Chemical Characteristics of Aerosol Composition over the Yellow Sea and the East China Sea in Autumn*

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(Manuscript received 17 August 2012, in final form 3 January 2013)

ABSTRACT

The total suspended particulate (TSP) samples over the Yellow Sea and the East China Sea were collected to determine the major compositions of water-soluble ionic species during two cruises in autumn 2007. The aerosol compositions exhibited an obvious regional variation between the two cruises, with higher concentrations (except Na\(^+\) and Mg\(^{2+}\)) over the northern Yellow Sea during the first cruise. The concentrations of the secondary ions [non–sea salt sulfate (nss-SO\(_4^{2-}\)), NO\(_3^-\), and NH\(_4^+\)] were 11 ± 4.9, 3.1 ± 2.1, and 3.7 ± 2.6 \(\mu g\) m\(^{-3}\), respectively, which together contributed over 72% of the total determined ion concentrations. Significant correlations between these secondary ions were found within each sampling period, while nss-K\(^+\) and nss-Ca\(^{2+}\) showed strong correlation with each other. The calculated results of equivalent concentrations of anions (nss-SO\(_4^{2-}\) and NO\(_3^-\)) and cations (NH\(_4^+\) and Ca\(^{2+}\)) showed that the acidic species were mostly neutralized with the alkaline species over the study areas. The mass ratio of nss-SO\(_4^{2-}\)/NO\(_3^-\) was 1.4 during the investigation period. In addition, the concentrations of MSA were 0.011 ± 0.044 and 0.0081 ± 0.0047 \(\mu g\) m\(^{-3}\) during the two cruises, respectively. Based on the measured MSA, nss-SO\(_4^{2-}\), and their ratios, the relative biogenic sulfur contribution to the total nss-SO\(_4^{2-}\) was estimated to be only 2.0% during the two cruises, further suggesting the major contribution of anthropogenic source to sulfur budget over the marginal seas of China.

1. Introduction

Knowledge of the physical and chemical properties of airborne aerosols over the oceans is relevant for global change studies because of the roles that these aerosol particles play in a number of important atmospheric processes, especially their influence on the earth’s climate variations (Fitzgerald 1991; Russell et al. 1994). Because marine aerosols can affect radiation budget directly by scattering and absorbing radiation and indirectly by influencing the droplet number and size distribution and albedo of marine boundary layer clouds. Corresponding to the large-scale upward emission of particles, large portions of the loss will in turn be balanced under steady-state condition by their deposition to the ocean surface. Therefore, atmospheric deposition may serve as one of the main supplies for not only major components but also trace-level pollutants to the ocean cycling system (Duce et al. 1991; Kim et al. 2002).

The water-soluble ions are important constituent of the marine atmospheric aerosols, mainly including sea salts, mineral aerosols, and secondary aerosols [non–sea salt sulfate (nss-SO\(_4^{2-}\)), NO\(_3^-\), and NH\(_4^+\)], which mainly come from the chemical conversions of anthropogenic SO\(_2\), nitrogen oxide (NO\(_x\)), and NH\(_3\) from the continent. Over the coastal and shelf areas influenced by human activities, nss-SO\(_4^{2-}\) is the major contributor of condensation nuclei (CN), accounting for over 90% of the total particle numbers (Fitzgerald 1991) and eventually cloud condensation nuclei (CCN). Changes in CCN concentration affect the cloud droplet number concentrations, which influences the cloud albedo and subsequently the climate (Charlson et al. 1987). NO\(_3^-\) and NH\(_4^+\) are the central existing forms of N nutrient, and thus their deposition from the atmosphere would have a significant impact on the marine ecosystem, especially for the remote ocean. In addition, nss-SO\(_4^{2-}\) and NO\(_3^-\) are the most common compounds contributing to the atmospheric
acidity and their deposition affects the pH value of surface water (Larssen and Carmichael 2000; Lestari et al. 2003).

East Asia can be a seriously polluted region in which human activities impose a heavy load on the atmosphere (Uematsu et al. 1983). Aerosol particles formed from the anthropogenic pollutants affect not only the atmospheric quality of the Asian continent but also the marine aerosol compositions over the Pacific Ocean. These aerosol particles with high levels can be transported to the remote ocean over the Chinese marginal seas from a long-range distance. Thus the marginal seas [the Yellow Sea (YS) and the East China Sea (ECS)] are well known for their favorable geographical location to study the diverse source processes of the atmospheric aerosols that are best reflected by relatively systematic seasonal wind patterns (Carmichael et al. 1996; Gao et al. 1996; Hsu et al. 2010). Uematsu et al. (2010) conducted a survey about the atmosphere transport and deposition of different size-fractioned aerosols from Asia to the ECS. In addition, Zhu et al. (2013) estimated the dry deposition fluxes of nutrients over the ECS by collecting different size-segregated samples separated into eight size intervals. However, the previous observations made over the coastal seas and at several local monitoring sites (e.g., Qianliyan, Yellow Sea; Cheju Island, Korea) were mostly focused in spring and early summer owing to the frequent occurrence of Asian dust events under the strong westerly monsoon (Chen et al. 1997; Kim et al. 1998; Lee et al. 2002; Zhang et al. 2002; Kim et al. 2009) but only a few in autumn (Nakamura et al. 2005). Moreover, China has become the world’s largest emitter of SO2 with the rapid pace of economic and industrial progresses since 2005 (Su et al. 2011). Facing the formidable pressure of environment protection, the industrial restructuring emission has been conducted to reduce SO2 discharge in the past decade. Overall, the dataset establishes a quantitative budget of the anthropogenic input of nss-SO4$^{2-}$ and NO3$^{-}$ to the marine boundary of the marginal seas of China.

2. Materials and methods

a. Sampling areas and sampling facilities

Two cruises were conducted over the YS and the ECS in autumn on board the research vessel (R/V) Dong Fang Hong 2. Figure 1 shows the track of the two cruises: the first cruise mainly covered the northern Yellow Sea (NYS) (14–25 October 2007), while the second cruise covered the southern Yellow Sea (SYS) and the ECS (2–24 November 2007). A high-volume sampler (Model KB-1000, Jinshida Electronic Technology Co. Ltd., Qingdao, China) was used to collect the TSP samples, with Whatman 41 filters (20.3 × 25.4 cm$^2$) (Whatman International Ltd., Maidstone, England) used as the substrates. The size of TSP particles was between 0.05 and 100 μm. The average sampling interval was approximately 24 h with a start flow rate of 1.0 m$^3$ min$^{-1}$. As the sampling time increased, the accumulation of particulate would cause instantaneous flow fluctuation and thus the flow rate might be slightly less than 1.0 m$^3$ min$^{-1}$. A water-borne Asian dust is expected to be present in low levels. In addition, we identified the main source of all measured ions and provided valuable information for understanding the input pathway of aerosols over the study areas.

b. Ion analyses

For determination of the water-soluble ionic species, a quarter of each Whatman 41 filter was extracted ultrasonically with 10 mL purified water made from a Milli-Q system (resistivity > 18 MΩ cm, Millipore Co.). Ion Chromatography (Model ICS-1000, Dionex Co., United States) was used to determine the concentrations of major water-soluble ionic components and methanesulfonic acid (MSA). Special emphasis has been placed on examining the chemical features and correlations of aerosol compositions during autumn when airborne Asian dust is expected to be present in low levels. In addition, we identified the main source of all measured ions and provided valuable information for understanding the input pathway of aerosols over the study areas.
within 0.01 mg L$^{-1}$ for the cations and within 0.02 mg L$^{-1}$ for the anions, respectively. During the two cruises, a total of seven filter blanks were taken and analyzed along with the samples and the background concentrations had been subtracted from the detected concentrations. In addition, those with significant sources besides the maritime origin (e.g., SO$_4^{2-}$, K$^+$, and Ca$^{2+}$) are separated into sea salt and non–sea salt parts by regarding sodium as the conservative element from the seawater. The non–sea salt part is calculated by the following formula: nss-$X = X_{aerosol} \cdot \frac{(X/Na)_{seawater}}{Na_{aerosol}}$. In the present study, the mass ratios of $(X/Na)_{seawater}$ (SO$_4^{2-}$, K$^+$, and Ca$^{2+}$) of 0.2515, 0.037 01, and 0.038 21 are used to calculate the concentrations of $X$ in the bulk seawater (Millero 2006).

c. Backward trajectory analysis

Three-day backward trajectories were calculated using the National Oceanic and Atmospheric Administration (NOAA) Air Resources Laboratory Hybrid Single-Particle Lagrangian Integrated Trajectory, version 4 (HYSPLIT 4), model (http://www.arl.noaa.gov/ready/hysplit4.html) to verify the sources of air mass that influenced the observational areas during the sampling period. The backward trajectories were plotted based on the Global Data Assimilation System (GDAS) archived meteorological data starting from the midpoint of one certain sampling interval (usually lasted for approximately 24 h). In general, at the three different altitudes (500, 1000, and 1500 m) trajectories were obtained to identify the origin and flow of typical air masses.

3. Results and discussion

a. Meteorological conditions

During autumn, the observed areas over the YS and the ECS are under the influence of circulation systems Siberian high pressure and the low pressure formed over the northwestern Pacific Ocean. The synoptic conditions showed relatively similar circulation patterns during the two cruises (Fig. 2). During the first cruise, the circulation pattern was dominated by the cold high pressure system over the adjacent Mongolia and Russia and the low pressure system over the northwestern Pacific Ocean. While during the second cruise, the cold high pressure system increased as well as the high pressure...
system formed over the coastal area of the YS, introducing relatively higher wind speed. The circulation patterns during the two sampling periods caused the winds to come mainly from the northwest and west, then the observational areas were under the influence of both long- and medium-range transport from the continent.

The meteorological data during the two cruises were summarized in Table 1. The average wind speed and temperature for the first cruise were $6.6 \pm 2.8$ m s$^{-1}$ and $16.8 \pm 2.1$°C, respectively. The data for the second cruise appeared to be relatively higher than the first one, with average values of $7.7 \pm 3.1$ m s$^{-1}$ and $18.8 \pm 3.4$°C, respectively. Moderate precipitations were encountered on 14 and 18 October during the first cruise and on 8 and 16 November during the second cruise, which caused the aerosol concentrations to drop sharply because of the scavenging by precipitation.

### b. Overview of aerosol compositions

During the two cruises, a total of 30 samples were collected: 12 over the NYS and 18 over the SYS and the ECS. The concentrations of all determined ions in TSP samples ranged from 14.5 to 42.3 µg m$^{-3}$ in the NYS and from 12.3 to 44.8 µg m$^{-3}$ in the SYS and the ECS, respectively, with average values of 26.2 ± 9.88 and 24.9 ± 8.88 µg m$^{-3}$ (note that Cl$^-$ was not analyzed and thus not included in the total mass of ionic species). The TSP samples collected over the two investigating areas exhibited no obvious difference in the total concentrations. Table 1 presents the statistical overview of aerosol compositions over the two observational areas, including the arithmetic-mean value, the standard deviation, and the range of the water-soluble ionic species in the aerosol samples. The mass concentrations of

<table>
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<th>NYS</th>
<th>SY and ECS</th>
<th>Overall</th>
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<tbody>
<tr>
<td></td>
<td>Mean</td>
<td>St dev</td>
<td>Range</td>
</tr>
<tr>
<td>MSA</td>
<td>0.011</td>
<td>0.0044</td>
<td>0.0041–0.017</td>
</tr>
<tr>
<td>$\text{SO}_4^{2-}$</td>
<td>13</td>
<td>6.1</td>
<td>5.0–23</td>
</tr>
<tr>
<td>$\text{NO}_3^-$</td>
<td>3.5</td>
<td>1.9</td>
<td>0.53–7.5</td>
</tr>
<tr>
<td>Na$^+$</td>
<td>1.8</td>
<td>1.5</td>
<td>0.58–6.1</td>
</tr>
<tr>
<td>NH$_4^+$</td>
<td>4.6</td>
<td>2.2</td>
<td>0.76–9.0</td>
</tr>
<tr>
<td>K$^+$</td>
<td>1.0</td>
<td>0.51</td>
<td>0.42–2.0</td>
</tr>
<tr>
<td>Mg$^{2+}$</td>
<td>0.59</td>
<td>0.31</td>
<td>0.18–1.4</td>
</tr>
<tr>
<td>Ca$^{2+}$</td>
<td>1.0</td>
<td>0.47</td>
<td>0.37–2.0</td>
</tr>
<tr>
<td>nss-$\text{SO}_4^{2-}$</td>
<td>12</td>
<td>6.2</td>
<td>3.5–22</td>
</tr>
<tr>
<td>nss-K$^+$</td>
<td>0.94</td>
<td>0.52</td>
<td>0.20–2.0</td>
</tr>
<tr>
<td>nss-Ca$^{2+}$</td>
<td>0.97</td>
<td>0.46</td>
<td>0.33–1.9</td>
</tr>
<tr>
<td>Wind speed</td>
<td>6.6</td>
<td>2.8</td>
<td>0.60–13</td>
</tr>
<tr>
<td>Temperature</td>
<td>16</td>
<td>2.1</td>
<td>11–20</td>
</tr>
</tbody>
</table>
3. Na mass concentrations for Na concentrations during the two cruises with average pedogenic influence from the continent. The two observational areas were under strong anthropogenic input that can reflect on the aerosol compositions. On the other hand, the ECS covers a more vast area and opens to the Pacific Ocean, which can make it relatively clean and strong winds from the ocean could bring about more powerful input for marine ions.

d. Relationships among ionic species in aerosol

Correlation coefficient matrix was applied to investigate the internal relationships among different species, and the results are presented in Table 2. It could be seen that although the differences of individual ion concentrations were highly significant over the two observational areas, the correlations between internal species within each sampling period exhibited rather similar patterns. NH$_4^+$ showed strong correlations with both nss-SO$_4^{2-}$ and NO$_3^-$, while the correlations between nss-SO$_4^{2-}$ and NO$_3^-$ were relatively weak; nss-K$^+$ corresponded well with both NH$_4^+$ and NO$_3^-$ and the same applied to nss-Ca$^{2+}$ to a lesser extent; nss-K$^+$ and nss-Ca$^{2+}$ showed strong correlation with each other. The correlation between Na$^+$ and Mg$^{2+}$ was strong during the second cruise and the regression result of Mg versus Na [slope = 0.11, standard error (SE) = 0.0043, correlation coefficient $R = 0.99$] was rather close to the Mg/Na ratio in seawater (slope = 0.12; Millero 2006), which indicates that both share the marine source; however, no significant correlation occurred in the NYS during the first cruise, implying that the sea salt components in the aerosols were interfered by other continental transport. Combined with the enrichment factor (EF) in the following discussion, it can be easily seen from Table 3 that EFs of Mg$^{2+}$ relative to crust and seawater sources were 1.8 and 2.8, respectively. This suggests that a quite large part of Mg$^{2+}$ might be attributed to the mineral aerosol source during the first cruise.

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1) ENRICHMENT FACTOR FOR THE WATER-SOLUBLE IONS

In an effort to further separate and identify the main source of the determined water-soluble ions, we calculated the EFs in aerosol relative to their contents in seawater and crust. Here Na\(^+\) and Ca\(^{2+}\) are regarded as the conservative elements for marine and crustal sources (Nishikawa et al. 1991; Millero 2006), respectively, and the EFs of other ions are defined as follows:

\[
\text{EF}_{\text{seawater}} = \frac{(X/Na)_{\text{aerosol}}}{(X/Na)_{\text{seawater}}}
\]

and

\[
\text{EF}_{\text{crust}} = \frac{(X/Ca)_{\text{aerosol}}}{(X/Ca)_{\text{crust}}}
\]

where the subscript “aerosol” represents the mass concentration ratio between \(X\) and Na or Ca in the atmospheric aerosol, while the subscripts “seawater” and “crust” mean the ratio of \(X\) to Na in seawater and the ratio of \(X\) to Ca in crust, respectively.

As shown in Table 3, EFs of the secondary ions (nss-SO\(_4^{2-}\), NO\(_3^-\), and NH\(_4^+\)) relative to the crustal source were very high (minimum value > 700), suggesting the three kinds of water-soluble ions were not from the crust source. At the same time, EF_{seawater} of nss-SO\(_4^{2-}\) ranged from 6.6 over the SYS and the ECS to 29 over the NYS, indicating its non–sea salt source. It can be seen from Fig. 4 that the air masses reaching the study areas had to pass through eastern China coastal areas with developed economy and dense population, where human activities could contribute to the main source of the secondary ions. As far as K\(^+\) and Ca\(^{2+}\) are concerned, their EF_{seawater} varied from 3.8 to 15 and from 4.4 to 14 over the two observational areas, though greater wind speeds brought more marine ions into the atmosphere. However, the mean EF_{crustal} of K\(^+\) was 1.5 over the NYS and 1.3 over the SYS and the ECS, respectively, suggesting that K\(^+\) and Ca\(^{2+}\) have the crustal source. Combined with the 3-day backward trajectory (Fig. 4), the arid and semiarid soil of Outer Mongolia and northwestern China is the primary source of crustal compositions (K\(^+\) and Ca\(^{2+}\)) in aerosol.

2) ALKALINE AND ACIDIC IONIC SPECIES

As mentioned above, East Asia is featured by its high-level emissions of SO\(_2\), NO\(_x\), and many studies have discussed on the basis of measurement or model assessment (Kato and Akimoto 1992; Wang et al. 2006).

### Table 2. Correlation coefficient matrix of aerosol samples over the NYS and the SYS and ECS. Correlation coefficients with statistical significance of \(p < 0.01\) are shown in boldface.

<table>
<thead>
<tr>
<th></th>
<th>MSA</th>
<th>nss-SO(_4^{2-})</th>
<th>NO(_3^-)</th>
<th>NH(_4^+)</th>
<th>Na(^+)</th>
<th>Mg(^{2+})</th>
<th>nss-K(^+)</th>
<th>nss-Ca(^{2+})</th>
</tr>
</thead>
<tbody>
<tr>
<td>MSA</td>
<td>1.0</td>
<td>0.68</td>
<td>0.27</td>
<td>0.41</td>
<td>0.12</td>
<td>-0.27</td>
<td>0.029</td>
<td>0.012</td>
</tr>
<tr>
<td>nss-SO(_4^{2-})</td>
<td></td>
<td>1.0</td>
<td>0.64</td>
<td>0.86</td>
<td>0.34</td>
<td>-0.028</td>
<td>0.70</td>
<td>0.043</td>
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<tr>
<td>NO(_3^-)</td>
<td></td>
<td></td>
<td>1.0</td>
<td>0.92</td>
<td>0.28</td>
<td>-0.024</td>
<td>0.083</td>
<td>0.43</td>
</tr>
<tr>
<td>NH(_4^+)</td>
<td></td>
<td></td>
<td></td>
<td>1.0</td>
<td>-0.34</td>
<td>-0.12</td>
<td>0.093</td>
<td>0.79</td>
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<tr>
<td>Na(^+)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1.0</td>
<td>0.13</td>
<td>-0.26</td>
<td>-0.034</td>
</tr>
<tr>
<td>Mg(^{2+})</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1.0</td>
<td>0.19</td>
<td>0.19</td>
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<tr>
<td>nss-K(^+)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1.0</td>
<td>0.88</td>
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<tr>
<td>nss-Ca(^{2+})</td>
<td></td>
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### Table 3. Enrichment factors for the aerosol samples collected over the two research areas.

<table>
<thead>
<tr>
<th></th>
<th>NYS</th>
<th></th>
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<tbody>
<tr>
<td></td>
<td>Crust*</td>
<td>Seawater**</td>
<td>Crust*</td>
<td>Seawater**</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>nss-SO(_4^{2-})</td>
<td>3250</td>
<td>29</td>
<td>2500</td>
<td>6.6</td>
<td></td>
<td></td>
<td></td>
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<td></td>
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<tr>
<td>NO(_3^-)</td>
<td>875</td>
<td>—</td>
<td>725</td>
<td>—</td>
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<tr>
<td>NH(_4^+)</td>
<td>1150</td>
<td>—</td>
<td>775</td>
<td>—</td>
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<td>Na(^+)</td>
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<td>K(^+)</td>
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<tr>
<td>Ca(^{2+})</td>
<td>1.0</td>
<td>14</td>
<td>1.0</td>
<td>4.4</td>
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** Seawater data from Millero (2006).
FIG. 4. Three-day backward trajectory analysis for typical days during the two cruises in 2007: (a) 14 Oct, (b) 21 Oct, (c) 24 Oct, (d) 2 Nov, (e) 10 Nov, and (f) 23 Nov. For detailed discussion of origins of the air mass, refer to the text.
The oxidation of SO\textsubscript{2} and NO\textsubscript{x} can contribute to the high levels of secondary aerosols of SO\textsubscript{4}\textsuperscript{2-} and NO\textsubscript{3} and bring risks to acid deposition resulting to air quality deterioration and ecosystem destruction. On the other hand, the high-level emission of NH\textsubscript{3}, which is mainly due to the agricultural activities and livestock farming (Galloway et al. 1995) together with the mineral dust from long-range transport that is rich in calcium-containing aerosol can play an important role in the neutralization of acidic aerosols. The neutralization conditions of marine aerosol over the marginal seas of China can serve as an indicator to determine the reactions of alkaline and acidic aerosol components.

Table 2 shows that the correlations were significant between the alkaline and acidic ionic species. NH\textsubscript{4}\textsuperscript{+} was closely correlated with both nss-SO\textsubscript{4}\textsuperscript{2-} and NO\textsubscript{3} over the two observational areas; nss-Ca\textsuperscript{2+} also showed strong correlation with NO\textsubscript{3}—however, it was not associated with nss-SO\textsubscript{4}\textsuperscript{2-} during the two cruises. To quantify the relationship between the two groups of ionic species, both cations (NH\textsubscript{4}\textsuperscript{+} and nss-Ca\textsuperscript{2+}) and anions (nss-SO\textsubscript{4}\textsuperscript{2-} and NO\textsubscript{3}) were converted to equivalent concentrations and compared. A strong correlation was found between the two groups and the slope was 1.1 (Fig. 5), which was comparable with the result observed by Chen et al. (1997) at Cheju Island over a 3-yr period. These results indicated that the acidic ionic species were mostly neutralized with alkaline species over the study areas. As for the role of nss-Ca\textsuperscript{2+}, it may be due to the following reason. In the long-distance transport, nss-SO\textsubscript{4}\textsuperscript{2-} and NO\textsubscript{3} from anthropogenic SO\textsubscript{2} and NO\textsubscript{x} might adsorb on the wet sand aerosol particles, and then combine with Ca\textsuperscript{2+} by replacing CO\textsubscript{3}\textsuperscript{2-} in CaCO\textsubscript{3} from crustal source. Through the analysis of chemical compositions over the Korean peninsula and Japan during the occurrence of wet deposition, Hirai (1991) found that about 75% of CO\textsubscript{3}\textsuperscript{2-} was replaced by SO\textsubscript{4}\textsuperscript{2-} and NO\textsubscript{3} when dust particles reached those sampling areas from their origins. Recently, Sullivan et al. (2007) pointed out that the alkaline calcium carbonate easily neutralized nitric acid and led to the accumulation of NO\textsubscript{3} in calcium-rich mineral dust, which could further illustrate the good correlation of nss-Ca\textsuperscript{2+} and NO\textsubscript{3} observed in this study. Thus, the transforming processes of Ca\textsuperscript{2+} may play an important role in reducing or neutralizing the atmospheric deposition acid (mainly depending on nss-SO\textsubscript{4}\textsuperscript{2-} and NO\textsubscript{3}) over the marginal seas of China.

3) RATIO OF NSS-SO\textsubscript{4}\textsuperscript{2-} TO NO\textsubscript{3}^{-}

The ratio of nss-SO\textsubscript{4}\textsuperscript{2-} to NO\textsubscript{3} in aerosol can be used to track the relative contributions from the stationary and mobile sources to these secondary aerosols in China (X.-P. Wang et al. 2005). Atmospheric SO\textsubscript{2} and NO\textsubscript{3} over continent and marginal seas mainly come from the oxidation of gaseous SO\textsubscript{2} and NO\textsubscript{x} emitted into the atmosphere. Many studies have been carried out on the emission inventories of air pollutant species over East Asia, especially China (Foell et al. 1996; Chen et al. 1997). Arimoto et al. (1996) estimated the characteristic SO\textsubscript{4}\textsuperscript{2-}/NO\textsubscript{3} ratio of China by converting the emissions of SO\textsubscript{2} and NO\textsubscript{x} to SO\textsubscript{4}\textsuperscript{2-} and NO\textsubscript{3} quantitatively and calculated the mass ratio of SO\textsubscript{4}\textsuperscript{2-}/NO\textsubscript{3} to be 3.0 over China by the emission inventory in 1987. However, the emission patterns of major air pollutants over China (i.e., SO\textsubscript{2} and NO\textsubscript{x}) have changed a lot in recent years. First, because of the extensive application of flue gas desulfurization (FGD) technology and the phasing out of small, high emitting units, the emission of SO\textsubscript{2} began to decline slowly after 2006 (Su et al. 2011). Second, the emission of NO\textsubscript{x} tends to increase over China, especially the industrialized areas, primarily because of the rapid growth of the transportation sector (Richter et al. 2005). According to the report of emission inventory by Streets et al. (2008), the estimated characteristic mass ratio of SO\textsubscript{4}\textsuperscript{2-}/NO\textsubscript{3} was 2.0 over China and 1.4 over Asia in the year 2000. While by adopting the emission inventory by Y. Wang et al. (2005), the calculated SO\textsubscript{4}\textsuperscript{2-}/NO\textsubscript{3} mass ratio over eastern China was 1.7 in the same year, and the authors ascribed the higher emission of air pollutants to the inclusion of rural coal consumption and the higher NO\textsubscript{x} emission factor for mobile sources. Thus we can see that because of the change of the emission pattern over China in the past decade, the calculated SO\textsubscript{4}\textsuperscript{2-}/NO\textsubscript{3} ratio tends to change gradually as expected.

![Fig. 5. Correlation between the sum of acidic ionic species (nss-SO\textsubscript{4}\textsuperscript{2-} and NO\textsubscript{3}) and the sum of alkaline ionic species (NH\textsubscript{4}\textsuperscript{+} and Ca\textsuperscript{2+}) in the form of equivalent concentrations in the aerosol samples collected over the two observational areas. The dashed lines indicate the 95% confidence bands for the sum of NH\textsubscript{4}\textsuperscript{+} and Ca\textsuperscript{2+}.](http://journals.ametsoc.org/jas/article-pdf/70/6/1784/3632914/jas-d-12-0232_1.pdf)
In this study, the linear regression results show that the mass ratio of $\text{nss-SO}_4^{2-}/\text{NO}_3^-$ in the aerosol samples over the YS and the ECS (slope = 1.4, SE = 0.37; $R = 0.59$; intercept = 5.7, SE = 1.4) is comparable with the ratios in TSP samples observed in the vicinity areas such as Cheju Island by Arimoto et al. (1996) (slope = 1.7, SE = 0.14; $R = 0.89$; intercept = −1.9, SE = 0.72) and the ECS by Hatakeyama et al. (2004) (slope = 1.8, SE = 0.17; $R = 0.91$; intercept = 4.0, SE = 0.86). Although the application of FGD and the continued increase of vehicles have occurred in China for several years, the ratios of $\text{nss-SO}_4^{2-}/\text{NO}_3^-$ during the cruises were more than 1, revealing that stationary source emissions are still more significant contributor to atmospheric particles. In addition, it should be noted that the concentrations of $\text{nss-SO}_4^{2-}$ and $\text{NO}_3^-$ in aerosols are not so well correlated as compared with the latter two investigations. This may be partly attributed to the wider spatial coverage of our observational areas than the others, which can make it undergo various air masses and thus introduce diversified $\text{SO}_4^{2-}$ and $\text{NO}_3^-$ sources.

4) $\text{nss-SO}_4^{2-}$ and MSA

The concentrations of MSA in the aerosols during the two cruises were $0.011 \pm 0.0044$ and $0.0081 \pm 0.0047 \text{ gm}^{-3}$, respectively, without significant difference existing between the two observational areas [one-way analysis of variance (ANOVA), $p = 0.12$]. To estimate the biogenic contribution to the total $\text{nss-SO}_4^{2-}$, MSA is used as a tracer for biogenic $\text{SO}_4^{2-}$ according to the following formula: biogenic $\text{SO}_4^{2-} = \text{MSA}_{\text{aerosol}} \times (\text{nss-SO}_4^{2-}/\text{MSA})$ (Savoie and Prospero 1989). $\text{MSA}_{\text{aerosol}}$ means the MSA concentration in the atmospheric aerosol, while $\text{nss-SO}_4^{2-}$/MSA indicates their ratio in the remote ocean air. Many observations have been made over the Pacific Ocean to evaluate the relationship between $\text{nss-SO}_4^{2-}$ and MSA in the marine aerosol (Saltzman et al. 1986; Bates et al. 1992; Kim et al. 2000). Based on a long term record of data at Samoa, a site with little continental influence in the tropical Pacific, Savoie et al. (1989) suggested that an $\text{nss-SO}_4^{2-}/\text{MSA}$ ratio of approximately 18–20 could be applied to the world’s oceans at latitudes between 30°S and 30°N. Several studies have adopted this ratio at coastal areas of East Asia to determine the biogenic contribution to the total nss-$\text{SO}_4^{2-}$ (Gao et al. 1996; Arimoto et al. 1996) and a comparison with them will be discussed below.

Here we used the typical $\text{nss-SO}_4^{2-}/\text{MSA}$ ratio of 19 to evaluate the biogenic contribution to the total $\text{nss-SO}_4^{2-}$ over the YS and the ECS. The results showed that biogenic $\text{SO}_4^{2-}$ only accounted for 2.0% of the total nss-$\text{SO}_4^{2-}$ over the two observational areas (Fig. 6). The scatterplots show that the ratios span an order of magnitude, ranging from 0.86% to 6.6%, and the correlation of biogenic nss-$\text{SO}_4^{2-}$ with total nss-$\text{SO}_4^{2-}$ was not significant because of the poor relationship between MSA and total nss-$\text{SO}_4^{2-}$ (Table 2). Comparisons with other studies conducted previously in the vicinity areas indicated that the calculated biogenic portion in our research was relatively lower. On the basis of the same calculation method, Gao et al. (1996) reported the biogenic contribution to be 10%–19% over the ECS, while Arimoto et al. (1996) found that marine biogenic sources accounted for 3.6% and 10.9% at the eastern and western sides of Cheju Island, respectively. Further insight into the low biogenic contribution may include the discussion of both high concentrations of nss-$\text{SO}_4^{2-}$ and low concentrations of MSA. As discussed above, the total nss-$\text{SO}_4^{2-}$ over the East Asia marginal seas were under strong continental influence, resulting in high loadings of nss-$\text{SO}_4^{2-}$. On the other hand, the concentration of MSA in atmospheric aerosol shows a significant seasonal variation owing to its biogenic origin. Mukai et al. (1995) summarized a 9-yr period observation at the coastal island in the Sea of Japan, and reported that the MSA concentrations ranged from 0.003 to 0.095 $\text{gm}^{-3}$ with the maximum occurring during spring and early summer and the minimum in winter. So the difference could be explained partly by the sampling period and the temporal variation in MSA concentrations. The sampling period in Gao et al. (1996) was from March to June, and thus the MSA concentration tended to be high (average value of 0.029 $\text{gm}^{-3}$). For the Cheju Island data, the eastern side shared the similar sampling period with this study, and the biogenic portion was of the same order of magnitude, although

![Fig. 6. Relationship between total nss-$\text{SO}_4^{2-}$ and biogenic $\text{SO}_4^{2-}$. The solid lines (0.86% and 6.6%) represent the lowest and highest contributions of biogenic nss-$\text{SO}_4^{2-}$ to total nss-$\text{SO}_4^{2-}$ over the ECS and the YS during the two cruises.](attachment:fig6.png)
a little bit higher than our result. While for the western side of Cheju Island, the sampling time scales extended to nearly a year, and thus the result tended to reflect annual average conditions.

Fortunately, an investigation over the NYS was conducted in spring (23 April–5 May 2007), which allowed us to assess the biogenic contribution at high bioactivity period. The MSA concentration was 0.073 ± 0.034 μg m⁻³ during the spring cruise over the NYS (unpublished data), and thus the biogenic portion over the NYS occupied 12% by assuming that the total nss-SO₄²⁻ in spring remained the same as in autumn, which is of the same order of magnitude with previously reported results (Yang et al. 2009). It should be pointed out that the ratio of nss-SO₄²⁻/MSA was derived from clearly tropical oceans, and hence there may be some uncertainties related to the application of the ratio to the coastal and shelf regions. However, this preliminary calculation could be regarded as an approximate assessment. Despite the overwhelming anthropogenic influence from the Asian continent, the nss-SO₄²⁻ derived from bioactivities cannot be ignored especially in spring and early summer with elevated biological activity.

4. Conclusions

We studied the chemical characteristics and sources of water-soluble ions in atmospheric aerosols over the YS and the ECS during autumn. The regional difference of aerosol composition was significant over the observational areas, and most species except the sea salt compounds exhibited relatively higher concentrations over the NYS than over the SYS and the ECS. However, the correlations between internal ions within each sampling period showed rather similar patterns. Of the overall determined aerosol species, the enrichment factors of the secondary ions in aerosol relative to their contents in seawater and crust were extremely high, revealing that the aerosol compositions were under strong anthropogenic influence from the continent, even if the Asian dust input is thought to be relatively low during autumn. In contrast with the previous observations, the relatively low mass ratio of nss-SO₄²⁻/NO₃⁻ in aerosol suggests the gradually increasing air pollution from mobile sources in China, even though stationary emissions are still the primary source. Moreover, a high nss-SO₄²⁻ level and low MSA/nss-SO₄²⁻ ratio in aerosols were observed over the YS and the ECS, further suggesting that the contribution of biogenic SO₄²⁻ to total nss-SO₄²⁻ in aerosols was not pronounced because of the anthropogenic source from East Asia.

Acknowledgments. The authors are grateful to the captain and crew of the R/V Dong Fang Hong 2 for help and cooperation during the two cruises. We also wish to thank three anonymous reviewers for valuable comments and suggestions, which greatly improved the manuscript. This work was financially supported by the National Natural Science Foundation of China (Project 41030858), the National Basic Research Program of China (973 Program Project 2010CB428904), the Changjiang Scholars Programme, Ministry of Education of China, and the Taishan Scholars Program of Shandong Province, China.

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