MICS-Asia II: Model intercomparison and evaluation of particulate sulfate, nitrate and ammonium

Hiroshi Hayami\textsuperscript{a,*}, T. Sakurai\textsuperscript{b}, Z. Han\textsuperscript{b}, H. Ueda\textsuperscript{c}, G.R. Carmichael\textsuperscript{d}, D. Streets\textsuperscript{e}, T. Holloway\textsuperscript{f}, Z. Wang\textsuperscript{g}, N. Thongboonchoo\textsuperscript{d}, M. Engardt\textsuperscript{h}, C. Bennet\textsuperscript{h}, C. Fung\textsuperscript{i}, A. Chang\textsuperscript{j}, S.U. Park\textsuperscript{j}, M. Kajino\textsuperscript{c}, K. Sartelet\textsuperscript{k}, K. Matsuda\textsuperscript{l}, M. Amann\textsuperscript{m}

\textsuperscript{a}Central Research Institute of Electric Power Industry, 1646 Abiko, Abiko, Chiba 270-1194, Japan
\textsuperscript{b}Acid Deposition and Oxidant Research Center, Niigata 950-2144, Japan
\textsuperscript{c}Disaster Prevention Research Institute, Kyoto University, Kyoto 611-0011, Japan
\textsuperscript{d}Center for Global and Regional Environmental Research, University of Iowa, Iowa city, IA 52242, USA
\textsuperscript{e}Argonne National Laboratory, Argonne, IL 60439, USA
\textsuperscript{f}The University of Wisconsin-Madison, New York, NY 10027, USA
\textsuperscript{g}Institute of Atmospheric Physics, Beijing 100029, China
\textsuperscript{h}Swedish Meteorological and Hydrological Institute, 601 76 Norrkoping, Sweden
\textsuperscript{i}Hong Kong Environmental Protection Department, Hong Kong SAR, China
\textsuperscript{j}Meisei University, 2-1-1 Hodokubo, Hino City, Tokyo 191-8506, Japan
\textsuperscript{k}Swedish Meteorological and Hydrological Institute, 601 76 Norrkoping, Sweden
\textsuperscript{l}Institute of Atmospheric Physics, Beijing 100029, China
\textsuperscript{m}Centre d’Enseignement et de Recherche Eau, Ville, Environnement, 6 et 8, avenue Blaise Pascal, Cite Descartes, Champs-sur-Marne, 77455 Marne-la-Vallee Cedex 2, France
\textsuperscript{l}Meisei University, 2-1-1 Hodokubo, Hino City, Tokyo 191-8506, Japan
\textsuperscript{m}International Institute for Applied System Analysis, A-2361 Luxenburg, Austria

Received 23 March 2007; received in revised form 30 August 2007; accepted 30 August 2007

Abstract

Eight chemical transport models participate in a model intercomparison study for East Asia, MICS-Asia II. This paper analyzes calculated results for particulate matter of sulfate, nitrate and ammonium through comparisons with each other and with monthly measurements at EANET (the acid deposition monitoring network in East Asia) and daily measurements at Fukue, Japan.

To the EANET measurements, model ensemble means better agree with model individual results for sulfate and total ammonium, although total nitrate is consistently and considerably underestimated. To measurements at Fukue, the models show better agreement than for the EANET measurements. This is likely because Fukue is centered in many of the model domains, whereas the EANET stations are mostly in Southeast Asia and Russia. Moreover, it would be important that Fukue is in Northeast Asia, where the emission inventory is more reliable than Southeast Asia.

\textsuperscript{*}Corresponding author. Tel.: +81 4 7182 1181; fax: +81 4 7183 2966.
E-mail addresses: haya@criepi.denken.or.jp (H. Hayami), sakurai@adorc.gr.jp (T. Sakurai), han@adorc.gr.jp (Z. Han), ueda@storm.dpri.kyoto-u.ac.jp (H. Ueda), gcarmich@icaen.uiowa.edu (G.R. Carmichael), dstreets@anl.gov (D. Streets), taholloway@wisc.edu (T. Holloway), zifawang@mail.iap.ac.cn (Z. Wang), nthongbo@cgrer.uiowa.edu (N. Thongboonchoo), magnuz.engardt@smhi.se (M. Engardt), Cecilia.Bennet@smhi.se (C. Bennet), cfung@epd.gov.hk (C. Fung), alick@epd.gov.hk (A. Chang), supark@snu.ac.kr (S.U. Park), mimizu@storm.dpri.kyoto-u.ac.jp (M. Kajino), sartelet@cereve.enpc.fr (K. Sartelet), matsuda@adorc.gr.jp, matsuda@es.meisei-u.ac.jp (K. Matsuda), amann@iiasa.ac.at (M. Amann).

1352-2310/$ - see front matter © 2007 Elsevier Ltd. All rights reserved.
doi:10.1016/j.atmosenv.2007.08.057
The model–model comparisons are made in view of the total amount in the atmosphere, vertical profile, coefficient of variation in surface concentrations, and transformation changes with distance. All the models show reasonable tendencies in vertical profiles and composition ratios. However, total amounts in the atmosphere are discrepant among the models. The consistency of the total amount in the atmosphere would influence source–receptor analysis. It seems that model results would be consistent, if the models take into account the primitive processes like emission, advection/diffusion, chemical transformation and dry/wet deposition, no matter the processes are modeled simply or comprehensively.

Through the comparison study, we learned that it would be difficult to find any problems from one comparison (model-observation comparison with one data or many but at one station or in a short period). Modelers tend to examine model performances only from model-observation comparisons. However, taking budget in a certain or whole model domain would be important, before the models are applied to source–receptor analysis.

1. Introduction

MICS-Asia is a model intercomparison study of long-range transport models for East Asia. It was initiated by the inconsistency in source–receptor relationships for acid deposition found in the Fifth International Conference on Acid Deposition held in 1995 (Ichikawa et al., 2001). In the first phase of MICS-Asia (MICS-Asia I), the target species were sulfur compounds (Carmichael et al., 2002). In the present stage of MICS-Asia, or MICS-Asia II, nitric acid/nitrate, ammonia/ammonium, ozone and relevant species were added. To date, eight models have participated and submitted computed results (Carmichael et al., 2008). Here in this paper, we analyze the model results by focusing on aerosol quantities.

In recent years, urban air pollution by aerosol is high priority because of their health effects. However, aerosols can be transported over long distances, because their retention times in the atmosphere can be a few days to a week, resulting in transport scales of 100–1000 km. Due to this nature, a certain part of aerosol found in a city could be contributed by precursors emitted in distant cities. Thus, emission controls policies inside a city or a country might not be so effective as expected, and it is important to estimate source–receptor relationships of aerosol in discussing the emission control. Apart from the urban air pollution, aerosol is related to a variety of environmental issues like climate change, visibility, acid deposition and nitrification. It is also important to estimate and predict local, regional and global impacts of aerosol.

Chemical transport models (CTMs) play an important role in assessing environmental impacts, estimating source apportionment and predicting future changes. Before providing scientifically and/or socially meaningful information, the performance of CTMs must be evaluated. MICS-Asia II gives an opportunity to see predictability and consistency among present models. In MICS-Asia II, the eight participating models were required to submit concentrations of particulate sulfate, nitrate and ammonium as aerosol components. We will take a model-observation comparison with monthly and daily measurements to see the predictability, and take a model–model comparison to see the consistency. For other analysis topics, see Han et al. (2008) for ozone and relevant species, Wang et al. (2008) for deposition, and Holloway et al. (2008) for effects of boundary conditions. Some other related papers are also to be published (Sartelet et al., 2008; Kannari et al., 2008).

2. Description on models themselves and their results, and measurements

2.1. Brief introduction to MICS II

Here we briefly introduce MICS-Asia II. See Carmichael et al. (2008) for more detailed information. Model input datasets on emissions, meteorological fields and boundary concentrations were prepared for the MICS-Asia II, and it was strongly recommended to use the datasets. However, no groups used the meteorological fields, because all the eight models were designed to run with specific meteorological models or analysis datasets. The emission and boundary datasets were used by all. The emission inventory was on a monthly basis at 0.5° in longitude and latitude.

At this moment, eight regional CTMs participated in MICS-Asia Phase II. The model domains...
in the MICS II study domain are shown in Fig. 1 along with monitoring sites and emissions of SO$_2$. The name of each model or modeling group is not opened, because this project aims at understanding the uncertainty of the state-of-the-art CTMs applied to East Asia but not at ranking the models. Instead, the models are called M+numbers like M1. Following the data protocol given by the MICS-Asia II organizer (ADORC, 2003), the modeling groups submitted simulated atmospheric concentrations of seven gases (SO$_2$, NO, NO$_2$, HNO$_3$, PAN, NH$_3$ and O$_3$) and three aerosol components (sulfate, nitrate and ammonium), dry and wet depositions of some of those gases and aerosol components, and concentrations of three ionic species in precipitation (SO$_4^{2-}$, NO$_3^-$ and NH$_4^+$) in the study domain covering East and Southeast Asia during 4 months of March, July and December 2001 and March 2002. However, not all the models gave everything requested. M3 did not submit nitrate and ammonium, while M5 submitted only gaseous and particulate results in March 2001. The model domains of M1, M6 and M7 mostly cover the MICS study domain, but the other models just focus on China, Korea and Japan. This paper uses the submitted results of monthly and daily ground-level concentrations and monthly column total amounts of sulfate/sulfur dioxide, nitrate/nitric acid and ammonium/ammonia.

![Fig. 1. Participating models' domains, EANET stations, Fukue Island, and SO$_2$ emissions in MICS-Asia II study domain.](image-url)
2.2. Modeling information relevant to aerosol

General information on the models is summarized in Table 1.

M1 takes the most comprehensive aerosol model among the participating models. It accounts for processes of nucleation, coagulation and dynamic condensation/evaporation. Aerosol is divided into 16 bins from 0.02 to 19.8 \( \mu m \). The equilibrium concentration on the aerosol surface is calculated by SCAPE 2 (Meng et al., 1995). SCAPE 2 is an aerosol chemistry model that calculates concentrations and state of sulfate, nitrate, chloride, carbonate, ammonium, sodium, potassium, magnesium and calcium in aqueous and solid phases at equilibrium. M1 chooses one of two equilibrium options of SCAPE 2, where gaseous concentrations on the aerosol surface are calculated for the dynamic approach to the condensation/evaporation process. The nucleation process of \( H_2SO_4/H_2Oi \) is modeled as a function of temperature and relative humidity (Wexler et al., 1994). Heikes and Thompson (1983) are taken for heterogeneous reactions to form nitrate.

M2 assumes equilibrium between the gas and aerosol phases in the condensation/evaporation process. This process is calculated by MARS (Saxena et al., 1986). MARS treats sulfate, ammonium and nitrate. The size of aerosol is not defined. Nucleation and coagulation are not considered. Most importantly, M2 does not take into account the dry-deposition process for aerosol, because M2 was developed focusing on gaseous species but not on aerosol. However, the dry deposition process is very important in determining the atmospheric concentration of aerosol, and, for example, the sulfate concentration by M2 is extremely high, especially in a dry month of December 2001. Therefore, we do not analyze results by M2 in this paper, because the subject of this paper is aerosol.

M3 does not treat the aerosol processes explicitly. No other processes and no size dependency are modeled. Sulfate is assumed to form through both gas and aqueous phase transformation, whereas only aqueous phase formation through cloud process is considered for nitrate and ammonium. M3 submitted results only for sulfate.

M4 takes the gas–aerosol equilibrium, which is calculated by SCAPE 2. This model is unique in treating heterogeneous reactions as follows:

\[
\begin{align*}
Cl^- + HNO_3 & \leftrightarrow HCl + NO_3^- \\
NO_3^- + H_2SO_4 & \leftrightarrow HNO_3 + SO_4^{2-}.
\end{align*}
\]

No other processes and no size dependency are included.

M5 has the second most detailed model of aerosol. It considers nucleation, coagulation, and condensation/evaporation at equilibrium in four size bins of 0.1–0.3, 0.3–1.0, 1.0–2.5 and 2.5–10 \( \mu m \). The coagulation process is considered in the smallest two bins by following Whitby (1978). The nucleation of sulfate is by Wexler et al. (1994). The equilibrium model is SCAPE 2. The heterogeneous reactions taken are

\[
\begin{align*}
o_3 & \rightarrow 1.5O_2 \\
SO_2 & \rightarrow SO_4^{2-} \\
NO_2 & \rightarrow NO_3^- \\
HNO_3 & \rightarrow NO_3^-.
\end{align*}
\]

Details on the aerosol model in M5 are given in Tang et al. (2004). The wet deposition process is not taken into account in M5. M5 submitted results only for March 2001.

M6 considers sulfate, nitrate and ammonium. Ammonium nitrate is produced at an equilibrium constant as a function of temperature and relative humidity (Mozurkewich, 1993). Sulfuric acid formation in cloud droplets is considered by following Berge (1993). The formation of ammonium sulfate \( (NH_4)_2SO_4 \) and ammonium nitrate \( NH_4NO_3 \) is modeled following Hov et al. (1994) with some modification. Sulfuric acid produced in the gas and aqueous phases is assumed to react irreversibly with available ammonia producing aerosol phase \( (NH_4)_2SO_4 \):

\[
H_2SO_4 + 2NH_3 \rightarrow (NH_4)_2SO_4.
\]

This formulation is slightly different from Hov et al. (1994), who assumes the production of \( (NH_4)_1.5SO_4 \), which is a combination of ammonium bisulfate \( NH_4HSO_4 \) and \( (NH_4)_2SO_4 \). If there is any ammonia left after the full neutralization of sulfuric acid, it enters into equilibrium with HNO_3 and NH_4NO_3:

\[
NH_3 + HNO_3 \rightarrow NH_4NO_3.
\]

This equilibrium is dependent on temperature and relative humidity. The production of aerosol nitrate through the reaction of HNO_3 with sea salt...
and dust particles is described in a simplified way by
\[ \text{HNO}_3 \rightarrow \text{NO}_3^- \]

In addition, nitrate radicals NO and N\textsubscript{2}O\textsubscript{5} also produce aerosol nitrate through a first order loss process:
\[ \text{NO}_3 \rightarrow \text{NO}_3^- \]
\[ \text{N}_2\text{O}_5 \rightarrow 2 \text{NO}_3^- \]
This is slightly different compared to Hov et al. (1994), since the current scheme also predicts NO₃ and N₂O₅. No sizing is considered.

M7 expresses the size distribution by three modes, Aitken, accumulation and coarse modes. Sulfate produced in the nucleation is added into the Aitken mode. The coagulation process is taken into account in the Aitken and accumulation modes. Heterogeneous formation of nitrate is modeled by Riemer et al. (2003). The parameterization of the sulfate nucleation is based on Kulmala et al. (1998). Concentrations at the gas–aerosol equilibrium are calculated by ISORROPIA (Nenes, 2004). ISORROPIA is a successor model of SCAPE 2 and treats ammonium, sulfate, nitrate, chloride and sodium.

M8 expresses the size distribution by three bins from 0.01 to 10 µm. The nucleation process is modeled by Vehkamaki et al. (2002). The coagulation and heterogeneous reaction processes are not considered. The gas–aerosol equilibrium is assumed and calculated by ISORROPIA.

In summary, aerosol size distributions are taken into account in M1, M5, M7 and M8. The other models do not explicitly define the aerosol size, although it is implicitly assumed in calculating dry-deposition velocities. The gas–aerosol equilibrium is assumed by all the models except M1, in which the dynamic model is applied. Equilibrium models used are SCAPE 2 in M1, M4 and M5, MARS in M2, the model of Hov et al. (1994) in M6 and ISORROPIA in M7 and M8.

2.3. Measurements used for the model-observation comparisons

Model results submitted to MICS-Asia II were compared with monthly mean concentrations measured at EANET (Acid Deposition Monitoring Network in East Asia) stations (EANET, 2001, 2002) and daily mean concentrations in Fukue Island, Japan (Hayami, 2005).

In the comparative 4 months, March, July and December 2001 and March 2002, the aerosol chemical composition was monitored with high completeness at 14 of 43 active EANET stations (Table 2). Among the 14 stations, six stations are located in the northern domain, in Russia and Mongolia, seven stations are located in Southeast Asia, and one station, No. 32 (Imsil, Korea) is in the middle. No EANET stations with aerosol measurements were located in China and Japan. Some of the 14 stations did not obtain all data required for the comparison. We used monthly mean measurements observed over 80% of the days in each month. At all the 14 stations, aerosol and related gas samples were collected by four-stage filter-pack samplers. Four kinds of filters were set in each filter holder; in the order of air inflow, a PTFE filter for aerosol, a polyamide filter for whole of HNO₃ and part of SO₂, HCl and NH₃, a K₂CO₃-impregnated filter for the rest of SO₂ and HCl, and an H₃PO₄-impregnated filter for the rest of NH₃. See EANET (2003) for details. It is well known that filter-pack samples are influenced by artifacts through condensation or evaporation of semi-volatile species like nitrate and ammonium. Therefore, the model-observation comparisons were made for

<table>
<thead>
<tr>
<th>ID</th>
<th>Site name</th>
<th>Country</th>
<th>Characteristics</th>
<th>Latitude (N)</th>
<th>London (E)</th>
<th>Altitude (m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>11</td>
<td>Serpong</td>
<td>Indonesia</td>
<td>Rural</td>
<td>6.25</td>
<td>106.57</td>
<td>46</td>
</tr>
<tr>
<td>24</td>
<td>Petaling-Jaya</td>
<td>Malaysia</td>
<td>Urban</td>
<td>3.10</td>
<td>101.65</td>
<td>87</td>
</tr>
<tr>
<td>25</td>
<td>Tanah-Rata</td>
<td>Malaysia</td>
<td>Remote</td>
<td>4.47</td>
<td>101.38</td>
<td>1470</td>
</tr>
<tr>
<td>26</td>
<td>Ulaanbaatar</td>
<td>Mongolia</td>
<td>Urban</td>
<td>47.90</td>
<td>106.82</td>
<td>1282</td>
</tr>
<tr>
<td>27</td>
<td>Terelj</td>
<td>Mongolia</td>
<td>Remote</td>
<td>47.98</td>
<td>107.48</td>
<td>1540</td>
</tr>
<tr>
<td>28</td>
<td>Metro-Manila</td>
<td>Philippines</td>
<td>Urban</td>
<td>14.63</td>
<td>121.07</td>
<td>54</td>
</tr>
<tr>
<td>29</td>
<td>Los-Banos</td>
<td>Philippines</td>
<td>Rural</td>
<td>14.18</td>
<td>121.25</td>
<td>35</td>
</tr>
<tr>
<td>32</td>
<td>Imsil</td>
<td>Republic of Korea</td>
<td>Rural</td>
<td>35.60</td>
<td>127.18</td>
<td>–</td>
</tr>
<tr>
<td>33</td>
<td>Mondy</td>
<td>Russia</td>
<td>Remote</td>
<td>51.67</td>
<td>101.00</td>
<td>2000</td>
</tr>
<tr>
<td>34</td>
<td>Listvyanka</td>
<td>Russia</td>
<td>Rural</td>
<td>51.85</td>
<td>104.90</td>
<td>700</td>
</tr>
<tr>
<td>35</td>
<td>Irkutsk</td>
<td>Russia</td>
<td>Urban</td>
<td>52.23</td>
<td>104.25</td>
<td>400</td>
</tr>
<tr>
<td>36</td>
<td>Primorskaya</td>
<td>Russia</td>
<td>Rural</td>
<td>43.70</td>
<td>132.12</td>
<td>84</td>
</tr>
<tr>
<td>42</td>
<td>Hanoi</td>
<td>Vietnam</td>
<td>Urban</td>
<td>21.02</td>
<td>105.85</td>
<td>5</td>
</tr>
<tr>
<td>43</td>
<td>Hoa-Binh</td>
<td>Vietnam</td>
<td>Rural</td>
<td>20.82</td>
<td>105.33</td>
<td>23</td>
</tr>
</tbody>
</table>
particulate sulfate, total nitrate (\(=\) gaseous HNO\(_3\) + particulate nitrate) and total ammonium (\(=\) gaseous NH\(_3\) + particulate ammonium).

Hayami (2005) monitored daily concentrations of gases and aerosol components in Fukue Island, Japan, in March 2001. Fukue is located between Japan and Korea and surrounded by no large emissions. PM\(_{2.5}\) was collected for chemical analysis by an impactor/denuder/filter-pack sampling system. The impactor was used to cut off larger particles than PM\(_{2.5}\), and the denuder was used to collect gaseous HNO\(_3\), HCl and NH\(_3\). Three kinds of filters were used in each filter pack; a PTFE filter, a nylon filter for volatilized nitrate from the PTFE filter and a citric acid-impregnated quartz filter for volatilized ammonium from the PTFE filter. Thus, samples collected on those filters could be considered as PM\(_{2.5}\) components (not including gases or larger particles). Denuded filter-pack samples are much less influenced by the artifacts than the filter-pack samples. Therefore, we used measurements of sulfate, nitrate and ammonium in PM\(_{2.5}\) for the comparisons.

For both of the EANET monthly and Fukue daily comparisons, non-sea-salt sulfate concentrations were calculated by assuming a sea-salt ratio of sulfate to sodium, 0.25 by mass. Hereinafter, sulfate is referred to as non-sea-salt sulfate.

3. Model-observation comparison

In this section, surface concentrations predicted by the participating models are compared with monthly EANET measurements of particulate sulfate, total nitrate and total ammonium and daily measurements of particulate sulfate, nitrate and ammonium at Fukue.

3.1. Comparison with EANET monthly measurements

Table 3 shows statistics of mean bias errors (MBE), root-mean squared errors (RMSE), correlation coefficients (\(r\)) between the observed and model-predicted monthly mean concentrations at all the EANET stations in all the four months. Numbers of samples are small for M5 and M8, because M5 submitted results only for March 2001, and because only two EANET stations observing aerosols exist inside the model domain of M8. For sulfate, M2 and M7 show overestimation, while the others tend to underestimate. RMSEs by M5 and M8 are smaller than the observed mean concentration of 2.59 \(\mu g m^{-3}\). The correlations are low in general, \(<0.55\) by M5. The overestimation by M2 is extremely large, because M2 does not take into account the dry deposition processes for aerosols. For total nitrate, M4 shows considerable overestimation, but the other models tend to underestimate. M8 has a smaller RMSE than the observed mean of 1.83 \(\mu g m^{-3}\). For total ammonium, M6 and M8 tend to underestimate, while the others show overestimation. RMSEs by M5 and M8 are smaller than the observed mean of 3.01 \(\mu g m^{-3}\). The correlation by M5 is very high (\(r = 0.83\)).

Table 3
Statistics of the participating models to EANET monthly measurements for whole of the four comparative months

<table>
<thead>
<tr>
<th></th>
<th>M1</th>
<th>M2</th>
<th>M3</th>
<th>M4</th>
<th>M5</th>
<th>M6</th>
<th>M7</th>
<th>M8</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulfate observed mean = 2.59</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MBE</td>
<td>-1.16</td>
<td>6.33</td>
<td>-1.15</td>
<td>-1.22</td>
<td>-0.09</td>
<td>-1.00</td>
<td>0.57</td>
<td>-1.40</td>
</tr>
<tr>
<td>RMSE</td>
<td>2.69</td>
<td>9.15</td>
<td>3.30</td>
<td>3.96</td>
<td>1.45</td>
<td>2.86</td>
<td>2.71</td>
<td>2.42</td>
</tr>
<tr>
<td>(r)</td>
<td>0.26</td>
<td>0.30</td>
<td>0.41</td>
<td>-0.03</td>
<td>0.55</td>
<td>0.11</td>
<td>0.32</td>
<td>-0.37</td>
</tr>
<tr>
<td>(n)</td>
<td>40</td>
<td>23</td>
<td>14</td>
<td>14</td>
<td>8</td>
<td>40</td>
<td>38</td>
<td>6</td>
</tr>
<tr>
<td>Total nitrate observed mean = 1.83</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MBE</td>
<td>-1.41</td>
<td>-1.80</td>
<td>7.87</td>
<td>-0.94</td>
<td>-1.71</td>
<td>-1.27</td>
<td>-1.01</td>
<td></td>
</tr>
<tr>
<td>RMSE</td>
<td>2.47</td>
<td>3.12</td>
<td>8.50</td>
<td>2.10</td>
<td>2.76</td>
<td>2.51</td>
<td>1.42</td>
<td></td>
</tr>
<tr>
<td>(r)</td>
<td>0.44</td>
<td>0.30</td>
<td>0.36</td>
<td>0.33</td>
<td>0.13</td>
<td>0.22</td>
<td>0.57</td>
<td></td>
</tr>
<tr>
<td>(n)</td>
<td>39</td>
<td>22</td>
<td>0</td>
<td>13</td>
<td>8</td>
<td>39</td>
<td>37</td>
<td>5</td>
</tr>
<tr>
<td>Total ammonium observed mean = 3.01</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MBE</td>
<td>0.06</td>
<td>1.76</td>
<td>14.00</td>
<td>0.01</td>
<td>-1.25</td>
<td>1.17</td>
<td>-1.42</td>
<td></td>
</tr>
<tr>
<td>RMSE</td>
<td>4.06</td>
<td>7.56</td>
<td>17.69</td>
<td>1.55</td>
<td>3.54</td>
<td>5.66</td>
<td>2.21</td>
<td></td>
</tr>
<tr>
<td>(R)</td>
<td>0.31</td>
<td>0.00</td>
<td>0.39</td>
<td>0.83</td>
<td>0.20</td>
<td>0.26</td>
<td>0.03</td>
<td></td>
</tr>
<tr>
<td>(n)</td>
<td>37</td>
<td>21</td>
<td>0</td>
<td>12</td>
<td>8</td>
<td>37</td>
<td>35</td>
<td>4</td>
</tr>
</tbody>
</table>
Fig. 2 shows the same statistics as Table 3, but calculated for each of the month. For sulfate and total ammonium, correlations in both of March 2001 and 2002 are relatively high, although correlation coefficients are near zero or minus in July and December, 2001. This must be a reason why the performance of M5, which submitted results only for March 2001, seems to be the best in Table 3, compared with the others that submitted all the 4 months. Another finding in Fig. 2 is that monthly correlations for sulfate and total ammonium are relatively consistent among the models. In contrast, correlations for total nitrate are much different by models. This indicates that various processes related to nitrate are differently expressed among the participating models.

There are a variety of statistical measures proposed to evaluate model performance in comparisons with measurements. Ideally, such statistical measures should be applied in cases where observation sites are evenly distributed in a study domain, identical sampling techniques are used at all the sites, and the number of measurements are large sufficiently to satisfy statistical reliabilities. However, the EANET stations with aerosol measurements in the comparative months in 2001 and 2002 were unevenly distributed, near model boundaries (see Fig. 1), and the number of samples (number of the stations multiplied by 4 months) was small (about 10 stations × 4 months) for each species, although the quality-assurance/quality-control program worked well. Therefore, it is difficult to judge the model performances only from the statistics described above.

Next, we take model-observation comparisons by each of the stations and the months (Fig. 3). Here, M2 is excluded for all the species and M4 is excluded total nitrate and ammonium from the comparisons below, because they overestimated extremely as shown in Fig. 2. For sulfate, the models tend to slightly underestimate measurements in both of the March (2001 and 2002), except for stations with lower measurement values. In these months, model ensemble means, which were calculated from all the model estimates for each of the stations, fall within a factor of 2 of the measurements at many of

![Fig. 2. Statistics between observed and predicted monthly concentrations at EANET stations.](image)
the stations. In July, the models tend to overestimate the measurements in general. The model predictions agree well with measurements in December 2001, except for certain stations like Nos. 34–36 and 42. For total nitrate, low concentrations are well predicted by the models. However, in general, the models consistently underestimate relatively high concentrations with some exceptions. The remarkable underestimation in July 2001 might be related to the overestimation of sulfate which could transfer.
particulate nitrate to gaseous HNO₃ that has a larger deposition velocity. At stations Nos. 42 and 43, the models agree with measurements in March 2001 but show considerable underestimation in March 2002. Measurements at No. 24 are extremely underestimated in all the months by all the models. For total ammonium, model predictions better agree with measurements than for sulfate and total nitrate in both of the March (2001 and 2002), although there are some exceptions. The models extremely overestimate measurements at Nos. 42 and 43 in December 2001 and extremely underestimate at No. 24 in March, July and December 2001 (no data for March 2002). In summary, the model ensemble means better agree with measurements of sulfate and total ammonium than individual estimates by each of the models, but the models consistently underestimated total nitrate concentrations.

All the models show relatively good agreement with all measurements at Vietnamese stations Nos. 42 and 43 (Hanoi and Hoa-Binh). However, large increases are found in measurements at No. 43 in March from 2001 to 2002. Emissions near the station might have changed during that 1 year. At Russian stations Nos. 34–36 (Listvyanka, Irkutsk and Primorskaya), the models consistently underestimate measurements in December 2001. These stations are located near the northern boundary of the MICS-Asia study domain where emissions are not estimated around (see Fig. 1). In December, the dominant flows come from the north, bringing boundary concentrations which are very low. Russian emissions should be considered in order to improve the model predictions at those stations. The total nitrate and ammonium concentrations at No. 24 (Petaling Jaya, Malaysia) are underestimated in all the months. However, total nitrate and ammonium observed at this station are mainly (84–89%) dominated by the corresponding gaseous species, HNO₃ and NH₃, which was also predicted by the models. It is indicated that the partitioning of the volatile species are well modeled (for this station).

### 3.2. Comparison with daily measurements at Fukue, Japan

Comparisons between daily measurements and model predictions at Fukue are made for sulfate and nitrate in March 2001. Table 4 shows statistics (MBE, RMSE, r) for daily concentrations of PM$_{2.5}$ sulfate and nitrate at Fukue in March 2001. For sulfate, all the models except M5 tend to underestimate the measurements. All the RMSEs are smaller than the averaged measurement (7.9 $\mu$g m$^{-3}$). Correlations are relatively high. For nitrate, three of the seven models tend to underestimate the measurements. M4 and M5 considerably overestimated compared with the averaged measurement (1.3 $\mu$g m$^{-3}$). Correlations are also high. It is curious that M2, which was an outlier in the comparisons with EANET measurements, is not an outlier here. This suggests that it is dangerous to evaluate the performance of a model by comparing with measurements at one site.

The air quality in springtime of Fukue is characterized by big events lasting for a few days or more. According to Fig. 4, at least two events appeared from 1–3 to 18–21 in March 2001. Many of the models capture both of the events. In general, the consistency between the

<table>
<thead>
<tr>
<th></th>
<th>M1</th>
<th>M2</th>
<th>M3</th>
<th>M4</th>
<th>M5</th>
<th>M6</th>
<th>M7</th>
<th>M8</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulfate</td>
<td>MBE</td>
<td>−6.62</td>
<td>−2.04</td>
<td>−6.28</td>
<td>−4.35</td>
<td>1.16</td>
<td>−4.64</td>
<td>−0.96</td>
</tr>
<tr>
<td></td>
<td>RMSE</td>
<td>7.66</td>
<td>4.52</td>
<td>7.60</td>
<td>6.17</td>
<td>3.09</td>
<td>6.25</td>
<td>2.69</td>
</tr>
<tr>
<td></td>
<td>r</td>
<td>0.60</td>
<td>0.64</td>
<td>0.11</td>
<td>0.26</td>
<td>0.79</td>
<td>0.28</td>
<td>0.83</td>
</tr>
<tr>
<td></td>
<td>n</td>
<td>30</td>
<td>29</td>
<td>30</td>
<td>30</td>
<td>30</td>
<td>30</td>
<td>30</td>
</tr>
<tr>
<td>Nitrate</td>
<td>MBE</td>
<td>−0.74</td>
<td>−1.29</td>
<td>−2.40</td>
<td>2.35</td>
<td>−0.57</td>
<td>0.45</td>
<td>0.47</td>
</tr>
<tr>
<td></td>
<td>RMSE</td>
<td>1.27</td>
<td>1.69</td>
<td>−2.78</td>
<td>2.93</td>
<td>1.22</td>
<td>1.33</td>
<td>1.01</td>
</tr>
<tr>
<td></td>
<td>r</td>
<td>0.53</td>
<td>0.74</td>
<td>0.54</td>
<td>0.75</td>
<td>0.46</td>
<td>0.72</td>
<td>0.70</td>
</tr>
<tr>
<td></td>
<td>n</td>
<td>30</td>
<td>29</td>
<td>0</td>
<td>30</td>
<td>30</td>
<td>30</td>
<td>30</td>
</tr>
</tbody>
</table>
model predictions and measurements at Fukue is much better than that shown above in the comparisons with EANET monthly measurements. One plausible reason is the location of Fukue. Fukue is surrounded by China, Korea and Japan and nearly centered in the MICS-Asia II study domain (see Fig. 1). As shown later in 4.3, the consistency among the models is relatively high around Fukue. For sulfate, some of the models agree well with measurements, but the others underestimate. As a result, model ensemble means show a tendency of underestimation. In contrast, ensemble means are mostly consistent with measurements for nitrate, because of the balance between overestimation by some of the models and underestimation by the others.

4. Model–model comparison

In this section, aerosol distributions calculated by the participating models are compared with each other. Model–model comparisons are implemented over a comparison-domain, which is equal to the domain of M3 and M4 and mostly covered by many of the models. That is, as shown in Fig. 1, the comparison-domain is covered fully by M3, M4, M5 and M6 and mostly by M1 and M7 with lack of small part at the southeastern corner, but certain part of the comparison-domain is not covered by M8 (and M2, which is not analyzed).

4.1. Total amounts

It is important to check the budget in the whole domain of a model, before applied to comparisons with measurements or source–receptor analysis. Here, we look at total amounts in the atmosphere over the comparative domain. Fig. 5 shows total amounts of each of total sulfur (SO$_2$ + sulfate), total nitrate (HNO$_3$ + nitrate) and total ammonium (NH$_3$ + ammonium) by each of the months and the models. The total amount was calculated by vertically integrating submitted results of monthly mean concentrations at 0, 300, 1000, 1500, 3000 and 6000 m over the comparison-domain.

For total sulfur, the models can be divided into two groups by smaller or larger total amounts in the atmosphere. The total amount by the former group of M1, M4 and M6 is about half of the latter group of M3, M5, M7 and M8. In MICS-Asia II, all the models were supposed to use the same emission data and the boundary conditions. However, those
common data were actually used after modified in order to fit to the map projection, the vertical coordinate, and the species modeled. Such modifications could introduce differences in total inputs of emissions and lateral fluxes to the models. Total amounts of particulate sulfate by M8 are much smaller than those by M3, M5 and M7, although total amounts of total sulfur by these models are comparable. A large difference in modeling between M8 and the others is that M8 does not have the in-cloud formation process of sulfate. This process would be important in East Asia. For total nitrate, total amounts by M4 are larger compared with the other models. Based on monthly deposition data submitted by M4, the monthly total (= wet + dry) deposition of total nitrate in the comparison-domain, or the whole domain of M4, was estimated to be 30–86 Gmol, which is larger than the monthly emitted NO\textsubscript{x} in the comparison-domain (29–30 Gmol). It is likely because a large amount of nitrogen compounds were supplied from out of the domain of M4. Other than M4, the same features as total sulfur are also found for total nitrate, such as larger differences among the models than those
among the months and the existence of two groups. All the models predict that particulate nitrate represents the majority of total nitrate in March 2001 and 2002, and December 2001. In July, gaseous HNO₃ increases in all the models. This seasonality is considered to reflect the temperature dependency of the gas–aerosol equilibrium of nitrate. For total ammonium, intermediate features between total sulfur and total nitrate described above are found.

Overall, total amounts by M1 and M6 are very comparable. As described in Section 2.2, M1 has the most comprehensive aerosol model, whereas the aerosol model of M6 is simplified for long-term calculations. It is considered that the simplified model of M6 well approximates complex aerosol processes in a long-term, long-range scale.

4.2. Vertical profile

Fig. 6 shows mean vertical profiles of particulate and total sulfur, nitrate and ammonium in March 2001, averaged over the comparison-domain for each of the models. Note that M3 did not submit results for nitrate and ammonium, and M4 is removed in the analysis for nitrate and ammonium due to the extreme overestimation.

The models show identical features in vertical profiles of particulate and total sulfur; that is, the total sulfur concentration decreases with increasing altitude, and the particulate sulfate concentration is uniform at <1500 m and decreases with increasing altitude >1500 m. Such a vertical profile of total sulfur indicates that SO₂, which is a primary pollutant, is much influenced by area sources. In contrast, sulfate is a secondary pollutant and relatively slowly transformed from SO₂, which results in sulfate being well mixed in the boundary layer. Sulfur concentrations at 6000 m by M7 are higher than the other models. It seems unlikely that the vertical motion in M7 is much more active than the others. It is possible that boundary concentrations of sulfur in upper layers used by M7 are higher than the others. Vertical profiles of total and particulate nitrate are similar to those of sulfate, because both HNO₃ and nitrate are secondary pollutants. In addition, particulate nitrate concentrations increase relatively to total nitrate concentrations with altitude. These features are captured by all the models. The vertical profile of total and particulate ammonium is similar to that for total and particulate sulfate, because ammonium is associated with sulfate, and NH₃ is emitted from area sources as well as SO₂.

In Section 4.1, it was found that total amounts in the atmosphere by M3, M5, M7 and M8 are larger than those by M1 and M6. However, as shown above, tendencies in the vertical profiles are consistent among the models. That is, concentrations by the former models are higher than those by the latter models at all the vertical levels.

4.3. Variation in surface concentration

Here, we examine the model results for spatial distributions of variations in monthly mean surface concentrations in the comparison-domain. Fig. 7 shows spatial distributions of coefficients of variation and mean concentrations of particulate sulfate, nitrate and ammonium in the surface layers in March 2001. The coefficient of variation (hereinafter, CV) is defined as the standard deviation divided by the mean. The larger CV, the lower the consistency among the models. Note that M4 is removed in the analysis for nitrate and ammonium.

Mean concentrations of sulfate are high near Chongqing, Shanghai and Seoul and in the volcanic plume from Mt. Miyake. In general, areas with relatively low CVs (<0.5) are nearly consistent with areas with high concentrations (>6 µg m⁻³). However, the CV is not so low near the volcanic plume. Actual release height of the volcanic plume is different among the models, even though it should be at about 1500 m. This high CV is probably due to the different modeling of vertical mixing in addition to the chemical transformation process. High concentrations of nitrate are centered in the Yellow Sea and in the large cities like Shanghai, Taipei, Osaka and Tokyo. CVs are <0.5 in relatively high concentration areas, as shown above for sulfate. CVs outside of the domain of M8 (see Fig. 1) are larger than those inside of the domain. However, very high CVs appear in the northwestern part of the domain, where concentrations are low (<0.5 µg m⁻³). This is likely because these concentrations are heavily influenced by boundary concentrations, and because boundary concentrations are not consistent among the models due to domain sizes and other modeling features (Holloway et al., 2008). For ammonium, CVs are lower than those for sulfate and nitrate in eastern China. Ammonium is associated with acidic particulate components of sulfate and nitrate. The models are more consistent in predicting the
The summed concentration of sulfate and nitrate but more variable in predicting sulfate-to-nitrate ratios.

4.4. Transformation as a function of distance from land

Fig. 8 shows monthly mean ground-level particulate sulfate/nitrate ratio (S/N), particulate ratio to total sulfur (Fs) and particulate to total nitrate ratio (Fn) from 120°E to 140°E along 27°N in March 2001. 120°E and 27°N is on the eastern coast of China, and, to the east, there is the Pacific Ocean. Note that S/N by M3 is not shown, because M3 does not treat nitrate, and S/N and Fn by M4 are not shown because of the extremely high concentrations predicted by M4, as presented in Section 4.1.

It is expected that S/N increases eastward with distance from source areas on the Asian Continent, because the formation of sulfate from SO₂ is slower than the formation of nitrate from NOₓ. The models show that S/N consistently increases in from 120°E to 130°E. However, from 130°E to
E, M8 decreases, but M7 increases, while the others keep constant. All the models show that Fs increases eastward, except for local reductions around 129°E and 134°E where ship lanes with large emissions SO₂ cross 27°N. Fs values by M3 and M8 are very consistent with each other but are lower than those by the other models. As described in Section 2.2, M3 takes into account both gas and aqueous phase transformation of SO₂ to sulfate, whereas only the gas-phase formation is considered in M8. It is considered that this difference in modeling of the sulfate formation process leads to

Fig. 7. Spatial distributions of coefficients of variation in mean surface concentrations in March 2001.
lower Fs by M8 than that by M3, based on the total and particulate sulfur in the atmosphere shown in Fig. 5. However, monthly precipitation of >100 mm appears along 27°N in meteorological data used in M3 as well as M8, which should have made Fs by M3 larger than M8. Therefore, the reason of the consistency in Fs between M3 and M8 remains unclear. It is possible that Fs is different between M3 and M8, when they are compared at cloud levels. In contrast to Fs, Fn decreases eastward in general. This is likely because nitrate is driven out from aerosol by newly produced sulfate. Due to this reason, Fn by M8, which estimates very low sulfate concentrations, remains high.

5. Summary

In this paper, calculated results by the eight participating models in MICS-Asia II were compared with measurements and with each other for sulfate, nitrate and ammonium. Note that M2 was excluded from the comparisons except for the statistical analysis, because it did not take into account the dry deposition process for aerosol.

Model-observation comparisons were made with monthly mean measurements of sulfate, total nitrate and total ammonium at EANET stations and daily measurements of sulfate and nitrate at Fukue, Japan. To EANET measurements, model ensemble means agreed better with measurements than model individual estimates for sulfate and total ammonium, although total nitrate was consistently and considerably underestimated by all the models. To Fukue measurements, the models showed better agreement than for EANET measurements. This is likely because Fukue is centered in many of the model domains, whereas the EANET stations are mostly in Southeast Asia and Russia. Moreover, it would be important that Fukue is in Northeast Asia, where emissions are high, and the emission inventory is more reliable than Southeast Asia.

Model–model comparisons were made in view of the total amount in the atmosphere, vertical profile, CV in surface concentrations, and transformation changes with distance from the continent. All the models showed reasonable tendencies in vertical profiles and composition ratios. However, total amounts in the atmosphere were discrepant among the models. The reasons could be resolved by looking at budget among emissions, depositions and lateral fluxes. The consistency of the total amount in the atmosphere would influence source–receptor analysis. It seems that model results would be consistent, if the models take into account primitive processes like emission, advection/diffusion, chemical transformation and dry/wet deposition. The model results would not be altered by the magnitude of details of each process, in a long scale in space and time.

In the analysis, M2 and M4 did not fully participate, because the dry deposition process for aerosol is not modeled in M2, and M4 seems to have a problem on lateral boundary conditions for nitrogen compounds. However, in preliminary comparisons with daily measurements at Fukue, their predictions were comparative to the other models and modestly agreed with measurements. It would be difficult to find any problems from one comparison (model-observation comparison with one data or many but at one station or in a short period). Modelers tend to examine model performances only
References


Engardt, M., 2000. Sulphur simulations for East Asia using the MATCH model with meteorological data from ECMWF. Swedish Meteorological and Hydrological Institute RMK No. 88, p. 33.


