

## Soluble species in aerosols collected on the route of the Second Chinese National Arctic Research Expedition

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**Abstract** Aerosol samples are collected on the route of the Second Chinese National Arctic Research Expedition from July 15 to September 28, 2003. The concentration of water soluble ions ( $\text{Na}^+$ ,  $\text{NH}_4^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Cl}^-$ , MSA,  $\text{SO}_4^{2-}$  and so on) are analyzed. By correlation analysis, the ions can be divided into three groups: (1)  $\text{Na}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ , mainly from sea salt; (2)  $\text{NH}_4^+$ ,  $\text{NO}_3^-$ , markedly from coastal regions of the continents; (3) Acetate, MSA,  $\text{C}_2\text{O}_4^{2-}$ , from other sources. Marine aerosols are the dominant origin,  $\text{Cl}^-$  and  $\text{Na}^+$  are the most dominant anion and cation, respectively and these two ions ( $\text{Na}^+ + \text{Cl}^-$ ) account for 55.6% of the total aerosol loading. The mean equivalence ratio of  $\text{NH}_4^+/\text{SO}_4^{2-}$  is 0.45, we suggest that ammonium and sulfate exist mainly as  $\text{NH}_4\text{HSO}_4$ . The concentration of  $\text{NO}_3^-$  shows three different patterns on the route of expedition: Japan Sea with median value of  $15.2 \text{ neq} \cdot \text{m}^{-3}$ ; Sea of Okhotsk and Bering Sea of  $1.8 \text{ neq} \cdot \text{m}^{-3}$  and Arctic Ocean of  $0.4 \text{ neq} \cdot \text{m}^{-3}$ . Bering Sea is a high MSA area. Through the comparison of the concentration of main water soluble ions between the First and Second Chinese National Arctic Research Expedition, the variation matches each other.

**Key words** Marine aerosol, Arctic, Soluble species, MSA.

### 1 Introduction

Knowledge of the physical and chemical properties of marine aerosol particles is important because of the role these particles play in a number of important atmospheric processes. Marine aerosols affect radiative transfer and climate directly by scattering and absorbing the radiation and indirectly by influencing the droplet size distribution and albedo of marine boundary layer clouds. In addition, marine aerosol particles play an important role in the marine portion of the atmospheric sulfur cycle (Fitzgerald 1991). The number, size distribution and composition of marine aerosol particles vary in time and space in response to a number of different processes including long-range transport of continental air; aerosol production by the bursting of whitecap bubbles and by homogeneous nucleation involving the

oxidation products of precursor gases emitted by the ocean; removal of particles by deposition and precipitation scavenging.

In the past dozens of years, a large number of studies on the sea-salt aerosol have been published (Junge 1972; Warneck 1988; Sun 2002). This paper analyzes soluble species in aerosol samples collected on the Route of the Second Chinese National Arctic Research Expedition from July 15 to September 28, 2003, and estimates their existence formation of each ion. Finally, we compare the results of the First and Second Chinese National Arctic Research.

## 2 Experimental methods

Fifty aerosol samples (including eight blank samples) were collected on the route of the Second Chinese National Arctic Research Expedition (Table 1). The route covers Japan Sea, Okhotsk Sea, Bering Sea and Arctic Ocean (Fig. 1).

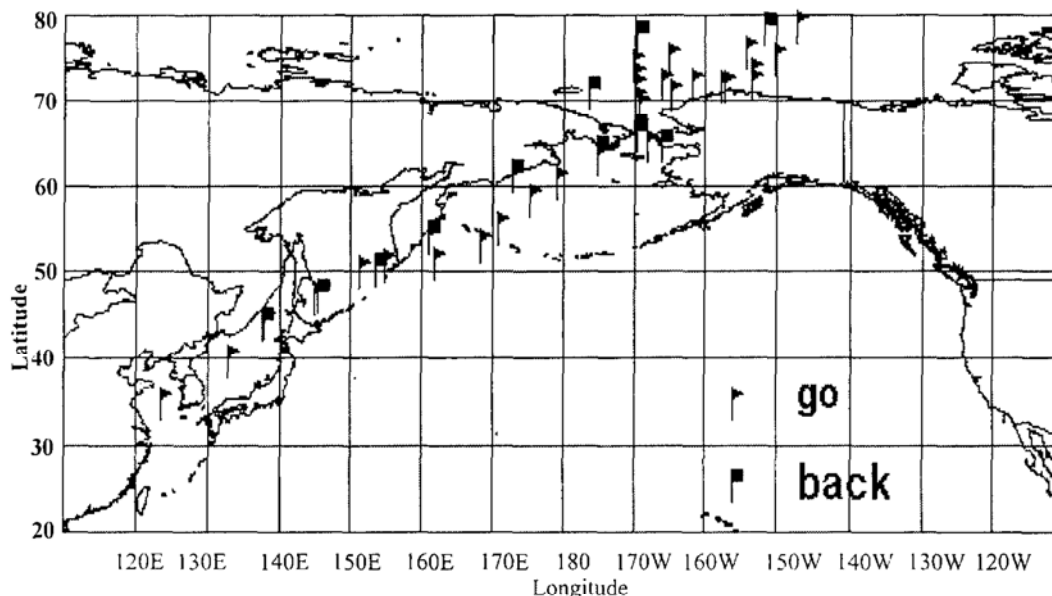


Fig. 1 The track along which aerosols were collected on the route of the Second Chinese National Arctic Research Expedition in 2003.

Aerosol samples were recovered on 2  $\mu\text{m}$ , 4.7 cm diameter Zefluor Teflon filters (Gelman Sciences<sup>TM</sup>) using a 220 V vacuum pump. The filters were placed on the vessel-top about 25 m above the sea surface in a cylindrical polyethylene protective cover. The mean flow rate was 0.39 standard cubic meter per hour ( $\text{m}^3 \text{STP} \cdot \text{h}^{-1}$ ), yielding a velocity at the face of the filter of 18.74 cm/s. This velocity is high enough for this kind of filter to have a collection efficiency greater than 97% for the aerosol particles which diameter is larger than 0.035  $\mu\text{m}$  (Liu *et al.* 1984). The major parts of the sample represent 1 day sampling intervals. The air volume through the filter was measured by an in-line meter. Pressure, temperature and other meteorological parameters were recorded by the meteorological stations on the vessel. After sampling, the filters were removed from the filter holder, put into a cleaned airtight plastic container and stored in the refrigerator at 4°C on the

vessel.

All sample and blank filters were wetted with 200  $\mu\text{l}$  pure ethanol, then extracted with 25 mL Milli-Q water, ultrasonated for about 30 min. Soluble ions in aerosol samples were analyzed using a Dionex model<sup>TM</sup> 300 ion chromatograph.

Major ions were detected in all aerosol samples. Average concentrations of five blanks were (in  $\text{ng} \cdot \text{g}^{-1}$ ):  $\text{Na}^+$  (44.4),  $\text{NH}_4^+$  (39.0),  $\text{K}^+$  (4.9),  $\text{Mg}^{2+}$  (0.5),  $\text{Ca}^{2+}$  (1.8),  $\text{CH}_3\text{COO}^-$  (13.8),  $\text{MSA}$  (0.0),  $\text{Cl}^-$  (23.0),  $\text{SO}_4^{2-}$  (31.4),  $\text{C}_2\text{O}_4^{2-}$  (0.0),  $\text{NO}_3^-$  (20.5).

### 3 Results and discussion

Concentrations of water soluble ions in the aerosol are presented in Table 1. The average total aerosol loading (total anions + total cations) was  $170.6 \text{ neq} \cdot \text{m}^{-3}$ , the maximum and the minimum total aerosol loading are 1304.1 and  $29.2 \text{ neq} \cdot \text{m}^{-3}$  respectively. The samples of A1-A30 are collected on go-way (A14-A30 are collected in the Arctic Ocean), the A31-A42 are collected on back -way.

The statistical data of water soluble ions in the aerosol are presented in Table 2. The mean concentrations are significantly different for all species; the dominant ions are  $\text{Na}^+$ ,  $\text{Cl}^-$ , and  $\text{SO}_4^{2-}$ .

These three ions account for more the 75% of the total burden of measured ions. The difference of mean concentration of water soluble ions, in general, relates with the source intensity and distance from the sources. Some ions have several sources, for example  $\text{SO}_4^{2-}$ , besides marine origin, it also origin from anthropogenic emissions (Wang 1999). The standard deviations of  $\text{Na}^+$ ,  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$  are large, indicating these three ions concentrations are severely influenced by alteration of marine.

#### 3.1 Sources

All correlation coefficients are shown in Table 3. On the basis of their correlation coefficients, we divided them into three groups: (1)  $\text{Na}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ , mainly origin from marine aerosol; except for  $\text{SO}_4^{2-}$ , all correlation coefficients are more than 0.90 ( $p=0.01$ ). The correlation coefficients between  $\text{SO}_4^{2-}$  and other marine aerosol ions are less than 0.90, indicating that there is other sources for  $\text{SO}_4^{2-}$ . The correlation coefficients between  $\text{Ca}^{2+}$  and  $\text{Na}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{K}^+$  are relatively low, and the correlation coefficient of  $\text{Ca}^{2+}/\text{SO}_4^{2-}$  is the biggest, suggesting that they may have common sources; (2)  $\text{NH}_4^+$ ,  $\text{NO}_3^-$ , originated from anthropogenic emissions; (3)  $\text{CH}_3\text{COO}^-$ ,  $\text{MSA}$ ,  $\text{C}_2\text{O}_4^{2-}$  originated from differenced sources.

#### 3.2 Formation

Cations originated from marine aerosol include  $\text{Na}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$  and anions include  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ . The sum of ( $\text{Na}^+ + \text{Cl}^-$ ) accounts for more than 50% of total aerosol loading. It is noteworthy that marine aerosol is the main formation of aerosol.  $\text{Cl}^-/\text{Na}^+$  ratio

Table 1. Soluble species concentration in aerosols collected on the route of the Second Chinese National Arctic Research Expedition in 2003 (neq · m<sup>-3</sup>)

Sample	Date	Lat (°)	Lon (°)	Cations					Anions					Σ <sub>+</sub>	Σ <sub>-</sub>	NH <sub>4</sub> <sup>+</sup> /SO <sub>4</sub> <sup>2-</sup>	Cl <sup>-</sup> /Na <sup>+</sup>	DCI <sup>-</sup>	
				Na <sup>+</sup>	NH <sub>4</sub> <sup>+</sup>	K <sup>+</sup>	Mg <sup>2+</sup>	Ca <sup>2+</sup>	CH <sub>3</sub> COO <sup>-</sup>	MSA	Cl <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	C <sub>2</sub> O <sub>4</sub> <sup>2-</sup>						NO <sub>3</sub> <sup>-</sup>
A1	7-16	34.83N	124.51E	90.1	28.8	3.3	24.0	4.3	0.0	0.4	61.7	69.3	2.8	22.5	150.4	156.7	0.4	0.7	-43.6
A2	7-18	39.64N	133.71E	62.2	11.4	1.6	16.5	1.9	0.0	0.2	60.1	21.1	0.9	8.7	93.5	91.0	0.5	1.0	-12.6
A3	7-19	44.17N	138.86E	90.3	18.2	2.1	24.9	2.9	0.0	0.4	82.6	44.3	1.7	21.7	138.2	150.7	0.4	0.9	-23.0
A4	7-20	46.81N	145.90E	43.7	15.5	1.0	8.2	1.7	0.0	0.2	31.5	35.5	1.1	5.5	70.1	73.7	0.4	0.7	-19.6
A5	7-21	49.79N	152.23E	10.3	9.0	0.3	1.0	1.8	0.1	0.5	4.2	37.4	0.2	0.4	22.3	42.8	0.2	0.4	-7.9
A6	7-22	50.48N	155.72E	36.4	18.0	1.1	7.2	1.5	0.0	1.1	9.6	53.5	1.1	1.1	64.2	66.4	0.3	0.3	-33.0
A7	7-23	50.82N	162.60E	50.3	6.6	1.3	11.7	3.8	0.0	0.5	43.2	23.2	0.4	1.1	73.7	68.4	0.3	0.9	-15.6
A8	7-24	52.78N	169.36E	11.1	14.8	0.3	2.2	0.9	0.0	1.6	1.5	23.3	0.8	0.1	29.3	27.3	0.6	0.1	-11.5
A9	7-25	54.98N	171.86E	40.5	17.2	1.2	7.6	1.3	0.1	1.6	26.1	27.3	2.9	3.7	67.8	61.6	0.6	0.6	-21.3
A10	7-26	58.04N	176.26E	23.0	16.5	1.7	2.9	0.8	0.1	1.7	12.0	15.5	2.2	1.3	44.8	32.8	1.1	0.5	-14.8
A11	7-27	60.14N	179.91W	56.6	11.4	1.4	15.0	2.8	0.3	0.7	54.7	20.8	3.8	1.4	87.2	81.6	0.6	1.0	-11.6
A12	7-28	62.93N	174.19W	56.1	8.0	1.1	14.8	3.5	0.1	0.5	64.7	12.6	1.4	1.0	83.5	80.3	0.6	1.2	-1.0
A13	7-29/30	64.35N	167.00W	83.5	5.6	2.0	30.6	4.2	0.1	0.2	117.5	15.7	0.9	0.7	125.9	135.1	0.4	1.4	19.8
A14	7-31	69.76N	168.99W	14.8	3.4	0.3	2.6	0.5	0.1	0.2	12.7	3.4	0.5	0.2	21.6	17.1	1.0	0.9	-4.6
A15	8-1	72.50N	168.99W	7.5	6.9	0.3	0.8	0.8	0.1	0.1	1.3	23.4	0.0	0.1	16.3	25.0	0.3	0.2	-7.5
A16	8-3	71.59N	165.00W	17.4	5.5	0.4	2.0	2.8	0.1	0.4	10.5	19.2	0.5	0.4	28.1	31.1	0.3	0.6	-9.9
A17	8-4/5	71.45N	156.37W	23.1	2.3	0.4	5.2	1.9	0.1	0.1	24.6	9.3	0.3	0.2	32.8	34.4	0.3	1.1	-2.4
A18	8-6	71.72N	152.44W	63.9	8.0	1.5	16.0	2.3	0.3	0.4	77.5	15.9	0.5	0.7	91.7	95.3	0.5	1.2	2.8
A19	8-7	70.49N	163.94W	25.2	6.3	0.5	5.2	1.6	0.1	0.3	21.0	17.4	0.5	0.4	38.7	39.6	0.4	0.8	-8.5
A20	8-8	68.92N	168.35W	56.6	5.2	1.2	14.9	2.6	0.0	0.2	65.0	0.0	15.3	0.7	80.4	81.4	0.0	1.2	-1.2
A21	8-9	71.13N	168.98W	20.6	7.1	0.7	4.2	1.2	0.0	0.2	9.4	0.4	18.7	0.8	33.8	29.9	18.9	0.5	-14.8

Table 1. (Continued)

Sample	Date	Lat (°)	Lon (°)	Cations					Anions					$\Sigma_+$	$\Sigma_-$	$\text{NH}_4^+/\text{SO}_4^{2-}-\text{Cl}^-/\text{Na}^+$	DCI-	
				$\text{Na}^+$	$\text{NH}_4^+$	$\text{K}^+$	$\text{Mg}^{2+}$	$\text{Ca}^{2+}$	$\text{CH}_3\text{COO}^-$	MSA	$\text{Cl}^-$	$\text{SO}_4^{2-}$	$\text{C}_2\text{O}_4^{2-}$					$\text{NO}_3^-$
A22	8-10	74.01N	169.18W	16.4	7.7	0.5	2.5	1.6	0.2	0.1	13.6	0.0	25.0	0.0	28.7	38.8	0.8	-5.5
A23	8-11	74.72N	164.07W	25.6	14.7	0.5	3.0	1.6	0.4	0.1	20.4	45.1	0.0	0.5	45.4	66.4	0.8	-9.5
A24	8-12	74.01N	169.18W	5.8	7.8	0.2	0.4	0.2	0.1	0.1	2.8	11.8	0.0	0.0	14.4	14.8	0.5	-4.1
A25	8-13	75.46N	153.34W	8.4	5.0	0.1	0.4	0.1	0.4	0.1	4.7	10.2	0.4	0.2	13.9	15.5	0.5	-5.1
A26	8-14	74.63N	149.29W	13.8	6.3	0.3	1.1	0.7	0.2	0.1	9.3	11.5	0.0	0.2	22.1	21.1	0.5	-6.8
A27	8-15	73.07N	152.57W	87.5	6.9	2.0	22.7	4.2	0.0	0.1	90.7	28.2	0.0	0.9	123.2	120.4	0.2	-11.7
A28	8-16	71.64N	160.93W	24.1	7.6	0.5	5.0	1.2	0.0	0.1	25.9	9.1	0.0	0.4	38.4	35.7	0.8	-2.3
A29	8-17	71.34N	156.88W	35.9	6.0	0.4	4.3	0.6	0.4	0.2	29.3	15.8	0.0	1.0	47.1	46.7	0.4	-12.7
A30	8-29-9-4	78.56N	146.40W	11.2	21.7	0.7	2.0	8.3	0.2	0.3	0.3	176.9	0.0	0.7	43.8	178.5	0.1	-12.8
A31	9-5	78.27N	151.03W	5.0	8.4	0.2	1.6	1.4	0.4	0.2	4.5	21.0	0.0	0.0	16.5	25.6	0.4	-1.3
A32	9-7	77.32N	168.87W	6.2	6.1	0.4	2.0	1.4	0.4	0.2	5.9	25.3	0.0	0.0	16.0	31.7	0.2	-1.3
A33	9-10	70.78N	175.67W	19.3	1.6	0.5	4.4	0.9	0.0	0.1	24.4	4.8	0.7	0.4	26.8	30.3	0.3	1.8
A34	9-11	66.14N	169.00W	73.3	11.4	2.0	18.9	4.3	0.3	0.2	85.5	27.6	2.5	2.3	109.9	118.5	0.4	-0.3
A35	9-12	64.47N	165.44W	82.4	21.7	2.3	19.8	6.1	0.0	0.3	81.7	64.2	5.0	2.5	132.4	154.1	0.3	-14.8
A36	9-13	65.57N	168.90W	33.1	4.8	0.8	8.9	2.7	0.4	0.3	39.4	10.9	1.0	1.3	50.3	51.0	0.4	0.7
A37	9-14	63.69N	174.39W	21.6	10.7	1.3	4.7	1.7	0.3	0.8	10.8	25.5	5.3	6.6	39.9	49.2	0.4	-14.4
A38	9-15/16	60.94N	173.59E	273.9	13.5	6.7	91.3	17.3	0.2	0.8	379.1	158.8	2.6	3.6	402.7	545.0	0.1	58.6
A39	9-17	53.97N	161.72E	390.8	19.2	9.0	117.0	21.5	0.2	1.0	500.0	238.7	1.1	5.6	557.5	746.6	0.1	42.8
A40	9-18	50.05N	154.19E	33.8	19.0	1.7	9.0	2.3	0.2	0.5	25.4	39.5	1.9	2.2	65.7	69.7	0.5	-14.1
A41	9-19	47.06N	146.16E	30.4	9.2	1.1	9.0	2.0	0.3	0.1	34.0	12.4	1.6	3.6	51.6	52.0	0.7	-1.6
A42	9-20	43.88N	138.42E	32.3	8.9	1.5	6.5	6.8	0.2	0.1	31.8	11.6	2.7	2.9	56.0	49.4	0.8	-6.0

The latitude and longitude in the Table1 are the starting position, and the ending position are the start position of next sample, except that the end position of A1 ,A15 ,A29 ,A31 ,A32 ,A42 are (34.83 °N;129.33 °E) ,(73.78 °N;168.62 °W) ,(73.05 °N;158.07 °W) ,(77.59 °N;160.44 °W) ,(76.00 °N;171.99 °W) ,(39.70 °N;133.76 °E).

Table 2. Statistical parameter of soluble species in aerosols collected on the route of the Second Chinese National Arctic Research Expedition in 2003 ( $\text{neq} \cdot \text{m}^{-3}$ )

	$\text{Na}^+$	$\text{NH}_4^+$	$\text{K}^+$	$\text{Mg}^{2+}$	$\text{Ca}^{2+}$	$\text{CH}_3\text{COO}^-$	MSA	$\text{Cl}^-$	$\text{SO}_4^{2-}$	$\text{C}_2\text{O}_4^{2-}$	$\text{NO}_3^-$
Average	50.3	10.6	1.3	13.1	3.1	0.2	0.4	52.6	34.2	7.0	2.6
Maximum	390.8	28.8	9.0	117.0	21.5	0.4	1.7	500.0	238.7	25.0	22.5
Minimum	5.0	1.6	0.1	0.1	0.1	0.0	0.1	0.3	0.0	0.0	0.0
Median	31.3	8.2	1.0	5.8	1.8	0.1	0.2	25.7	20.9	0.9	0.9
s. d.	69.9	6.1	1.7	22.2	4.1	0.1	0.4	93.4	47.8	5.1	4.8

Table 3. Inter-correlation between the water soluble ions in aerosols collected on the route of the Second Chinese National Arctic Research Expedition in 2003

	$\text{NH}_4^+$	$\text{K}^+$	$\text{Mg}^{2+}$	$\text{Ca}^{2+}$	Ace	MSA	$\text{Cl}^-$	$\text{SO}_4^{2-}$	$\text{C}_2\text{O}_4^{2-}$	$\text{NO}_3^-$
$\text{Na}^+$	.344*	.979**	.994**	.916**	.179	.223	.991**	.770**	-.027	.297
$\text{NH}_4^+$		.457**	.312*	.369*	.074	.461**	.253	.591**	-.040	.590**
$\text{K}^+$			.975**	.919**	.169	.290	.961**	.786**	-.013	.367*
$\text{Mg}^{2+}$				.921**	.160	.211	.995**	.766**	-.029	.276
$\text{Ca}^{2+}$					.278	.172	.921**	.878**	-.035	.175
Ace						-.197	.186	.267	.192	-.194
MSA							.187	.251	-.049	.075
$\text{Cl}^-$								.752**	-.032	.207
$\text{SO}_4^{2-}$									-.160	.232
$\text{C}_2\text{O}_4^{2-}$										-.023

\* :Correlations is significant at the 0.05 confidence level; \*\* :Correlations is significant at the 0.01 confidence level.

is 0.83, less than sea-water  $\text{Cl}^-/\text{Na}^+$  ratio (1.17). There is a deficiency in  $\text{Cl}^-$  concentration in the aerosol compared to the sea-water  $\text{Cl}^-/\text{Na}^+$  ratio (Table 1).  $\text{Cl}^-$ -deficit shows an inverse relationship with  $\text{SO}_4^{2-}$  in our samples (with the exception of A13, A30, A38 and A39) (Fig. 4). This suggests that  $\text{Cl}^-$  was depleted due to the reaction between sea salt and  $\text{H}_2\text{SO}_4$  in the air (Shrestha *et al.* 1997). Based on meteorological record, the A13, A30, A38 and A39 were collected under the bad weather (condition). The wind speed is more than  $10 \text{ m} \cdot \text{s}^{-1}$  sometimes, thus strong wind may bring much sea-water bubble into air, and the sea-salt aerosol concentration were higher. This result may weak the relationship between  $\text{Cl}^-$ -deficit and  $\text{SO}_4^{2-}$ .

The total measured cations are less than that of anions in most of samples, and the deficiencies are more than 5%, indicating that some ions have not been detected (Legrand and Delmas 1984). It is likely that  $\text{H}^+$  can account for a significant percentage of the missing cations composition, with  $\text{H}_2\text{SO}_4$ ,  $\text{HCOOH}$  the principal acidic gases; the summertime troposphere in the Arctic and sub-Arctic is an acidic environment ( $\text{pH} < 5$ ) (Talbot *et al.* 1997). In all samples, most of the ratio  $\text{NH}_4^+/\text{SO}_4^{2-}$  are less than 1 (Table 1). Except the

A20, A21 and A22 samples, the average  $\text{NH}_4^+/\text{SO}_4^{2-}$  ratio of other samples is 0.45. Sun and Qin (1998) suggested that local atmosphere environment and the ions equivalence of aerosol should be considered in explaining the association between ammonium and sulfate using the ratio of these two species. Out of 42 samples, 29 are acidic aerosols, and the  $\text{NH}_4^+/\text{SO}_4^{2-}$  ratio is close to 0.5, so we suggest that  $\text{NH}_4^+$  and  $\text{SO}_4^{2-}$  exist in the form of  $\text{NH}_4\text{HSO}_4$ .

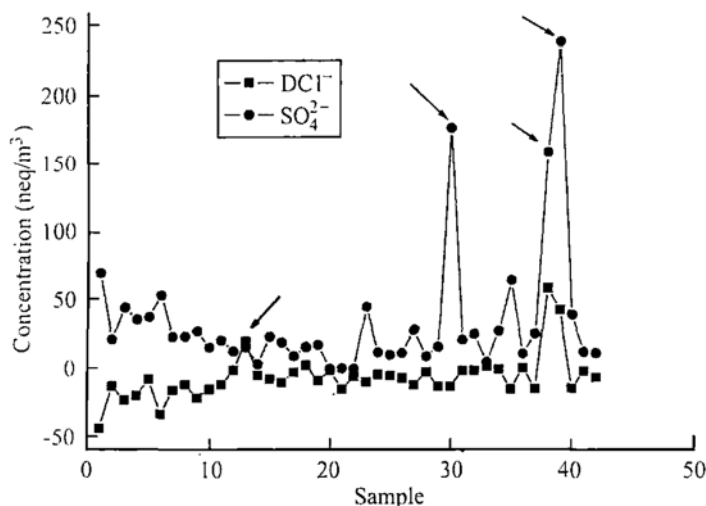


Fig. 2 Relationship between deficit  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$  in the aerosol. The arrows indicate anomalous data points, which don't follow the general inverse relationship.

It has been suggested that acidic aerosols can be contaminated by ammonia in ambient air while processing filter in laboratories (Shrestha *et al.* 1997). If the samples were contaminated in a laboratory, then the amount of anions would equal to the amount of cations. But the phenomena was not observed in our laboratory, which means the collected samples are uncontaminated.

Compared with  $\text{SO}_4^{2-}$ , the source of  $\text{NO}_3^-$  on the route of the expedition is simple relatively, the contribution originated from the marine or the lands is not obvious, which can be proved from the inter-correlation between the  $\text{NO}_3^-$  and the water soluble ions in aerosols (Table 3). The oxidation of biogenic-produced organic nitrogen gases from the ocean may be an important source of nitrate, however, this process mainly occurred around the equator. The source of  $\text{NO}_3^-$ ,  $\text{HNO}_3$  in mid-high latitude may be augmented by anthropogenic inputs from long-range transport and regional forest fires (Talbot 1997; Jacob 1992; Singh 1992a, b; Wofsy 1992). Talbot's (1997) results indicated that in the free troposphere the concentration of  $\text{HNO}_3$  was significantly higher than that of aerosol  $\text{NO}_3^-$ , and most of  $\text{NO}_3^-$  is typically formed by sea-salt and  $\text{HNO}_3$ . It has been found that  $\text{HNO}_3$  deposition on Teflon filters do not influence nitrate concentrations, however there might have been some loss of nitrate by decomposition of  $\text{NH}_4\text{NO}_3$ , therefore the nitrate concentration reported here should be regarded as lower limit of true atmospheric concentration (Sun and Qin 1998). Fig. 3 shows that the concentration of  $\text{NO}_3^-$  decreased with increasing distance from the human activity, and may be divided into three area: Japan Sea with median value of  $15.2 \text{ neq} \cdot \text{m}^{-3}$ ; Sea of Okhostk and Bering Sea of  $1.8 \text{ neq} \cdot \text{m}^{-3}$  and Arctic Ocean of  $0.4 \text{ neq} \cdot$

$\text{m}^{-3}$ .

The values of MSA of 6 samples collected on the Bering Sea are high (Fig. 4), indicating that Bering Sea is a high-product area of MSA. The MSA values of A8, A9, A10 are higher than that of A37, A38, A39. Maybe the reason is the lower temperature benefit the transformation of DMS to MSA (Sun 2002). We observed high values of the ratio  $\text{MSA}/\text{nssSO}_4^{2-}$  over the Bering Sea (Fig. 4), also indicated that Bering Sea is a high-product area of MSA.

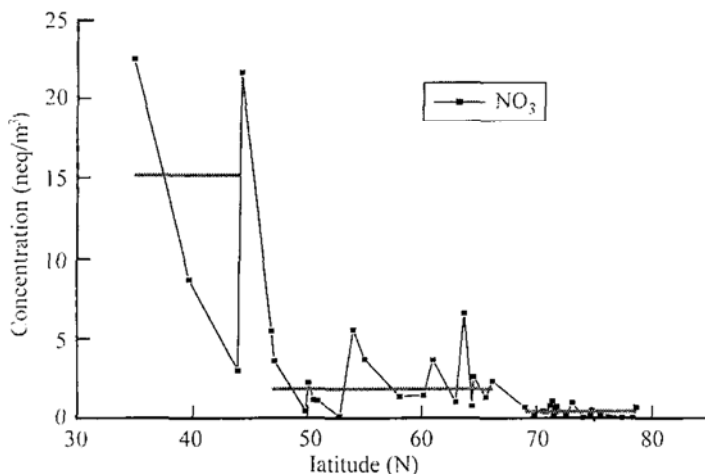


Fig. 3 The latitudinal distribution of the concentration of  $\text{NO}_3^-$

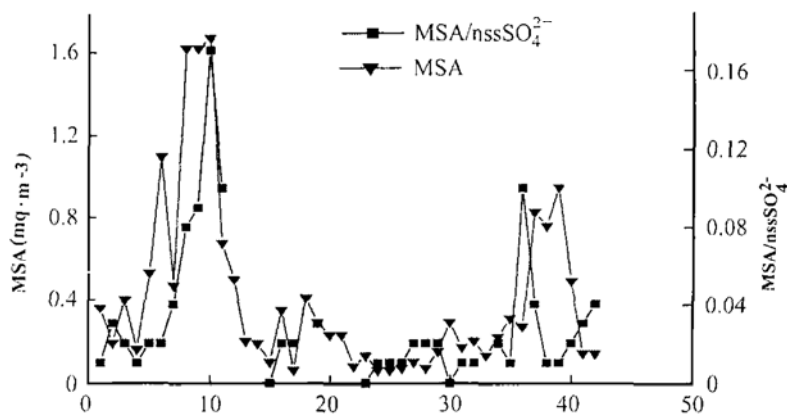


Fig. 4 The variation of MSA and  $\text{MSA}/\text{nssSO}_4^{2-}$  ratios in aerosols collected on the route of the Second Chinese National Arctic Research Expedition in 2003.

### 3.3 Comparison with the First Chinese National Arctic Research Expedition

There were 27 samples collected on the route of The First Chinese National Arctic Research Expedition (1999-07-01 — 1999-09-09). The routes of twice expedition are similar. Fig. 5 shows the mean concentration of soluble species collected during the two expeditions. The result indicates that the concentration of  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{C}_2\text{O}_4^{2-}$ ,  $\text{NH}_4^+$  are higher on the route of the Second Chinese National Arctic Research Expedition, however the concentration of  $\text{Cl}^-$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$  are higher on the First Chinese Nation-



al Arctic Research Expedition. The concentrations of MSA are same. The ions of  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{C}_2\text{O}_4^{2-}$ ,  $\text{NH}_4^+$  are mainly anthropogenic origins. Here the anthropogenic origins include anthropogenic sources and exhaust gas from the vessel. Although some protects had done to prevent exhaust gas from the vessel, the wind direction changed rapidly, it was possible that the samples were polluted more or less by the vessel exhaust. But as a whole, the concentrations of these 4 ions were high in the human area and were low in no-human area. So the concentrations of ions reflect truly the change in the atmosphere. The concentration of sea-salt ions are higher on the route of the Second Chinese National Arctic Research Expedition than that of the first time, may be due to the weather of the first expedition was more severely than the second expedition.

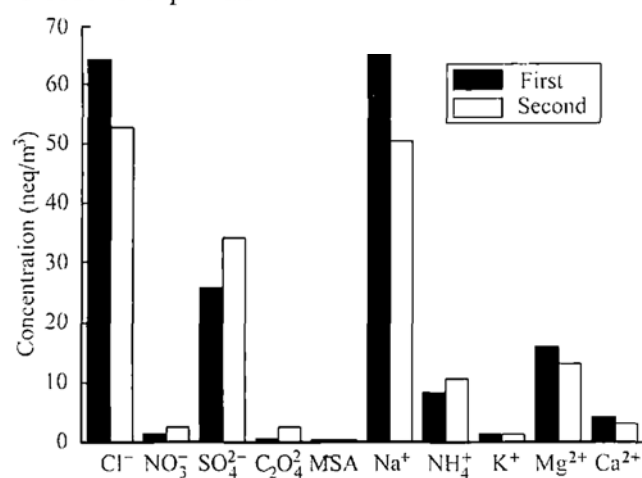


Fig. 5 Comparison of the mean concentration of soluble species in aerosols collected during the two expeditions.

We also compare the ions concentrations of  $\text{SO}_4^{2-}$ ,  $\text{Na}^+$ , MSA,  $\text{NO}_3^-$  along the route of two expeditions (Fig. 6), and find that the ions concentrations along the route of expedition are similar. But the concentrations of  $\text{Na}^+$ ,  $\text{SO}_4^{2-}$  in two expeditions have some differences. The two ions high values are more frequently occurred in the second expedition than in the first expedition, but the corresponding high values are resemble.

#### 4 Conclusions

Samples collected along the route of the Second Chinese National Arctic Research Expedition show that marine aerosols are the dominant origin,  $\text{Cl}^-$  and  $\text{Na}^+$  are the most dominant anion and cation, separately, and these two ions ( $\text{Na}^+ + \text{Cl}^-$ ) account for 55.6% of the total aerosol loading. The equivalent  $\text{Cl}^-/\text{Na}^+$  ratio is 0.83, less than sea-water  $\text{Cl}^-/\text{Na}^+$  ratio (1.17). There is a deficiency in  $\text{Cl}^-$  concentration in the aerosol compared to sea-water.  $\text{Cl}^-$ -deficit shows an inverse relationship with  $\text{SO}_4^{2-}$  in our samples (with the exception of A13, A30, A38 and A39) (Fig. 4.). This suggests that  $\text{Cl}^-$  was depleted due to the reaction between sea salt and  $\text{H}_2\text{SO}_4$  in the atmosphere. The mean equivalent ratio of  $\text{NH}_4^+/\text{SO}_4^{2-}$  is 0.45, we suggest that ammonium and sulfate exist mainly as  $\text{NH}_4\text{HSO}_4$ . The concentration of  $\text{NO}_3^-$  shows three different patterns along the route of ex-

pedition, i. e. Japan Sea with median value of  $15.2 \text{ neq} \cdot \text{m}^{-3}$ ; Sea of Okhotsk and Bering Sea of  $1.8 \text{ neq} \cdot \text{m}^{-3}$  and Arctic Ocean of  $0.4 \text{ neq} \cdot \text{m}^{-3}$ . Bering Sea is a high MSA area. Through the comparison of the concentration of main water soluble ions between the First and Second Chinese National Arctic Research Expedition, the variation matches each other.

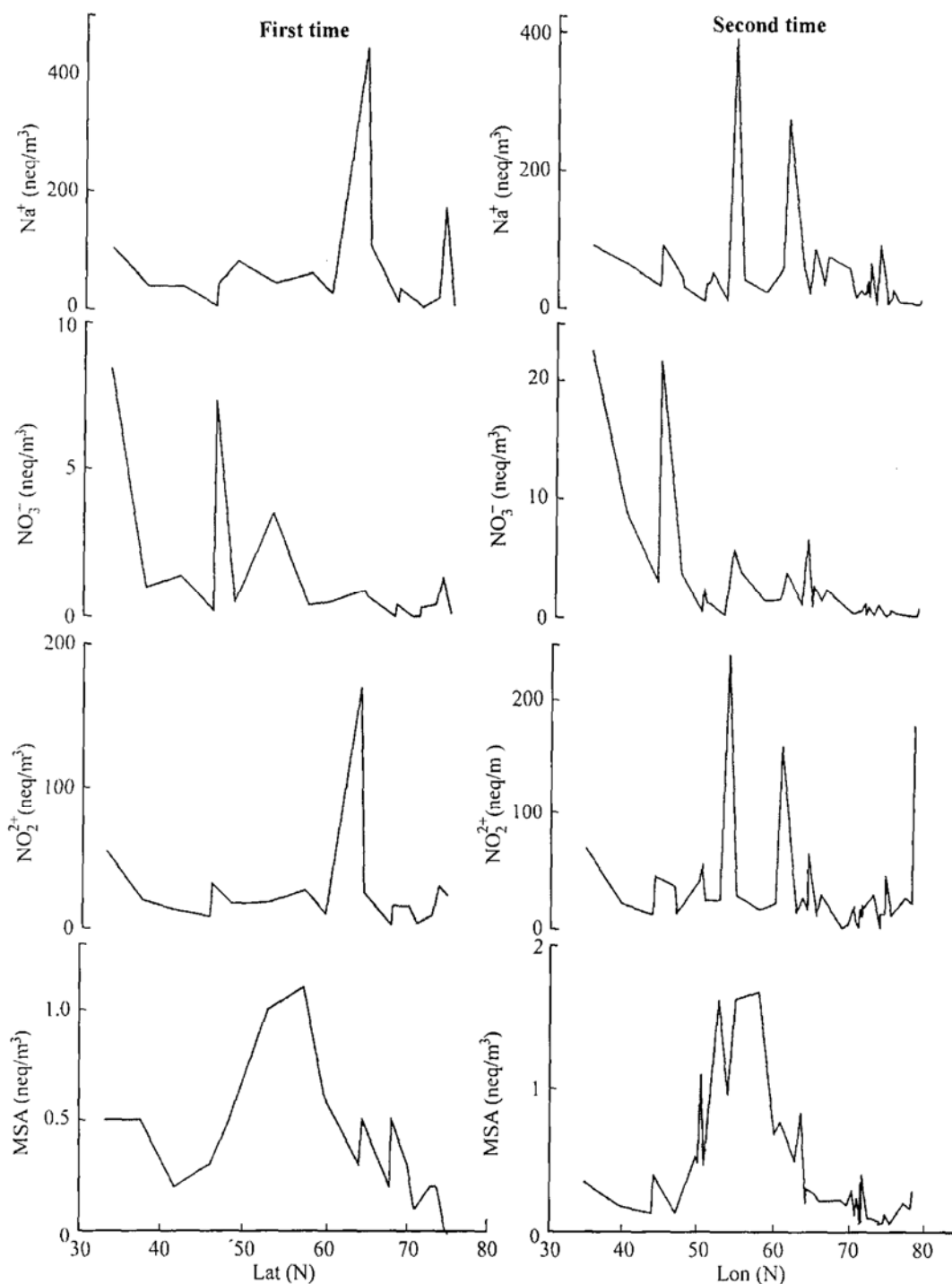


Fig. 6 Comparison of aerosol concentration with latitude during the two expeditions.

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