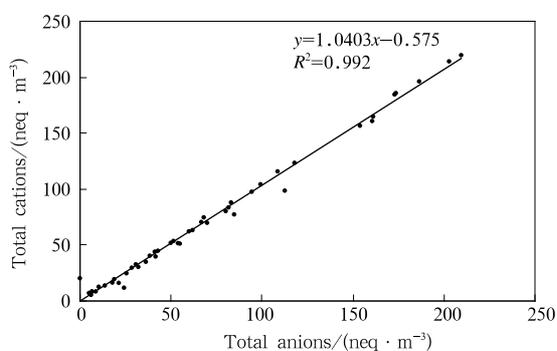


Figure 4 The charge balance between total anions and cations during the 26th CHINARE cruise.

In addition, the concentrations of Na⁺, K⁺, Mg²⁺ correlated obviously with Cl⁻, Br⁻ (Pearson Correlation Coefficient > 0.6, $p < 0.01$) from Table 3. This may indicate that the ions were present as NaCl, KCl, MgCl₂, NaBr, KBr, MgBr₂ and so on. This would be similar to the components in sea water.

2.2 The latitudinal distribution characteristics of various components

To examine the distribution of aerosol ions along the route of 26th CHINARE, latitudinal distributions of aerosol ions are shown in Figure 5. The sea salt concentration was used to represent the concentration of marine aerosol sea salt particles, and the sea salt was calculated from:

$$\text{Sea Salt}(\text{ng} \cdot \text{m}^{-3}) = \text{Cl}^{-}(\text{ng} \cdot \text{m}^{-3}) + \text{Na}^{+}(\text{ng} \cdot \text{m}^{-3}) \times 1.47$$

Where 1.47 is the value of $(\text{Na}^{+} + \text{K}^{+} + \text{Mg}^{2+} + \text{Ca}^{2+} + \text{SO}_4^{2-} + \text{HCO}_3^{-})/\text{Na}^{+}$ in sea water. This assumes

that all of the Na⁺ and Cl⁻ in the aerosol is sourced from the sea water, and all non-sea-salt components of K⁺, Mg²⁺, Ca²⁺, SO₄²⁻ and HCO₃⁻ have been excluded^[18]. Figure 5(a) shows the latitudinal distribution of sea salt on the route of the 26th CHINARE, and the high values were found south of 40°S. Some previous work^[19] reports that Na⁺ and Cl⁻ are mainly sourced from the sea, and their concentrations are controlled by the wind speed over the sea surface. In this study, the sea salt concentration was also affected by the wind speed. In the south of 40°S, which was close to the latitudes of prevailing westerly winds. Both wind-speed and waves were high and sea spray, which was enriched with sea salt, was emitted into the atmosphere. So the general tendency of sea salt concentrations was high. As for NH₄⁺, shown in Figure 5(b), the general concentrations were about 50–100 ng·m⁻³, and high values (295.4 ng·m⁻³) occurred over the East China Sea. This sample was collected at the end of spring, 2010, when Western and Northern China were experiencing severe sandstorms, so the dust could be transported long distances to the Chinese marginal seas. Therefore, a series of atmospheric photochemical reactions occurred on the surface of the particles and produced high concentrations of secondary aerosols. The concentrations of SO₄²⁻ and NO₃⁻ were also high, demonstrating that chemical reactions (1), (2) and (3) took place on the aerosols surface. Hence these samples were very altered by the influence of the transported terrestrial substances. The latitudinal distribution of NO₃⁻ is shown in Figure 5(c). The tendency of the NO₃⁻ is clearly similar to that of NH₄⁺, and high values also occurred in the samples collected in Chinese marginal seas, Fremantle port and the offshore of Philippines. These high concentrations were inevitably affected by the emissions from anthropogenic activities, and chemical reactions (1), (4) happened on the surface of particles with the participation of HNO₃. And chemical reaction (4) may be the main process of NO₃⁻ production in the remote ocean.

The MSA in marine aerosols was produced by a series of oxidation reaction of DMS, and the latitudinal distribution is shown in Figure 5(d). According to the distance of M/V Xuelong away from the continent and the specific characteristics of different ocean areas, the voyage track could be divided into 3 parts, i.e. Shanghai to Fremantle (32°S–30°S), Indian Ocean (30°S–60°S) and the Southern Ocean-Antarctic floating ice region

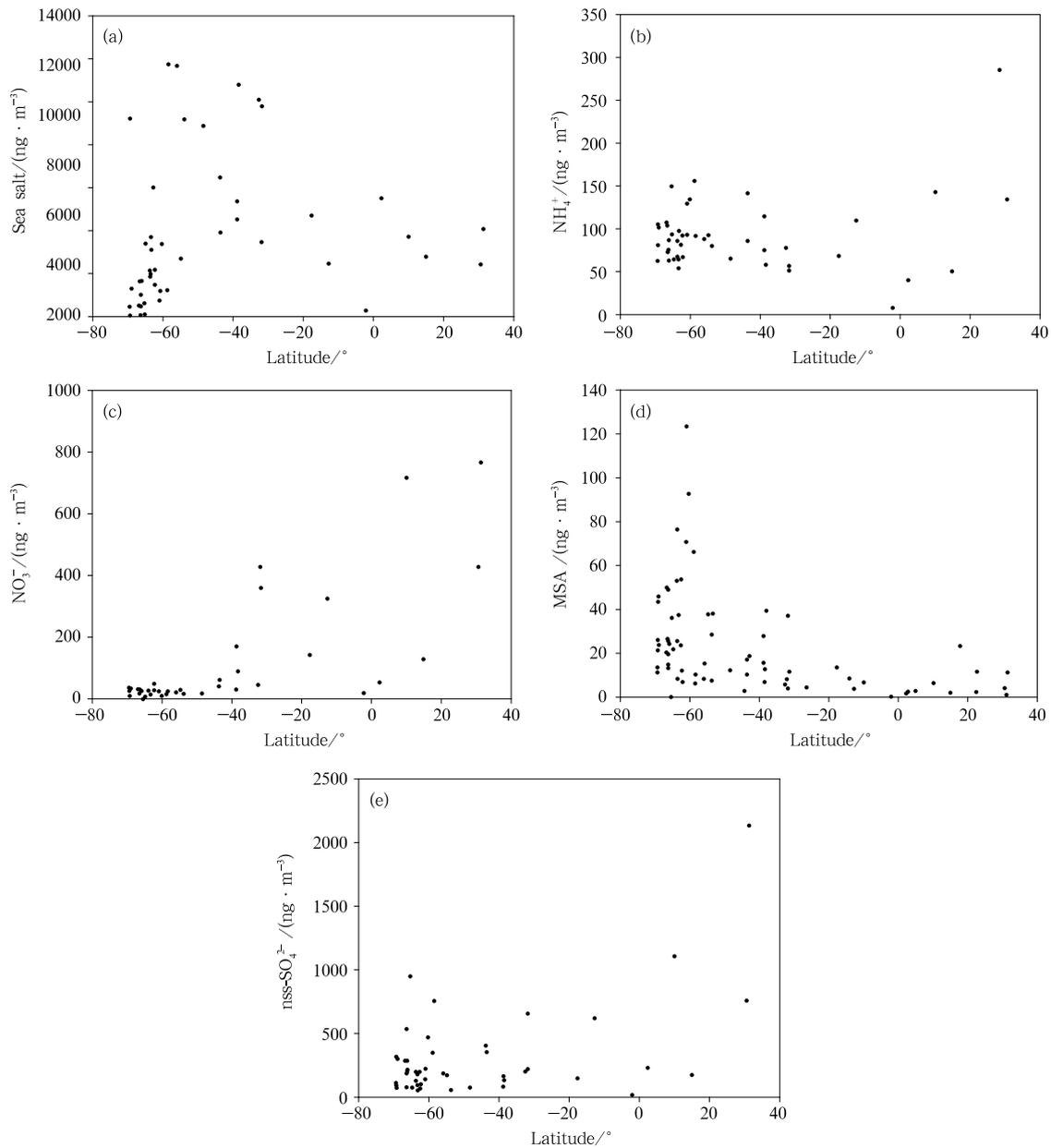


Figure 5 Latitudinal distributions of aerosol ions concentration. (a) sea salt, (b) NH₄⁺, (c) NO₃⁻, (d) MSA and (e) nss-SO₄²⁻.

(south of 60°S). The MSA concentration increased sharply from north to south in these three regions. That is, as the latitude increased, the MSA concentration increased, especially in the south of 60°S, where the concentration of MSA was three times higher than that in 30°S–60°S region. This could be explained by the air temperature and related algal emissions in Southern Ocean^[12,20].

The concentrations of nss-SO₄²⁻ was low in the Open Oceans and the seas around Antarctica, while the concentrations were high in the marginal seas (Figure 5(e)).

It has been reported^[3] that nss-SO₄²⁻ concentrations decrease from north to south, and the nss-SO₄²⁻ concentration in the West Pacific Ocean was twice as high as that in South Pacific Ocean, while the nss-SO₄²⁻ concentration in South Pacific Ocean was twice as high as that in Antarctic Peninsula region. In the Northern Hemisphere, the non-sea-salt sulfate accounted for 59% of the total sulfate, while in Pacific Ocean that was 39%, and in the seas around Antarctica it was 28%. This study suggested that pollution accounted for 90% of the source of sulfur to the atmosphere in the Northern Hemisphere, probably from

the combustion of fossil fuel which emitted SO_2 , which is oxidized into SO_4^{2-} in the atmosphere. In the Northern Hemisphere, sulfate aerosol is transported over the seas by winds, and this gives a large contribution to the nss- SO_4^{2-} . By way of contrast, in the Southern Hemisphere the sea area spanned vastly greater distances than in the North, not only across marginal oceans, but also across the open ocean. Therefore, the average concentrations of nss- SO_4^{2-} during the whole 26th CHINARE was relatively higher than that in Open Oceans, but the value was lower than that in Chinese marginal seas. Comparisons of the marine aerosol nss- SO_4^{2-} and MSA ions concentration over the various concerned regions appears in Table 2^[21–27]. The results consistently show that the nss- SO_4^{2-} concentrations were high in the Chinese marginal seas, while the nss- SO_4^{2-} concentrations were low in Southern Ocean and in the seas around Antarctica. This indicated that the nss- SO_4^{2-} concentration was mostly controlled by the distance away from the anthropogenic sources; According to Table 2 and this study, the MSA concentration of marine aerosol in the Southern Ocean and the seas around Antarctica were relatively high, marine organisms contributed much to the nss- SO_4^{2-} and MSA concentrations in those regions. That is to say, in marginal seas, the concentration of nss- SO_4^{2-} was high, while the concentration of MSA was low. Hence, the contribution of biogenic sources to nss- SO_4^{2-} was little, the main part of the nss- SO_4^{2-} being sourced from anthropogenic emissions. However, the concentrations of MSA were high, while the concentration of nss- SO_4^{2-} was low in the Antarctic coastal area. Here, the nss- SO_4^{2-} to some extent may be formed by the oxidation of biogenic sulfur. To sum up, the source of nss- SO_4^{2-} was

not uniformly distributed, anthropogenic sources mostly focused on marginal ocean, while the marine biogenic sources mostly focused on Southern Hemisphere (especially Southern Ocean and the seas around Antarctica). Meanwhile the complicated air conditions and solar radiation change together made the process of identifying different air masses, and hence different sources of nss- SO_4^{2-} ^[28] rather complex.

The correlation between MSA and MSA/nss- SO_4^{2-} was significant, and the Pearson correlation coefficient was 0.780, $p < 0.01$. Our results indicate a good linear relationship between the MSA/nss- SO_4^{2-} ratio and MSA, $R^2 > 0.6$, see Figure 6. As the concentration of MSA increased, the contribution of biogenic sulfur to total nss- SO_4^{2-} also increased. To some degree, as the only precursor of MSA, the concentration and the oxidation processes of DMS determined the MSA/nss- SO_4^{2-} . Cosme et al.^[29] studied the aerosol sulfate over Dumont d’Urville station in East Antarctica and the inland Vostok Station. The contribution of DMS to the sulfate in aerosols in that study was more than 90% in summer. Contributions from anthropogenic and volcanic emissions contributed less than 3% to the sulfate, so the DMS contributed mostly of the nss- SO_4^{2-} in Antarctic area.

In Figure 7, the correlation between the concentration of MSA and air temperature showed that the concentration of MSA decreased when air temperature rose. There was a significant negative correlation between the concentration of MSA and air temperature, and the Pearson correlation coefficient was -0.462 , $p < 0.01$. The lab simulation showed that the rate of the abstraction reaction between DMS and OH was the function of air temperature, the rate of the addition reaction between

Table 2 Comparison of the nss- SO_4^{2-} and MSA concentrations in marine aerosols for the various concerned regions

Area	Location	nss- $\text{SO}_4^{2-}/(\mu\text{g}\cdot\text{m}^{-3})$	MSA/ $(\mu\text{g}\cdot\text{m}^{-3})$	Reference
East China Sea	26°N–34°N, 122°E–130°E	8.7±6.8 (0.96–24)	0.027±0.020 (N.D.-0.068)	Nakamura T et al. ^[21]
South China Sea	21°N–23°N, 113°E–115°E	14.6(3.9–29.8)	0.006–0.102	Zhang X et al. ^[22]
New Zealand	41.42°S, 174.88°E	0.246 (0–0.96)	0.024 (0–0.162)	Allen A G et al. ^[23]
Southern Ocean (March–April)	60°S	0.02–0.032	0.018–0.037	Berresheim ^[24]
West Antarctica (King George Island)	64.77°S, 64.05°W	0.0985±0.121	0.0488±0.0892	Savoie D L et al. ^[25]
East Antarctica	78°S, 139°E	0.021 (0.09–0.041)	0.088 (0.065–0.13)	Mora S J de et al. ^[26]
Mawson Station	67.6°S, 62.6°E	0.09	0.02	Savoie D L et al. ^[27]

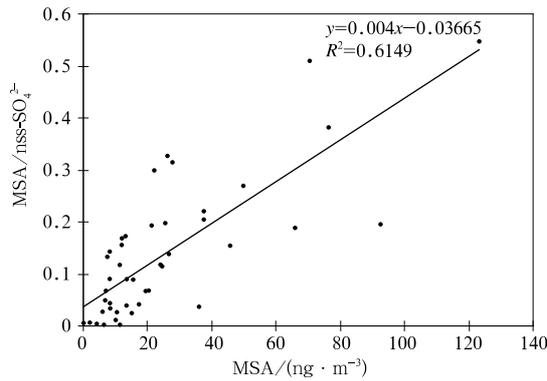


Figure 6 The relationship between the concentration of MSA and $\text{MSA}/\text{nss-SO}_4^{2-}$.

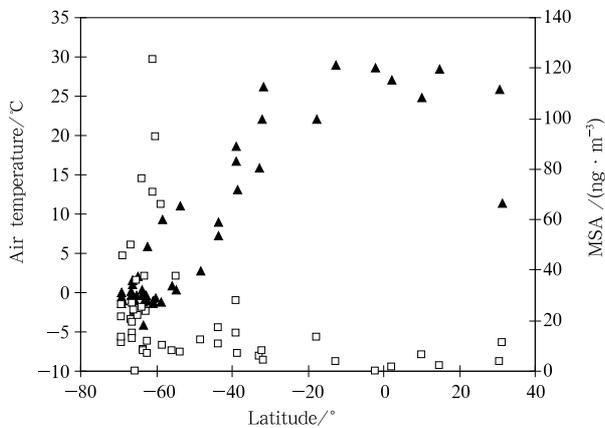


Figure 7 Latitudinal distribution of air temperature and MSA. (▲ represents air temperature, □ represents the concentration of MSA).

the two increased as the air temperature fell.

At 300 K, about 25% of DMS reacted with OH, while at 250 K, 75% of DMS reacted with OH^[30], so the concentration of MSA in part depended on the air temperature change, and the lower air temperature may produce more

MSA^[31–33]. But the especially high value of MSA in the 60°S sea area deserves closer study. The other sources may derive from the oxidation of DMS in Southern Ocean and the coastal area of Antarctica should be studied further.

2.3 The source analysis of components

As discussed above, marine aerosol ions generally can be divided into sea salt and non-sea-salt components. The correlations between aerosol ions in Table 3 showed that:

1. Sea salt components Na^+ , K^+ , Mg^{2+} , Cl^- , Br^- had obvious correlations (Pearson value >0.6 , $p < 0.01$), which represented the common characteristics of sea salt ions.

2. Secondary aerosol ions nss-SO_4^{2-} , NO_3^- , NH_4^+ had obvious positive correlations each other (Pearson value >0.5 , $p < 0.01$), which demonstrated that these three ions had the similar sources.

Factor analysis is a multiple statistical analysis method, it was used to explore the correlations among observed variables and potential major sources of chemical species. The factor score indicated the relative impact of the factor on sample compositions. In this study, factor analysis was carried out on 48 samples for 11 water soluble ions with measurable concentrations, and represented the various sources of aerosols. Three factors explaining 91.3% of the variance in the data were obtained and rotated according to the orthogonal varimax method. Na^+ , Mg^{2+} , Ca^{2+} , K^+ , Cl^- , SO_4^{2-} , Br^- had a high Factor 1 score; NH_4^+ , SO_4^{2-} , NO_3^- , F^- had a high Factor 2 score; MSA had a high Factor 3 score. According to the discussion above, it could be concluded that Factor 1 may be concerned with marine sources, Factor 2

Table 3 Correlations between soluble ions concentration during the 26th CHINARE cruise

Ions	Na^+	NH_4^+	K^+	Mg^{2+}	F^-	MSA	Cl^-	Br^-	NO_3^-	nss-SO_4^{2-}	Ca^{2+}
Na^+	1										
NH_4^+	-0.118	1									
K^+	0.981*	-0.015	1								
Mg^{2+}	0.994*	-0.079	0.980*	1							
F^-	-0.253	0.691*	-0.113	-0.218	1						
MSA	-0.271	0.215	-0.316	-0.277	-0.067	1					
Cl^-	0.997*	-0.126	0.967*	0.988*	-0.304	-0.274	1				
Br^-	0.975*	-0.148	0.940*	0.965	-0.272	-0.264	0.977*	1			
NO_3^-	0.076	0.511*	0.246	0.116	0.669*	-0.267	0.003	-0.032	1		
nss-SO_4^{2-}	0.047	0.713*	0.180	0.098	0.782*	-0.050	-0.030	0.006	0.757*	1	
Ca^{2+}	0.707*	0.086	0.732*	0.734*	0.099	-0.311	0.669*	0.665*	0.467*	0.410*	1

*represents the obvious correlation under the 0.01 confidence interval (two-tailed test).

may be concerned with anthropogenic sources, and Factor 3 may be concerned with the emission from organic marine sources.

To sum up, the water soluble ions of aerosols collected on the route of the 26th CHINARE could be ascribed to marine sources, anthropogenic sources and marine biogenic sources. The SO_4^{2-} can be impacted both by Factor 1 and Factor 2, this demonstrated the importance of separating the ss-SO_4^{2-} and nss-SO_4^{2-} .

Table 4 Rotated component matrix of ions in aerosols during the 26th CHINARE cruise^a

Ions	Factor 1	Factor 2	Factor 3
Na^+	0.991	-0.053	-0.090
Mg^{2+}	0.990	-0.005	-0.094
NH_4^+	-0.016	0.842	0.406
Ca^{2+}	0.738	0.347	-0.263
K^+	0.971	0.102	-0.141
Cl^-	0.986	-0.112	-0.066
SO_4^{2-}	0.652	0.710	-0.047
NO_3^-	0.080	0.856	-0.319
MSA	-0.209	-0.051	0.933
Br^-	0.971	-0.115	-0.068
F^-	-0.227	0.887	-0.058
Eigen values	6.111	2.843	1.089
Variance /%	55.558	25.842	9.902
Accumulation /%	55.558	81.400	91.302

^aValues of factor loading higher than 0.60 are in bold.

3 Conclusions

Aerosol samples collected on the route of the 26th CHINARE were analyzed by IC. The main results include:

1. Cl^- , Na^+ , SO_4^{2-} , NO_3^- , and Mg^{2+} were the most prevalent ion components, and Na^+ and Cl^- contributed to ~75% of the total ions. Sea salt is the primary component of aerosols, and sulfate aerosol is the second major aerosol component. As a secondary aerosol ammonium existed in the forms of NH_4NO_3 , NH_4HSO_4 and $(\text{NH}_4)_2\text{SO}_4$.

2. The sea salt concentration peaked at 40°S, which may correlate with the wind speed. The concentration of MSA increased from the low latitudes to high latitudes, possibly caused by temperature change and algal emissions. The concentrations and the oxidation processes of DMS determined the MSA/nss-SO_4^{2-} ratio to some degree. The concentrations of NO_3^- and NH_4^+ were gen-

erally influenced by the distance from the continents and the anthropogenic activities. The nss-SO_4^{2-} had low concentrations in open ocean and Southern Ocean area and high concentrations in the marginal sea.

3. Cl^- , Br^- , Na^+ , K^+ , Mg^{2+} and Ca^{2+} came mainly from marine sources; F^- , NO_3^- and NH_4^+ were mostly from anthropogenic sources; MSA was mostly from marine biogenic sources; The concentration of SO_4^{2-} was influenced both by marine and anthropogenic sources. Therefore separating ss-SO_4^{2-} and nss-SO_4^{2-} was important for climate evaluation models.

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