Nitrate transboundary heavy pollution over East Asia in winter

Syuichi Itahashi1, Itsushi Uno2, Kazuo Osada3, Yusuke Kamiguchi3,a, Shigekazu Yamamoto4, Kei Tamura5, Zhe Wang2,6, Yasunori Kurosaki7, and Yugo Kanaya8

1Environmental Science Research Laboratory, Central Research Institute of Electric Power Industry, 1646 Abiko, Abiko-shi, Chiba 270-1194, Japan
2Research Institute for Applied Mechanics, Kyushu University, 6-1 Kasuga Park, Kasuga, Fukuoka 816-8580, Japan
3Graduate School of Environmental Studies, Nagoya University, D2-1 (510) Furo-cho, Chikusa-ku, Nagoya, Aichi 464-8601, Japan
4Fukuoka Institute of Health and Environmental Sciences, 39 Mukaizano, Dazaifu-shi, Fukuoka 818-0135, Japan
5Nagasaki Prefectural Environmental Affairs Department, 2-1306-11 Ikeda, Omura, Nagasaki 856-0026, Japan
6Institute of Atmospheric Physics, Chinese Academy of Sciences, 40 Huayanli, Chaoyang, Beijing 100029, China
7Arid Land Research Center, Tottori University, 1390 Hamasaka, Tottori 680-0001, Japan
8Japan Agency for Marine-Earth Science and Technology, 3173-25 Showa-machi, Kanazawa-ku, Yokohama, Kanagawa 236-0001, Japan

Correspondence to: Syuichi Itahashi (isyuichi@criepi.denken.or.jp)

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Abstract. High PM$_{2.5}$ concentrations of around 100 µg m$^{-3}$ were observed twice during an intensive observation campaign in January 2015 at Fukuoka (33.52°F, 130.47°E) in western Japan. These events were analyzed comprehensively with a regional chemical transport model and synergistic ground-based observations with state-of-the-art measurement systems, which can capture the behavior of secondary inorganic aerosols (SO$_4^{2-}$, NO$_3^-$, and NH$_4^+$). The first episode of high PM$_{2.5}$ concentration was dominated by NO$_3^-$ (type N) and the second episode by SO$_4^{2-}$ (type S). The concentration of NH$_4^+$ (the counterion for SO$_4^{2-}$ and NO$_3^-$) was high for both types. A sensitivity simulation in the chemical transport model showed that the dominant contribution was from transboundary air pollution for both types. To investigate the differences between these types further, the chemical transport model results were examined, and a backward trajectory analysis was used to provide additional information. During both types of episodes, high concentrations of NO$_3^-$ were found above China, and an air mass that originated from northeast China reached Fukuoka. The travel time from the coastline of China to Fukuoka differed between types: it was 18 h for type N and 24 h for type S. The conversion ratio of SO$_2$ to SO$_4^{2-}$ ($F_4$) was less than 0.1 for type N, but reached 0.3 for type S as the air mass approached Fukuoka. The higher $F_4$ for type S was related to the higher relative humidity and the concentration of HO$_2$, which produces H$_2$O$_2$, the most effective oxidant for the aqueous-phase production of SO$_4^{2-}$. Analyzing the gas ratio as an indicator of the sensitivity of NO$_3^-$ to changes in SO$_4^{2-}$ and NH$_4^+$ showed that the air mass over China was NH$_3$-rich for type N, but almost NH$_3$-neutral for type S. Thus, although the high concentration of NO$_3^-$ above China gradually decreased during transport from China to Fukuoka, higher NO$_3^-$ concentrations were maintained during transport owing to the lower SO$_4^{2-}$ for type N. In contrast, for type S, the production of SO$_4^{2-}$ led to the decomposition of NH$_4$NO$_3$, and more SO$_4^{2-}$ was transported. Notably, the type N transport pattern was limited to western Japan, especially the island of Kyushu. Transboundary air pollution dominated by SO$_4^{2-}$ (type S) has been recognized as a major pattern of pollution over East Asia. However, our study confirms the importance of transboundary air pollution dominated by NO$_3^-$, which will help refine our understanding of transboundary heavy PM$_{2.5}$ pollution in winter over East Asia.

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1 Introduction

Particulate matter (PM) presents major environmental problems globally, especially in East Asia. A typical example is the episode of severe air pollution that occurred in January 2013 above China (e.g., Wang et al., 2014; Uno et al., 2014). During this episode, PM with aerodynamic diameters of less than 2.5 μm (PM$_{2.5}$) reached record-breaking concentrations of 772 μg m$^{-3}$ on 12 January 2013 (Y. Pan et al., 2016). Transboundary air pollution in downwind regions resulting from the severe air pollution in China is also an important environmental problem. For example, the possible long-range transport of PM$_{2.5}$ was based on the comparison of observations in metropolitan areas and remote islands in western Japan (Kaneyasu et al., 2014). They highlighted the dominant effect of the transboundary transport of sulfate (SO$_2^{2-}$) as a major PM$_{2.5}$ component in western Japan throughout most of the year. In spring, due to the prevailing westerly wind over East Asia, the transboundary air pollution of both aerosols and gases, e.g., carbon monoxide (CO) and ozone (O$_3$), has been thoroughly discussed (Itahashi et al., 2010, 2013, 2015; Kanaya et al., 2016; Nagashima et al., 2010). In summer, the clean air mass from the oceans is moved over Japan by the southerly wind caused by the Pacific High; however, some studies have discussed the importance of transboundary air pollution from China over western Japan (Itahashi et al., 2012; Ikeda et al., 2014). Recently, 1-year source-receptor relationships for SO$_4^{2-}$ were evaluated, and China was identified as the main influence on downwind regions throughout the year with local sulfur dioxide (SO$_2$) emissions making an important contribution in summer (Itahashi et al., 2017). Compared with the analyses for spring and summer, transboundary air pollution events in winter are less well understood.

In this study, we also focused on nitrate (NO$_3^-$), which is an important PM$_{2.5}$ component. The NO$_3^-$ in PM$_{2.5}$ is produced via the reaction of gas-phase nitrate (nitric acid: HNO$_3$) and ammonia (NH$_3$), and this process is reversible. The reaction favors a shift toward the aerosol phase at low temperatures and high humidity (Seinfeld and Pandis, 2006). The simulated spatial distribution over East Asia showed the possible impact of transboundary NO$_3^-$ pollution in winter over western Japan (Zhang et al., 2007; Ying, 2014). However, a quantitative evaluation over downwind regions was not presented in previous studies. This is partly because the model ability was not evaluated owing to the difficulty in measuring NO$_3^-$. Particulate NH$_4$NO$_3$ may be volatilized after collection on the filter, either through an increase in the pressure drop across the particle-collecting medium or changes in the gas–aerosol equilibrium during sampling (Sickles II et al., 1999; Chang et al., 2000). This volatilization could occur even in winter because the temperature in the instrument shelter can be increased by heat from the pump. Therefore, the ground-based Acid Deposition Monitoring Network in East Asia uses the four-stage filter pack method: NH$_4$NO$_3$ is collected on the first filter and gas-phase HNO$_3$ and NH$_3$ are detected on the subsequent filters. The artifacts might not be significant; however, to avoid the possibility of volatilization, total nitrate (the sum of NO$_3^-$ and HNO$_3$) has been used to evaluate the model ability in previous studies (e.g., Kajino et al., 2013).

To improve our understanding of the behavior of NO$_3^-$, accurate measurements and the evaluation of the model ability are needed. In this study, we used a state-of-the-art automated monitoring system for SO$_4^{2-}$ and NO$_3^-$, an aerosol chemical speciation analyzer (ACSA). This system measures SO$_4^{2-}$ and NO$_3^-$ with high temporal resolution, and 1 h intervals were used in this study, minimizing the possibility of volatilization. In addition, the behavior of ammonium (NH$_4^+$), which is the counterion for SO$_4^{2-}$ and NO$_3^-$, was captured by the well-validated NH$_4$ monitoring system. Therefore, the secondary inorganic aerosols (sulfate (SO$_4^{2-}$), nitrate (NO$_3^-$), and ammonium (NH$_4^+$); hereafter summarized as SNA) were fully observed by our synergic monitoring system. The denuder filter pack (D–F pack) method with 6–8 h cycles was also used during the intensive observation period from 7–17 January 2015. This intensive observation was designed to capture the heavy PM$_{2.5}$ pollution episode in the wintertime and to support and validate the ACSA and NH$_4$ monitoring systems. Based on these measurement systems, gas-phase HNO$_3$ and NH$_3$ can be measured by the D–F pack method and the NH$_4$ monitor, respectively. The related gas-phase behavior analysis is valuable for improving our understanding of the formation of NO$_3^-$. The observations were conducted at the Chikushin Campus of Kyushu University, which is in the suburbs of Fukuoka (33.52° N, 130.47° E) in western Japan. The synergic ground-based observation dataset was systematically interpreted by using the regional chemical transport model, and we also examined the impact of the domestic and transboundary air pollution in winter. Chemical transport model studies are one type of critical approach for analyzing the behavior of three-dimensional air pollutants and estimating source impacts. A systematic comparison of model results with observations, including gas-phase precursors, will promote understanding and improve the model ability for Asia. This will also contribute to the Model Intercomparison Study for Asia (MICS-Asia), which focuses on providing a common understanding of the model performances and uncertainties, especially for models of long-range transport in Asia (Carmichael et al., 2002, 2008; Li et al., 2017). This paper is constructed as follows. Section 2 documents the observation dataset and the model simulation. Section 3 discusses the results with respect to the temporal variations at the observation sites and the model results combined with the backward trajectory analysis. Finally, a summary and conclusions are given in Sect. 4.
2 Observation and model simulation

2.1 Observation sites

The synergetic observations for capturing SNA behavior were conducted at the Chikushi Campus of Kyushu University located in the suburbs of Fukuoka (33.52° N, 130.47° E). Fukuoka is the largest center of commerce on the island of Kyushu. The population of Fukuoka is 1.5 million and that of the Fukuoka metropolitan area is 2.5 million. This is the fourth largest metropolitan area in Japan after Tokyo (34.8 million), Osaka (12.2 million), and Nagoya (5.5 million). This site is an urban site. In addition to the observations at Fukuoka, observations from the Goto Islands (32.68° N, 128.83° E) and Tsushima Island (32.20° N, 129.28° E) were also used. The Goto Islands are located in the East China Sea, 190 km southwest of Fukuoka, and have a population of 70,000. Tsushima Island is located in the Tsushima Strait, 140 km northwest of Fukuoka, and has a population of 34,000. These islands have negligible anthropogenic emission sources and are regarded as remote sites. In addition to these three sites over Kyushu, to investigate the regions affected by transboundary air pollution, observations from Tottori (35.54° N, 134.21° E) in western Japan were also used. Tottori has a population of 190,000, and this site is also regarded as a remote site in western Japan. The locations of these four observation sites over Japan are shown in Fig. 1. In addition to these observations over Japan, PM$_{2.5}$ observations in China from the US Embassy in Beijing and the US consulates in the provincial capitals of Shanghai and Shenyang were used. The locations of these three sites over China are shown in Fig. 2.

2.1.1 Aerosol chemical speciation analyzer (ACSA)

An ACSA-12 monitor (Kimoto Electric Co., Ltd., Osaka, Japan) for PM$_{10}$ and PM$_{2.5}$, which were separated by a US Environmental Protection Agency inlet and a virtual impactor, were measured with high temporal resolution (Kimoto et al., 2013). PM was collected on a tape filter made of Teflon (PTFE). Hourly observations were conducted for SO$_4^{2-}$ and NO$_3^-$ at Fukuoka. The mass concentrations of PM were determined by using the beta ray absorption method. The ACSA-12 measured NO$_3^-$ using an ultraviolet spectrophotometric method and SO$_4^{2-}$ by turbidimetry after the addition of BaCl$_2$ to form BaSO$_4$ and polyvinyl pyrrolidone as a stabilizer. The analytical period was within 2 h of sampling; therefore, the volatilization of particulate NH$_4$NO$_3$ after collection was regarded as small compared with the traditional filter pack observation method. An ACSA has been tested (Osada et al., 2016) and used to analyze the severe winter haze in Beijing (Zheng et al., 2015; Li et al., 2016) and to identify the aerosol chemical compositions at Fukuoka (X. Pan et al., 2016).

2.1.2 NH$_4$ monitor

The behavior of NH$_3$ and NH$_4^+$ is also important because they are the counterions for SO$_4^{2-}$ and NO$_3^-$. The concentrations of gaseous NH$_3$ and aerosol NH$_4^+$ were measured with a semicontinuous microflow analytical system (MF-NH$_3$A; Kimoto Electric Co., Ltd.; Osada et al., 2011) at Fukuoka. The atmospheric NH$_3$ was dissolved in ultrapure water with a continuous air–water droplet sampler and quantified by fluorimetry (excitation, 360 nm; emission, 420 nm) of the o-phthalaldehyde–sulfite–NH$_3$ reaction product (Genfa et al., 1989). Two inlet lines were used to differentiate the total amounts of NH$_3$ and particulate NH$_4^+$ after gaseous NH$_3$ was removed by a phosphoric acid-coated denuder from the sample air stream. The cutoff diameter of the inlet impactor was about 2 µm.

2.1.3 Denuder filter pack method (D–F pack)

During the intensive observation period from 7–17 January 2015, D–F pack measurements were conducted at Fukuoka to validate the ACSA and NH$_4$ monitor measurement systems. An annular denuder multistage filter sampling system was used for HNO$_3$ and size-segregated aerosol sampling. The sampling interval was 6–8 h. At the inlet, coarse-mode aerosols were removed by nuclepore membrane filters (111114; Nomura Micro Science Co., Ltd., Atsugi, Japan; pore size 8 µm), and then gas-phase HNO$_3$ was collected with the annular denuder (2000-30x242-3CSS; URG Co., Chapel Hill, NC, USA) coated with NaCl (Perrino et al., 1990). Fine-mode aerosols were collected with a PTFE filter (J100A047A; ADVANTEC, Tokyo, Japan; pore size 1 µm), and a nylon filter (66509; Pall Co., Port Washington, NY, USA) captured volatized NO$_3^-$ from the PTFE filter (Appel et al., 1981; Vecchi et al., 2009). Because of the use of an annular denuder system before PTFE filter collection, the adsorption of HNO$_3$, which would otherwise lead to the overestimation of NO$_3^-$, was low. The sample airflow rate was 16.7 L min$^{-1}$ (1 atm, 25°C). Under these conditions, the aerodynamic diameter of 50% cutoff for the nuclepore filter was about 1.9 µm (John et al., 1983). The samples were analyzed by ion chromatography (IC). Comparing size-segregated SO$_4^{2-}$ and NO$_3^-$ data based on the D–F pack method with data from the ACSA showed systematic differences. A linear regression analysis of fine-mode and coarse-mode SO$_4^{2-}$ and NO$_3^-$ showed good correlation, but the slope was not uniform. Fine-mode aerosols were underestimated by the D–F pack relative to the ACSA measurements, and coarse-mode aerosols were overestimated by the D–F pack relative to the ACSA measurements. However, by summing the fine- and coarse-mode data, the slope between the D–F pack and ACSA results was close to unity. The difference in the cutoff diameter of the D–F pack method was considered to be the most important factor in explaining the differences between the results from the D–F pack and the ACSA.
Figure 1. The temporal variation in PM$_{2.5}$ over Japan at Fukuoka, the Goto Islands, Tsushima Island, and Tottori from 7–17 January 2015. The blue and red shading shows the episodes focused on in this study. The red lines indicate the observations. The black lines indicate the base case simulation, and the dotted black lines indicate the sensitivity simulation in which the anthropogenic emissions from Japan were switched off; the differences between these results, shown in gray, represent local contributions.

details of the comparison and validation of the ACSA data are reported in Osada et al. (2016).

2.1.4 PM-712

Hourly PM$_{10}$ and PM$_{2.5}$ concentrations were measured by a PM monitor (PM-712; Kimoto Electric Co., Ltd.) at the Goto Islands, Tsushima Island, and Tottori. The PM-712 used the beta ray attenuation method to measure the mass concentrations of PM$_{10}$ and PM$_{2.5}$. The ionic constituents of the species on the PTFE tape filters were also analyzed by IC to compare the aerosol behavior at Fukuoka and the other sites. At all sites, the sample spots collected on the tape filter were covered with polyester tape to avoid contamination and cross talk interference during storage. The sampling duration for the PM-712 tape filters was 1 h, except for Tottori where it was 3 h. For chemical analysis, four consecutive 1 h tape samples were combined into one sample for the Goto Islands and Tsushima Island. For Tottori, tape samples for 1 or 0.5 days were combined. Because of a temperature change during PM sample storage, some NO$_3^-$ may have escaped via volatilization of HNO$_3$ from the sample. Therefore, NO$_3^-$ data from the Goto Islands, Tsushima Island, and Tottori were not used. NH$_4^+$ is also affected by volatilization when it forms NH$_4$NO$_3$, but it preferentially forms (NH$_4$)$_2$SO$_4$. The data for NH$_4^+$ were used to indicate the concentration trapped by SO$_4^{2-}$. Hereafter, we call these datasets from the PM tape samples “tape filters”.

2.1.5 Beta attenuation monitors (BAMs)

Hourly PM$_{2.5}$ concentrations in China were measured by beta attenuation monitors (BAMs) (1020; Met One Instruments, Inc., Grants Pass, OR, USA) at the US Embassy in Beijing on 8 April 2008, at the US consulates in Shanghai on 21 December 2011, and at the US consulates in Shenyang on 22 April 2013 (Ministry of Environment, 2016). In the BAM technique, PM is collected on a quartz filter tape over a given time interval and the attenuation of beta rays through the sample is measured and correlated directly with the PM mass. The details and the statistical analysis results of the BAM observation at the US Embassy and consulates are found in the work of San Martini et al. (2015).

2.1.6 Multi-angle absorption photometer (MAAP)

Observations of black carbon (BC), a primary aerosol that directly reflects local emission contributions, from Fukuoka
and the Goto Islands were also used to distinguish domestic and transboundary air pollution. BC is observed by using a multi-angle absorption photometer (MAAP) (MAAP5012; Thermo Fisher Scientific, Waltham, MA, USA) (Petzold et al., 2005). In this method, the absorbance of the particles deposited on the filter is distinguished from scattering by reflectance measurements at multiple angles and by transmittance. This is to minimize the effects of coexisting aerosol particles other than BC on filter-based absorption photometers. The comparison measurements of BC from the Goto Islands were previously performed by Kanaya et al. (2013), and they reported that the BC MAAP measurements were strongly correlated with measurements by other techniques but had a positive bias. From the results reported by Kanaya et al. (2013), the MAAP absorption cross section of 6.6 m$^2$g$^{-1}$ at 639 nm. There were no MAAP BC measurements from the Goto Islands before 11 January 2015 during the intensive observation period.

### 2.2 Chemical transport model

The chemical transport model simulation was performed by using the Community Multiscale Air Quality (CMAQ) modeling system version 4.7.1 (Byun and Schere, 2006) with nesting over East Asia. The meteorological fields of CMAQ were prepared with the Weather Research and Forecasting Model version 3.3.1 (Skamarock et al., 2008) with analysis nudging applied to the National Centers for Environmental Prediction final operational global analysis data. The model domain covers the whole of East Asia with an 81 km horizontal grid resolution and a 95 × 75 grid centered at 30°N and 115°E on a Lambert conformal projection. The nested domain covers eastern China and the whole of Japan with a 27 km horizontal grid resolution and a 145 × 145 grid. The vertical grid for sigma–pressure coordinates extends to 50 hPa with 37 layers with nonuniform spacing. The lateral boundary condition was as given by the global chemical transport model of Geos-Chem (Uno et al., 2014). The simulation period was from 1–17 January 2015, and the first 6 days were discarded as model spin-up time. The dry deposition velocity of HNO$_3$ over land was increased by a factor of 5 based on the model intercomparison results (Shimadera et al., 2014; Morino et al., 2015).

Emissions were set as follows. Anthropogenic emissions and natural sources of NO$_x$ from soil were obtained from the latest Regional Emission inventory in ASia (REAS) version 2.1 (Kurokawa et al., 2013), which covers 2000 to 2008. Therefore, the emissions for January 2008 were used in this study. This is because satellite observations of the NO$_2$ column showed a decreasing trend in NO$_x$ emissions from China of −6 % yr$^{-1}$ after 2011, and the levels for 2015 are similar to those for 2009 (Irie et al., 2016). In contrast, the NO$_2$ column over Japan decreased until 2013, and then began to increase from 2013 owing to the change in power plant use after the Fukushima Daiichi nuclear disaster (Morino et al., 2011). The level of the NO$_2$ column over Japan in 2015...
Table 1. The anthropogenic emission amounts used in this study. Units are Gg month\(^{-1}\) for January 2015.

<table>
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<tr>
<th></th>
<th>China</th>
<th>Republic of Korea</th>
<th>Japan</th>
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<tbody>
<tr>
<td>SO(_2)</td>
<td>2882.2</td>
<td>35.8</td>
<td>61.1</td>
</tr>
<tr>
<td>NO(_x)</td>
<td>2150.2</td>
<td>90.3</td>
<td>189.3</td>
</tr>
<tr>
<td>NH(_3)</td>
<td>642.1</td>
<td>15.0</td>
<td>15.3</td>
</tr>
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was close to that in 2008 (Irie et al., 2016). The installation of flue gas desulfurization systems in power plants in China decreased SO\(_2\) emissions in China from 2005 to 2006; after this turning point, SO\(_2\) emissions generally showed a decreasing trend but the variation in SO\(_2\) emissions is complicated (Xia et al., 2016). The assumption about the 2008 level of SO\(_2\) emissions may overestimate the actual status. In Japan, SO\(_2\) emissions are increasing for the same reasons as for NO\(_x\); however, there are no reliable references for the current status of SO\(_2\) emissions. Considering these factors in the variation of NO\(_x\) and SO\(_2\) emissions over China and Japan, it was assumed that the 2008 emissions would be within the range of uncertainty of the bottom-up emission inventories. Because REAS does not consider the monthly variation in NH\(_3\), we used the monthly variation estimated by Huang et al. (2012). The annual NH\(_3\) emission amount was also adjusted to match the estimate of Huang et al. (2012). Other anthropogenic emissions, such as BC, organic carbon (OC), and volatile organic compounds (VOC), were also assumed to be at the 2008 level due to the lack of information needed to update the status. The anthropogenic emission amounts of SO\(_2\), NO\(_x\), and NH\(_3\) in January 2015 are listed in Table 1. The biogenic emissions were prepared from the Model of Emissions of Gases and Aerosols from Nature (MEGAN; Guenther et al., 2012). As a biogenic source, dimethylsulfide (DMS) was not treated in the modeling system. The biomass burning emissions were used from the climatological database of REAnalysis of the TROpospheric chemical composition (RETRO; Schultz et al., 2008). The volcanic activity data were taken from the climatological database of REAnalysis of the TROpospheric chemical composition (RETRO; Schultz et al., 2008). The volcanic activity data were taken from the Climatic Data of the Japan Meteorological Agency (JMA) for available volcanoes (JMA, 2016). The 14 main active volcanoes in Japan, along with and Mount Mayon and Mount Bulusan on the island of Luzon in the Philippines, were considered. The model simulation using the above dataset is referred to as the base case simulation. The modeling system domain with overlaid anthropogenic NO\(_x\) emissions is shown in Fig. 3.

To investigate whether the effect of domestic or transboundary air pollution is dominant, we also conducted a sensitivity simulation in which the anthropogenic emissions in Japan are switched off. Here, the anthropogenic emissions were taken from the REAS inventory; because of this, emissions from agriculture were included. Shipping emissions were not treated in the sensitivity simulation. In terms of O\(_3\), which is involved in complex nonlinear chemistry, larger nonlinearities in the atmospheric concentration response to emission variation for China, but not Japan, were clarified due to the higher amount of emissions from China than from Japan (Itahashi et al., 2015). Therefore, the sensitivity simulation was designed to remove the anthropogenic emissions in Japan instead of those in China. Based on the differences between the base case simulation and this sensitivity simulation, the domestic contribution from Japan was estimated.

3 Results and discussion

3.1 Meteorological conditions

The meteorological conditions during the intensive observation campaign from 7–17 January 2015 are shown in Fig. 4 with the observations and model results. The meteorological observation stations of the JMA in the corresponding nested model grid of Fukuoka were used. Temperatures (Fig. 4a) were around 5 \(^\circ\)C at night and 10 \(^\circ\)C during the day in January 2015. On 9 January, the temperature was nearly 0 \(^\circ\)C at

Figure 3. The modeling domain for the horizontal resolutions of (a) 81 km and (b) 27 km with anthropogenic NO\(_x\) emissions.
Fukuoka. For the wind field (Fig. 4b and c), because of the dominance of the northwesterly wind system from the Asian continent in winter, the wind direction was generally 270–360° (west to north) and the wind speed was around 5 m s⁻¹, with the exception of 9 and 12–15 January. On 9 January when the coldest temperature during the intensive observation campaign was observed, the wind speed was less than 1 m s⁻¹ and the wind direction was from the south. From 13–15 January, the wind speed was also low at 2–3 m s⁻¹, and the wind direction was easterly, caused by a warm front passing over the south of Kyushu on 14 January. After the warm front had passed, the relative humidity was close to 100% on 15–16 January (Fig. 4d) with maximum rainfall of 10 mm h⁻¹ on 15 January (Fig. 4e). The model tended to underestimate the precipitation amount, as we have reported in a previous study (Itahashi et al., 2014). Comparing the observations with the model results shows that our modeling system generally captures the observed meteorological variations during this episode.

3.2 Temporal variation of particulate matter

3.2.1 PM$_{2.5}$

The temporal variation in PM$_{2.5}$ over Japan at Fukuoka, Tsushima Island, the Goto Islands, and Tottori are presented in Fig. 1. The PM$_{2.5}$ observation data are taken from the ACSA at Fukuoka and from the PM-712 at other sites. The temporal resolution is 1 h for all observations. During the analyzed period of 7–17 January 2015, episodic PM$_{2.5}$ peaks reached around 100 µg m⁻³ at Fukuoka twice. The first peak, observed at 12:00 LT on 11 January (shown in blue in Fig. 1), reached a maximum concentration of 86.4 µg m⁻³ at Fukuoka and 105.1 µg m⁻³ at the Goto Islands. During this first peak, the concentration at Tsushima Island was 63.9 µg m⁻³, which was lower than at the other remote island sites in the Goto Islands, and there was no distinctive peak at Tottori. The second peak, observed at 00:00 LT on 17 January (shown in red in Fig. 1), reached a maximum concentration at Fukuoka of 106.2 µg m⁻³. During this second peak, the remote sites of the Goto Islands and Tsushima Island also recorded high PM$_{2.5}$ concentrations of 104.8 and 89.1 µg m⁻³, respectively, and the PM$_{2.5}$ concentration reached 37.6 µg m⁻³ at Tottori. In Fig. 1, we show the model results as black lines. Generally, the model captured the observed temporal PM$_{2.5}$ behavior, although it underestimated the first peaks at Fukuoka and the Goto Islands and the second peak at the Goto Islands. The timing of the high PM$_{2.5}$ concentration was reproduced well by the modeling system. A statistical analysis of the model reproducibility demonstrated that all paired datasets for PM$_{2.5}$ showed good correlations between the observations and the model at the four sites in Japan, with a correlation coefficient ($R$) of 0.86. The mean fractional bias (MFB) and mean fractional error (MFE) were −42.6 and 67.4 %, respectively, and these results satisfied the model performance criteria (MFB $\leq \pm 60\%$ and MFE $\leq +75\%$) proposed by Boylan and Russell (2006). Figure 1 also shows the model results of a sensitivity simulation performed by switching off the Japanese anthropogenic emissions. The sensitivity simulation results are shown as dotted black lines, and the difference between the base case and the sensitivity simulation is shown in gray, which indicates the domestic contribution of Japan. Except for Fukuoka, there were few domestic contributions for PM$_{2.5}$; therefore, transboundary air pollution was dominant in January 2015 at remote sites in western Japan. At Fukuoka, although domestic contributions for PM$_{2.5}$ were found in some cases (from 8–10 and on 14 January), the
concentration of PM$_{2.5}$ was lower compared with the two peaks. During the two episodes when PM$_{2.5}$ concentration reached around 100 µg m$^{-3}$ over Japan, the model simulation suggested that the effect of transboundary air pollution was dominant, even at Fukuoka.

The temporal variations in PM$_{2.5}$ over China at Beijing, Shanghai, and Shenyang are shown in Fig. 2. The PM$_{2.5}$ observation data are taken from the BAMs, and the temporal resolution is 1 h. The model results of a sensitivity simulation suggested that the impact on three Chinese sites from Japanese anthropogenic emissions was negligible during this period. At Beijing, there were high concentrations of PM$_{2.5}$ that correspond to the high concentration of PM$_{2.5}$ found over Japan. One high concentration was approximately 300 µg m$^{-3}$ on 10–11 January and another was around 600 µg m$^{-3}$ on 16 January. These peak times were almost 1 day before the high concentration was observed over Japan. At Shanghai, there were two clear peaks with a PM$_{2.5}$ concentration of 200 µg m$^{-3}$ on 11 and 17 January. The time corresponded well to the peak time over Japan. At Shenyang, where the local emissions from domestic sources were dominant in winter, the temporal variation was complex compared with Beijing and Shanghai. PM$_{2.5}$ showed sharp peaks several times with concentrations of around 300 µg m$^{-3}$, whereas the model only showed gentle peaks. An analysis of the model reproducibility showed that all for PM$_{2.5}$ paired datasets for the observations and the model at three sites over China, $R$ was 0.73 and MFB and MFE were $-9.8$ and 46.8 %, respectively; these numbers satisfy the model goal criteria (MFB $\leq \pm 30$ % and MFE $\leq \pm 50$ %) proposed by Boylan and Russell (2006). The evaluation of the model performance over China supports the discussion on downwind regions.

### 3.2.2 SNA

The temporal variations in SNA are shown in Figs. 5 and 6. In Fig. 5, SO$_4^{2-}$ and NH$_4^+$ are shown for four sites in Japan. At Fukuoka, the ACSA and D–F pack observations are shown for SO$_4^{2-}$. The NH$_4$ monitor and D–F pack results are shown for NH$_4^+$. The temporal resolutions of the ACSA and the NH$_4$ monitor were 1 h, and those of the D–F packs were 6–8 h depending on the samples. For the Goto Islands, Tsushima Island, and Tottori, the PM-712 tape filter data were used. The temporal resolution was 4 h at the Goto Islands and Tsushima Island and 1 or 0.5 days at Tottori. In Fig. 6, NO$_3^-$, HNO$_3$, NH$_3$, and total ammonia (sum of NH$_4^+$ and NH$_3$) are shown for Fukuoka. The ACSA and D–F pack observations for NO$_3^-$ are shown, the D–F pack observations are shown for HNO$_3$, and the NH$_4$ monitor observations are shown for NH$_3$ and total ammonia. Because of a temperature change during the PM-712 sample storage, the NO$_3^-$ concentrations could have been affected by volatilization; hence, only the NO$_3^-$ analysis at the Fukuoka site was used. At Fukuoka, the SNA concentration contributed 52 and 46 % of the PM$_{2.5}$ concentration in the first and second episodes, respectively. For SO$_4^{2-}$ (Fig. 5; left), the concentration during the second episode was larger than during the first episode at Fukuoka, the Goto Islands, and Tsushima Island. At Tottori, there was no peak for the first episode for SO$_4^{2-}$. In contrast to SO$_4^{2-}$, a higher NO$_3^-$ concentration was observed during the first episode instead of the second episode (Fig. 6). NH$_4^+$ showed high concentrations during both episodes because it is the counterion for SO$_4^{2-}$ and NO$_3^-$ (Fig. 5; right). Based on the analysis of the PM$_{2.5}$ (Fig. 1) and SNA (Figs. 5 and 6) observations, the PM$_{2.5}$ concentrations were similar during the episodes on 11 and 17 January; however, the main component of SNA was NO$_3^-$ during the first episode and SO$_4^{2-}$ during the second episode. At Fukuoka, the relative portions of SO$_4^{2-}$, NO$_3^-$, and NH$_4^+$ within the PM$_{2.5}$ were respectively 18, 20, and 14 % during the first episode, and 27, 6, and 14 % during the second episode. Therefore, the first episode (shown in blue in Figs. 1, 5, 6, 7 and 8) is referred to as "type N", and the second episode (shown in red in Figs. 1, 5, 6, 7 and 8) is referred to as "type S" hereafter.

The model results for the base case and sensitivity simulations are overlaid with the same temporal resolution as the observations in Figs. 5 and 6. The model tended to underestimate the SO$_4^{2-}$ concentration (Fig. 5; left); however, the model reproduced the features of types N and S, and the sensitivity simulation indicated the dominance of transboundary air pollution for SO$_4^{2-}$ during the intensive observation campaign in January 2015, even at Fukuoka. For NO$_3^-$ (Fig. 6), the model reproduced the features of the type N and S peaks well, although the model overestimated the dip in NO$_3^-$ concentration found from the evening of 10 January to before the type N episode. The D–F pack observations generally underestimated NO$_3^-$ compared with the ACSA observations because of the difference in the cutoff diameter between these measurement systems. Except for the type N and S episodes, domestic contributions were seen for NO$_3^-$ from 8–10 and on 14 January. However, the sensitivity simulation confirmed that transboundary NO$_3^-$ air pollution was dominant for types N and S. Because NH$_4^+$ is the counterion for both SO$_4^{2-}$ and NO$_3^-$, small domestic contributions for NH$_4^+$ were observed at Fukuoka (Fig. 5; right). This result corresponded to the domestic contribution for NO$_3^-$ peak. For the other three remote sites, there were no domestic contributions for NH$_4^+$.

The behavior of SNA, gas-phase HNO$_3$, and NH$_3$ was analyzed comprehensively based on the NH$_4$ monitor and D–F pack observations (Fig. 6) to support our understanding of NO$_3^-$ behavior. There are few synergistic analyses including gas-phase behavior over the downwind region of the Asian continent. Peaks for gas-phase HNO$_3$ were found for types N and S, whereas the concentration of gas-phase NH$_3$ was nearly zero (less than 1 µg m$^{-3}$ for 24 h average) for types N and S on 8, 10, 12, and 15 January (the green arrows in Fig. 6). Type S, in particular, showed an almost zero concentration of NH$_3$. The concentration of total am-
Figure 5. The temporal variation in \( \text{SO}_4^{2-} \) and \( \text{NH}_4^+ \) over Japan at Fukuoka, the Goto Islands, Tsushima Island, and Tottori from 7–17 January 2015. The blue and red shading shows the type N and S patterns focused on in this study. The red lines indicate \( \text{SO}_4^{2-} \) observations by ACSA, and the green lines indicate \( \text{NH}_4^+ \) observations by the \( \text{NH}_x \) monitor at Fukuoka. The open circles are D–F pack observations at Fukuoka. The open squares are tape filter measurements at the Goto Islands, Tsushima Island, and Tottori. The black lines indicate the base case simulation, and the dotted black lines indicate the sensitivity simulation in which the anthropogenic emissions from Japan were switched off; the differences between these results, shown in gray, represent local contributions.

monia showed distinct peaks for types N and S; therefore, the nearly zero concentration of \( \text{NH}_3 \) suggested the full conversion of \( \text{NH}_3 \) to produce \( \text{NH}_4^+ \) as a counterion for \( \text{SO}_4^{2-} \) and \( \text{NO}_3^- \). The sensitivity simulation, in which Japanese anthropogenic emissions were switched off, clarified the different features of related gas-phase species. The base case simulation and sensitivity simulation were similar for \( \text{HNO}_3 \), suggesting that it originated from transboundary air pollution. A slight increase in \( \text{HNO}_3 \) in the sensitivity simulation was found from 8–10 and on 12 January (the red arrows in Fig. 6). These were the complex cases connected to overseas and domestic emissions. If there are no Japanese \( \text{NH}_3 \) emissions, the transported \( \text{HNO}_3 \) cannot produce \( \text{NO}_3^- \) in Japan, and so it remains as gas-phase \( \text{HNO}_3 \). The synergistic analysis for gas-phase \( \text{HNO}_3 \) and \( \text{NH}_3 \) indicated that abundant \( \text{HNO}_3 \) was transported from abroad and reacted with domestic \( \text{NH}_3 \), producing \( \text{NO}_3^- \) from 8–10 January. Compared with these cases, domestic \( \text{HNO}_3 \) and \( \text{NH}_3 \) produced \( \text{NO}_3^- \) on 14 January (orange arrows in Fig. 6). The concentrations were lower than for types N and S, which were dominated by transboundary air pollution.

3.2.3 Coarse-mode aerosols

Coarse-mode aerosols were also partly analyzed in this study. Because of the effect of transboundary air pollution on \( \text{HNO}_3 \) (Fig. 6), we focused on coarse-mode \( \text{NO}_3^- \). Coarse-mode \( \text{NO}_3^- \) is produced by reactions of \( \text{HNO}_3 \) with mineral dust or sea salt particles. In general, mineral dust mainly has an effect in spring over East Asia (Itahashi et al., 2010), whereas sea salt particles play an important role throughout the year. Recently, we reported the importance of coarse-mode \( \text{NO}_3^- \).
The temporal variation in NO$_3^-$, HNO$_3$, NH$_3$, and total ammonia at Fukuoka from 7–17 January 2015. The red lines indicate NO$_3^-$ observations by the ACSA, the green lines indicate NH$_3$ observations by the NH$_x$ monitor, and the open circles indicate D–F pack observations. For NH$_3$, periods of nearly zero concentration (24 h average of less than 1 µg m$^{-3}$) are indicated by arrows. The black lines indicate the base case simulation, and the dotted black lines indicate the sensitivity simulation in which the anthropogenic emissions from Japan were switched off; the differences between these results, shown in gray, represent local contributions.

Based on the model results and because the domestic contribution for HNO$_3$ was found on 14 January (Fig. 6), the domestic contribution for coarse-mode NO$_3^-$ was found only on 14 January, but the concentration was below 1 µg m$^{-3}$. Na$^+$ and Cl$^-$ from sea salt particles also had peaks for types N and S. Sea salt particles are mechanically produced by high winds; therefore, these peaks generally corresponded to high wind speeds (Fig. 4b). High winds were observed on 15 January; Na$^+$ and Cl$^-$ peaks occurred, but the coarse-mode NO$_3^-$ concentration was close to zero. This was because there was no HNO$_3$ to react with NaCl from 12–15 January or the wet deposition of coarse-mode NO$_3^-$ with the precipitation from noon on 14 January to the evening of 15 January. For coarse-mode NO$_3^-$, transboundary air pollution was the dominant factor. This means that a large amount of HNO$_3$ was transported from abroad (Fig. 6), reacted with sea salt particles over the ocean, and reached Fukuoka in the air mass.
3.2.4 BC

To support the discussion of the domestic and transboundary contributions to SNA, the behavior of BC at Fukuoka and the Goto Islands is shown in Fig. 8. The sensitivity simulation would suffer from a nonlinear chemical response if complex atmospheric chemistry were involved; hence, we focused on BC, which is a primary aerosol. The temporal variation of BC also showed distinctive peaks for types N and S at Fukuoka and the Goto Islands. The model results reproduced these peaks well, and the sensitivity simulation also suggested the dominance of transboundary air pollution for both peaks N and S. The temporal variation at the Goto Islands showed only two peaks of types N and S, although many short-term peaks were seen at Fukuoka. The sensitivity simulation confirmed that domestic air pollution contributed to these short-term peaks at Fukuoka; however, the model could not fully capture the peaks observed on 7, 13, and 14 January. To improve the performance of the model to capture these short-term peaks, a higher resolution model simulation and a revision of the emission inventory are needed. An analysis of the primary aerosol confirmed that transboundary air pollution was dominant for types N and S in January 2015.

Consequently, the well-validated model simulation indicated that two high PM$_{2.5}$ episodes with concentrations of around $100 \mu g \text{ m}^{-3}$ occurring over western Japan in January were dominated by NO$_3^-$ for the first peak (type N) and by SO$_4^{2-}$ for the second peak (type S); the NH$_4^+$ concentration was high for both types. The model sensitivity simulation clarified that these high SNA concentrations in the type N and S episodes were dominated by transboundary air pollution. In addition to the transport of SNA, abundant gas-phase HNO$_3$ and coarse-mode NO$_3^-$ reacted with sea salt particles over the ocean and were also transported to western Japan. NH$_3$, which mainly came from domestic emissions, showed concentrations of around zero during type N and S events, suggesting that NH$_3$ was depleted to neutralize SO$_4^{2-}$ and NO$_3^-$. The high NO$_3^-$ concentration of more than $10 \mu g \text{ m}^{-3}$ covered Fukuoka. The spatial distribution patterns indicated an outflow of SO$_4^{2-}$ and NO$_3^-$ from continental Asia to western Japan. The dominance of transboundary air pollution suggested by these spatial distributions was consistent with the model sensitivity simulation results (Figs. 5 and 6). High-concentration regions of SO$_4^{2-}$ and NO$_3^-$ stretched from the eastern coastline of China to the East China Sea and western Japan. The spatial distribution implied the direct transport from continental Asia to the downwind regions. In addition, the high-concentration region stretched from eastern China to western Japan, which is consistent with the corresponding PM$_{2.5}$ peak on 11 January at Shanghai and over Japan.

To investigate the air mass origin for type N, the HYSPLIT backward trajectory (Stein et al., 2015) was analyzed over 72 h starting from Fukuoka ($T_N$ in Fig. 9; left). The backward trajectory during type N transport suggested that the air mass originated from Shaanxi Province and passed over Shanxi Province, southern Hebei Province, and Shandong Province, and then reached Fukuoka. The traveling time from the coast of China to Fukuoka was about 18 h. The distance from the coastline of China to Fukuoka is approximately 1000 km, so the air mass speed for type N was 55.6 km h$^{-1}$. Figure 9 (left) shows the spatial distribution when the air mass was located over China. A high concentration of NO$_3^-$ of more than $60 \mu g \text{ m}^{-3}$ occurred over the east coast of China before the air mass arrived in Fukuoka, whereas the SO$_4^{2-}$ concentration was as high as $10 \mu g \text{ m}^{-3}$ above the East China Sea.

3.3 Trajectory analysis

Analyzing the synergetic observations at Fukuoka and the other three remote sites in Japan with the regional chemical transport model demonstrated that the two PM$_{2.5}$ episodic peaks were dominated by transboundary heavy pollution, even at Fukuoka. The two peaks had different SNA compositions. The first episode on 11 January showed a high NO$_3^-$ (type N) concentration and the second episode on 17 January was dominated by SO$_4^{2-}$ (type S). The differences in these episodes were investigated further by a model simulation combined with a backward trajectory analysis. The spatial distributions of SO$_4^{2-}$ and NO$_3^-$ during type N and S patterns are shown in Figs. 9 and 10, respectively.

In type N (Fig. 9; right), the model results showed that a low SO$_4^{2-}$ concentration of less than $5 \mu g \text{ m}^{-3}$ and a

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In type S (Fig. 10; right), the model calculated that a high SO\textsubscript{4}\textsuperscript{2-} concentration of more than 20 µg m\textsuperscript{-3} and a low NO\textsubscript{3} concentration of around 5 µg m\textsuperscript{-3} covered Fukuoka. The HYSPLIT backward trajectory is shown as T\textsubscript{S} in Fig. 10. The air mass during type S transport originated from Shanxi Province and slowly moved over northern Henan Province and Shandong Province, and reached Fukuoka within about 24 h. The high-concentration regions stretched from eastern China to western Japan, which is consistent with the simultaneous PM\textsubscript{2.5} peak at Shanghai and over Japan. The air mass was stagnant over China compared with type N transport. The spatial distribution when the air mass arrived at Fukuoka compared with that in China, suggesting the fast production of SO\textsubscript{4}\textsuperscript{2-} during the transport process. A high concentration of SO\textsubscript{4}\textsuperscript{2-} of 20 µg m\textsuperscript{-3} spread over the East China Sea and western Japan. A high NO\textsubscript{3} concentration of more than 60 µg m\textsuperscript{-3} occurred over China, similar to type N; however, the NO\textsubscript{3} concentration was immediately reduced during the transport. The high NO\textsubscript{3} concentration of more than 10 µg m\textsuperscript{-3} did not reach Fukuoka in this type S transport. Comparing the spatial distribution of the air mass over Fukuoka (Fig. 10; right) and China (Fig. 10; left) showed a 1-day delay in the high-concentration peaks over Japan compared with the peak for Beijing (Figs. 1 and 2).

The backward trajectories for types N and S both showed similar transport patterns from China and Fukuoka. However, the spatial distribution patterns demonstrated clear differences between SO\textsubscript{4}\textsuperscript{2-} and NO\textsubscript{3} distributions for type N and S patterns. To discuss the different mechanisms for types N and S further, the model results were analyzed along the backward trajectories of T\textsubscript{N} and T\textsubscript{S}. The path analyses are shown in Figs. 11 and 12, along with additional indexes. The conversion ratio of SNA from the gas phase to the aerosol phase is an important indicator. For SO\textsubscript{4}\textsuperscript{2-}, considering the concentration of the gas-phase species of SO\textsubscript{2}, the conversion ratio of F\textsubscript{s} is defined as follows and calculated based on molar concentrations, shown in square brackets (Khoder, 2002):

$$F_s = \frac{[SO_4^{2-}]}{[SO_2] + [SO_4^{2-}]} \text{[mol mol}^{-1}]$$

(1)
Figure 10. The simulated spatial distribution of (a) SO$_4^{2-}$ and (b) NO$_3^-$ during a type S pattern. The contours shown by the white lines for NO$_3^-$ represent 40 and 60 µg m$^{-3}$. The 72 h HYSPLIT backward trajectory from Fukuoka is overlaid with orange lines and orange circles at 12 h intervals. (Left) 00:00 LT on 16 January 2015 when the air mass left China and (right) 00:00 LT on 17 January 2015 when the air mass reached Fukuoka.

A ratio of 0 indicates that SO$_4^{2-}$ was not produced, and a ratio of 1 indicates that SO$_2$ was converted completely to SO$_4^{2-}$. To confirm the $F_n$ analysis, the concentration of the highly reactive hydroperoxy radical (HO$_2$) was also analyzed. The self-reaction of HO$_2$ produces hydrogen peroxide (H$_2$O$_2$), and this is the most effective oxidant of aqueous-phase SO$_2$ (Pandis and Seinfeld, 1989). Because the analyzed period was in winter, aqueous-phase reactions would be the main pathway for producing SO$_4^{2-}$.

For NO$_3^-$, the conversion ratios of $F_n$ are defined by considering the concentration of NO$_2$ as a precursor and calculated based on molar concentrations (Khoder, 2002):

$$F_n = \frac{[\text{HNO}_3] + [\text{NO}_3^-]}{[\text{NO}_2] + [\text{HNO}_3] + [\text{NO}_3^-]} \text{[mol mol}^{-1}] ,$$

(2)

To investigate the ratio of NO$_3^-$ to gas- and aerosol-phase components analogous to the calculation for SO$_4^{2-}$, the conversion ratio of $F'_n$ is introduced:

$$F'_n = \frac{[\text{NO}_3^-]}{[\text{HNO}_3] + [\text{NO}_3^-]} \text{[mol mol}^{-1}] .$$

(3)

The behavior of SNA is determined by introducing candidate indicators according to the work of Ansari and Pandis (1998) and Pinder et al. (2008). The gas ratio (GR) is an indicator of the sensitivity of NO$_3^-$ to changes in SO$_4^{2-}$ and NH$_4^+$ concentrations. The GR is defined as the ratio of free ammonia to total nitrate as

$$GR = \frac{[\text{NH}_3 + \text{NH}_4^+]}{[\text{HNO}_3 + \text{NO}_3^-]} \text{[mol mol}^{-1}] ,$$

(4)

where it is assumed that SO$_4^{2-}$ is fully neutralized, as indicated by the coefficient of 2 for [SO$_4^{2-}$]. The GR value implies the following condition for NO$_3^-$ production:

$$\begin{cases} 
GR > 1 : \text{NH}_3\text{-rich} \\
0 < GR < 1 : \text{NH}_3\text{-neutral} . \\
GR < 0 : \text{NH}_3\text{-poor}
\end{cases}$$

(5)

Here, NH$_3$-rich means that there is sufficient NH$_3$ to neutralize both SO$_4^{2-}$ and NO$_3^-$, NH$_3$-neutral means that there is sufficient NH$_3$ to neutralize SO$_4^{2-}$, and NH$_3$-poor means that there is insufficient NH$_3$ to neutralize SO$_4^{2-}$ or NO$_3^-$. Free ammonia, which can form NH$_4$NO$_3$ in the equilibrium
process, is quantified more accurately by adjusting $[\text{SO}_2^{2-}]$ with the degree of sulfate neutralization (DSN). The DSN is defined as

$$\text{DSN} = \frac{[\text{NH}_4^+]}{[\text{SO}_2^{2-}]} \text{[mol mol$^{-1}$]},$$

where DSN is equal to or greater than 2 if there is sufficient NH$_4^+$. By substituting the coefficient 2 before $[\text{SO}_2^{2-}]$ in Eq. (2) with Eq. (4), the adjusted GR (adjGR) can be defined as

$$\text{adjGR} = \frac{[\text{NH}_3 + \text{NH}_4^+] - \text{DSN} \times [\text{SO}_2^{2-}]}{[\text{HNO}_3 + \text{NO}_2^\text{y}]}
= \frac{[\text{NH}_3] + [\text{NO}_2^\text{y}]}{[\text{HNO}_3] + [\text{NO}_2^\text{y}]} \text{[mol mol$^{-1}$]}$$

Figure 11. The path analysis of the model results along trajectory $T_N$. (a) Temperature and relative humidity; (b) $\text{SO}_2^{2-}$ (with expansion at the bottom) and $\text{SO}_2^\text{y}$; (c) $\text{HO}_2$ concentration; (d) $\text{NO}_2^\text{y}$, HNO$_3$, NO, NO$_2$, other NOy (NO$_3$, HNO$_2$, N$_2$O$_5$, and PANs), and coarse-mode NO$_2^\text{y}$; (e) NH$_4^+$ and NH$_3$; (f) adjGR, $F_s$, and $F''_n$. In (b), (d), and (e), BC and CO concentrations normalized to the maximum value are also shown. The time axis indicates the backward time from Fukuoka. The brown and blue bars at the bottom are schematic images of the trajectory location over land and ocean.
Figure 12. The path analysis of the model results along trajectory T₅. (a) Temperature and relative humidity; (b) SO₄²⁻ (with expansion at the bottom) and SO₂; (c) HO₂ concentration; (d) NO₃⁻, HNO₃, NO, NO₂, other NOₓ (NO₃, HNO₂, N₂O₅, and PANs), and coarse-mode NO₃⁻; (e) NH₄⁺ and NH₃; and (f) adjGR, Fₖ, and Fₚ. In (b), (d), and (e), BC and CO concentrations normalized to the maximum value are also shown. The time axis indicates the backward time from Fukuoka. The brown and blue bars at the bottom are schematics of the trajectory location over land and ocean.

by using the indexes, and the path analysis of the backward trajectories for the model results are shown in Figs. 11 and 12 and summarized in Table 2. The analyses are shown for the following: (a) the meteorological components of temperature and relative humidity; (b) SO₄²⁻ and SO₂ with an enlarged view for SO₄²⁻; (c) HO₂ concentration; (d) NO₃⁻, HNO₃, NO, NO₂, other NOₓ consisting of NO₃, HNO₂, N₂O₅, and peroxyacyl nitrates (PANs), and coarse-mode NO₃⁻; (e) NH₄⁺ and NH₃; and (f) adjGR, Fₖ, and Fₚ. The concentrations of the air pollutants were reduced by chemical reactions, dispersion, and deposition during the transport; therefore, as an index of the dispersion and deposition processes, BC and CO concentrations normalized to their maximum concentrations during the transport were used in the variation of the total concentration in (b), (d), and (e). Table 2 shows the meteorological components and the air pollutant concentrations.
of each component and total sulfate, total nitrate, and total ammonia. The indexes were averaged over China, the transport time above the ocean, and Fukuoka. The SNA concentration was balanced between NH$_4^+$ and SO$_4^{2−}$ with NO$_3^−$ during both types N and S.

During the type N pattern (Fig. 11), the concentration of air pollutants increased after the air mass moved into Hebei Province (−30 h). The relative humidity was lower than 40 % when the air mass traveled over Shanxi Province and Hebei Province (Fig. 11a). The SO$_4^{2−}$ concentration was around 1 µg-S m$^{-3}$ during transport (Fig. 11b and Table 2), and SO$_2$ was dominant in the total sulfate concentration. In this type N pattern, the concentration of the most effective oxidant of HO$_2$ for the SO$_2$ aqueous-phase reaction was smaller due to the lower relative humidity (Fig. 11c), and the conversion ratio was less than 0.1 (Fig. 11f and Table 2). Compared with the SO$_4^{2−}$ variation, as the trajectory passed from Shanxi Province (−36 h) to Shandong Province (−18 h) and over the ocean (−12 h), the NO$_3^−$ and NH$_4^+$ concentrations increased. The concentrations of NO$_3^−$ and NH$_4^+$ decreased as the air mass traveled to Japan (Figs. 11d and 11e). Over China (−30 to −18 h), gas-phase NH$_3$ was abundant and HNO$_3$ was fully consumed to produce NH$_4$NO$_3$ (Figs. 11d and e). The excess HNO$_3$ over the ocean contributed to producing coarse-mode NO$_3^−$ by reacting with sea salt particles as the air mass traveled over the ocean (Fig. 11d). The adjGR was super NH$_3$-rich over China (Fig. 11f). After the air mass left Shandong, HNO$_3$ increased and NH$_3$ was close to zero (Fig. 11d and e), so the adjGR shifted to an NH$_3$-neutral status (Fig. 11f). Consequently, the proportion of NO$_3^−$, indicated by $F_n^r$, remained around 80 % during transport from China to Japan (Fig. 11f). The rates of the decrease in total sulfate, total nitrate, and total ammonia were generally consistent with the rates of decrease in normalized BC and CO, suggesting that the budget was almost satisfied during transport (Table 2). The decrease in BC was larger than that in CO because of wet deposition (e.g., Pan et al., 2011; Kanaya et al., 2016).

During the type S pattern (Fig. 12), SNA concentrations were higher compared with the type N pattern (Fig. 11), partly due to the slower motion of the air mass compared with type N. SO$_4^{2−}$ concentration was around 2 µg-S m$^{-3}$ over Shanxi Province to Henan Province (−72 to −36 h). It increased slightly to 3 µg-S m$^{-3}$ over Henan Province to Shandong Province (−36 to −24 h) and subsequently increased to 3 µg-S m$^{-3}$ over the ocean (Fig. 12b and Table 2). The aqueous-phase reaction contributed to the production, as suggested by the variation in HO$_2$ concentration. Over the oceans, the relative humidity was around 80 %, which is 20 % larger than in the case of the type N pattern (Fig. 12a and Table 2). The $F_s$ conversion ratio was 0.3 when the air mass reached Fukuoka (Fig. 12f). The increase in SO$_4^{2−}$ over Fukuoka compared with over China was +67.2 % (Table 2). The behavior of gas-phase HNO$_3$ and NH$_3$ was similar in type N patterns (Figs. 12d and e); the NH$_3$ concentration was high over China, and HNO$_3$ gradually increased after the air mass approached the ocean, partly because coarse-mode NO$_3^−$ was produced. However, the NH$_3$ concentration was smaller compared with type N patterns and remained near zero when the air mass passed over Henan Province (Fig. 12e). The adjGR showed a slight NH$_3$-rich status over China (−54 to −36 h) and shifted to an NH$_3$-neutral status before the air mass left China (−36 h). At the same time, the ratio of NO$_3^−$, indicated by $F_n^r$, decreased to 0.45 (Fig. 12f and Table 2). Similar to type N, the rates of decrease in total sulfate, total nitrate, and total ammonia were generally consistent with the rates of decrease in normalized BC and CO.

To summarize the key points for type N and S patterns, the behavior of SO$_4^{2−}$, NO$_3^−$, and HNO$_3$ concentrations during transport from China to Japan is shown in Fig. 13. The relative percentages of the concentration of each species to the total concentration of SO$_4^{2−}$, NO$_3^−$, and HNO$_3$ are shown. It is clear that NO$_3^−$ was not produced, whereas SO$_4^{2−}$ was produced during transport from China to Fukuoka. Types N and S both showed the dominance of NH$_4$NO$_3$ (over 70 %) when the air mass was over China (−48 h). For the air mass close to Fukuoka, because there was no NH$_3$, NH$_4$NO$_3$ decomposed into gas-phase NH$_3$ and HNO$_3$. Therefore, HNO$_3$ concentration increased as the air mass reached Fukuoka for types N and S. At this time, the SO$_4^{2−}$ concentration was important in determining the NO$_3^−$ concentration. SO$_4^{2−}$ production (Figs. 11b and 12b) through an aqueous-phase reaction was indicated by the HO$_2$ concentration (Figs. 11c and 12c), and $F_n$ showed a large difference between types N (lower than 0.1 during transport; Fig. 11f) and S (around 0.3 at Fukuoka; Fig. 12f). Once H$_2$SO$_4$ was produced via an aqueous-phase reaction, it reacted with gas-phase NH$_3$ to produce (NH$_4$)$_2$SO$_4$, leading to the further decomposition of NH$_4$NO$_3$. The ratio of NO$_3^−$ ($F_n^r$) showed different behavior for types N (around 0.8 during transport; Figs. 11f) and S (lower than 0.5 at Fukuoka; Fig. 12f). The transport pattern under similar conditions over China was determined by the low SO$_4^{2−}$ concentration maintaining a higher NO$_3^−$ concentration at Fukuoka (type N), or by SO$_4^{2−}$ production under a higher relative humidity resulting in the dominance of SO$_4^{2−}$ with further NH$_4$NO$_3$ decomposition (type S).

### 3.4 Outflow analysis

Finally, the outflow of SO$_4^{2−}$ and NO$_3^−$ from China to western Japan during the intensive observation campaign is summarized in Fig. 14. In this figure, the modeled SO$_4^{2−}$ and NO$_3^−$ concentrations were averaged at 32–36°N to cover the four sites in Japan (Fig. 1) and are shown as a time–longitude cross section. The longitudes of Shanghai, the Goto Islands, Tsushima Island, Fukuoka, and Tottori are indicated at the bottom of the figure. This outflow analysis can help to identify the areas affected by transboundary heavy pollution. A main outflow from China to western Japan occurred twice.
Table 2. Summary of the path analysis for types N and S.

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<th>Type</th>
<th>Arrival time at Fukuoka</th>
<th>Type N</th>
<th>Over China</th>
<th>During transport</th>
<th>Over Fukuoka</th>
<th>Type S</th>
<th>Over China</th>
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<td>15:00 LT, 11 Jan</td>
<td></td>
<td>18 h</td>
<td></td>
<td></td>
<td></td>
<td>00:00 LT, 17 Jan</td>
<td>24 h</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Temperature [°C]</td>
<td></td>
<td>6.6</td>
<td>6.7</td>
<td>9.3</td>
<td></td>
<td>3.1</td>
<td>4.0</td>
<td>6.5</td>
<td></td>
</tr>
<tr>
<td>Relative humidity [%]</td>
<td></td>
<td>32.7</td>
<td>60.5</td>
<td>50.5</td>
<td></td>
<td>66.3</td>
<td>74.4</td>
<td>67.0</td>
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</tr>
<tr>
<td>$\text{SO}_4^{2-}$ [µg-S m$^{-3}$]</td>
<td></td>
<td>0.9</td>
<td>1.1</td>
<td>1.1</td>
<td></td>
<td>3.3</td>
<td>3.7</td>
<td>6.2</td>
<td></td>
</tr>
<tr>
<td>$\text{SO}_2$ [µg-S m$^{-3}$]</td>
<td></td>
<td>55.9</td>
<td>25.0</td>
<td>14.1</td>
<td></td>
<td>72.1</td>
<td>40.0</td>
<td>17.0</td>
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</tr>
<tr>
<td>Total sulfate [µg-S m$^{-3}$]</td>
<td></td>
<td>56.8</td>
<td>26.1</td>
<td>15.2</td>
<td></td>
<td>75.4</td>
<td>43.8</td>
<td>23.1</td>
<td></td>
</tr>
<tr>
<td>$F_\text{s}$ [mol mol$^{-1}$]</td>
<td></td>
<td>0.02</td>
<td>0.04</td>
<td>0.07</td>
<td></td>
<td>0.04</td>
<td>0.10</td>
<td>0.27</td>
<td></td>
</tr>
<tr>
<td>$\text{NO}_3^-$ [µg-N m$^{-3}$]</td>
<td></td>
<td>4.9</td>
<td>7.5</td>
<td>3.3</td>
<td></td>
<td>15.9</td>
<td>9.4</td>
<td>2.8</td>
<td></td>
</tr>
<tr>
<td>$\text{HNO}_2$ [µg-N m$^{-3}$]</td>
<td></td>
<td>0.0</td>
<td>2.1</td>
<td>1.7</td>
<td></td>
<td>1.9</td>
<td>6.1</td>
<td>5.2</td>
<td></td>
</tr>
<tr>
<td>Other NO$_3$ [µg-N m$^{-3}$]</td>
<td></td>
<td>22.2</td>
<td>8.5</td>
<td>3.3</td>
<td></td>
<td>16.7</td>
<td>6.4</td>
<td>0.9</td>
<td></td>
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<tr>
<td>Coarse-mode NO$_3$ [µg-N m$^{-3}$]</td>
<td></td>
<td>0.0</td>
<td>1.1</td>
<td>1.4</td>
<td></td>
<td>0.4</td>
<td>0.7</td>
<td>1.4</td>
<td></td>
</tr>
<tr>
<td>Total NO$_3$ [µg-N m$^{-3}$]</td>
<td></td>
<td>27.1</td>
<td>19.1</td>
<td>9.7</td>
<td></td>
<td>34.8</td>
<td>22.5</td>
<td>10.4</td>
<td></td>
</tr>
<tr>
<td>$F'_\text{s}$ [mol mol$^{-1}$]</td>
<td></td>
<td>1.00</td>
<td>0.81</td>
<td>0.73</td>
<td></td>
<td>0.90</td>
<td>0.61</td>
<td>0.45</td>
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<tr>
<td>NH$_4^+$ [µg-N m$^{-3}$]</td>
<td></td>
<td>5.6</td>
<td>8.7</td>
<td>4.4</td>
<td></td>
<td>18.8</td>
<td>12.6</td>
<td>8.2</td>
<td></td>
</tr>
<tr>
<td>$\text{NH}_3$ [µg-N m$^{-3}$]</td>
<td></td>
<td>7.5</td>
<td>0.4</td>
<td>0.2</td>
<td></td>
<td>0.6</td>
<td>0.1</td>
<td>0.0</td>
<td></td>
</tr>
<tr>
<td>Total ammonia [µg-N m$^{-3}$]</td>
<td></td>
<td>13.2</td>
<td>9.1</td>
<td>4.6</td>
<td></td>
<td>19.5</td>
<td>12.7</td>
<td>8.2</td>
<td></td>
</tr>
<tr>
<td>adjGR [mol mol$^{-1}$]</td>
<td></td>
<td>2.56</td>
<td>0.87</td>
<td>0.77</td>
<td></td>
<td>0.93</td>
<td>0.61</td>
<td>0.46</td>
<td></td>
</tr>
<tr>
<td>BC [µg m$^{-3}$]</td>
<td></td>
<td>6.5</td>
<td>5.2</td>
<td>2.6</td>
<td></td>
<td>9.7</td>
<td>6.1</td>
<td>4.0</td>
<td></td>
</tr>
<tr>
<td>CO [ppbv]</td>
<td></td>
<td>904.4</td>
<td>737.6</td>
<td>440.2</td>
<td></td>
<td>1260.0</td>
<td>887.0</td>
<td>564.9</td>
<td></td>
</tr>
<tr>
<td>Key points</td>
<td></td>
<td>– Dominance of NO$_3^-$ compared with $\text{SO}_4^{2-}$</td>
<td>– Dominance of $\text{SO}_3^-$ compared with NO$_3^-$</td>
<td>– Under 10 % conversion ratio for $\text{SO}_4^{2-}$</td>
<td>– Approximately 30 % conversion ratio for $\text{SO}_4^{2-}$</td>
<td>– Lower relative humidity</td>
<td>– Higher relative humidity of around 70 %</td>
<td>– No NH$_3$ in the gas phase</td>
<td>– NH$_3$-rich air mass maintaining neutralization of NO$_3^-$</td>
</tr>
</tbody>
</table>

Note: the parentheses indicate the multiplying factors compared with the status over China. The status is averaged over 6 h before the air mass leaves China, during the transport time from China to Fukuoka above the ocean, and over 3 h before the air mass reaches Fukuoka. Other NO$_3$ consists of NO, NO$_2$, NO$_3$, HNO$_2$, N$_2$O$_5$, and PANs.

4 Conclusion

Using state-of-the-art observation systems to capture SNA behavior and a chemical transport model, two episodes of high PM$_{2.5}$ concentrations of around 100 µg m$^{-3}$ were analyzed that occurred in winter over western Japan. The first episode (11 January) was dominated by NO$_3^-$ (type N) and the second episode (17 January) by SO$_4^{2-}$ (type S). The chemical transport model captured the behavior of SNA and the related gas-phase species of HNO$_3$ and NH$_3$ as well as coarse-mode NO$_3$ observed over Japan. The model also reproduced PM$_{2.5}$ variation over China. To evaluate the domestic contributions, a sensitivity analysis was performed. In this analysis, the anthropogenic emissions from Japan were switched off in the chemical transport model. The results showed some domestic contributions for NO$_3^-$, although the...
type N and S patterns were dominated by transboundary air pollution, even at Fukuoka. The effects of transboundary air pollution on type N and S patterns were also confirmed by analyzing the behavior of BC at Fukuoka and the remote Goto Islands. The importance of transboundary air pollution for coarse-mode NO$_3^-$, produced by abundant HNO$_3$ and sea salt particles, was also revealed. To investigate the characteristic differences between type N and S patterns, the chemical transport model results were analyzed by backward trajectory analysis from Fukuoka to continental Asia. We also evaluated the adjusted gas ratio (adjGR), which indicates the sensitivity of NO$_3^-$ to changes in SO$_2^{2-}$ and NH$_4^+$, and examined $F_s$, which is the conversion ratio of SO$_2$ to SO$_2^{2-}$.

For the SO$_2$ aqueous-phase reaction, H$_2$O$_2$ is the most effective oxidant. Thus, HO$_2$, which produces H$_2$O$_2$ through self-reaction, was also analyzed. The features of type N and S patterns are summarized as follows.

- In the type N transport pattern, NO$_3^-$ was mainly the NH$_4^+$ counterion during transport from China to Japan. A high NO$_3^-$ concentration of more than 10 $\mu$g m$^{-3}$ was observed at Fukuoka. NH$_3$ was abundant and HNO$_3$ was completely consumed to produce NO$_3^-$ over China; hence, the adjGR indicated an NH$_3$-rich status, which meant full neutralization of both SO$_2^{2-}$ and NO$_3^-$ over China. After the air mass left China, HNO$_3$ increased and NH$_3$ was close to zero, so the adjGR shifted to an NH$_3$-neutral status. The SO$_2^{2-}$ concentration was always lower than the NO$_3^-$ concentration. This was because the HO$_2$ concentration was less than 3 pptv during transport from China to Fukuoka, and $F_s$ suggested a slow conversion ratio for SO$_2^{2-}$ of less 0.1. SO$_2^{2-}$ production via an aqueous-phase reaction was also inhibi-
ited. This also explained why the air mass maintained a higher NO$_3^-$ concentration during transport.

- In the type S transport pattern, the ion balance between NH$_4^+$ and NO$_3^-$ with SO$_4^{2-}$ showed that the count- rion of NH$_4^+$ was mainly NO$_3^-$ over China and then became SO$_4^{2-}$ as the air mass left China and approached Fukuoka. A high concentration of SO$_4^{2-}$ of more than 20 µg m$^{-3}$ was observed at Fukuoka. The change in $F_4$ from 0.1 to 0.3 when the air mass reached Fukuoka was consistent with this observation. Higher $F_4$ values were related to higher relative humidity and HO$_2$ concentrations, indicating the high production of SO$_4^{2-}$ via an aqueous-phase reaction (H$_2$SO$_4$). The production of H$_2$SO$_4$ promoted the reaction with NH$_3$ to produce (NH$_4$)$_2$SO$_4$ and the further decomposition of NH$_4$NO$_3$ during the transport process from China to Fukuoka. The temporal behavior of gas-phase HNO$_3$ and NH$_3$ was similar for type N; however, the NH$_3$ concentration was lower. The adjGR showed almost NH$_3$-neutral conditions during type S. The production of SO$_4^{2-}$ and the insufficient supply of NH$_3$ contributed to the rapid decomposition of NH$_4$NO$_3$ in this case.

In this study, we clarified two types of transport patterns for SNA. The spatial distribution pattern of the outflow over East Asia in January 2015 showed that the outflow of SO$_4^{2-}$ stretched over the whole of western Japan, whereas transbound- ary NO$_3^-$ air pollution played an important role over Kyushu in western Japan. Generally, transboundary air pol- lution dominated by SO$_4^{2-}$ (type S) has been recognized over East Asia, but we have elucidated the effect of transboundary heavy pollution dominated by NO$_3^-$ (type N). Our findings demonstrate the importance of NO$_3^-$ long-range transport.

The study period was limited to January 2015, so the ana- lyzed period should be extended to investigate the type S and N transport patterns further. The variation in the gas ratio for emissions (GRe), which considers the balance between SO$_2$, NO$_x$, and NH$_3$ (analogous to Eq. 4), may be useful for fu- ture analysis. The emission reductions achieved by the 12th Chinese Five Year Plan for 2011–2015 (Asia Society, 2016) resulted in a GRe increase, which consider an NH$_3$-rich status compared with the current status. Moreover, the target for the 13th Chinese Five Year Plan for 2016–2020 suggests that there will be further increases in GRe. The effects of different reduction rates for SNA precursor gases on transbound- ary NO$_3^-$ air pollution, especially over western Japan, should be modeled.

Data availability. To request observation data used in this study for scientific research purposes, please contact Itsushi Uno at Kyushu University via email (uno@riam.kyushu-u.ac.jp). Model simulations were based on CMAQ, open-source and publicly available software. The model and related software can be downloaded from https://www.cmascenter.org/download.cfm for registered users.

Author contributions. Itsushi Uno designed the synergetic observations at the Chikushi Campus of Kyushu University and other re- mote sites in western Japan. Shigekazu Yamamoto and Kazuo Osada respectively carried out the ground-based ACSA and NH$_4^-$ mon- itor observations at Fukuoka. Yusuke Kamiguchi and Kazuo Osada conducted air sampling and chemical analysis for D–F pack sam- ple during the intensive observation period at Fukuoka. Kazuo Osada and Yasunori Kurosaki measured PM$_{2.5}$ and analyzed samples at Tottori. Kei Tamura analyzed the observations from the remote sites on Tsushima Island and the Goto Islands. Yugo Kanaya conducted the BC observations at Fukuoka and the Goto Islands. Zhe Wang and Syuichi Itahashi discussed the modeling configuration, and Zhe Wang conducted the model comparison to brush up the model results. Syuichi Itahashi developed the modeling system, performed the model simulations and analysis, and prepared the pa- per with the contributions from all coauthors.

Competing interests. The authors declare that they have no conflict of interest.

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