Chinese province-scale source apportionments for sulfate aerosol in 2005 evaluated by the tagged tracer method

Syuichi Itahashi a, * , Hiroshi Hayami a , Keiya Yumimoto b , Itsushi Uno c

a Environmental Science Research Laboratory, Central Research Institute of Electric Power Industry, 1646 Abiko, Abiko, Chiba 270-1194, Japan
b Meteorological Research Institute, Japan Meteorological Agency, 1-1 Nagamine, Tsukuba, Ibaraki 305-0032, Japan
c Research Institute for Applied Mechanics, Kyushu University, 6-1 Kasuga Park, Kasuga, Fukuoka 816-8580, Japan

ARTICLE INFO

Article history:
Received 12 August 2016
Received in revised form 30 September 2016
Accepted 30 October 2016
Available online 22 November 2016

Keywords:
Sulfate aerosol
Source apportionment
Tagged tracer method
Regional chemical transport model
East Asia

ABSTRACT

Appropriate policies to improve air quality by reducing anthropogenic emissions are urgently needed. This is typified by the particulate matter (PM) problem and it is well known that one type of PM, sulfate aerosol ($\text{SO}_4^{2-}$), has a large-scale impact due to long range transport. In this study we evaluate the source–receptor relationships of $\text{SO}_4^{2-}$ over East Asia for 2005, when anthropogenic sulfur dioxide (SO$_2$) emissions from China peaked. SO$_2$ emissions from China have been declining since 2005–2006, so the possible maximum impact of Chinese contributions of $\text{SO}_4^{2-}$ is evaluated. This kind of information provides a foundation for policy making and the estimation of control effects. The tagged tracer method was applied to estimate the source apportionment of $\text{SO}_4^{2-}$ for 31 Chinese province-scale regions. In addition, overall one-year source apportionments were evaluated to clarify the seasonal dependency. Model performance was confirmed by comparing with ground-based observations over mainland China, Taiwan, Korea, and Japan, and the model results fully satisfied the performance goal for PM. We found the following results. Shandong and Hebei provinces, which were the largest and second largest SO$_2$ sources in China, had the greatest impact over the whole of East Asia with apportionments of around 10–30% locally and around 5–15% in downwind receptor regions during the year. Despite large SO$_2$ emissions, the impact of south China (e.g., Guizhou, Guangdong, and Sichuan provinces) was limited to local impact. These results suggest that the reduction policy in south China contributes to improving the local air quality, whereas policies in north and central China are beneficial for both the whole of China and downwind regions. Over Taiwan, Korea, and Japan, the impact of China was dominant; however, local contributions were important during summer.

© 2016 The Authors. Published by Elsevier Ltd. This is an open access article under the CC BY license (http://creativecommons.org/licenses/by/4.0/).

1. Introduction

Sulfate aerosol ($\text{SO}_4^{2-}$) is generally present in particulate matter with aerodynamic diameters of less than 2.5 $\mu$m (PM$_{2.5}$) and is, globally, an important aerosol component (Zhang et al., 2007). It plays an important role in the global energy budget, cloud properties, precipitation efficiency, and atmospheric circulation. SO$_2^-$ is mainly produced by the oxidation of sulfur dioxide (SO$_2$), and over East Asia, especially in China, anthropogenic SO$_2$ is emitted in significant amounts. In 1950, the contribution of Chinese SO$_2$ emissions to the global total was only 2%. However, China’s contribution surpassed that of the U.S. and Europe during the decade 1990–2000, and China became the largest global emitter in 2000, contributing more than 20% of the global total (Smith et al., 2011). Due to the long lifetime of $\text{SO}_4^{2-}$ in the atmosphere, trans-boundary pollution is likely to be a significant problem. Ground-based observations of the impact of trans-boundary $\text{SO}_4^{2-}$ air pollution over downwind regions of Korea (Kim et al., 2009) and Japan (Kaneyasu et al., 2014) have been made. By compiling data from the observation network over Japan, a significant longitudinal gradient for SO$_2^-$, with higher concentrations over western Japan and lower concentrations over eastern Japan, has been found (Aikawa et al., 2010). This suggests the large impact of long range transport of SO$_2$ from China to downwind regions.

Recently, it has been recognized that Chinese SO$_2$ emissions peaked during 2005–2006; the subsequent decrease was due to the introduction of flue–gas desulfurization systems on power plants under the Chinese government policies of the Eleventh Five-
Year Plan during 2006–2010 (Lu et al., 2011; Kurokawa et al., 2013). As a result, it has been reported that SO$_2$ concentration at observation sites located over western Japan exhibited an upward and then downward trend during 1998–2012, with peaks in 2005–2007 (Kaneyasu et al., 2014). Satellite observed aerosol optical depth, mainly arising from SO$_2^-$, also increased up to 2005–2006 and subsequently decreased to 2010 over oceans adjacent to East Asia (Itahashi et al., 2012a). These previous studies all indicate the strong relationship of SO$_2^-$ variation over East Asia to SO$_2$ emission changes in China.

To improve air quality in East Asia, especially in China, appropriate control policies to regulate anthropogenic emissions and reduce subsequent air pollution are necessary, as has been indicated by the relationship between SO$_2^-$ variation over East Asia and SO$_2$ emission change in China. For an accurate evaluation of source–receptor (S–R) relationships, a chemical transport model can offer valuable insights. Scenario analysis, which is a type of sensitivity analysis in which one model parameter (e.g., emission amount) is varied at a time, can be used in combination with the chemical transport model to highlight the importance of particular regions. Based on scenario analysis using a global-chemical transport model, Zhang et al. (2015) found that, SO$_2$ emissions reduction over north China was most effective in reducing national mean SO$_2$ and SO$_2^-$, but that reduction over south China was least efficient on the national scale, albeit with large benefits within the region. Although scenario analysis is a common approach, there are other ways to evaluate S–R relationships. In our previous study, we used the sophisticated decoupled direct method (DDM) to estimate the source contribution of SO$_2^-$, and we found that the dominant impact at a remote island in western Japan was from China, especially from central eastern China (Itahashi et al., 2012b). However, DDM is computationally intensive, so the analysis period was limited to two episodes in summer. Another approach is the tagged tracer method. This method tags the emission sources and traces them, and it can estimate the source apportionment. Focusing on SO$_2^-$ in PM$_{2.5}$, the significant impact of inter-regional transport over China was found by tagging seven Chinese regions (Ying et al., 2014). However, this analysis was limited to 1 month in winter and 1 month in summer, and did not discuss the impact on downwind regions. A long-term (1 year) simulation using the tagged tracer method for particulate matter with aerodynamic diameters of less than 10 μm (PM$_{10}$) over East Asia with seven source regions in China has been conducted (Li et al., 2014). Annual mean results showed that the largest contributions were self-contributions in China (49%), Korea (42%), and Japan (39%), and long-range transport from China formed the second and third largest attributions in Korea (26%) and Japan (14%), respectively. High seasonal variability was also reported. However, the source contributions of each component of PM$_{10}$ were not presented.

Because emission regulations depend on the chemical species, we focus on the S–R relationships of SO$_2^{-}$ for which we have been discussing the impact of long-range transport. China is divided into 31 province-scale source regions, and the S–R relationships of SO$_2^-$ are presented for China, Taiwan, Korea, and Japan. For computational efficiency, the tagged tracer method is adopted to evaluate the source apportionment of SO$_2^-$ over the whole year. To the best of our knowledge, no research has previously been conducted to estimate Chinese province-scale S–R relationships over an entire year. Throughout this manuscript, SO$_2^-$ is used for simplicity to indicate non-seasalt SO$_2^-$, which excludes the effects of sea salt.

Before discussing the improvement arising from recent SO$_2$ emissions reduction in China, knowledge of the possible maximum SO$_2^-$ impact over East Asia will give us foundation information about which source regions have large impacts locally and regionally. Therefore, we focused on the year 2005 when SO$_2$ emissions from China peaked. The selection of 2005 has the additional advantage that differences of emission amounts among inventory datasets are smaller than those for recent years because the bottom-up emissions inventory takes a few years to compile.

2. Material and methods

2.1. Chemical transport model

Model simulations were performed by using the regional chemical transport model of the Comprehensive Air Quality Model with extensions (CAMx) version 6.00 (ENVIRON, 2013). CAMx was configured with 220 × 140 grid points, a 36 km horizontal resolution, and 37 non-uniformly spaced layers from the surface to 50 hPa, centered at 35 °N and 115 °E on a Lambert conformal projection (Fig. 1(a)). To drive CAMx, meteorological fields were prepared using the Weather Research and Forecasting (WRF) model version 3.3.1 (Skamarock et al., 2008). The detailed configuration of CAMx and the WRF model used for simulating air quality in East Asia was that reported in our previous paper (Itahashi et al., 2015a) with a modification to use the lateral boundary conditions from Geo-Chem (Uno et al., 2014). Emissions data were prepared as follows. Anthropogenic emissions were obtained from the Regional Emission inventory in Asia (REAS) version 2.1 (Kurokawa et al., 2013). Biogenic emissions were prepared from the Model of Emissions of Gases and Aerosols from Nature (MEGAN) (Guenther et al., 2006). Biomass burning emissions were obtained from the Global Fire Emissions Database (GFED) version 3.1 (van der Werf et al., 2010). Volcanic activity data were taken from the Ace-Asia and TRACE-P Modeling and Emission Support System (ACCESS) (Streets et al., 2003) and further modified by volcanic activity observation data from Japan Meteorological Agency (JMA) for available volcanoes (JMA, 2016). Fourteen main active volcanoes in Japan and Mt. Mayon in Luzon Island, Philippines were considered. The simulated period was 2005 with a spin-up time of 1 month, and all emissions corresponded to this period.

To evaluate the source apportionment, the Particulate Source Apportionment Technology (PSAT) algorithm in CAMx was applied (Wagstrom et al., 2008). To track SO$_2^-$, CAMx calculates the SO$_2$ tracer as SO$_2$ and the SO$_2^-$ tracer as PS$_4$, where $i$ $(i = 1, ..., N)$ indicates the source group (i.e., source region and category). PSAT is designed to apportion calculated atmospheric concentrations at each grid and time; hence, the sums of each tracer satisfy the mass consistency equations

$$SO_2(t) = \sum_{i=1}^{N} SO_2^i(t), \quad SO_2^-(t) = \sum_{i=1}^{N} PS_4^i(t)$$  \hspace{1cm} (1)

For SO$_2$, which has direct emission sources, the SO$_2$ tracer changes according to the emission amount

$$SO_2^i(t + \Delta t) = SO_2^i(t) + e_{SO_2}^i(t)$$  \hspace{1cm} (2)

where $e_{SO_2}^i$ represents the SO$_2$ emissions apportioned to source group $i$.

The variations of SO$_2$ and SO$_2^-$ produced by chemical reactions are apportioned to the variations of the tracers of SO$_2$ and PS$_4$,

$$SO_2^i(t + \Delta t) = SO_2^i(t) + \Delta SO_2^i(t) \frac{SO_2^i(t)}{\sum_{i=1}^{N} SO_2^i(t)}$$  \hspace{1cm} (3)

$$PS_4^i(t + \Delta t) = PS_4^i(t) + \Delta PS_4^i(t) \frac{SO_2^i(t)}{\sum_{i=1}^{N} SO_2^i(t)}$$  \hspace{1cm} (4)

The apportionment of the SO$_2$ tracer is used for the variation of...
the SO$_4^{2-}$ tracer in Eq. (4). This enables information about the source groups to be transferred from primary emitted species to secondary formed species. However, we note that the approximation of linearity is made here. The almost linear response of SO$_4^{2-}$ concentration to SO$_2$ emissions over East Asia was analyzed by comparing the PSAT approach with the traditional sensitivity approach. This comparison is presented in the Supporting Information (SI).

To estimate the source apportionment of SO$_4^{2-}$ in East Asia, we divided the source categories into anthropogenic and volcanic sources. Anthropogenic sources were separated further into 31 regions in China (22 provinces, 4 municipalities, and 5 autonomous regions), Taiwan, the Korean Peninsula, Japan, and the rest of the domain; the total number of source regions was 35. The apportionment from the lateral boundary is estimated separately. The special administrative regions of Hong Kong and Macau in China are included in Guangdong province because the model’s horizontal resolution is 36 km in this study and they cannot be fully resolved as source regions. Four main sources in China were defined: the Beijing, Tianjin, Hebei (Jing-Jin-Ji; JJJ) region; the Bohai Economic Rim (BER) region, which was defined as the JJJ region plus Shandong and Liaoning; the Yangtze River Delta (YRD), which was defined as Jiangsu, Shanghai, and Zhejiang; and the Pearl River Delta (PRD), which was defined as Guangdong (including Hong Kong and Macau). The source regions are illustrated in Fig. 1(a), and their emission amounts are shown as bar graphs in Fig. 1(c). The total amount from China was 96.3 Gg/day in 2005, and the largest emissions source was Shandong province with 11.8 Gg/day (approximately 12% of the total amount from China). The emissions from Taiwan, the Korean Peninsula, and Japan were 0.4, 1.8, 2.4 Gg/day, respectively. The SO$_2$ emissions from volcanoes, which are an important natural source of SO$_2$ in Japan, were 7.8 Gg/day. The injection height of volcanic emissions was assumed to be the mountain height; but this was revised if eruption plume height information was available.

2.2. Observation dataset

To evaluate the accuracy of the model in reproducing SO$_4^{2-}$ concentrations, we prepared the following ground-based observation dataset for China, Taiwan, Korea, and Japan. Over Asia, the Acid Deposition Monitoring Network in East Asia (EANET) provides atmospheric aerosol concentrations measured by the filter pack method (EANET, 2013). There was a total of 10 sites in Japan and three sites in Korea were available for 2005; the fraction of the period having available data was less for Korea than for Japan (EANET, 2006). In addition to EANET dataset, the observation dataset of the Japan Environmental Laboratories Association (JELA) acquired at 33 sites in Japan was used (JELA, 2006, 2016). Of these 33 sites, three sites were at the same locations as EANET sites; therefore, averaged EANET and JELA concentrations were used. Under the horizontal spatial resolution of the modeling in this study, two sites in Sapporo city and two sites in Niigata city were allocated to the same grid; therefore, observations from these pairs of sites were averaged. Monthly average EANET and JELA observations were used. Network datasets covering the whole of China for 2005 were not available, so we collected observation datasets from the literature for the best corresponding period. These observation datasets were over Beijing and Chongqing from March 2005 to
February 2006 (Yang et al., 2011); seasonally over Tsingdao from 1997 to 2000 (Hu et al., 2002); over Shanghai from March 1999 to March 2000 (Ye et al., 2003); over Guangzhou measured every sixth day in October 2002, December 2002, March 2003, and June 2003 (Hagler et al., 2006); and over Hong Kong in 2005 (Chan and Yao, 2008). Observations at the Taipei observation supersite in Taiwan from 2002 to 2008 were also used (Chang et al., 2010). These ground-based observation site locations are shown in Fig. 1(b).

3. Results and discussion

3.1. Evaluation of modeling ability

Before discussing the S–R relationships for \( \text{SO}_4^{2-} \), the model’s ability to reproduce observations was evaluated. The comparison between model and observation of annual means at each site in China and seasonal means for one site in Taiwan and all sites over Korea and Japan are shown in Fig. 2. Over China, although the observation period did not correspond exactly to the modeled period of 2005, the features of averaged \( \text{SO}_4^{2-} \) concentrations in each site were captured by our modeling system. Averaged concentrations were around 15 \( \mu g/m^3 \) at each site and a maximum concentration of 25 \( \mu g/m^3 \) was found at Chongqing. In Taiwan, the seasonal variation with summer minima was captured. Over Korea and Japan, the seasonal variations with summer maxima and winter minima were also well reproduced, but the model overestimated summer maxima over Korea. The results of statistical analysis of model reproducibility are given in Table 1: the correlation (R), skill score (S), mean fractional bias (MFB), mean fractional error (MFE), and the percentages within a factor of 2 (FAC2) and 3 (FAC3) were evaluated. For seasonal evaluation, observation sites in Taiwan, Korea, and Japan were used. The values of R ranged from 0.66 to 0.85, and were statistically significant (\( p < 0.001 \)) according to Student’s t-test. The value of S, which accounts for the correlation between the standard deviations of model and observations, ranged from 0.72 to 0.89, suggesting agreement between model and observations. In all seasons, MFB and MFE satisfied the model performance goals of MFB \( \leq +30\% \) and MFE \( \leq +50\% \), which were proposed as model performance metrics by Boylan and Russell (2006). More than 90% were within a factor of 2 of observed values, and over 97% were within a factor of 3. For annual evaluation, all observations were used. A scatter-plot of observations and model predictions is shown at the bottom right of Fig. 3. The annual averaged concentration of \( \text{SO}_4^{2-} \) was approximately 6 \( \mu g/m^3 \) over East Asia. The values of R and S were both 0.95, and the MFB of 11.9% and MFE of 19.8% also satisfied the performance goal criteria. More than 93% of predictions were within a factor of 2 of observed values, and all were within a factor of 3 in terms of annual average. These results show that our modeling system reproduces the observations over China, Taiwan, Korea, and Japan well, satisfying the level of model performance goal criteria from the viewpoint of statistical analysis.

Modeled seasonal and annual mean distributions at surface level are illustrated with the observation data overlaid in Fig. 3. For the annual mean, the model captured the observed \( \text{SO}_4^{2-} \) behavior well, with high concentrations of more than 10 \( \mu g/m^3 \) over most of China, concentrations of 7–10 \( \mu g/m^3 \) over the Korean Peninsula, concentrations around 5 \( \mu g/m^3 \) over Taiwan and western Japan, and concentrations around 3 \( \mu g/m^3 \) over northern Japan. From the viewpoint of the seasonal variation of \( \text{SO}_4^{2-} \) concentration, the high concentration shown in the annual mean spatial distribution was found throughout the year over China. Central China was covered by a high \( \text{SO}_4^{2-} \) concentration of over 10 \( \mu g/m^3 \) for all seasons, and high concentration areas moved northward during summer and southward during winter. During spring, because of the westerly wind, areas of high concentration of over 5 \( \mu g/m^3 \) stretched into western Japan. There was also a similar effect during autumn although it stretched a smaller distance towards Korea and Japan. Owing to the southerly wind from the Pacific High during summer, high concentration areas were spread over the Korean Peninsula and most of Japan, except the north. During this period, Taiwan experienced a marked minimum concentration throughout the year. In contrast, owing to the strong northwesterly wind from the
Table 1
Statistical analysis of model performance for SO$_4^{2-}$; seasonal evaluation for sites over Taiwan, Korea, and Japan, and annual evaluation for all sites.

|        | N  | Average | R       | S       | MFB    | MFE    | FAC2 | FAC3 |
|--------|----|---------|---------|---------|--------|--------|------|------|
|        |    | Observation | Model   |         |        |        |      |      |
| spring | 41 | 4.78    | 6.14    | 0.81 ($p < 0.001$) | 0.89  | 29.7   | 31.1 | 90.2 | 97.6 |
| summer | 40 | 7.27    | 7.66    | 0.66 ($p < 0.001$) | 0.72  | 0.3    | 21.6 | 90.0 | 100.0|
| autumn | 40 | 3.94    | 4.30    | 0.85 ($p < 0.001$) | 0.89  | 12.9   | 19.0 | 97.5 | 100.0|
| winter | 41 | 2.64    | 2.47    | 0.77 ($p < 0.001$) | 0.77  | 0.7    | 27.2 | 97.6 | 97.6 |
| annual | 48 | 6.02    | 6.29    | 0.95 ($p < 0.001$) | 0.95  | 11.9   | 19.8 | 93.8 | 100.0|

Fig. 3. Modeled spatial distribution of seasonal and annual mean SO$_4^{2-}$ concentrations at surface level overlaid with ground-based observations. A scatter-plot of observations and model predictions for annual means with standard deviations based on monthly means is shown in the bottom-right panel.
Asian continent during winter, high concentration areas extended to Taiwan and the north of Southeast Asian countries (Vietnam, Laos, and Thailand). The reproducibility for SO2, which is the precursor of SO4^2-/CO, compared with ground-based EANET (EANET, 2006) and satellite observations (Lee et al., 2011), is provided in the Supplementary Information. This indicated that the model can capture the observed SO2 behavior over East Asia. We have thus confirmed the adequate performance of our modeling system, and so we now turn to the annual mean S-E relationships over China and their seasonal variation over Taiwan, Korea, and Japan.

3.2. Assessment of annual mean source apportionment over China

The source apportionments as relative percentages of the modeled concentration over Beijing municipality, Shandong province, Shanghai municipality, Chongqing municipality, and Guangdong province in China, where the model reproducibility was evaluated at representative observation sites, are presented in Fig. 4. The top 10 source apportionment regions in China are indicated by numbers in each receptor region. In Beijing municipality (Fig. 4(a)), the source apportionment from Shandong and Hebei provinces, which were the largest and the second largest emission sources in China, were the largest at around 20%. The self-contribution was 4.0% and was the seventh largest source. The apportionment from JJJ was approximately 30%, and that from BER was 52.2%. In Shandong province (Fig. 4(b)), the self-contribution was over 30%. Jiangsu (12.4%), Hebei (8.8%), and Henan (6.7%), which are contiguous provinces, had the next largest apportionments. The apportionment of BER was 45.3%. YRD also had an impact on Shandong province, with an apportionment of 18.2%. In Shanghai municipality (Fig. 4(c)), the self-contribution was over 10% and Hebei and Jiangsu were the two largest
source regions; hence the apportionment from YRD was 41.4%. In Shanghai municipality, Shandong province also had a large impact (11.0%). In Chongqing municipality, the self-contribution was 9.2%, and the largest impact was from Guizhou province (12.8%), which is the third largest SO2 emissions source in China. In Guangdong province, the self-contribution was 29.0%.

Considering the ranking of SO2 emission amounts, it is remarkable that Shandong province had a significant impact over China, even in south China, including Chongqing municipality (5.9%) and Guangdong province (6.5%). Hebei, Henan, Jiangsu, and Shanxi provinces, which are in central to north China, also had a large impact over China. In contrast, Guizhou province had an impact that was limited to nearby regions. This was also the case for Guangdong and Sichuan provinces. These source regions in south China showed a large impact on only Chongqing. These results are based on annual means, but these significant inter-regional source contributions were qualitatively consistent to the results of another study (Ying et al., 2014).

The spatial variation of the source apportionments of the four main sources in China (JJJ, BER, YRD, and PRD), Taiwan, Korea, and Japan, and volcanoes are illustrated in Fig. 5. The impact of JJJ, BER, and YRD was dominant over the whole of China and in the downwind regions of Taiwan, Korea, and Japan. The source apportionment of JJJ was distributed over northeast China, Korea, and the Sea of Japan (Fig. 5(a)), whereas the source apportionment of YRD was distributed over the Yellow Sea, western Japan, and Taiwan (Fig. 5(c)). The impact of BER was the largest: its relative contribution to Korea was 30–40% and 10–20% to Taiwan, Japan, and even Southern China (e.g., Guangdong, Hainan) (Fig. 5(b)). In contrast, the impact from PRD was more local than that of JJJ, BER, and YRD (Fig. 5(d)). The source apportionments of each province in China are presented in the Supplementary Information. These results imply that emission control over north to central China (i.e., JJJ, BER, and YRD) would decrease the SO4\(^{2-}\) concentration over large parts of China, and emission control over south China (i.e., PRD) would reduce air pollution primarily in that region only.

The source apportionment of Taiwan peaked at 2.0 \(\mu g/m^3\) above north Taiwan, and it was distributed along the coastline of South China at a level of less than 0.5 \(\mu g/m^3\) (Fig. 5(e)). For Korea, the largest source apportionment of 2.5 \(\mu g/m^3\) was obtained in western Korea, which includes Seoul, the largest source in South Korea. It affected the northeast to eastern coastline of China and western Japan with an apportionment of less than 0.5 \(\mu g/m^3\) (Fig. 5(f)). The source apportionments for Japan and volcanoes, which are mainly located around Japan, were similar (Fig. 5(g) and (h)), but the apportionments were larger for volcanoes than for anthropogenic sources in Japan. The SO2 emission amounts were 2.4 Gg/day for anthropogenic sources in Japan and 7.8 Gg/day for volcanoes. The largest volcanic source was Miyakejima, 180 km south of Tokyo, with emissions of 4.2 Gg/day. Because of the height of volcanic sources and stronger winds at higher altitudes, the impact from volcanoes was distributed over a wide area, even to southeast China.

### 3.3. Assessment of seasonal mean source apportionments over Taiwan, Korea, and Japan

The seasonal variation and annual mean of SO4\(^{2-}\) concentration and its source apportionments are shown in Fig. 6. Here, the source apportionments of the 31 source regions in China are summarized as 'China'. In Taiwan (Fig. 6(a)), SO4\(^{2-}\) showed spring and winter maxima of 6.5 \(\mu g/m^2\) and a summer minimum of 2.9 \(\mu g/m^2\). The largest source was in April, with a maximum of 155% during high pressure pushing weather patterns originating from the Asian continent which are observed during all seasons except summer (Chuang et al., 2008); this corresponded to 61% of the
transboundary air pollution at Taipei, and was close to our source apportionment result of a 60.7% contribution from China to Taiwan, except for the summer (Fig. 6(a)).

In Korea (Fig. 6(b)), SO$_4^{2-}$ concentration had a summer maximum of 15.9 μg/m$^3$ and a winter minimum of 3.1 μg/m$^3$. The source apportionment of China was around 70% throughout the year, and the local contribution had a summer maximum (18.1%) and winter minimum (8.3%). The intensive measurement campaign at Gwangju super-observation site in Korea (126.85°E, 35.23°N) in spring 2008 concluded that the background concentration of SO$_4^{2-}$ was 8.5 μg/m$^3$ and this increased to 21.9–44.6 μg/m$^3$ during long-range transportation events (Cayetano et al., 2014). This corresponded to a 61–81% contribution from long-range transport, which is consistent with our source apportionment result of a 72.9% contribution from China to Korea in spring (Fig. 6(b)).

In Japan (Fig. 6(c)), the SO$_4^{2-}$ concentration showed a seasonal variation similar to that found in Korea (Fig. 6(b)): a summer maximum of 6.8 μg/m$^3$ and a winter minimum of 2.1 μg/m$^3$. In

\[ \text{concentration} \]
summer, when the maximum concentration was reached, the contributions from China (32.9%), Japan (26.2%), and volcanoes (28.7%) were similar. In other seasons, the impact of China dominated, and was around 50%. The low apportionment from volcanic sources in winter was related to the strong northwesterly wind, and a correspondingly high apportionment from volcanoes was found over the Pacific Ocean in the same period. Based on model estimation by setting the Chinese emissions to zero, a 50–70% Chinese contribution to Japan averaged over April 2003 to March 2006 has been reported (Aikawa et al., 2010); this represents an over-prediction compared to our source apportionments results. Considering the good correspondence between the source estimation methodologies discussed in the Supplementary Information, this difference is likely to be caused by the uncertainty of emissions. When lower estimates of SO2 amounts for China were used, a 40–60% Chinese contribution to Japan was obtained. Actually, REAS version 1.1 (Ohara et al., 2007), which was used in their study, estimated larger SO2 emissions from China, and this estimation was revised in REAS version 2.1 (Kurokawa et al., 2013), which is used in this study. This demonstrates the importance of the uncertainty of emission inventory to the estimation of S–R relationships, and the dependencies of S–R relationships on emission inventory should be examined carefully.

The impact from China was large in the downwind regions of Taiwan, Korea, and Japan; therefore, the S–R relationships of the source contributions from the 31 regions of China were analyzed further. The seasonal and annual mean source apportionments of the top 10 provinces and four main sources in China (JJJ, BER, YRD, PRD) over Taiwan, Korea, and Japan are presented in Fig. 7. The largest source was Shandong, which was the largest source of SO2 emissions in China. In Taiwan (Fig. 7(a)), the dominant source region in China did not change throughout the year, except during summer. BER and YRD both made contributions of around 15% except during summer. During summer, Guangdong (i.e., PRD) and Fujian were the dominant sources because of the southerly wind caused by the Pacific High. In Korea (Fig. 7(b)), the contribution from BER was larger, at around 35% throughout the year. At the province level, Shandong had the largest effect, with an impact more than twice that of other sources in China, and the source apportionment from Shandong was larger than the self-contribution of Korea throughout the year. The impact from Jiangsu, Zhejiang, and Shanghai (i.e., YRD) was small during winter, and the impact from Liaoning, Inner Mongolia, and Jilin, located in the north and northeast of China, was larger during winter due to the prevailing northwesterly wind from the Asian continent caused by the Asian monsoon. In Japan (Fig. 7(c)), the source apportionment was similar to that of Korea, although the relative contributions were smaller because volcanoes are also an important source in Japan. Heilongjiang, which was the most northeastern location in China, also had an impact on Japan during winter.

4. Conclusions

In this study, the source-receptor relationships of SO2− in 2005 were evaluated by applying the tagged tracer method. Due to the computational efficiency of the tagged tracer method, source regions were divided into 31 Chinese province-scale areas, and moreover, a full year of source apportionments was investigated. The S–R relationships over downwind regions of China suggest that emission control over northern and central China (e.g., BER and YRD), especially Shandong province, would effectively reduce SO2− concentration over the downwind region. For example, based on the almost linear correspondence of SO2 and SO2− concentrations, to reduce the SO2− concentration over Shandong province by 1 µg/m3, a 24.9% emission reduction over Shandong province is needed as the self source apportionment of Shandong province was 4.0 µg/m3 (see Fig. 4(b)). In this case, this 24.9% reduction of SO2 emissions over Shandong province would also lead to a reduction of SO2− concentration over Tianjin by 0.87 µg/m3, over Liaoning by 0.61 µg/m3, over Hebei by 0.52 µg/m3, over Henan by 0.50 µg/m3, and over Beijing by 0.46 µg/m3. Furthermore, there would be a reduction over downwind regions of Taiwan by 0.11 µg/m3, Korea by 0.39 µg/m3, and Japan by 0.09 µg/m3 (calculated with PS4 of Shandong province at each receptor region multiplied by 24.9%). Emission reduction policies over northern and central China would, therefore, benefit both China and downwind regions. Meanwhile, despite its large SO2 emissions, south China (e.g., Guangzhou, Guangdong, and Sichuan provinces) had only a local impact; this suggests that the reduction policy in south China contributes to the improvement of local air quality.

Zhang et al. (2015) reported that, although total national SO2 emissions were reduced by about 10% during the decline of SO2 emissions in China after 2005, there was high spatial variation: the reduction rates from 2006 to 2010 were 4.7%, 16.1%, and 23.1% over north, south, and southwest China, respectively. Considering our findings and the SO2 reduction estimation from 2006 to 2010, the SO2 emission reduction policy under the Eleventh Five-Year Plan during 2006–2010 in China will mainly contribute to the improvement of local air quality over south China rather than northeast China and downwind regions. To determine quantitatively the impact of policy making in China after 2005 at an East Asian scale, the evaluation of the long-term trends of S–R relationships is a priority for understanding the connection between policy decisions and their effects. To conduct these studies, the examination of emission source categories will be important (e.g., Zhang et al., 2012), because the SO2 reduction in China after 2005–2006 is mainly attributed to power plants (Lu et al., 2011; Kurokawa et al., 2013). In addition, because the emission inventory itself contains uncertainties, a comparison of S–R relationships derived from different emission inventories should be also made. The tagged tracer method applied successfully in this study has the advantage that detailed source groups (regions and categories) can be evaluated with computational efficiency. In addition, the link between the wet deposition over East Asia and anthropogenic emissions variation from China have been clarified recently (Itahashi et al., 2014, 2015b). Therefore the modeling of S–R relationships for evaluating both atmospheric concentration and deposition is important to further promote our understanding of air quality in East Asia.

Acknowledgements

The authors are grateful to EANET and JELA for providing measurement datasets. This study was supported in part by JSPS KAKENHI Grant Numbers JP25220101 and JP16K21690 and by the Global Environment Research Fund (No. S-12) of the Ministry of the Environment, Japan.

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.envpol.2016.10.098.

References

Aikawa, M., Ohara, T., Hiraki, T., Oishi, O., Tsuji, A., Yamagami, M., Murano, K., Mukai, H., 2010. Significant geographic gradients in particulate sulfate over Japan determined from multiple-site measurements and a chemical transport model: impacts of transboundary pollution from the Asian continent. Atmos. Environ. 44, 381–391.

Boylan, J.W., Russell, A.G., 2006. PM and light extinction model performance...
metrics, goals, and criteria for three-dimensional air quality models. Atmos. Environ. 40, 4946–4959.
Cayetano, M.G., Hoekse, P.K., Lee, K.H., Jung, J, Batmunkh, T., Lee, K, Kim, YJ, 2014. Investigations of the particle compositions of transported and local emissions in Korea. Aerosol Air Qual. Res. 14, 793–805.
Chan, C.K., Yao, X, 2008. Air pollution in mega cities in China. Atmos. Environ. 42, 1–42.
Chang, S.-C., Chou, C.C.-K., Chan, C.-C., Lee, C.-T., 2010. Temporal characteristics from continuous measurements of PM2.5 and speciation at the Taipei Aerosol Supersite from 2002 to 2008. Atmos. Environ. 44, 1088–1096.
Chuang, M.-T, Chiang, P.-C, Chan, C.-C, Wang, C.-T, Chang, E.-F, Lee, C.-T, 2008. The effects of synoptic weather pattern and complex terrain on the formation of aerosol events in the Greater Taipei area. Sci. Total. Environ. 399, 128–146.
EANET, 2006. Data Report on the Acid Deposition in the East Asia Region 2005., Network Center for EANET.
EANET, 2013. Technical Manual for Air Concentration Monitoring in East Asia. available from. Network Center for EANET. http://www.eanet.asia/product/index.html.
ENVIRON, 2013. User's Guide, Comprehensive Air Quality Model with Extensions Version 6.00. International Corporation, Novato, California, USA.
Guenther, A., Karl, T, Harley, P., Wiedinmyer, C, Palmer, P.L, Ceron, C, 2006. Estimates of global terrestrial isoprene emissions using MEGAN (model of emissions of gases and aerosols from nature). Atmos. Chem. Phys. 6, 3181–3210.
Hagler, G.S.W, Bergin, M.H, Salmon, L.G, Yu, J.Z, Wan, E.C.H, Zheng, M, Zeng, L.M, Kiang, C.S, Zhang, Y.H, Lau, A.K.H, Schauer, J.J, 2006. Source areas and chemical composition of fine particulate matter in the Pearl River Delta region of China. Atmos. Environ. 40, 3802–3815.
Hu, M, He, L.Y, Zhang, Y.-H, Wang, M, Kim, Y.-P, Moon, K.C, 2002. Seasonal variation of ionic species in fine particles at Qingdao, China. Atmos. Environ. 36, 5853–5859.
Itahashi, S, Uno, I, Yumimoto, K, Irie, H, Osada, K, Ogata, K, Fukushima, H, Wang, Z, Ohara, T, 2012a. Intermittual variation in the fine-mode MODIS aerosol optical depth and its relationship to the changes in sulfur dioxide emissions in China between 2000 and 2010. Atmos. Chem. Phys. 12, 2631–2640.
Itahashi, S, Uno, I, Kim, S.-T, 2012b. Source contributions of sulfate aerosol over East Asia estimated by CMAQ-DDM. Env. Sci. Tech. 46, 6733–6741.
Kaneyasu, N, Yamamoto, S, Sato, K, Takami, A, Hayashi, M, Hara, K, Kawamoto, K, Okuda, T, Hatakeyama, S, 2010. Impact of long-range transport of aerosols on the PM2.5 composition at a major metropolitan area in the northern Kyushu area of Japan. Atmos. Environ. 44, 416–425.
Kim, Y-J, Woo, J-H, Ma, Y-L, Kim, S, Nam, J.S, Sung, H, Choi, K-C, Seo, J, Kim, J.S, Kang, C-H, Lee, G, Ro, C-U, Chang, D, Sunwoo, Y, 2009. Chemical characteristics of long-range transport aerosol background in Korea. Atmos. Environ. 43, 5556–5566.
Kurokawa, J, Ohara, T, Morikawa, T, Hanayama, S, Janssens-Maenhout, G, Fukushima, T, Kawashima, K, Akimoto, H, 2013. Emissions of air pollutants and greenhouse gases over Asian regions during 2000–2008: regional emission inventory in Asia (REAS) version 2. Atmos. Chem. Phys. 13, 11019–11058.
Lee, C, Martin, R.V, Donkelaar, A, Lee, H, Dickerson, R.R, Hains, J.C, Krotkov, N, Richter, A, Vinnikov, K, Schwab, J.J, 2011. SO2 emissions and lifetimes: estimates from inverse modeling using in situ and global space-based (SCIAMACHY and OMI) observations. J. Geophys. Res. Atmos. 116, D06304.http://dx.doi.org/10.1029/2010JD014758.
Li, J, Yang, W, Wang, Z, Chen, H, Hu, B, Li, J, Sun, Y, Huang, Y, 2014. A modeling study of source-receptor relationships in atmospheric particulate matter over Northeast Asia. Atmos. Environ. 91, 40–51.
Lu, Z, Qiang, Z, Streets, D.G, 2011. Sulfur dioxide and primary carbonaceous aerosol emissions in China and India, 1996–2010. Atmos. Chem. Phys. 13, 9839–9864.
Ohara, T, Akimoto, H, Kurokawa, J, Horii, N, Yamaji, K, Yan, X, Hayasaka, T, 2007. An Asian emission inventory of anthropogenic emission sources for the period 1980–2020. Atmos. Chem. Phys. 7, 4419–4444.
Skamarock, W.C, Klemp, J.B, Dudhia, J, Gill, D.D, Barker, D.M, Duda, M.G, Huang, X-Y, Wang, W, Powers, G.C, 2008. A description of the advanced research WRF version 3. NCAR Tech. Note, NCAR/TN-475+STR, 113. Natl. Cent. for Atmos. Res. Boulder, Colorado, USA.
Smith, J, van Aardenne, J, Klimont, Z, Andres, R.J, Volke, A, Delgado Arias, S, 2011. Anthropogenic sulfur dioxide emissions: 1850–2005. Atmos. Chem. Phys. 11, 1101–1116.
Streets, D.G, Bond, T.C, Carmichael, G.R, Friedans, S.D, Fu, Q, He, D, Klimont, Z, Nelson, S.M, Tiai, N.Y, Wang, M.Q, Woo, J-H, Yabes, K.F, 2003. An inventory of gaseous and primary aerosol emissions in Asia in the year 2000. J. Geophys. Res. Atmos. 108, D21.http://dx.doi.org/10.1029/2002JD003093.
Uno, I, Sugimoto, N, Shizimu, A, Yumimoto, K, Hara, Y, Wang, Z, 2014. Record heavy PM2.5 air pollution over China in January 2013: vertical and horizontal distributions. SOLA 10, 136–140.
van der Werf, G.R, Randerson, J.T, Giglio, L, Collatz, G.J, Mu, M, Kasibhatla, P.S, Morton, D.C, Defries, R.S, Jin, Y, van Leeuwen, T.T, 2010. Global fire emissions and the contribution of deforestation, savanna, forest, agricultural, and peat fires (1997–2009). Atmos. Chem. Phys. 10, 11707–11735.
Wagstrom, K.M, Pandis, S.N, Yarwood, G, Wilson, G.M, Morris, R.E, 2008. Development and operation: a computationally efficient particulate matter apportionment algorithm in a three-dimensional chemical transport model. Atmos. Environ. 42, 5650–5659.
Yang, F, Tan, J, Zhao, Q, Du, Z, He, K, Ma, Y, Duan, F, Chen, G, Zhao, Q, 2011. Characteristics of PM2.5 specification in representative megacities and across China. Atmos. Chem. Phys. 11, 5207–5219.
Ye, B, Ji, X, Yang, H, Yao, X, Chan, C.K, Cadle, S.H, Chan, T, Mulawa, P.A, 2003. Concentration and chemical composition of PM2.5 in Shanghai for a 1-year period. Atmos. Environ. 37, 499–510.
Ying, Q, Wu, L, Zhang, H, 2014. Local and inter-regional contributions to PM2.5 nitrate and sulfate in China. Atmos. Environ. 94, 582–592.
Zhang, Q, Jimenez, J.L, Canagaratna, M.R, Allan, J.D, Coe, H, Ulbrich, I, Allan, M.R, Takami, A, Middlebrook, A.M, Sun, Y.L, Dzepina, K, Dunlea, E, Docherty, K, DeCarlo, P.F, Salcedo, D, Onasch, T, Jayne, J.T, Miyoshi, T, Shimono, A, Hatakeyama, S, Takegawa, N, Kondo, Y, Schneider, J, Drewnick, F, Borrmann, S, Wagner, S, Maki, R, Williams, K, Kondo, Y, Sokolik, I, 2007. Ubiquity and dominance of oxygenated species in organic aerosols in anthropogenically-influenced Northern hemisphere midlatitudes. Geophys. Res. Lett. 34, L13801.
Zhong, H, Li, J, Ying, Q, Yu, J.Z, Wu, D, Cheng, Y, He, K, Jiang, J, 2012. Source apportionment of PM2.5 nitrate and sulfate in China using a source-oriented chemical transport model. Atmos. Environ. 62, 228–242.
Zhang, Q.Q, Wang, Y, Ma, Q, Yao, Y, Xie, Y, He, K, 2015. Regional differences in Chinese SO2 emission control efficiency and policy implications. Atmos. Chem. Phys. 15, 6521–6533.