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### Long-range transport of acidifying substances in East Asia—Part II Source–receptor relationships

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### ABSTRACT

Region-to-grid source-receptor (S/R) relationships are established for sulfur and reactive nitrogen deposition in East Asia, using the Eulerian-type Community Multiscale Air Quality (CMAQ) model with emission and meteorology data for 2001. We proposed a source region attribution methodology by analyzing the non-linear responses of the CMAQ model to emission changes. Sensitivity simulations were conducted where emissions of  $SO_2$ ,  $NO_x$ , and primary particles from a source region were reduced by 25%. The difference between the base and sensitivity simulations was multiplied by a factor of four, and then defined as the contribution from that source region. The transboundary influence exhibits strong seasonal variation and generally peaks during the dry seasons. Long-range transport from eastern China contributes a significant percentage (>20%) of anthropogenic reactive nitrogen as well as sulfur deposition in East Asia. At the same time, northwestern China receives approximately 35% of its sulfur load and 45% of its nitrogen load from foreign emissions. Sulfur emissions from Miyakejima and other volcanoes contribute approximately 50% of the sulfur load in Japan in 2001. Sulfur inflows from regions outside the study domain, which is attributed by using boundary conditions derived from the MOZART global atmospheric chemistry model, are pronounced (10-40%) over most parts of Asia. Compared with previous studies using simple Lagrangian models, our results indicate higher influence from long-range transport. The estimated S/R relationships are believed to be more realistic since they include global influence as well as internal interactions among different parts of China.

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### 1. Introduction

Assessments of transboundary acidification in Europe have been carried out by European Monitoring and Evaluation Program (EMEP) since the late 1970s (e.g., Eliassen, 1978; Tarrasón et al., 2004, or www.emep.net). The importance of this topic is now realized in the rapidly developing countries of Asia, which are experiencing a large growth in industry and in automobile ownership. In the mid-1990s, a number of regional models for acid deposition began to be applied to estimate source-receptor (S/R) relationships for sulfur deposition in East Asia (e.g., Huang et al., 1995; Ichikawa and Fujita, 1995; Arndt et al., 1998; Calori et al., 2001). Early results indicated significant differences in calculated S/R relationships between different groups (Carmichael et al., 2002).





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Compared to the studies on sulfur, less work has been done to estimate S/R relationships for nitrogen deposition in Asia due to the complex chemistry involved. In the atmosphere NO is converted into a number of other oxides of nitrogen, generally denoted as reactive nitrogen NO<sub>y</sub> (in this work NO<sub>y</sub> = NO + NO<sub>2</sub> + NO<sub>3</sub> + 2N<sub>2</sub>O<sub>5</sub> + HONO+ HNO<sub>4</sub> + HNO<sub>3</sub> + aerosol nitrate + PAN + organic nitrates). Holloway et al. (2002) estimated S/R relationships for nitric acid (HNO<sub>3</sub>) deposition in Asia for the base year 1990 using a relatively simple and coarse-resolution Lagrangian model, ATMOS-N. ATMOS-N is the nitrogen version of the ATMOS model, one of the widely applied acidification models addressing sulfur transport in Asia (Arndt et al., 1998; Calori et al., 2001).

For long-range transport, it is necessary to account for the transport of pollutants in the free troposphere above the boundary layer. This is handled in the three-dimensional (3-D) Eulerian chemical transport models (CTMs), but is more difficult to account for in Lagrangian models. Major measurement campaigns over the Pacific and the Indian Ocean, have studied the outflow of Asian pollutants (Jacob et al., 2003; Lelieveld et al., 2001). The major findings from these campaigns were that regional pollution could be transported either in the boundary layer or in the free troposphere with vertical transport out of the boundary layer occurring by frontal lifting, convection, and orographic forcing (e.g., Bey et al., 2001; Liu et al., 2002). However, S/R relationships for reactive nitrogen deposition in East Asia have not yet, to date, been quantified by a 3-D Eulerian CTM using a recent emission inventory.

This study applied the state-of-the-art Community Multiscale Air Quality model (CMAQ version 4.5.1) (Byun and Ching, 1999; Byun and Schere, 2006) to examine and quantify long-range transport of sulfur and reactive nitrogen in East Asia. The meteorological data are prepared by the Mesoscale Meteorological Model version 5 (MM5) (Grell et al., 1994). CMAQ is run with the 81-km grid spacing and includes eight vertical layers from the surface to 14.6 km. Gas-phase chemistry is simulated with the carbon-bond IV mechanism. CMAQ is configured with the AERO-3 aerosol module. Detailed model configuration is described in Lin et al. (2008), which presented a comprehensive model evaluation with satellite and in situ measurements. The present paper is concerned with the estimates of S/R relationships for acid deposition in East Asia using the validated model system.

The S/R relationships in this work give the change in deposition over defined receptor areas resulting from a change in emissions from specific source areas. Section 2 presents the source region attribution methodology. The chemical and physical non-linearities in the sulfate–ni-trate–ammonia system are investigated on the basis of model responses to emission changes. Based on the analysis, a source region attribution methodology is proposed. Section 3 presents the region-to-region S/R relationships and the seasonal variability. Finally, the results derived in this study are compared with previous studies by other research groups.

### 2. Source region attribution methodology

The CMAQ modeling domain was divided into 18 geographical source areas including seven regions in China, seven regions in Southeast Asia, Japan, the Korean Peninsula, Mongolia, and remaining areas inside the model domain (Fig. 1). In addition, source attribution is also conducted for emissions from international shipping and volcanoes. The contribution from regions outside the study domain is attributed by the implementation of boundary conditions derived from the global Model for Ozone And Related Tracers (MOZART) as described in Lin et al. (2008). Emissions of primary sulfur (SO<sub>2</sub> and primary sulfate) and primary nitrogen ( $NO_x$  and primary nitrate) from the individual sources are summarized in Table 1. China is the largest source region within the study domain, including both the highly industrialized area along the eastern coast and the western developing area. To better reflect the S/R relationships between different parts of China and its neighboring source regions, we divided China into seven source regions roughly based on land-use types. To save computing time, some small neighboring regions are merged together and treated as one source region (e.g., KOR, IND, and RUS in Fig. 1).

With Eulerian models, changing the emissions from one source region has a non-linear effect on concentrations and depositions due to non-linearities in the atmospheric chemistry and deposition processes. Engardt et al. (2005) examined sulfur transport and deposition in Southeast Asia using a Eulerian model. They computed deposition from each country by running the model with only one country's emissions at a time. The major disadvantage of this straightforward approach is the underestimation of aerosol production, especially for nitrate aerosols, due to non-linear chemistry (Bartnicki, 1999).

The non-linear effects of emission perturbations are explicitly examined here. Section 2.1 briefly describes atmospheric chemistry in the sulfate–nitrate–ammonia



**Fig. 1.** Division map of source regions with identification code. RUS means parts of Russia, Kazakhstan, and Kyrgyzstan inside the model domain. KOR means South Korea and North Korea in combination. IND means the part of India inside the model domain, Nepal, Bhutan, and Bangladesh.

### Table 1

Emissions of primary sulfur and primary nitrogen for designated source regions and source types<sup>a</sup>

Source region	Code	Sulfur emission (Gg S yr <sup>-1</sup> )	Nitrogen emission (Gg S yr <sup>-1</sup> )	
Northwest China	NW_CHN	891	266	
Northeast China	NE_CHN	764	460	
Central China	CTR_CHN	3193	825	
Southwest China	SW_CHN	1612	324	
South China	STH_CHN	1542	543	
Southeast China	SE_CHN	2376	880	
Taiwan, China	TWN_CHN	191	158	
Mongolia	MNG	45	17	
North/South Korea	KOR	532	473	
Japan	JPN	422	663	
Philippines	PHL	347	85	
Vietnam	VNM	98	54	
Laos	LAO	24	44	
Cambodia	KHM	26	30	
Thailand	THA	482	296	
Myanmar	MMR	61	119	
IND	IND	1133	495	
RUS	RUS	956	225	
Shipping	SHIP	495	351	
Volcanoes	VOLCANO	45937 <sup>b</sup>	-	

<sup>a</sup> Primary sulfur includes  $SO_2$  and primary sulfate. Primary nitrogen includes  $NO_x$  and primary nitrate.

<sup>b</sup> 43 801 Gg S yr<sup>-1</sup> is from Miyakejima Volcano.

system used in the CMAQ model. Section 2.2 presents sensitivity tests carried out to examine non-linear responses to the extent of emission changes. Finally, Section 2.3 outlines a source region attribution methodology based on the analysis in Section 2.2.

# 2.1. Atmospheric chemistry in sulfate-nitrate-ammonia system

The aerosol module of CMAQ uses an equilibrium approach to predict gas/particulate equilibrium and mass transfer between the gas and the particulate phases (Binkowski and Roselle, 2003). Sulfuric acid is formed by gas-phase reaction of SO<sub>2</sub> with hydroxyl radicals (OH) (R-1) and by aqueous conversion of SO<sub>2</sub> in cloud droplets:

$$SO_{2(g)} + OH_{(g)} \rightarrow H_2SO_4 + HO_2$$
 (R-1)

Particulate nitrate is produced predominantly from the equilibrium reaction between two gas-phase species, nitric acid (HNO<sub>3</sub>) and ammonia. The behavior of nitrate is one of the most intriguing aspects of inorganic atmospheric aerosols because particulate nitrate concentrations depend not only on the amount of nitric acid, but also on the availability of ammonia and sulfate, together with temperature and relative humidity (Yu et al., 2005). Nitric acid is mainly formed by reaction of NO<sub>2</sub> with OH during daytime (R-2) and by reaction of NO<sub>2</sub> with O<sub>3</sub> followed by hydrolysis of  $N_2O_5$  on aerosols at night (Dentener et al., 1993):

$$NO_{2(g)} + OH_{(g)} \leftrightarrow HNO_{3(g)}$$
 (R-2)

Generally, ammonia reacts preferentially with acidic sulfate particles  $(H_2SO_4 \text{ or } HSO_4^-)$  to form ammonium

bisulfate or ammonium sulfate:

$$NH_3 + H_2SO_4 \Leftrightarrow (NH_4)HSO_4$$
 (R-3)

$$NH_3 + (NH_4)HSO_4 \iff (NH_4)_2SO_4$$
 (R-4)

If excess ammonia is available beyond that required for sulfate neutralization to ammonium sulfate, the gaseous nitric acid can be neutralized by ammonia and therefore partitions into the aerosol phase to yield ammonium nitrate (NH<sub>4</sub>NO<sub>3</sub>):

$$NH_4NO_{3(s)} \Leftrightarrow NH_{3(g)} + HNO_{3(g)}$$
 (R-5)

### 2.2. Non-linear investigations

Modeled non-linear responses to emission changes are examined for a winter month (January 2001) when the meteorological conditions and atmospheric compositions favored aerosol nitrate formation in East Asia (Tie et al., 2005). Firstly, the model was executed with all the emissions included (referred to as the baseline simulation). Then sensitivity simulations are carried out for each source region with the following scenarios of emission reductions, respectively:

- 100RM\_SN\_NH<sub>3</sub>: a 100% reduction of SO<sub>2</sub>, primary sulfate, NO<sub>x</sub>, primary nitrate, and NH<sub>3</sub> simultaneously from regional emissions;
- 25RM\_SN\_NH<sub>3</sub>: a 25% reduction of SO<sub>2</sub>, primary sulfate, NO<sub>x</sub>, primary nitrate, and NH<sub>3</sub> simultaneously from regional emissions;
- 25RM\_SN: a 25% reduction of SO<sub>2</sub>, primary sulfate, NO<sub>x</sub>, and primary nitrate simultaneously from regional emissions.

By comparing 100RM\_SN\_NH<sub>3</sub> and 25RM\_SN\_NH<sub>3</sub>, modeled non-linear responses to the extent of emission changes are investigated. By comparing 25RM\_SN\_NH<sub>3</sub> and 25RM\_SN, we can examine the modeled non-linear responses to reductions of ammonia emissions. For each case, 18 sensitivity simulations were conducted. The contribution of reduced emissions from region *k* to the grid (i, j),  $C_{ij,k}$  can be defined as:

$$C_{ij,k} = D_{ij,\text{base}} - D_{ij,k}$$

where  $D_{ij,base}$  and  $D_{ij,k}$  are the deposition load in the grid (i,j) predicted, respectively, by the base run and by the sensitivity run with emissions from region k perturbed. If modeled responses to emission perturbation had been linear in deriving the deposition load, the sum of the contributions from every single source for every grid cell, should then be equal to the total amount of deposited pollutant predicted by the baseline simulation:

$$D_{ij,\text{base}} = \sum_{k=1}^{n} C_{ij,k} / \text{RD}$$

where RD is the reduction percentage.

Figs. 2 and 3 show the scatter plots between  $D_{ij,\text{base}}$  and  $\sum_{k=1}^{n} C_{ij,k}$ . The relationships are shown in the same plot for three cases of emission reductions. The non-linear effects

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**Fig. 2.** Relationship of dry depositions of gases (a -  $SO_2$ , c -  $HNO_3$ ) and aerosols (b - sulfate, d - nitrate) in January 2001 between baseline simulation and sum of all regional contributions due to emission perturbation. The dashed lines are 1:1 and 1:0.25 reference lines. See text for details about the three emission reduction simulations (unit: mg m<sup>-2</sup>).

can be evaluated with the slope of regression line as well as the correlation coefficient  $R^2$  for each reduction case. If the relationship had been linear, the slope of regression line should be equal to 1.00 for the 100% reduction case while equal to 0.25 for the 25% reduction cases. We find that emissions perturbation has large non-linear effects in deriving the deposition of sulfate (Fig. 2b) and nitric acid (Fig. 2c). A 100% reduction of regional emissions perturbs the atmospheric chemistry significantly. The correlation factors in the cases of perturbing ammonia emissions (100RM\_SN\_NH<sub>3</sub> and 25RM\_SN\_NH<sub>3</sub>) are much lower than the value for the case of reducing  $SO_2$  and  $NO_x$  only (25RM\_SN).

As presented in Section 2.1, the reductions of ammonia emissions not only decrease the formation of ammonium sulfate ((R-3) and (R-4)), but also have significant effects on the gas/aerosol partitioning between nitric acid and aerosol nitrate (R-5). Fig. 4 shows the contribution from Central China to dry deposition of HNO<sub>3</sub> and aerosol nitrate in January 2001, due to 25% emission reductions in the sensitivity simulations of 25RM\_SN\_NH<sub>3</sub> (upper panels) and 25RM\_SN (lower panels). As shown in Fig. 4a, a deficit

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Fig. 3. Same as Fig. 2, but for wet depositions of sulfate (left panel) and nitrate (right panel) in January 2001 (unit: mg m<sup>-2</sup>).

in the availability of ammonia and ammonium over Central China in the case of 25RM\_SN\_NH<sub>3</sub>, results in higher HNO<sub>3</sub> concentrations that are effectively dry deposited over source areas. This indicates that the reduction of ammonia emissions is unfavorable for nitrate to exist in the aerosolphase. The aerosol NH<sub>4</sub>NO<sub>3</sub> has a longer atmospheric residence time compared to the corresponding precursor gases (NH<sub>3</sub> and HNO<sub>3</sub>) and can therefore be transported over larger distances. A reduction of ammonia emissions in the source region increases the dry deposition of nitric acid over the perturbation region and may therefore reduce the transport of aerosol nitrate downwind of the source region.

Is it applicable to perturb emissions of  $SO_2$  and  $NO_x$  in combination? We found that a reduction of  $NO_x$  emissions slightly increases the deposition of sulfate in source areas (Fig. 3a, blue). This is likely caused by changes in the oxidation of  $SO_2$  to sulfate as a reduction in  $NO_x$  emissions will affect the radical chemistry (e.g., (R-2) and (R-1)). At the same time, a reduction of SO<sub>2</sub> emissions slightly decreases the deposition of HNO<sub>3</sub> (Fig. 2c, blue). With reduced emissions of SO<sub>2</sub>, the sulfate concentration levels above source areas decrease, thus allowing for enhanced conversion of nitric acid to form ammonium nitrate (R-5). Overall, the slopes of regression lines for the case of 25RM\_SN are within the range of 0.20-0.30. The departure from the linear relationship with a slope of 0.25 is lower than 5% for all species. The correlations are all higher than 0.9.

### 2.3. Method proposal

The analysis presented above suggests that the nonlinear responses of the CMAQ Eulerian model depend on the extent of the emission perturbation. To further analyze the reduction case when  $SO_2$  and  $NO_x$  emissions only are reduced by 25%, we calculated non-linear effects ( $NLE_{ij}$ ) for annual total deposition of sulfur and reactive nitrogen as follows:

$$\text{NLE}_{ij} = \sum_{k=1}^{n} C_{ij,k} / D_{ij,\text{base}} - 25\%$$

As shown in Fig. 5, non-linear effects for most areas are generally lower than 2% for sulfur, and lower than 5% for reactive nitrogen. Uncertainties of S/R relationships caused by the method itself should be within the range of the non-linear effects. Therefore, we proposed a 25% reduction of  $SO_2$ ,  $NO_x$  and its primary particles in combination from regional emissions for the source region attribution both for sulfur and reaction nitrogen. In addition, since both  $SO_2$  and  $NO_x$  are combustionrelated emissions, the simultaneous reductions of these two pollutants are realistic. A 25% reduction is also large enough for the model to give responses for emission changes. With the assumption of linear relationships, the difference between the base and sensitivity simulations was multiplied by a factor of four, and then defined as the contribution from that source region.

### 3. Results and discussion

The S/R calculations are done on a region-to-grid basis. These region-to-grid values are integrated to assess region-to-region S/R matrices, which provide an important connection between emissions and acid deposition over different time and spatial scales.

### 3.1. Region-to-region S/R relationships

Fig. 6 depicts the region-to-region S/R relationships for total depositions of sulfur and reactive nitrogen over 18

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**Fig. 4.** Contribution from 25% reduced emissions in Central China to dry depositions of nitric acid and aerosol nitrate in January 2001, derived from the sensitivity simulations, 25RM\_SN\_NH<sub>3</sub> (upper panels) and 25RM\_SN (lower panels).

receptor regions in East Asia. Total deposition includes both the locally driven dry deposition and the more longrange transport effects of wet deposition. Values in Fig. 6 are given as percentage of total deposition load over a receptor area contributed by emissions from various sources. Supplemental data can be found in Appendix A.

In this study, boundary conditions of chemical species derived from the MOZART global model were used to conduct source attribution for regions outside the CMAQ domain, i.e., other parts of the Indian subcontinent and European outflow across Eurasia to Asia. Previous studies using global CTMs (e.g., Liu et al., 2002; Wild et al., 2004; Holloway et al., 2007) and analysis of backward trajectories (Newell and Evans, 2000) suggested substantial contributions of North American and European emissions to Asian levels of ozone and carbon monoxide. Our results show that the contribution of global inflows (gray bars in Fig. 6) is significant (>30%) for the deposition loads of sulfur and reactive nitrogen over the northern and western receptor areas of the study domain, i.e., parts of Russia, Mongolia, Northwest China, parts of India and Myanmar. Sulfate has a longer atmospheric lifetime (1-2 weeks) than nitrate. Therefore, boundary contribution to sulfur deposition (Fig. 6a) is evident (>10%) even for the receptors located in the central parts of study domain, i.e., Central China, Korea, and Taiwan.

The contribution from China, including all the seven source regions shown as red bars in Fig. 6, is significant to the deposition load throughout the study area. Long-range transport from the industrialized areas of China (red series) contributes a significant percentage (>20%) of anthropogenic sulfur and reactive nitrogen depositions throughout East Asia. At the same time, northwest China receives approximately 35% of its sulfur load and 45% of its nitrogen load from foreign emissions mainly from the Indian subcontinent either in domain or through boundary inflows.

For the receptor areas in Southeast Asia, except Thailand and parts of India, the dominating sources (>50%) are foreign emissions from Thailand, South China and Southeast China. In addition, the contributions of NO<sub>x</sub> emissions from international shipping are considerable

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Fig. 5. Spatial distributions of non-linear effects on annual total depositions of sulfur (a) and reactive nitrogen (b).

for nitrogen deposition over Southeast Asia, especially the Philippines.

S/R relationships for reactive nitrogen deposition (Fig. 6b) show a somewhat different pattern as contrasted to S/R relationships for sulfur deposition (Fig. 6a). In considering the internal relationships among source regions of China, for instance, the relative contribution from Southeast China is more significant for the reactive

nitrogen load in other regions than for the sulfur load. Local emissions are the dominant source of sulfur deposition in Southwest and South China (Fig. 6a), whereas for reactive nitrogen loading over these two areas, Southeast China sources contribute up to 20-30%. NO<sub>x</sub> emissions are expected to change dramatically in the future because of rapid motorization in most cities of China. There is concern that nitrate could decrease the pH

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**Fig. 6.** Region-to-region source-receptor relationships for total sulfur (a) and total reactive nitrogen (b) deposition in East Asia. Vertical bars show the origin of substances deposited in each "receptor" region. Values given show percentage of total deposition in a "receptor" region contributed from different "source" regions. Red series is used for seven source regions in China, whereas blue series shows source regions in Southeast Asia.

level of rainwater and undermine the success of  $SO_2$  control strategies for acid rain in China. The anticipated increase of  $NO_x$  emissions will not only lead to an increase in acid deposition, but also pose additional environmental concerns through increases in tropospheric ozone.

### 3.2. Seasonal variability of S/R relationships

Seasonal variability of S/R relationships is examined here by considering wet deposition alone in order to

better reflect the effects of long-range transport. Wet deposition occurs only during precipitation, therefore air pollutants have a possibility to be transported far from the source area before being deposited (Holloway et al., 2002). Asian monsoon circulation plays an important role either in long-range transport or in scavenging and wet depositions of acid precursors. Vietnam, Taiwan, and Japan were chosen as typical receptors to reflect the patterns of longrange transport for different seasons on a sub-continental scale for Southeast Asia, East Asia, and Northeast Asia, respectively. Fig. 7 shows the contributions from major

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**Fig. 7.** Seasonality of wet sulfur (left panels, Gg S) and wet nitrogen (right panels, in Gg N) deposition in Vietnam, Taiwan of China, and Japan with contributions from major sources. The left/bottom axis refers to individual source contribution, whereas the right/top axis refers to monthly precipitation (cm) averaged over the receptor area.

sources to wet sulfur and wet nitrogen deposition over these three receptors as a function of season in 2001. Each line in Fig. 7 corresponds to the contribution to wet deposition load over the receptor from emissions in the individual source region or source type, as determined from the sensitivity simulation.

(1) Sources of acid deposition in Vietnam: The seasonal behavior of source contributions to acid deposition in Vietnam reflects what is seen in most of the countries in Southeast Asia, where emissions from South China, Thailand, and India dominate the deposition load over the smaller countries. In winter and autumn, a predominant feature at lower latitudes (south of 25°N) is southwest transport of Asian pollution kept in the boundary layer toward the tropics (de Laat and Lelieveld, 2002; Liu et al., 2002). The contributions of long-range transport from Southeast China and Central China are significant for both

sulfur and nitrogen deposition in Vietnam during winter and autumn. Compared with wet S deposition, sources contributing to wet N deposition in Vietnam exhibit stronger seasonal variation with its minimum in summer. The results show that wet N deposition in Vietnam due to emissions from international shipping is comparable with contributions from Thailand. The impacts of NO<sub>x</sub> emission from international shipping are discussed further in the next section.

(2) Sources of acid deposition in Taiwan, China: Sources of acid deposition in Taiwan exhibit strong seasonal variation reflecting the monsoonal precipitation pattern. In contrast to the situation in Vietnam, local emissions are the dominant source of sulfur and reactive nitrogen deposited in Taiwan. Long-range transport contributions are maximum in late spring and in autumn, when continental outflow of Asian pollution are efficiently removed by the precipitation over Taiwan. The contribution from Southeast Asia is maximum in spring and insignificant in other seasons. In spring biomass burning dominates the emission sources in Southeast Asia (Woo et al., 2003). In summer, when South and Southeast China receive a large portion of annual precipitation, acid precursors emitted from these areas experience the maximum wet removal closer to their source areas and thus contributions to other regions are insignificant. We found that in August volcanic sulfur accounts for about 50% of wet S deposition in Taiwan. During this time, elevated volcanic plume from the northern Philippines is carried by marine air mass blowing from the western Pacific and experiences wet removal over Taiwan. The contribution of international shipping emissions to wet N deposition in Taiwan is also noticeable.

(3) Sources of acid deposition in Japan: Volcanic plume significantly dominates sulfur deposition in Japan. Since July 2000, Miyakejima Volcano located in the northwest Pacific Ocean and 180 km south from Tokyo Metropolitan area, has begun to erupt and emitted huge amounts of SO<sub>2</sub> (Kajino et al., 2004). The present study included monthly emission flux from Miyakejima Volcano in 2001 as well as annual emissions of other inactive volcanoes located within the study domain (Table 1). In winter, most of the volcanic sulfur is deposited over the northwest Pacific Ocean. During August through October, however, volcanic sulfur accounts for more than 80% of total sulfur deposition in the terrestrial area of Japan. In terms of anthropogenic sulfur deposition in Japan, the contributions of domestic anthropogenic emissions as well as long-range transport from Central China and Southeast China are significant. Compared with wet deposition of anthropogenic sulfur, contribution due to anthropogenic emissions in Japan is more significant for anthropogenic nitrogen. This reflects the relatively strong signature of  $NO_x$  emission from transportation sources in Japan, which account for 60% of total amount (Streets et al., 2003). For a similar reason, NO<sub>x</sub> emissions from the Korean Peninsula also have a larger contribution to wet N deposition in Japan than to anthropogenic sulfur.

#### 3.3. Comparison with previous estimates

Several independent research groups have investigated S/R relationships for sulfur deposition in East Asia (Huang et al., 1995; Ichikawa and Fujita, 1995; Ichikawa et al., 1998; Arndt et al., 1998; Calori et al., 2001; Engardt et al., 2005). It should be noted that there are considerable differences in spatial resolution, emission inventory, meteorological fields, and study base year as well as sensible parameters applied in the models used in these studies. The definition of regional territory may not necessarily be the same, either. This makes the comparison basis somewhat inconsistent. Tables 2 and 3 present comparisons of major sources contribution to sulfur deposition in Japan and Vietnam, as calculated in this study and previous studies.

In considering source contributions to sulfur deposition in Japan (Table 2), initial calculations by Huang et al.

#### Table 2

Comparison with previous studies: major sources contributing to total sulfur deposition in Japan (in percent)

References	Year	China	N/S Korea	Japan	Volcano
Huang et al. (1995)	1989	3.5	2 <sup>a</sup>	93 <sup>b</sup>	-
Ichikawa and Fujita (1995)	1990	(45)	(16)	(33)	20
Ichikawa et al. (1998)	1990	25.0	16	40	18
Arndt et al. (1998)	1990	(17)	(14)	-	-
Calori et al. (2001)	1997	36.0	12	-	-
This study <sup>c</sup>	2001	15.4	3.5 (7)	18.4	50.4
		(31)		(37.2)	

Note that the values in parentheses are the percentage contributions to anthropogenic sulfur deposition in Japan excluding the deposition originating from volcano sources.

<sup>a</sup> South Korea only.

<sup>b</sup> Combined contribution from anthropogenic and volcanic sources in Japan.

<sup>c</sup> Boundary contribution in this study is 8.9 (17.8)%.

### Table 3

Comparison with previous studies: major sources contributing to total sulfur deposition in Vietnam (in percent)

References	Year	China	Vietnam	Thailand	Boundary	Shipping
Arndt et al. (1998) Engardt et al. (2005)	1990 2000	40 38 <sup>a</sup>	36 41	19 7	- 9	- 1
This study <sup>b</sup>	2001	51.4	15.3	10.5	5.3	3.0

<sup>a</sup> Parts of Southern China only.

 $^{\rm b}$  Other noticeable (>2.0%) contributors are IND (2.9%), PHL (3.3%), and volcano (2.5%).

(1995) and Ichikawa and Fujita (1995) differ substantially due to large differences in removal rates and chemical conversion rates assumed in the models (Arndt et al., 1998). The results calculated by the ATMOS model (Arndt et al., 1998; Calori et al., 2001) fall between these two initial calculations. The present study indicates a marked contribution from volcanic sources due to the inclusion of emissions from Miyakejima Volcano which began to erupt in July 2000. Excluding the contributions of volcanic sources, we estimated that 37% of anthropogenic sulfur deposition in Japan is due to Japanese anthropogenic emissions, 31% to emissions from China, 18% to sources outside the study region, and 7% to emissions from the Korean Peninsula. As discussed in Section 3.1, the results presented here indicate a considerable inflow of sulfur compounds from the northern and western boundaries.

In considering sources contributing to sulfur deposition in Vietnam (Table 3), there are also some differences between the present and previous studies. Arndt et al. (1998) used the ATMOS Lagrangian model and estimated that domestic Vietnamese emissions contributed 36%. Engardt et al. (2005) applied a Eulerian model to a smaller study domain which includes the southern parts of China and Southeast Asia only. The contribution of southern China emissions (2255 Gg S yr<sup>-1</sup>) calculated by Engardt et al. (2005) can be compared with that of whole of China

#### Table 4

Comparison between CMAQ and ATMOS estimated source-receptor relationships for total nitrogen deposition (in percent)

Receptors $\rightarrow$	Taiwan, China		N/S Korea		Japan		Mainland China	
Sources ↓	CMAQ	ATMOS	CMAQ	ATMOS	CMAQ	ATMOS	CMAQ	ATMOS
Taiwan, China	46.0	80	1.1	-	0.9	2	1.6	2
N/S Korea	4.2	-	46.9	61.5 <sup>a</sup>	14.9	15 <sup>a</sup>	2.6	1 <sup>a</sup>
Japan	1.8	1	4.6	2.5 <sup>b</sup>	55.7	65	0.5	-
Mainland China	34.1	18	39.1	36 <sup>b</sup>	20.6	18	79.7	90
SE Asia	6.6	-	0.6	-	0.6	-	4.0	-
Shipping	6.5	-	2.1	-	3.4	-	1.1	-
Boundary	0.6	-	4.3	-	2.7	-	8.1	-

<sup>a</sup> Taken as combined contribution from emissions in South and North Korea.

<sup>b</sup> Taken as averaged contribution to deposition in South Korea and deposition in North Korea.

emissions (9935 Gg Syr<sup>-1</sup>) calculated by Arndt et al. (1998). The present study estimated that emissions from whole of China (10 378 Gg Syr<sup>-1</sup>) contribute 51% to total sulfur deposition in Vietnam. In detail, 27% is from South China, 11% from Southeast China, 6% from Central China, and 6% from Southwest China according to this study. The comparison indicates that long-range transport, which is better handled in Eulerian models than in simple Lagrangian models, plays a significant role in Vietnam's sulfur deposition.

S/R relationships for nitrogen deposition derived in this study can be compared with Holloway et al. (2002) who presented transfer of reactive nitrogen in Asia calculated with the ATMOS-N model. Table 4 compares the impact of major sources of emissions to total nitrogen deposition in mainland China, Taiwan of China, Japan, and the Korean Peninsula. Both studies agree that domestic emissions are the primary source of nitrogen deposition in the receptors shown in Table 4. Overall, our results calculated by the CMAQ Eulerian model show higher long-range transport effects from foreign sources than those calculated by the ATMOS-N Lagrangian model. This is related to the Eulerian model's ability to describe vertical pollution transport in the free troposphere, whereas the Lagrangian model cannot manage to trace the fate of pollution above the atmospheric boundary layer with the same accuracy (Tarrasón et al., 2004). In the Lagrangian model, species trapped in the boundary layer may be dry deposited too quickly, rather than being transported downwind in a more realistic manner as suggested by Holloway et al. (2002).

### 4. Summary

The complex CMAQ regional Eulerian CTM and related components developed in this study have been applied for the first time, to date, to quantify region-to-grid S/R relationships both for sulfur and reactive nitrogen in East Asia. Source attributions are conducted for volcanoes, boundary conditions and international shipping as well as the 18 source regions within the study domain.

Investigation of model responses to emission changes has suggested that reductions of ammonia emissions have significant non-linear effects on the deposition of sulfur and reactive nitrogen as a result of non-linearity in the atmospheric chemistries of sulfate–nitrate–ammonia system and the deposition processes. We have analyzed the non-linear effects quantitatively and proposed a source regional attribution methodology. Sensitivity simulations were conducted where emissions of SO<sub>2</sub>, NO<sub>x</sub>, and its primary particles from a specific source region were reduced by 25%. The difference between the base and sensitivity simulations was multiplied by a factor of four, and then defined as the contribution from that source region.

The region-to-region quantitative S/R relationships provide an important connection between emissions and fates of pollutants over different time and spatial scales. Long-range transport of anthropogenic sulfur and reactive nitrogen from central eastern China contributes a significant percentage (>20%) to the deposition throughout East Asia. At the same time, northwestern China receives approximately 35% of its sulfur load and 45% of its nitrogen load from foreign emissions, mainly from the Indian subcontinent. Sulfur emissions from Miyakejima and other volcanoes contribute approximately 50% of sulfur load in Japan in 2001. Sulfur inflows from regions outside the study domain, which is attributed by using the boundary conditions derived from the MOZART global CTM, are pronounced (10-40%) over many parts of East Asia. We found that long-range transport of pollutants exhibits strong seasonal variation. The transboundary acid deposition generally peaks during the dry season. Compared with previous studies using simple Lagrangian models, the results derived in this study indicate higher influence from long-range transport. The relationships presented here are believed to be more realistic since they include the global influence as well as internal interactions among different parts of China.

This study is the first attempt to quantify transboundary influence both for sulfur and reactive nitrogen deposition in East Asia using a 3-D Eulerian CTM. Although the results need to be interpreted with caution because of the meteorological variability, sensitivity to emission changes, and model limitations, region-to-region S/R relationships predicted in this study could provide quantitative information for environmental negotiation, cost allocation, and possible international initiatives to mitigate global air pollution and climate change.

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### Appendix A. Supplementary data

Supplementary data associated with this article can be found in the online version at 10.1016/j.atmosenv. 2008.03.039.

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