Long-term trends of sulfur deposition in East Asia during 1981–2005

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Abstract

We used a chemical transport model to investigate the long-term trends of sulfur deposition in East Asia during 1981–2005. The model reproduced the observed spatial distributions in East Asia of the rate of wet deposition of non-seasalt sulfate (nss-SO_4^{2-}), volume-weighted mean concentrations of nss-SO_4^{2-} in precipitation, precipitation, and concentrations in air of gaseous sulfur dioxide and particulate nss-SO_4^{2-} . The model also reproduced well observed seasonal variations and long-term trends of wet deposition of nss-SO_4^{2-} in Japan from 1988 to 2005. The increasing rate of wet deposition of nss-SO_4^{2-} in Japan during 1991–2005 was demonstrated with 99.9% significance for both observed and modeled data. The annual rate of total (wet + dry) sulfur deposition in Japan increased from 15.6 Gmol S y^{-1} in 1981–1985 to 23.9 Gmol S y^{-1} in 2001–2005 in response to both increasing contributions from Chinese emissions and the eruption of Miyakejima volcano in 2000. During that 25-year period, approximately 2.1% of the sulfur from Chinese emissions was deposited in Japan. Over the same period, the rate of deposition of sulfur in East Asia increased gradually from 14.2 mmol S m^{-2} y^{-1} to 24.0 mmol S m^{-2} y^{-1} , and the contribution of emissions from China to total sulfur deposition in East Asia increased from 65% to 77%. The contribution of Miyakejima volcano was 3% during 2001–2005. The increase in the sulfur deposition rate was remarkably high on the North China Plain, around Guangzhou, and south of Chongqing. The rate of increase in East Asia was greatest in winter, although the

27 rate of sulfur deposition was highest in summer. Sulfur flux from
28 China to Japan increased by a factor of 2.5 at altitudes of 0–3000 m
29 from 1981 to 2005.

30

31 *Keywords:* Sulfur deposition; Long-term trends; East Asia; Chemical
32 transport model; China; Miyakejima volcano

1. Introduction

Deposition of atmospheric sulfur causes acidification of soil and water, which is harmful to ecosystems (Krug and Frink, 1983; Likens et al., 1996); thus, it is important to understand spatiotemporal variations of rates of sulfur deposition. Dentener et al. (2006) showed that, in global terms, the regions worst affected by sulfur deposition are North America, Europe, and Asia. Observations of sulfur deposition by national and international networks (European Monitoring and Evaluation Programme and National Atmospheric Deposition Program/National Trends Network) have revealed that sulfur deposition rates in Europe and North America have decreased since the 1970s because of continuous decreases of sulfur dioxide (SO_2) emissions in those regions (Likens et al., 2001; Fowler et al., 2007). In Asia, by contrast, SO_2 emissions from China, which account for 64–71% of the total emissions from Asia, increased rapidly from the 1980s to the mid-1990s, decreased slightly during 1995–1999, and increased dramatically in the early 2000s (Ohara et al., 2007; Lu et al., 2010). Since 1992, Asia's contribution to global SO_2 emissions has been greater than any other region (Stern, 2005). Although modeling by Carmichael et al. (2002) indicated that the rate of sulfur deposition in Asia increased during 1975–2000, there were no monitoring programs covering the entire Asian continent during that 25-year period.

In 1983, the Japan Environment Agency (now the Ministry of the Environment) started a nationwide monitoring network, the Japanese Acid Deposition Survey (JADS). JADS data indicated that the wet deposition rate of non-seasalt sulfate (nss-SO_4^{2-}) in Japan decreased significantly from 1989 to 1998 (Seto et al., 2004). In 2000, monitoring of atmospheric deposition by the Acid Deposition Monitoring Network in East Asia (EANET) commenced, with the aim of creating a common understanding of acid deposition problems in East Asia. Seto et al. (2007) analyzed EANET data from 2000–2004 and showed that continental emissions made a large contribution to wet deposition of nss-SO_4^{2-} over remote areas in Japan during

high-deposition episodes. Considering the rapid increase of SO₂ emissions in China during 2000–2005 and the huge SO₂ emissions from the eruption of Miyakejima volcano in 2000 (Kajino et al., 2004; Lu et al., 2010), there is a need to evaluate the trends of deposition of atmospheric sulfur in East Asia, particularly since 2000.

Chemical transport models (CTMs) can provide a comprehensive understanding of air pollution by simulating emissions, transportation, chemical and aerosol processes, and deposition. CTMs are useful tools for evaluating the factors controlling sulfur deposition as they can differentiate deposition processes (e.g., dry or wet, gaseous or particulate) and quantify source contributions. Several studies have estimated region-to-region source–receptor (S/R) relationships for sulfur deposition in East Asia (e.g., Arndt et al., 1998; Ichikawa et al., 1998; Lin et al., 2008) and improved our understanding of origin of sulfur deposited in East Asia. However, few modeling studies have addressed the need to understand the factors that control the long-term trends of sulfur deposition in East Asia.

We evaluated the long-term trends of sulfur deposition in East Asia during 1981–2005 by using a Community Multiscale Air Quality (CMAQ) model and Regional Emission inventory in Asia (REAS) data. Our objective was to characterize the long-term trends of sulfur deposition. First, we compared the results of our simulations with observational data (*Section 3.1*). Then, we determined the long-term trends of the rate of sulfur deposition in Japan from both the observed and simulated data and quantified the source contributions (*Sections 3.1* and *3.2*). We also considered spatial and seasonal variations of sulfur deposition in East Asia (*Sections 3.3* and *3.4*). Finally, we evaluated the vertical variations of atmospheric sulfur from various sources during 1981–2005 (*Section 3.5*).

2. Data and methodology

2.1. Numerical model

Our model was based on the CMAQ version 4.4 system released by the US Environmental Protection Agency (Byun and Schere, 2006). This model is driven by meteorological fields generated by the Regional Atmospheric Modeling System (RAMS) version 4.4 (Pielke et al., 1992). The domain of the CMAQ simulation covers $6240 \text{ km} \times 5440 \text{ km}$ on a rotated polar stereographic map projection centered at 25°N , 115°E (Fig. 1), with $80 \text{ km} \times 80 \text{ km}$ grid resolution and a 14-layer vertical structure up to an elevation of 23 km set on a terrain following the sigma-z coordinate system.

We adopted the Statewide Air Pollution Research Center 99 scheme (Carter, 2000) for gas-phase chemistry. The dry deposition velocity of gaseous species is defined as the reciprocal of the sum of the aerodynamic resistance, the quasilaminar sublayer resistance, and the bulk surface resistance (Wesely, 1989).

For aerosol calculations, we applied the third-generation CMAQ aerosol module, which includes the ISORROPIA model (Nenes et al., 1998) as an inorganic aerosol model, and the piecewise parabolic method of Binkowski and Shankar (1995) as the regional particulate model. In addition, the cloud scheme in CMAQ complies in basic terms with the diagnostic model used in the Regional Acid Deposition Model of Chang et al. (1987).

Meteorological fields for each year were generated using RAMS with initial and boundary conditions defined by National Centers for Environmental Prediction—National Center for Atmospheric Research Reanalysis 1 data sets (Kalnay et al., 1996; Kistler et al., 2001). The reanalysis data sets were available with $2.5^\circ \times 2.5^\circ$ horizontal resolution at 6-h intervals.

Initial fields of chemical compounds were prepared using the initial conditions processor of the CMAQ modeling system (Byun and Schere, 2006). Monthly averaged lateral boundary conditions for most chemical tracers were obtained from a global CTM: the Chemical Atmospheric General

Circulation Model for Study of Atmospheric Environment and Radiative Forcing (Sudo et al., 2002).

For these simulations, we prepared data sets for anthropogenic emissions of SO₂, nitrogen oxides, carbon monoxide, non-methane volatile organic compounds, black carbon, organic carbon, and ammonia (NH₃) by using REAS version 1.1 over Asia with about 0.5° × 0.5° horizontal resolution (Ohara et al., 2007). The REAS data sets include most anthropogenic sources for 1980–2003, such as fuel combustion and industrial processes. Additionally, we used the emission data sets for 2004 and 2005 of Kurokawa et al. (2009), which extended the REAS data to 2005 using the same methodology as Ohara et al. (2007). SO₂ emissions in 2000 in the REAS data agreed with four other emission inventories within a range from –20% to 36% in Asia and from –26% to 24% in China (Ohara et al., 2007). The estimate of SO₂ emissions in China during 2000–2003 in the REAS data is 1.27–1.37 times greater than the recent estimate of Lu et al. (2010). These results serve as an indication of emission uncertainty.

Streets et al. (2003) and Lu et al. (2011) estimated that monthly SO₂ emissions in China are largest in winter and that the ratio between maximum and minimum monthly emissions is 1.2–1.4, whereas the REAS data did not include seasonal variation of SO₂ emissions. Thus, our estimate may underestimate SO₂ emissions in winter and overestimate them in low-emission seasons by a factor of 1.1–1.2.

We also considered SO₂ emissions from the 2000 eruption of Miyakejima volcano (Kajino et al., 2004; Japan Meteorological Agency) and from 12 other active volcanoes in Japan (Fujita et al., 1992). We used climatological inventories of biomass burning emissions from Streets et al. (2003) and took biogenic emissions of isoprene and monoterpene from monthly emissions presented by Guenther et al. (1995).

The effective heights of the stacks of large point sources were uniformly set to 240–675 m above ground level. Although there is uncertainty in the smoke height, the influence of smoke height below 1000 m on dry deposition rate is

not significant at distances beyond 150 km from the emission source (Hayami and Ichikawa, 2001). The influence of smoke height on wet deposition rate is expected to be smaller still, because wet deposition rate is less sensitive than dry deposition to the vertical profile of atmospheric sulfur concentrations. On the other hand, the effective injection height of volcanic plumes was uniformly set to 1000–2500 m above the altitude of all active volcanic craters in the study area. The influence of the effective injection height (above 1000 m) on sulfur deposition was not estimated in previous studies and this study. This point should be evaluated in future studies.

The modeling system we used has been applied previously for analyses of East Asian sulfur transport and deposition (Aikawa et al., 2010), nitrogen transport and deposition (Morino et al., 2011), and tropospheric ozone content (Kurokawa et al., 2009). The simulation results of these studies generally show good agreement with observational data.

We conducted three sets of numerical experiments. First, we performed a simulation from 1 January 1981 to 31 December 2005 (control run). Second, to estimate the contributions from China and Miyakejima volcano to sulfur deposition in East Asia, we conducted two perturbation runs: one with emissions from China set to zero, the other with emissions from Miyakejima volcano set to zero. We defined the individual contributions of China and Miyakejima volcano as the difference between the control run and the respective perturbation runs. All runs used the same meteorological field, initial conditions, and boundary conditions for chemical tracers. We should note that our sensitivity analyses with zero emission for all precursor species may include errors because of nonlinearity in chemical processes related to NH_3 . Lin et al. (2008) compared a baseline simulation to sensitivity analyses with zero emissions from different regions and showed that the experiment with zero regional emissions overestimated the contribution of wet (dry) deposition of particulate nss-SO_4^{2-} by about 20% (64%) over the baseline simulation and underestimated the contribution of dry deposition of gaseous SO_2 by about 2%. Thus, this nonlinearity may cause the contributions of each

source to total sulfur deposition to be overestimated by approximately 20% in regions where the wet process is dominant.

2.2. Observational data

We used monthly observed data from EANET for 2000–2005 (Network center for EANET, 2006) and from JADS for 1988–2005 (Japanese Ministry of the Environment, 2002, 2009) to validate the CMAQ simulation.

2.2.1. EANET data

The EANET measurement sites were classified as remote, rural, or urban, where remote sites were defined as those more than 50 km from large pollution sources, rural sites were those between 20 and 50 km from such sources, and urban sites were those less than 20 km from such sources. We used the data from rural and remote sites in this study. Figure 1 and Table 1 provide the locations and other details of EANET monitoring sites used in this analysis. The EANET data for monthly rates of wet deposition of nss-SO_4^{2-} and volume-weighted mean concentrations of nss-SO_4^{2-} in precipitation satisfy the EANET criteria for completeness of precipitation data (Network center for EANET, 2006). In this analysis, we set criteria for monthly concentrations in air of gaseous SO_2 and particulate SO_4^{2-} (temporal data coverage of >80% in each month). To calculate annual (seasonal) average deposition and concentration from EANET data, we excluded data where less than 7 months (2 months) of data were available. Details of the monitoring techniques, including sampling, chemical analysis, definitions of data completeness, and quality control and quality assurance are documented in the EANET monitoring manual (Network center for EANET, 2000a, 2000b, 2001, 2006).

2.2.2. JADS data

The JADS measurement sites were classified as remote, rural, and urban on the similar basis as the EANET sites (Japanese Ministry of the

Environment, 2002). We used the data from rural and remote sites in this analysis. The number of JADS sites has changed over time so they were considered in five phases: I (1983–1987; 29 sites), II (1988–1992; 29 sites), III (1993–1997; 48 sites), IV (1998–2000; 55 sites), and post-2000 (31 sites). In addition, the monitoring techniques used for JADS have changed in response to technical developments. The most important change was the introduction of automated wet-only samplers for every site in 1988 (Japanese Ministry of the Environment, 2002, 2009).

3. Results and discussion

3.1. Model validation

3.1.1. Validation of annual means of wet deposition of sulfur, precipitation, and atmospheric sulfur concentration

The model reproduced 81% of wet deposition rates of nss-SO_4^{2-} and 79% of nss-SO_4^{2-} concentrations in precipitation within a factor of 2 (Figs. 2a and 2b and Table 2). However, the model underestimated both of these in Chongqing (ID = 1 and 2; see Fig. 1 and Table 1) and Xian (ID = 3–5) in China, yielding results smaller than observations by factors of about 2–6 (Table 2). At Jinyunshan in Chongqing, the model also underestimated precipitation and gaseous SO_2 concentrations (Figs. 2c and 2d), suggesting that the model did not capture the local structure of pollution and precipitation. The model better reproduced precipitation and gaseous SO_2 concentrations at Weishuiyuan in Xian. As shown in Figure 3, observed wet deposition rates of nss-SO_4^{2-} at Weishuiyuan drastically decreased from 2003 to 2004, and the model better reproduced the observations in year 2004 and 2005. The cause of this drastic decrease is undetermined.

In contrast, the model overestimated both the wet deposition rate and concentration in precipitation of nss-SO_4^{2-} by a factor of 5 at Chiang Mai, Thailand (Figs. 2a and 2b and Table 2), possibly because of overestimation of SO_2 emissions from a coal-fired power generation plant at a mine in Mae Moh district about 90 km southeast of Chiang Mai. Installation of a flue-gas desulfurization system at the Mae Moh power plant in 2000 may have reduced SO_2 emissions by as much as 90–97% (Sampattagul et al., 2005); REAS data do not reflect this change.

The simulation reproduced 79% of observed annual precipitation values within a factor of 2 (Fig. 2c), but the model consistently underestimated precipitation at sites in China, Japan, Mongolia, and Korea (Table 2). In Japan, these underestimates were greater at the southern sites (ID = 13–16) than at the other sites (ID = 7–12) (Table 2). In addition, Yoshida et al. (2006) showed that RAMS, using the same setup as this study, reproduced the

temporal variations of temperature, wind speed, and precipitation well in East Asia but underestimated the total precipitation amount in Japan and the Pacific Ocean by 20–40%.

The model reproduced 60% and 75% of the observed concentrations of gaseous SO_2 and particulate SO_4^{2-} , respectively, within a factor of 2 (Figs. 2d and 2e). The model could not reproduce the gaseous SO_2 concentrations at Ijira, Japan (ID = 12), and at sites in Mongolia, Russia, and Southeast Asia (ID = 21, 25–27) (Fig. 2d). There are two possible explanations for the underestimations in Mongolia and Russia. First, these sites are close to the northern boundary of the model domain (Fig. 1) and are thus strongly influenced by the lateral boundary condition (SO_2 concentration close to zero). Second, the REAS data sets do not include emission sources in Russia. The modeled concentrations of particulate SO_4^{2-} overestimated observed concentrations by a factor of 1.5 at most sites in Japan (Table 2), and observation data for particulate SO_4^{2-} concentrations are not available for China and Korea.

3.1.2. Validation of seasonal variations in wet deposition rates of nss- SO_4^{2-}

Comparison of simulated monthly wet deposition rates of nss- SO_4^{2-} with observed data at representative EANET sites in each country shows that the model has successfully reproduced observed seasonal variations at all sites except Weishuiyuan (Fig. 3). The problem in Weishuiyuan is discussed in *Section 3.1.1*.

Scatter plots comparing observed and simulated average seasonal wet deposition rates of nss- SO_4^{2-} (Fig. 4) show that the model reproduced 57%, 67%, 68%, and 44% of nss- SO_4^{2-} wet deposition within a factor of 2 in spring (Mar–May), summer (June–Aug), autumn (Sept–Nov), and winter (Dec–Feb), respectively. The consistency between observations and the model is worse for seasonal data than for annual data. As shown in *Section 3.1.1*, observed annual wet deposition rates of nss- SO_4^{2-} were largely underestimated in China and largely overestimated at Chiang Mai. This discrepancy was found

in all seasons in China and in three seasons other than winter at Chiang Mai (Fig. 4). The model did not overestimate wet deposition at Chiang Mai in winters with little rain. In Japan and Korea, the model generally reproduced seasonal variations well. It reproduced wet deposition rates in spring at almost all stations within a factor of 2 (Fig. 4a). However, it underestimated rates observed in southern Japan (ID = 12, 14–16) in summer because of underestimation of precipitation. It also overestimated wet deposition rates observed in northern Japan (ID = 7, 8) in autumn, and at Imsil, Korea, in winter, as a result of overestimating nss-SO_4^{2-} concentration in precipitation. In the northwestern part of the CMAQ domain (ID = 17, 23, 24) and Southeast Asia (ID = 21, 25, 26), the discrepancies between observations and simulations were large in winter (Fig. 4d). However, the wet deposition rate of nss-SO_4^{2-} is small in winter as a result of low precipitation (Fig. 3), thus these discrepancies do not affect the model performance for annual wet deposition rates of nss-SO_4^{2-} .

3.1.3. Validation of long-term trends of the rate of wet deposition of nss-SO_4^{2-} in Japan

Comparison of simulated and JADS observed long-term trends of wet deposition rates of nss-SO_4^{2-} in Japan show that the model reproduced well monthly variations (Fig. 5a), although it underestimated some local maxima in the JADS data. Discrepancies between observed data and modeled annual average deposition rates are less than the range of the standard deviation (Fig. 5b). The simulation agreed better with observed monthly data after 1991, when the number of observation sites increased from 7 to 12 (Fig. 5a). Simulation results averaged over the grids including the observation sites also agreed with the model data averaged over all of Japan (117 grids) after 1991, but not before 1991 (Fig. 5b). These results suggest that JADS data averaged over fewer than 10 observation sites may poorly represent the deposition rates over all of Japan. Therefore, we compared the observed and simulated long-term trends of sulfur deposition rates after 1991.

The annual increase rates of observed and simulated (average of grids over observation sites) monthly wet deposition of nss-SO_4^{2-} during 1991–2005 were $1.96\% \text{ y}^{-1}$ and $3.04\% \text{ y}^{-1}$, respectively (Fig. 5a). These rates were calculated as a percentage of a linear regression coefficient to the average during the 25-year period. Applying the Student's t -test to these rates, the t values of both the observed trend (t value: 3.74 for 177 degrees of freedom) and simulated trend (t value: 6.85 for 177 degrees of freedom) exceeded the 0.001 significance level (t value: 3.35 for 177 degrees of freedom) and can be considered statistically significant (99.9%). On the other hand, the corresponding annual increase rates of observed and simulated monthly precipitation during 1991–2005 were $2.65\% \text{ y}^{-1}$ and $1.82\% \text{ y}^{-1}$, respectively (Fig. 5c). Therefore the model underestimated the increase rate of monthly precipitation but overestimated the increase rate of monthly wet deposition of nss-SO_4^{2-} . The overestimate of wet deposition can be partly explained by underestimations during 1991–1992 and overestimations during 2004–2005 (Fig. 5b). The increase rates of observed and simulated wet deposition during 1993–2003 were $3.56\% \text{ y}^{-1}$ and $4.00\% \text{ y}^{-1}$, respectively, a better match than that for 1991–2005.

3.2. Long-term trends of sulfur deposition in Japan

We calculated total (wet + dry) sulfur deposition in Japan from 1981 to 2005 as the sum of deposition from each SO_2 emission source (China, Miyakejima volcano, and others) in 117 grids ($748,800 \text{ km}^2$) shown in Fig. 1. We also calculated sulfur inflow to Japan, defined as the sum of sulfur flux passing through the western edge of Japan shown in Fig. 1 from west to east or from north to south. The cross-sectional area used to calculate sulfur flow into Japan is $68,733 \text{ km}^2$ (length: 3,200 km, height: 21.479 km).

The contribution of wet deposition to the total sulfur deposition in Japan was about 78%, and the contribution of particulate nss-SO_4^{2-} deposition was about 82% (Fig. 6a). These values changed little during 1981–2005, and their interannual variations were less than 3%. On the other hand, annual sulfur

deposition in Japan increased from 15.6 Gmol S y⁻¹ during 1981–1985 to 23.9 Gmol S y⁻¹ during 2001–2005 (Fig. 6a). This increase can be explained by increased contributions from China (an increase of 7.0 Gmol S y⁻¹) and Miyakejima volcano (2.4 Gmol S y⁻¹). Sulfur deposition from other sources decreased marginally (–1.0 Gmol S y⁻¹). The contribution of China to the rate of sulfur deposition in Japan increased from 34% in the early 1980s to 51% in the early 2000s, and the contribution of Miyakejima volcano was about 10% during 2001–2005. The annual inflow of sulfur over the western edge of Japan also increased during the 25 years (Fig. 6c). The contribution of China to sulfur inflow to Japan increased from 43% in 1981 to 76% in 2005. The interannual trend of SO₂ emissions in China explains well the trend of China’s contribution to sulfur deposition in Japan ($R = 0.96$) and sulfur inflow to Japan ($R = 0.98$) (Figs. 6a–c). Approximately 29.4% of SO₂ emissions from China reached Japan (Figs. 6b and 6c), and 2.06% of SO₂ emissions from China were deposited on the 117 grids covering Japan (Figs. 6a and 6b).

For a comparison among several studies (Fig. 7), we scaled the sulfur deposition in Japan by simply multiplying the ratio of a land area of Japan (377,880 km²) to the area of Japan defined in individual studies. The studies shown as red symbols in Fig. 7 had explicit definitions of the area of Japan: 812,800 km² in Ikeda and Higashino (1997), and 813,000 km² in Inoue et al. (2005). Ichikawa et al. (1998) was shown as green symbol, because we could read the area of Japan (610,844 km²) from figures without explicit definition. The studies shown as light gray symbols did not indicate the area of Japan clearly, and thus we did not scale the results of these studies. Approximately 1.04% of SO₂ emissions from China were deposited on the land area of Japan in this study (Fig. 7). It was estimated as 0.88% by Ikeda and Higashino (1997), 0.63% by Ichikawa et al. (1998), 0.71% by Arndt et al. (1998), 1.18% by Carmichael et al. (2000), 0.78% by Carmichael et al. (2002), 1.58% by Inoue et al. (2005), and 0.42% by Lin et al. (2008) (Fig. 7). The differences among these studies should reflect differences in the defined region of Japan,

the CTM used, the interannual variation of meteorology, and emission data. We estimate that meteorological variation scatter these percentages less than 0.42%, because the percentage of Chinese emissions deposited in Japan was 1.26% in 2002 (maxima) and 0.84% in 1990 (minima) in this study. The percentage of Chinese emissions deposited in Japan for each season was estimated to be 1.21%, 0.84%, 0.91%, and 1.24%, in spring, summer, autumn, and winter, respectively (Fig. 7). These differences are attributed to seasonal meteorological conditions (see *Section 3.4*).

3.3. Long-term trends of sulfur deposition in East Asia

The rate of total sulfur deposition in East Asia increased remarkably from the early 1980s to the early 2000s (Fig. 8), reflecting the rapid increase of SO₂ emissions from China and emissions from Miyakejima volcano (Fig. 6b). The area where China's contribution to total sulfur deposition was more than 60% extended gradually from the coast of the Asian continent to the west coast of Japan during 1981–2005 (Figs. 8a–e), and the contribution of Miyakejima volcano was 10–20% in eastern Japan during 2001–2005 (Fig. 8f). The rates and source contributions of sulfur deposition in East Asia are summarized in Table 3. The 9.8 mmol S m⁻² y⁻¹ increase of the total rate of sulfur deposition from 1981 to 2005 can be explained by the increases of contributions from China (9.1 mmol S m⁻² y⁻¹) and Miyakejima volcano (0.8 mmol S m⁻² y⁻¹). From 1981 to 2005, the contribution of emissions in China to sulfur deposition rates in East Asia increased from 65% to 77% and sulfur deposition from China emissions doubled. The emissions from Miyakejima volcano contributed to 3% of the rate of sulfur deposition in East Asia during 2001–2005.

The areas of high sulfur deposition during 1981–2005 did not clearly correspond to the areas of large increase rates of sulfur deposition (Figs. 9a and b). The increase rate of sulfur deposition was more than 3% y⁻¹ on the North China Plain, the south region of 25°N in China, the south of Chongqing, and the area east of Miyakejima volcano. The increase around

Miyakejima volcano was caused by the sudden eruption of 2000, whereas the considerable increase in China was caused by steady growth of SO₂ emissions in China during 1981–2005 (Ohara et al., 2007), which was greatest in the North China Plain (Lu et al., 2010). Growth rates of SO₂ and NH₃ emissions are both important for analyses of the nonlinearities of the S/R relationship (Fowler et al., 2007). REAS estimated growth rates of SO₂ and NH₃ emissions in East Asia during 1981–2005 as 2.98% y⁻¹ and 1.90% y⁻¹, respectively (Kurokawa et al., 2009).

SO₂ emissions from China made the predominant contribution (>90%) to the increased rate of sulfur deposition over the Asian continent (Fig. 9b). In Japan, emissions from both China and Miyakejima volcano contributed to the increasing trend. Emissions from China were the main contributor (90%) to the increases to the west of the coast of Japan, whereas both China (<60%) and Miyakejima volcano contributed to the increase to the east of Japan. Even though Taiwan is close to mainland China, the increase rate of the amount of sulfur deposition indicated negative value (Fig. 9b). This might be attributed partly to the location of Taiwan in the trade wind zone windward of the mainland and partly to decreasing SO₂ emissions in Taiwan (Streets and Waldhoff, 2000).

The proportion of wet deposition in total sulfur deposition from 1981 to 2005 was more than 85% on the Japan Sea side of northern Japan and northeastern China, and less than 40% in the coast of the North China Plain and Chongqing (Fig. 9c). The proportion of wet deposition was relatively high in areas of high rainfall (Figs. 9c and 9d).

The total rate of wet deposition was approximately twice the total rate of dry deposition in East Asia (Table 4). Wet deposition of sulfur was dominated by particulate nss-SO₄²⁻, whereas dry deposition was associated with gaseous SO₂. During 1981–2005 in East Asia, the rate of dry deposition of gaseous SO₂ increased by a factor of 2.1 and the rate of wet deposition of particulate nss-SO₄²⁻ increased by a factor of 1.5. The share of the increase in wet deposition to the increase in total sulfur deposition was more than 75%

in Japan and northeastern China, less than 50% in the North China Plain and south of Chongqing, and 50–75% south of 25°N in China (Fig. 9e).

3.4. Seasonal variations of sulfur deposition and long-term trends in East Asia

Average seasonal sulfur deposition rates over East Asia during 1981–2005 were 4.7, 5.7, 4.3, and 3.8 mmol S m⁻² (3 months)⁻¹, for spring (Mar–May), summer (Jun–Aug), autumn (Sep–Nov), and winter (Dec–Feb), respectively. Sulfur deposition was highest in summer over the Asian continent, reflecting high precipitation in summer (Figs. 10a–d). In Japan, the rate of sulfur deposition was 6.8, 6.2, 6.0, and 5.7 mmol S m⁻² (3 months)⁻¹, for spring, summer, autumn, and winter, respectively. The amount of sulfur coming from China to Japan was greater in spring and winter than in summer and autumn (Fig. 7). Sulfur deposition was highest along the Japan Sea coast in winter because of the influence of the winter monsoon (Fig. 10d).

The rate of increase in annual sulfur deposition averaged over East Asia was 2.34% y⁻¹, 2.55% y⁻¹, 2.65% y⁻¹, and 2.79% y⁻¹ for spring, summer, autumn, and winter, respectively. The corresponding increases in Japan were 2.10% y⁻¹, 2.24% y⁻¹, 2.53% y⁻¹, and 1.95% y⁻¹. The rate of increase around Guangzhou and on the North China Plain was higher in summer and winter than in spring and autumn (Figs. 10e–h). The rate of increase over Japan was higher in autumn than in other seasons, owing to the influence of Miyakejima volcano on deposition in Japan in autumn (Figs. 10e–h). The share of the increase in wet deposition to the increase in annual sulfur deposition was greatest in summer and smallest in winter over most of East Asia (Figs. 10i–l).

3.5. Vertical profile of atmospheric sulfur over Japan and sulfur flux from the west

To our knowledge, no previous study has investigated the contribution of the various sources of SO₂ and particulate nss-SO₄²⁻ to the vertical

distribution of sulfur in the atmosphere over the Japan Sea and East China Sea. We examined the contributions of three sources (China, Miyakejima volcano, and “others”) to the vertical distribution of sulfur concentrations over Japan and to sulfur flux across the western edge of Japan for 1981–1985 and 2001–2005 (Fig. 11). Our data show that 34% (34%), 57% (59%), and 72% (72%) of sulfur compounds (particulate nss-SO_4^{2-}) over Japan occurred below 1000, 2000, and 3000 m altitude, respectively (Fig. 11a). By contrast, lidar measurements indicated that spherical aerosols occurred mostly below 2000 m at Tsukuba (36.05°N, 140.12°E), Nagasaki (32.81°N, 129.85°E), and Hedo (Shimizu et al., 2004; Hara et al., 2011). This result suggests that the model overestimated the fraction of nss-SO_4^{2-} above 2000 m to a total vertical column abundance of nss-SO_4^{2-} , since particulate SO_4^{2-} is a major component of aerosols (Topping et al., 2004).

The simulated contribution of emissions from China to sulfur concentrations over Japan was 28% at the surface and 44% at 1500–2000 m altitude during 1981–1985 (Fig. 11a). The contribution from China to sulfur flux was 53% at the surface and 67% at 1500–2000 m during 1981–1985 (Fig. 11b). The simulated sulfur concentration below 5000 m increased remarkably from 1981–1985 to 2001–2005 in response to increased emissions from China and the eruption of Miyakejima volcano (Figs. 11a and c). The contribution of sulfur from China below 3000 m was about 2.2 times higher in 2001–2005 than in 1981–1985 (Figs. 11a and c). On the other hand, sulfur concentrations from other sources below 1500 m decreased 25% during this period. Sulfur flux from China to Japan below 3000 m was 2.5 times higher in 2001–2005 than in 1981–1985. Contributions of particulate nss-SO_4^{2-} to the total sulfur concentration and the total incoming sulfur flux decreased slightly over the 25 years (Fig. 11).

4. Summary and conclusions

To clarify the long-term trends of sulfur deposition in East Asia, we simulated spatiotemporal variations of sulfur deposition during 1981–2005. We used the CMAQ three-dimensional regional CTM coupled with the RAMS regional meteorological model and the REAS year-by-year emissions inventory for East Asia. CMAQ reproduced observed wet deposition rates of nss-SO_4^{2-} , nss-SO_4^{2-} concentration in precipitation, precipitation, and concentrations in air of gaseous SO_2 and particulate SO_4^{2-} within a factor of 2 for most EANET stations in East Asia. CMAQ also reproduced well the monthly variations and long-term trends of rates of wet deposition of nss-SO_4^{2-} observed at JADS stations in Japan from 1988 to 2005. The annual increase rates of observed and simulated monthly wet deposition of nss-SO_4^{2-} during 1991–2005 were $1.69\% \text{ y}^{-1}$ and $3.04\% \text{ y}^{-1}$, respectively. Application of the Student's t -test showed 99.9% significance for the increasing trends evident in both JADS data and the modeled data.

The annual rate of sulfur deposition in Japan, which consists of 117 grids ($748,800 \text{ km}^2$), increased from $15.6 \text{ Gmol S y}^{-1}$ during 1981–1985 to $23.9 \text{ Gmol S y}^{-1}$ during 2001–2005 in response to increased contributions from China ($7.0 \text{ Gmol S y}^{-1}$) and from Miyakejima volcano ($2.4 \text{ Gmol S y}^{-1}$). There was a small decrease in the rate of sulfur deposition from other sources ($-1.0 \text{ Gmol S y}^{-1}$). The contribution of China to sulfur deposition in Japan increased from 34% during 1981–1985 to 51% during 2001–2005; the eruption of Miyakejima volcano contributed about 10% during 2001–2005. The contribution from China to the sulfur inflow to Japan increased from 43% in 1981 to 76% in 2005. During this period, approximately 29.4% of SO_2 emissions from China reached Japan and 2.06% of these emissions were deposited on the 117 grids covering Japan. The China-to-Japan S/R ratio we determined was higher than those from previous modeling studies.

During 1981–1985, the rate of deposition of sulfur over the analytical domain was estimated to be $14.2 \text{ mmol S m}^{-2} \text{ y}^{-1}$, of which $9.3 \text{ mmol S m}^{-2} \text{ y}^{-1}$ originated from China. During 2001–2005, the corresponding rates were 24.0

mmol S m⁻² y⁻¹ and 18.4 mmol S m⁻² y⁻¹.

The contribution of emissions from China to the rate of sulfur deposition in East Asia increased from 65% to 77% during the 25 years covered by this study. The contribution of the 2000 eruption of Miyakejima volcano was 3% during 2001–2005. The increase in rate of sulfur deposition was remarkably high on the North China Plain, the region south of 25°N in China, and the area south of Chongqing. Sulfur deposition in East Asia was greatest in summer, reflecting high precipitation. Sulfur deposition in Japan was greatest in spring, reflecting higher transport of sulfur from China. The increase in sulfur deposition over East Asia was greatest in winter.

We found that most of the sulfur in the atmosphere over Japan was below 3000 m altitude. In Japan, atmospheric sulfur concentrations (flux) below 3000 m originating from China were about 2.2 (2.5) times higher in 2001–2005 than in 1981–1985. Contributions of particulate nss-SO₄²⁻ to total sulfur concentration and the total incoming sulfur flux decreased slightly over the 25 years covered by this study.

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Figure captions

Fig. 1. Spatial distribution of SO₂ emissions (averaged from 2001 to 2005) used in the CMAQ CTM for East Asia. Circles indicate locations of EANET monitoring sites in rural and remote areas and annotated numbers are IDs provided in Table 1. Red crosses denote locations of JADS monitoring sites already worked in 1991. The triangle marks the location of Miyakejima volcano. B, C, W, S, and G indicate locations of Beijing, Chongqing, Wuhan, Shanghai, and Guangzhou, respectively. The area (117 grids) surrounded by the outline of Japan was used to calculate the sulfur deposition in Japan. The western edge of Japan shown on the map was used to calculate sulfur flux into Japan. The CMAQ model domain covers the entire map area, and the inner black rectangle bounds the analytical domain of this study.

Fig. 2. Scatter plots of modeled versus observed annual (a) mean rates of wet deposition of nss-SO₄²⁻, (b) volume-weighted mean concentrations of nss-SO₄²⁻ in precipitation, (c) precipitation, (d) gaseous SO₂ concentrations, and (e) particulate SO₄²⁻ concentrations, from 2000 to 2005. The solid and open symbols indicate remote and rural sites, respectively. 1:1, 1:2, 2:1, 1:5, and 5:1 reference lines are shown. Observed data with temporal coverage of 7 months or more in each year were plotted (see Table 1). Annual means of simulated data were determined as an average over the period for which observed data were available.

Fig. 3. Observed and modeled monthly rates of wet deposition of nss-SO₄²⁻ at representative EANET monitoring sites from 2000 to 2005; these data show seasonal variations (indicated by annotations M and S for March and September, respectively). Observed and modeled

monthly levels of precipitation at each site are also shown. The spatial distribution of annual wet deposition rate of nss-SO_4^{2-} averaged from 2000 to 2005 is also indicated.

Fig. 4. Scatter plots of modeled versus observed seasonal means of rates of wet deposition of nss-SO_4^{2-} for (a) spring, (b) summer, (c) autumn, and (d) winter from 2000 to 2005. The solid and open symbols indicate remote and rural sites, respectively. 1:1, 1:2, 2:1, 1:5, and 5:1 reference lines are shown. Observed data with temporal coverage of 2 months or more in each season were plotted. Seasonal means of simulated data were determined as an average over the period for which observed data were available.

Fig. 5. Time series from 1988 to 2005 of (a) monthly rates of wet deposition of nss-SO_4^{2-} in Japan obtained from long-term acid deposition monitoring data and modeled data, (b) annual means from the same data sets, and (c) monthly precipitation in Japan from the same data sets. The blue and red shading in (b) signifies standard deviation of data at all observation sites and data at all grids over observation sites, respectively.

Fig. 6. Interannual variations from 1981 to 2005 of (a) sulfur deposition rates in Japan (see Fig. 1) differentiated by source, (b) SO_2 emissions in East Asia, and (c) sulfur inflows over the western edge of Japan (see Fig. 1) differentiated by source. In (a) and (c), percentages for contributions from China, wet deposition, and particulate nss-SO_4^{2-} are also shown.

Fig. 7. Relationship from 1981 to 2005 between deposition in Japan of sulfur originating from China and SO_2 emissions in China. The linear regression of data from this study (annual amount) is also shown.

Seasonal values represent average seasonal values for 1981 to 2005 multiplied by 4. The rate of sulfur deposition in Japan was scaled, multiplying by the ratio of the land area of Japan (377,880 km²) to the area of Japan defined in each study. The studies shown as red symbols had explicit definitions of the area of Japan. The study shown as green symbol allowed us to read the area of Japan from a figure without explicit definition. The studies shown as light gray symbols did not indicate the area of Japan clearly.

Fig. 8. Spatial distributions of average annual rate of sulfur deposition in East Asia for 5-year intervals between 1981 and 2005. Dashed purple contours (20% interval) in (a)–(e) show the contribution of anthropogenic emissions from China and those in (f) show the contribution (10% interval) from Miyakejima volcano. Vectors indicate average wind field below 1116 m. The definitions of B, C, W, S, G, and triangle are explained in Fig. 1.

Fig. 9. Spatial distributions averaged for 1981 to 2005 of (a) annual sulfur deposition (dashed purple contours indicate the percentage of China's contribution), (b) percentage of increase rate in annual amount of sulfur deposition (dashed purple contours indicate the percentage of China's contribution), (c) percentage of wet deposition in total sulfur deposition (d) annual precipitation amount, and (e) share of the increase in wet deposition to increase in total sulfur deposition. White areas in (b), (c) and (e) indicate values of less than 10 in (a) The definitions of B, C, W, S, G, and triangle are explained in Fig. 1.

Fig. 10. Spatial distributions of average (1981–2005) seasonal (a)–(d) rates of sulfur deposition (dashed purple contours indicate seasonal precipitation amount in mm per 3 months); (e)–(h) percentage of

annual change rate in seasonal amount of sulfur deposition; and (i)–(l) share of the increase in wet deposition to the increase in annual sulfur deposition. White areas in (e)–(h), and (i)–(l) indicate areas where values were less than 2 in (a)–(d). MAM, JJA, SON, and DJF indicate March–May, June–August, September–November, and December–February, respectively. Vectors indicate average wind field below 1116 m. The definitions of B, C, W, S, G, and triangle are explained in Fig. 1.

Fig. 11. (a) Vertical profiles of sulfur concentrations over Japan and (b) annual sulfur flux across the western edge of Japan (Fig. 1) during 1981–1985. (c) and (d) as above but for 2001–2005. Percentages of contributions from China and of particulate nss-SO_4^{2-} in total sulfur are also shown.

Table 1. Details of EANET site locations (see Fig. 1) and available data.

Table 2. Ratios of simulated to observed values at each station for sulfur and precipitation factors shown in Fig. 2.

Table 3. Total sulfur deposition rate from 1981 to 2005 in East Asia (analytical domain shown in Fig. 1) and contributions of sulfur from Chinese anthropogenic emissions and from the 2000 eruption of Miyakejima volcano.

Table 4. Wet and dry gaseous SO_2 and particulate nss-SO_4^{2-} deposition rates from 1981 to 2005 in East Asia (analytical domain shown in Fig. 1).

Figure 1

Figure 2

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Figure 11

1 Table 1 Details of EANET site locations (see Fig. 1) and available data.

ID	Country	Site name ^a		Lat.	Long.	Altitude	Precipitation	EANET annual data ^b		
				(°N)	(°E)	(m a.s.l.)	(mm y ⁻¹)	wet ^c	SO ₂ ^d	SO ₄ ²⁻ ^e
1	China	Nanshan	(Ru)	29.55	106.63	570	1259	00	—	—
2		Jinyunshan	(Ru)	29.82	106.37	800	1338	01-05	01-05	—
3		Weishuiyuan	(Ru)	34.37	108.85	360	534	00, 02-05	00-05	—
4		Dabagou	(Re)	33.90	108.85	1200	829	00	—	—
5		Jiwozi	(Re)	33.83	108.80	1800	423	01, 03-05	—	—
6		Xiaoping	(Re)	24.85	118.03	686	2283	00-05	—	—
7	Japan	Rishiri	(Re)	45.12	141.23	40	892	00-05	03-05	03-05
8		Ochiishi	(Re)	43.15	145.50	49	823	03-05	—	—
9		Tappi	(Re)	41.25	140.35	105	1168	00-05	00-05	03-05
10		Sado-seki	(Re)	38.23	138.40	136	1213	00, 01, 03-05	00-05	04, 05
11		Happo	(Re)	36.68	137.80	1850	2596	00-03, 05	00-05	03-05
12		Ijira	(Ru)	35.57	136.68	140	2703	00-05	00-05	03-05
13		Oki	(Re)	36.28	133.18	90	1363	00-05	00-05	02-05
14		Yusuhara	(Re)	33.37	132.93	790	2736	00-05	00-05	03-05
15		Hedo	(Re)	26.85	128.25	60	2073	00-03, 05	00-03, 05	03-05
16		Ogasawara	(Re)	27.08	142.22	230	1612	00-05	—	03-05
17	Mongolia	Terelj	(Re)	47.98	107.48	1540	231	00, 02-05	00, 02-05	02-05
18	Korea	Kanghwa	(Ru)	37.70	126.28	150	1040	01-05	02-05	—
19		Cheju	(Re)	33.30	126.17	72	1084	01-05	02-05	—
20		Imsil	(Ru)	35.60	127.18	—	1239	02-05	02-05	—
21	Vietnam	Hoa Binh	(Ru)	20.82	105.33	23	1880	00-05	00-05	01-05
22	Russia	Primorskaya	(Ru)	43.70	132.12	84	700	02-05	02-05	02-05
23		Mondy	(Re)	51.67	101.00	2000	330	00-05	00, 01, 03-05	01-05
24		Listvyanka	(Ru)	51.85	104.90	700	445	00-05	00-05	01-05
25	Philippines	Los Banos	(Ru)	14.18	121.25	35	2058	00-05	01-05	01-05
26	Thailand	Patumthani	(Ru)	14.03	100.77	2	1268	00-05	—	—
27		Chiang Mai	(Ru)	18.77	98.93	350	1186	01-05	03, 04	04, 05

^a (Ru) and (Re) indicate rural site and remote site, respectively.

^b EANET annual data are limited to years for which at least 7 months of monthly data cleared the EANET criteria for data completeness for 'wet' and the requirement we set about data completeness for 'SO₂' and 'SO₄²⁻'. (c.f. Section 2.2.1).

^c Data referred to in 'wet' column are nss-SO₄²⁻ wet deposition, volume-weighted mean concentration of nss-SO₄²⁻ in precipitation, and rainfall.

^d 'SO₂' means concentration in air of gaseous SO₂.

^e 'SO₄²⁻' means concentration in air of particulate SO₄²⁻.

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4 Table 2 Ratios of simulated to observed values at each station for sulfur and
5 precipitation factors shown in Fig. 2.

ID	Country	Site name ^a	Mean rates of wet deposition of nss-SO_4^{2-}	Volume-weighted mean concentrations of nss-SO_4^{2-} in precipitation	Precipitation	Gaseous SO_2 concentrations	Particulate SO_4^{2-} concentrations
1	China	Nanshan (Ru)	0.08	0.30	0.28	—	—
2		Jinyunshan (Ru)	0.16	0.42	0.39	0.39	—
3		Weishuiyuan (Ru)	0.27	0.52	0.86	1.54	—
4		Dabagou (Re)	0.26	0.53	0.48	—	—
5		Jiwozi (Re)	0.49	0.90	0.65	—	—
6		Xiaoping (Re)	0.76	0.84	0.90	—	—
7	Japan	Rishiri (Re)	1.43	1.55	0.94	1.95	1.62
8		Ochiishi (Re)	1.68	1.69	1.01	—	—
9		Tappi (Re)	0.77	1.41	0.56	1.23	1.45
10		Sado-seki (Re)	1.39	1.77	0.77	1.41	1.92
11		Happo (Re)	1.41	2.23	0.61	1.79	1.93
12		Ijira (Ru)	1.05	1.49	0.72	4.61	1.65
13		Oki (Re)	1.03	2.01	0.52	2.32	1.81
14		Yusuhara (Re)	0.82	1.76	0.46	0.78	1.36
15		Hedo (Re)	0.77	1.54	0.54	1.32	1.22
16		Ogasawara (Re)	0.52	1.31	0.41	—	2.48
17	Mongolia	Terelj (Re)	0.79	1.22	0.63	0.43	1.19
18	Korea	Kanghwa (Ru)	0.93	1.43	0.74	1.47	—
19		Cheju (Re)	0.80	1.41	0.59	1.04	—
20		Imsil (Ru)	1.58	2.10	0.79	1.42	—
21	Vietnam	Hoa Binh (Ru)	0.60	0.52	1.16	0.48	1.50
22	Russia	Primorskaya (Ru)	0.95	1.26	0.77	3.82	1.78
23		Mondy (Re)	1.33	1.46	1.00	0.31	1.07
24		Listvyanka (Ru)	0.58	0.57	1.02	0.12	0.55
25	Philippines	Los Banos (Ru)	1.10	1.22	0.91	2.70	1.39
26	Thailand	Patumthani (Ru)	1.27	0.77	1.68	—	—
27		Chiang Mai (Ru)	4.99	4.53	1.05	2.54	2.22

^a (Ru) and (Re) indicate rural site and remote site, respectively.

Table 3 Total sulfur deposition rate from 1981 to 2005 in East Asia (analytical domain shown in Fig. 1) and contributions of sulfur from Chinese anthropogenic emissions and from the 2000 eruption of Miyakejima volcano.

Period	Total	China's anthropogenic sources		Miyakejima volcano	
	Deposition rate (mmol S m ⁻² y ⁻¹)	Deposition rate (mmol S m ⁻² y ⁻¹)	Contribution ^a (%)	Deposition rate (mmol S m ⁻² y ⁻¹)	Contribution ^a (%)
1981–1985	14.2	9.3	65	—	—
1986–1990	16.5	11.5	70	—	—
1991–1995	17.9	13.0	73	—	—
1996–2000	20.0	14.9	75	—	—
2001–2005	24.0	18.4	77	0.8	3
1981–2005	18.5	13.4	72	—	—

^a Percentages of total sulfur deposition rate.

13 Table 4 Wet and dry gaseous SO₂ and particulate nss-SO₄²⁻ deposition rates
14 from 1981 to 2005 in East Asia (analytical domain shown in Fig. 1).

Period	Gaseous SO ₂		Particulate nss-SO ₄ ²⁻	
	Wet	Dry	Wet	Dry
	(mmol S m ⁻² y ⁻¹)		(mmol S m ⁻² y ⁻¹)	
1981–1985	0.10	3.53	9.84	0.76
1986–1990	0.13	4.31	11.18	0.84
1991–1995	0.12	4.80	12.08	0.88
1996–2000	0.14	5.29	13.52	1.00
2001–2005	0.19	7.34	15.24	1.18
1981–2005	0.14	5.05	12.37	0.93

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