Assessment of transboundary ozone contribution toward South Korea using multiple source–receptor modeling techniques

Ki-Chul Choia, Jong-Jae Leeb, Chang Han Bae, Cheol-Hee Kim, Soontae Kim, Lim-Seok Chang, Soo-Jin Ban, Suk-Jo Lee, Jongchoon Kim, Jung-Hun Woa,*

a Department of Advanced Technology Fusion, Konkuk University, Seoul, South Korea
b Department of Atmospheric Sciences, Pusan National University, Busan, South Korea
c Division of Environmental, Civil and Transportation Engineering, Ajou University, Suwon, South Korea
d National Institute of Environmental Research, Incheon, South Korea

HIGHLIGHTS

- We assessed the S–R relationships for ozone using three methods over East Asia.
- We evaluated S–Rs for not only anthropogenic emissions but biogenic emissions.
- Three methods showed similar S–Rs for anthropogenic emission sources.
- OPTM estimated higher biogenic contributions for ozone formation then HDDM.
- NOx limited regime was formed over South Korea for July periods.

ABSTRACT

Ozone concentrations in East Asia were simulated using the Community Multi-scale Air Quality (CMAQ) model, and its source contributions were estimated by multiple source–receptor modeling techniques. To study relationships between ozone concentrations and precursor emission sources, three approaches were applied to four months (January, April, July, and October 2009) to represent seasonal characteristics and compare results, with a particular focus on South Korea. Brute force (BF) is a traditional sensitivity analysis method used to estimate model output response to an input change. The high-order decoupled direct method (HDDM), a computational method, is an efficient and accurate alternative to the BF method for sensitivity. The Ozone and Particulate Precursor Tagging Methodology (OPTM) provides contribution information quantified by tracking emissions from selected sources throughout the simulation period. The approaches generally show that most of the receptor regions were substantially influenced by emissions from central China, which is the largest anthropogenic emissions source region in East Asia. Local emissions were still major contributors, especially South Korea and Japan during July 2009. On the other hand, a case study of maximum 8-h ozone concentrations derived from CMAQ–OPTM on April 9 in South Korea shows that the NOx and VOCs emissions from China contributed approximately 82% and 91%, respectively, to maximum 8-h ozone in Region 4 (South Korea) without boundary inflow, which indicates that Chinese emissions are the dominant contributor in this episode. A comparison study of the three approaches shows that HDDM tends to estimate biogenic source contributions lower than that from OPTM in China but similar to OPTM in South Korea and Japan. When comparing the BF method and HDDM, the sensitivity results show a reasonably good agreement during a given period. The location- and time-dependent maximum 8-h ozone isopleths over South Korea as a receptor region created by HDDM suggest that most ozone was being transported from central China, whereas almost no ozone was formed locally during April 2009, and local conditions were heavily VOC limited. On the other hand, local emissions were the dominant contributor during July 2009, and every source region showed a NOx-limited regime, which indicates that ozone concentrations in South Korea strongly depend on NOx emissions during this month.

© 2014 Elsevier Ltd. All rights reserved.

* Corresponding author.
E-mail address: jwoo@konkuk.ac.kr (J.-H. Woo).
1. Introduction

Both nitrogen oxides (NO\textsubscript{x}) and volatile organic compounds (VOCs) in the troposphere can have an impact on human health, either directly or because of their oxidation. This oxidation can lead to a variety of secondary oxidized products such as ozone, many of which are potentially more harmful than their precursors (Jenkin and Clemitshaw, 2000). Tropospheric ozone damages natural vegetation, agricultural crops, and human health, and is a greenhouse gas.

Previous research suggests that tropospheric ozone has increased over East Asia in the past decades and that the rate of increase is higher than in other regions (Akimoto et al., 1994; Oltmans et al., 1998; Lee et al., 1998; Meigen et al., 2004). Recently, NO\textsubscript{x}, which is a critical precursor of ozone, has rapidly increased over East Asia, chiefly because of emission increases in China during the last decade (Yamaji et al., 2008; Zhang et al., 2007) reported that China’s NO\textsubscript{x} emissions increased from 10.9 Tg in 1995 to 18.6 Tg in 2004, a 70% increase. Long-range transport of ozone and its precursors can influence other regions located downwind of emission source regions. For instance, Asian pollution enhanced surface ozone concentrations by 5–7 ppb over western North America in spring 2006 (Zhang et al., 2008).

The future ozone concentrations over East Asia will be significantly influenced by anthropogenic ozone precursor emissions, which in turn depend on future economic growth and environmental policies in East Asia (Yamaji et al., 2008). To support effective air quality management plans, contribution assessments of source regions as well as emission source categories are needed to better understand contributions from the East Asian countries. In the region, Lin et al. (2008) have estimated source–receptor (S–R) relations for sulfur and reactive nitrogen deposition, and Zhang et al. (2004) and Yamaji et al. (2008) have studied ozone over East Asia.

The Community Multi-scale Air Quality (CMAQ) model (Byun and Ching, 1999) is one of the photochemical grid models being used to investigate air quality degradation and to predict the effectiveness of emission control measures. Photochemical grid models such as CMAQ have also been used to estimate source contributions. To assess source contributions, various techniques have been developed based on this model to inform policy and scientific applications, such as control strategy development and source apportionment review. Here, we apply multiple S–R modeling techniques, including Brute Force (BF), High-Order Decoupled Direct Method (HDDM), and the Ozone and Precursor Tagging Methodology (OPTM), to assess source contributions and compare results from multiple modeling techniques over the East Asia region. The S–R modeling techniques used in this study are described in chapter 2.1.

The main objectives of this study were to assess contributions from specific emission source regions to ambient ozone concentrations in receptor regions and investigate ozone sensitivities toward South Korea. Source apportionment information for ozone has been investigated mainly by using source-tagging methodology, and the effects of emission perturbations on regionally averaged surface ozone have been derived by HDDM. The traditional BF method was applied to compare both of the alternative approaches. The three approaches were applied to examine the contributions of five source regions (South Korea, Japan, and three regions in China), and both anthropogenic and biogenic emissions in East Asia were applied to our modeling experiments.

2. Methodology

2.1. Source–receptor analysis methodologies

Sensitivity analysis generally measures how air concentrations respond to emissions perturbations at sources. In general, photochemical grid models have been used to estimate source contributions by performing a sensitivity case minus base case simulation. This approach is easily used for source contribution assessment when the relationship between model input and output is linear, such as sulfur transport. If emission perturbations have a nonlinear effect on concentrations because of nonlinearities in the atmospheric chemistry, such as ozone pollution, this method will underestimate source contribution. Sensitivity methods such as the BF method and the decoupled direct method (DDM) will not provide source apportionment if the relationship between model input and output is nonlinear (Yarwood et al., 2007).

On the other hand, source apportionment seeks to quantify contributions of various emission sources from specific geographic areas or of emissions sources to pollutant levels at particular locations (Cohan and Napelenok, 2011). This approach typically tracks target species separately from base model simulations and apportioned fractions of emission sources. However, the approach does not provide sensitivity results by an emission control scenario, because source apportionment seeks to determine the total contribution of each emission source to ambient concentration (Cohan et al., 2005). Source apportionment is most suited for identifying sources responsible for conditions present in a model.

The sensitivity approaches the BF method and HDDM were used in this study. The BF method calculates differences between concentrations in simulations with base case and perturbed emission scenarios from each source region or source category. In this respect, BF is one of the common methods used to estimate S–R relationships because of simplicity and ease of application in any model. However, the method is not always practical because computational cost increases linearly with the number of perturbations examined, and smaller concentration changes between simulations may be strongly influenced by numerical errors (Koo et al., 2009).

Several approaches have been attempted to use as substitutes for the traditional BF method to reduce the time needed for BF simulations within a photochemical grid model. DDM provides the same type of sensitivity information as the BF method but uses a computational method that is directly implemented in the host model (Dunker, 1981; Yarwood et al., 2007). Disadvantages of DDM include large computer memory requirements (Yarwood et al., 2007) and the nonlinearity of ozone formation. Instead, HDDM, which is an extension of DDM, is used to assess nonlinearity of ozone response to a variety of perturbations in emission rates (Cohan et al., 2005). Both DDM and BF methods are more suitable for looking at response rather than contribution to emission sources (Dunker et al., 2002; Cohan and Napelenok, 2011).

In this study, we applied HDDM (Hakami et al., 2003, 2004; Cohan et al., 2005) to assess nonlinearity of ozone response to a variety of emission perturbations. The sensitivity results calculated by HDDM have been compared with BF results to validate the HDDM estimates. HDDM was also used to explore comprehensive relationships between ozone and its perturbed precursor emissions over the S–R regions.

As the source apportionment approach, the CMAQ–OPTM source apportionment tool (Douglas et al., 2009) was used to estimate regional contributions to ozone in this study. OPTM was developed by the U.S. Environmental Protection Agency (EPA) as an applied tagging methodology for the CMAQ model (Arunchalam, 2009). OPTM provides contribution information for each emission source under unmodified simulated conditions. This method is a tracer-based technique that allows extra tagged species to be added to a grid model to track ozone or its precursors from specific sources. For ozone, aggregate modeled species are defined to track oxidants, NO\textsubscript{x}, and VOCs (Douglas et al., 2009). These techniques are useful evaluation tools in identifying which source categories or...
source regions contribute to receptor ozone concentrations. Major advantages of this method are less computational times and the ability to use unmodified simulated conditions. We demonstrate the CMAQ tagging with BF in terms of model runtime for six source areas and model boundaries (requires eight time simulations for BF, including the base case run) in the East Asia domain. The results show that the tagging method requires 0.18 times the model runtime than the BF method. Disadvantages of OPTM include limitation in distinguishing between NOx-limited and VOC-limited regimes. In addition, OPTM assumes that all VOC species have the same reactivity (Arunachalam, 2009). If the various tagged sources or categories have roughly similar reactivity, then OPTM results could produce reasonable results; otherwise, model accuracy may decrease. Therefore, we decided to use HDDM results as an alternative to distinguish between limited regimes for OPTM interpretations and selected broader regions as source definitions without source categories to retain similar reactivity for each tagged source. In this study, CMAQ–OPTM was used to assess quantitative information on the ozone contribution of each source region to each receptor region.

2.2. Modeling framework

Emissions information is one of the critical components of the modeling framework. In this study, both anthropogenic and biogenic emissions were used as inputs in the model. The Sparse Matrix Operator Kernel Emissions (SMOKE)-based emissions processing system (Woo et al., 2012), recently developed by the EPA, was also adopted for anthropogenic emissions. All pollutant emissions were adopted from the INTEX 2006 inventory (Zhang et al., 2009). If the various tagged sources or categories have roughly similar reactivity, then OPTM results could produce reasonable results; otherwise, model accuracy may decrease. Therefore, we decided to use HDDM results as an alternative to distinguish between limited regimes for OPTM interpretations and selected broader regions as source definitions without source categories to retain similar reactivity for each tagged source. In this study, CMAQ–OPTM was used to assess quantitative information on the ozone contribution of each source region to each receptor region.

Table 1
Summary of anthropogenic emissions over Asia (2009, unit: Gg/year).

<table>
<thead>
<tr>
<th>Country</th>
<th>CO</th>
<th>NOx</th>
<th>VOC</th>
<th>NH3</th>
<th>SO2</th>
<th>PM10</th>
<th>PM2.5</th>
</tr>
</thead>
<tbody>
<tr>
<td>S. Korea</td>
<td>790.6</td>
<td>1022.0</td>
<td>734.0</td>
<td>188.2</td>
<td>543.3</td>
<td>389.5</td>
<td>254.9</td>
</tr>
<tr>
<td>China</td>
<td>174,028.6</td>
<td>22,313.9</td>
<td>26,574.4</td>
<td>14,615.8</td>
<td>29,548.9</td>
<td>18,586.0</td>
<td>13,526.0</td>
</tr>
<tr>
<td>Japan</td>
<td>4870.4</td>
<td>2270.5</td>
<td>2135.4</td>
<td>357.7</td>
<td>795.3</td>
<td>167.3</td>
<td>121.3</td>
</tr>
<tr>
<td>OASIA</td>
<td>5442.5</td>
<td>906.1</td>
<td>1149.2</td>
<td>404.5</td>
<td>471.7</td>
<td>635.5</td>
<td>414.9</td>
</tr>
<tr>
<td>SEASIA</td>
<td>44,134.0</td>
<td>5468.0</td>
<td>14,563.8</td>
<td>3389.2</td>
<td>5814.8</td>
<td>4065.8</td>
<td>3438.6</td>
</tr>
<tr>
<td>SASIA</td>
<td>76,705.0</td>
<td>6168.3</td>
<td>14,384.4</td>
<td>10,482.7</td>
<td>9335.4</td>
<td>5611.6</td>
<td>4533.1</td>
</tr>
</tbody>
</table>

resolution and temporal resolution of 6 h. The WRF model has been run for four representative months (January, April, July, and October 2009) with a 5-day spin-up. A more comprehensive WRF model configuration is described in Table 2.

The CMAQ version 4.7 (Foley et al., 2010) model was used to assess contributions from specific emissions source regions to ambient ozone in each of the receptor regions and to provide an understanding of the characteristics of the atmospheric chemistry related to ozone formation over East Asia. The modeling domain was configured with a 60-km grid resolution, and the domain included 24 vertical layers. Model chemistry was simulated by the CB05 mechanism.

Table 2
Meteorological model configuration.

<table>
<thead>
<tr>
<th>Meteorological model</th>
<th>WRF</th>
</tr>
</thead>
<tbody>
<tr>
<td>Basic equation</td>
<td>Compressible, Non-hydrostatic</td>
</tr>
<tr>
<td>Domain structure</td>
<td>Nested grid (2 domains)</td>
</tr>
<tr>
<td>Horizontal resolution</td>
<td>D1: 180 km (51 x 47 grids)</td>
</tr>
<tr>
<td></td>
<td>D2: 60 km (109 x 82 grids)</td>
</tr>
<tr>
<td>Vertical coordinate</td>
<td>Sigma coordinate</td>
</tr>
<tr>
<td>Vertical layers</td>
<td>24</td>
</tr>
<tr>
<td>Data assimilation</td>
<td>FDDA with NCEP</td>
</tr>
<tr>
<td>Microphysics</td>
<td>WSM 6-class graupel scheme</td>
</tr>
<tr>
<td>Surface-layer options</td>
<td>Monin-Obukhov scheme</td>
</tr>
<tr>
<td>Boundary layer</td>
<td>YSU scheme</td>
</tr>
<tr>
<td>Cumulus</td>
<td>Kain-Fritsch (new Eta) scheme</td>
</tr>
<tr>
<td>Radiation</td>
<td>RRTM Longwave radiation</td>
</tr>
<tr>
<td></td>
<td>Dudhia Shortwave scheme</td>
</tr>
<tr>
<td>Land use type</td>
<td>MODIS (1 km global)</td>
</tr>
<tr>
<td></td>
<td>(20 categories)</td>
</tr>
</tbody>
</table>
2.3. Experimental design for source–receptor relationships

Each of the three methods used the same domains that cover 20°–50°N and 100°–150°E, as was agreed at the Long-range Transboundary Air Pollutants in Northeast Asia (LTP) modeling sub-working group meeting in August 2009. The LTP Project is a collaborative research framework on long-term monitoring and modeling launched by China, Japan, and Korea (Park et al., 2005; Kim et al., 2011). This CMAQ modeling domain was divided into six S–R regions, namely, northern China (Region 1), central China (Region 2), southern China (Region 3), South Korea (Region 4), Japan (Region 5), and the other East Asia (Mongolia, North Korea, and Taiwan) inside the model domain (Fig. 1). Our models have been run for four representative months (January, April, July, and October 2009) with a 5-day spin-up to explore seasonal ozone episodes. A time-independent set of vertical concentration profiles were used for initial and boundary conditions in our modeling domain (ozone concentrations range from 30 ppb to 35 ppb in our domain). To evaluate the model performance, we compared surface ozone and precursor monitoring data measured at 94 monitoring sites in the Seoul metropolitan area and 5 background monitoring sites in South Korea (Seongmo-Ri, Deokjeok-Do, Pado-Ri, Taha-Dong, and Gosan-Ri; Fig. 2) to the model results. Three model S–R runs were conducted to assess the S–R relationships of ozone and the sensitivity of area-averaged ozone to different magnitudes of anthropogenic precursor emission perturbations. Source apportionment information for ozone was investigated mainly by using CMAQ–OPTM source tagging methodology, and the effect of the emission perturbations on regionally averaged surface ozone was derived by CMAQ–HDDM. The traditional BF method was applied to evaluate the alternative approaches.

For the BF method application, we divided East Asia into five S–R regions based roughly on major source regions to minimize computing time and numerical errors. Modeled nonlinear responses to emission changes and sensitivity tests were examined using the BF method in East Asia. First, the model was run with all emissions (base case simulation). Then, sensitivity simulations were conducted for each source region with emission reduction scenarios. The emission reduction scenarios for the sensitivity test are shown in Table 3.

Table 3

<table>
<thead>
<tr>
<th>Reduction rate (%)</th>
<th>NOx 0%</th>
<th>NOx 25%</th>
<th>NOx 50%</th>
<th>NOx 75%</th>
<th>NOx 100%</th>
</tr>
</thead>
<tbody>
<tr>
<td>VOC 0%</td>
<td>Base case 1</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>VOC 25%</td>
<td></td>
<td>2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>VOC 50%</td>
<td></td>
<td></td>
<td>3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>VOC 75%</td>
<td></td>
<td></td>
<td></td>
<td>4</td>
<td></td>
</tr>
<tr>
<td>VOC 100%</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Note that each reduction scenarios are carried out for each source region with both precursor emissions from anthropogenic and biogenic sources at once.

Fig. 2. Location of monitoring sites in South Korea.

Fig. 3. Model simulated-monthly average of daily maximum 8-h surface ozone concentration from anthropogenic and biogenic emissions for (a) January, (b) April, (c) July, and (d) October 2009.

K.-C. Choi et al. / Atmospheric Environment 92 (2014) 118–129 121
3. Results and discussion

3.1. Model performance evaluation

The three S–R methodologies in the CMAQ model were simulated over four representative months (January, April, July, and October 2009) at a 60-km resolution. Figs. 3 and 4 show the estimated average monthly ozone concentrations for each of the study months and the average spatiotemporal ozone concentrations for each S–R region, respectively. Generally, the model estimated surface ozone concentrations in April and July are higher than in January and October because of the meteorological conditions. In Fig. 3, monthly averaged ozone concentrations in January and October are higher in the southern regions than in mainland China, which is a major ozone precursor emission region. This finding implies that relatively small amounts of ozone could be formed from precursor emissions over the mid-latitude regions because of the weak solar radiation in those months, while a significant amount of ozone could be transported from outside the model boundaries. For this reason, we focused on springtime (April) and summertime (July) simulations to estimate source contributions for ozone.

Fig. 4. Box and Whiskers plot of daily maximum 8-h surface ozone concentrations for each receptor region (area-wide average concentrations). Black dots indicate monthly average of daily maximum 8-h surface ozone concentrations.

Temporal variations in the simulated and observed surface hourly ozone and precursor (NO, NO2) concentrations in the Seoul metropolitan area during July 2009 (includes 94 monitoring stations; average values were used) are shown in Fig. 5.

We used the Index of Agreement in order to interpret performance of the modeling results (Willmott and Wicks, 1980; Willmott, 1981). For IOA, a value of 1 indicates a perfect match and 0 indicates no agreement at all. Overall, the simulation appears to underestimate the concentrations of NOx (NO and NO2). In the case of ozone, Fig. 5 shows that the model simulated hourly ozone concentrations reasonably well, with overall IOA of 0.68. The model showed higher performance for daytime ozone concentrations (IOA 0.77) compared to the nighttime ones (IOA 0.34). These findings may be explained as the result of reduced titration by NO.
during the nighttime because of the underestimated NO concentrations in the model. Another reason for underestimating NO\textsubscript{x} is the coarse grid resolution (60 km), which would be too coarse to adequately capture urban-scale phenomena. For the contribution analysis, which was focused on long-term regional interpretation, the grid resolution issue would be less problematic.

**Fig. 6** shows the hourly variations in the simulated and observed surface ozone concentrations over the Korea background sites (five monitoring stations) during July 2009. The intercomparison using the background sites was conducted to observe the background level and long-range transport effect from outside Korea. The figure shows that the model reproduced ozone concentrations reasonably...
well over that period, even the model-estimated concentrations presented with course grid structure. However, for several days for each of the sites show model overestimation, especially at sites Pado-Ri and Gosan-Ri, which indicates that the ozone contribution from outside Korea may be slightly overestimated.

3.2. Results of source–receptor relationships

The results of the source apportionment simulations were analyzed for regional ambient ozone concentrations and for regional contributions to Region 4 (South Korea). The Korea ozone standard is expressed as 1-h ozone and daily 8-h ozone concentrations, with thresholds of 100 ppb and 60 ppb, respectively. For ozone, impacts on the daily maximum 8-h average were evaluated for the four simulation periods.

Fig. 7 shows the model-estimated 8-h ozone concentrations for April 2009 (left panel) and for July 2009 (right panel) base case simulations in the South Korea region (Region 4). The maximum model-estimated 8-h ozone concentration during the April simulation is 77 ppb, which occurs on April 9 in South Korea. During the July 2009 simulation, the 8-h ozone concentrations for the base case are in the 30–71 ppb range, which is a wide concentration range compared with other regions during the same period. On July 1 and July 10, the concentrations exceeded the Korea ozone standards, at 66 ppb and 71 ppb, respectively. These cases were also analyzed for their S–R relationship for ozone by using CMAQ–OPTM; they are described below and shown in Fig. 8.

Fig. 8 shows the contribution of NOx and VOC emissions from source regions to the maximum 8-h ozone concentration on April 9 in receptor Region 4 (South Korea) by using the CMAQ–OPTM source-tagging methodology. Overall, nearly half of maximum 8-h ozone concentrations in Region 4 were contributed by model domain boundary input, which is the biggest contributor in this region. Previous studies have reported that ozone levels over East Asia could be found in association with continental outflow, and the contribution from outside of the East Asia domain is predominant in winter and early spring (Zhang et al., 2002; Yamaji et al., 2006).

The model’s default boundary conditions were used in the modeling domain, and the domain does not fully reflect temporal variation and concentrations of boundary ozone. This may act as a limitation of our study, which will be focused on in the next phase of this research. The assessment of ozone contributions by internal emissions by region is the focus of our research in this study. Without boundary impacts, the major contributor to the high 8-h ozone episode in Region 4 was Region 2 (central China), which contributed more than 70%. The NOx and VOC emissions from China (Regions 1, 2, and 3) contributed approximately 82% and 91%, respectively, to maximum 8-h ozone in Region 4, which indicates that Chinese emissions are the dominant contributor in this episode. As mentioned in chapter 2.1, OPTM cannot distinguish between NOx- and VOC-limited regimes; this means that OPTM only estimated contribution by total ozone concentration. Alternatively, HDDM generates both limited regimes in the same condition. The results show that anthropogenic NOx and VOC emissions from China contributed to maximum 8-h ozone in Region 4 as approximately 33 ppb and 14 ppb, respectively, in this episode.

Fig. 9 shows the contribution of NOx and VOC emissions from source regions to maximum 8-h ozone on July 1 (left panel) and July 10 (right panel) in receptor Region 4 (South Korea) using CMAQ–OPTM. Both cases show that boundary condition (BC) was ranked as the biggest contributor, but they represented different contribution ratios. About half of maximum 8-h ozone concentrations in Region 4 were contributed to by model domain boundaries in the July 1 case. For the July 10 case, however, the contributions are 31–38%, which is much less than in other cases. Without BC, the contribution of Chinese emissions were as high as 57% of total NOx and 69% of total VOC contributed to maximum 8-h ozone in Region 4 for the July 1 case. The VOC emissions from biogenic sources were approximately 60% of total VOCs contributed to maximum 8-h ozone, which is likely a result of increased vegetation during the summertime. For VOCs contributed to ozone, emissions from China (both anthropogenic and biogenic sources) made up 70% of contributions without BC. Of the NOx emissions contributed to ozone in receptor Region 4, the contribution from local emissions made up approximately 57%, while the contribution from China emissions made up approximately 33% on July 10. In contrast, the VOC emissions contributed to ozone concentrations from local sources was approximately 35%, which is relatively low compared with that
Fig. 9. Contribution of NO\textsubscript{x} and VOC emissions from source regions to maximum 8-h ozone concentrations for the July 1 (left panel) and July 10 (right panel) cases in receptor Region 4. S1–S5 indicate source regions, and A and B represent anthropogenic and biogenic sources, respectively. Other sources involved domain-wide emissions without predefined source region.

Fig. 10. Comparison of S–R relationships for monthly average of daily maximum 8-h surface ozone concentrations for July 2009 between HDDM (left) and OPTM (right) results. “A” and “Biog.” represent anthropogenic and biogenic sources, respectively. Both NO\textsubscript{x} and VOC-limited regimes derived from HDDM for each receptor regions are applied to OPTM to combine the NO\textsubscript{x} and VOC contributions.

Fig. 11. Comparison of S–R relationships for monthly average of daily maximum 8-h surface ozone concentrations for July 2009 between (a) BF, (b) HDDM, and (c) OPTM. Both NO\textsubscript{x} and VOC-limited regimes derived from HDDM for each receptor region are applied to OPTM to combine the NO\textsubscript{x} and VOC contributions. S1–S5 indicates source regions that include anthropogenic and biogenic sources. The other total indicates the rest of the ozone contribution with exception of predefined five source regions, e.g., domain-wide emissions without predefined source region and boundary inflow.
in the NOx case. The other sources, including North Korea, Mongolia, and Taiwan, generally showed low contributions to Region 4. However, they showed larger contributions in the July 10 case because of increased North Korea impact (anthropogenic and biogenic emissions) in addition to local (South Korea) contributions and stagnant meteorological conditions. HDDM results applied to both cases show that anthropogenic emissions from China are the more dominant contributor in the July 1 case (NOx, 29 ppb; VOC, 3 ppb) than in the July 10 case (NOx, 11 ppb; VOC, 1 ppb). Anthropogenic emissions from local sources (Region 4) are major sources in the July 10 case (NOx, 25 ppb; VOC, 1 ppb) compared with that in the July 1 case (NOx, 11 ppb; VOC, 0.3 ppb). Overall, OPTM results suggest that episodic high ozone concentrations could be influenced mainly by local sources, as well as transported from outside of the region. The HDDM results show that reduction plans for NOx emissions are more effective than VOC controls for reducing high ozone concentration in the three ozone episodes.

To compare the three approaches and to assess the representative S–R relationships for ozone, source contributions to monthly average of maximum 8-h ozone concentrations for each of the receptor regions were performed using HDDM, source-tagging, and the traditional BF method for the July 2009 period. Fig. 10 shows that S–R relationships contributed to monthly average of maximum 8-h ozone concentrations for each receptor region derived from CMAQ–HDDM and CMAQ–OPTM. Most of the receptor regions were substantially influenced by Region 2 emissions, which is the largest anthropogenic emissions source region in East Asia. Nevertheless, local emissions are still major contributors, especially Region 4 (South Korea) and Region 5 (Japan). When comparing the two approaches, S–R results from anthropogenic sources are reasonably well matched except in regions 3 and 4. HDDM estimated a higher contribution from local anthropogenic emissions in receptor Region 3, and from Regions 2 and 5 anthropogenic emissions in the receptor Region 4 compared with source-tagging results. HDDM tends to estimate biogenic source contributions lower than OPTM in China but similar to OPTM results in regions 4 and 5.

Monthly average of daily maximum 8-h ozone contributions from anthropogenic sources derived from the three approaches for the July 2009 case are presented in Fig. 11. The three approaches showed a slightly different contribution for each receptor region. The other total, which included boundary inflows and domain-wide emissions without predefined source regions, was ranked as a biggest contributor, but the total represented different contribution rates for each method. HDDM tends to estimate the other total contributions as lower than OPTM and BF estimates in China (Regions 1, 2, and 3), whereas OPTM tends to overestimate the other total compared with HDDM and BF estimates. In Region 4, the local contribution rate was estimated as 38% by BF, 30% by HDDM, and 28% by OPTM, which shows that the BF method estimates higher contributions from local emissions than HDDM and OPTM. However, local contribution in Region 3 was estimated as 21% by BF, 40% by HDDM, and 28% by OPTM, which shows that HDDM estimates higher contributions from local sources than OPTM and BF, and this is the opposite of the Region 4 case.

3.3. Sensitivity analysis for ozone

Figs. 12 and 13 show the maximum 8-h ozone sensitivity simulation results carried out for each source region to receptor region 4 for April and July by the BF method (Fig. 12) and the whole target period by HDDM (Fig. 13). To investigate the ozone sensitivity, sensitivity simulations are carried out with 25%, 50%, 75%, and 100% reduction of both of NOx and VOCs for each source region. When comparing between the BF method and HDDM, the sensitivity results show reasonably good agreements during the same period. For the April simulations, central China emissions (S2) strongly influenced receptor region 4 (South Korea), with more than 7 ppb (100% reduction) ozone concentration. Local emissions are major contributors to ozone sensitivity, with more than 11 ppb (100% reduction) of ozone concentration during the July period. The effect of the emission reductions on receptor region 4 ozone is near-linear for reductions less than 50%. However, for emission reductions more than 50%, the response of ozone became nonlinear. It is assumed that more than 50% reduction of regional emissions generally perturbs the atmospheric chemistry.

Figs. 14 and 15 show the location- and time-dependent maximum 8-h ozone isopleths in receptor region 4 (South Korea) derived from HDDM during April and July, respectively. During April 2009, most ozone is being transported from Region 1 and especially Region 2, whereas almost no ozone is formed locally. When local NOx emission increase results in substantial ozone decrease, the local conditions are heavily VOC-limited. In this month, ozone is being formed in upwind regions (Regions 1 and 2) and transported into Region 4. On the other hand, Fig. 15 shows that local emissions are the dominant contributor during July 2009, which are comparable to April 2009 results. During July simulations, every source region showed a NOx-limited regime, which
indicates that ozone concentrations in South Korea strongly depend on NO\textsubscript{x} emissions during this month. When the NO\textsubscript{x} emissions from northern and central China are reduced, ozone concentrations in South Korea are expected to decrease during the April and July periods. Further, in July, reduced NO\textsubscript{x} from local sources is the most important source of maximum 8-h ozone concentrations in South Korea, with Regions 1, 2, and 5 emissions playing a smaller but still substantial role.

Fig. 13. Maximum 8-h ozone sensitivity results from NO\textsubscript{x} and VOC emissions derived by HDDM over the entire target period in South Korea (receptor Region 4, S1–S5 indicate source regions).

Fig. 14. Monthly average of daily maximum 8-h ozone isopleths for receptor region 4 (South Korea) during April 2009 (a) Source region 1, (b) Source region 2, (c) Source region 3, (d) Source region 4, and (e) Source region 5.
4. Summary and conclusions

The CMAQ chemical transport model with multiple source–receptor modeling techniques was used for the first time to estimate S–R relationships and sensitivity for ozone in East Asia. Source contributions were estimated for biogenic sources, as well as for five anthropogenic source regions, within the study area. Three approaches to study relationships between ozone concentrations and precursor emission sources were applied to four months (January, April, July, and October 2009) as representative of seasonal characteristics and compared over East Asia, with a particular focus on South Korea.

The quantitative S–R relationships derived from multiple approaches provided various possible scenarios relating ozone concentrations and emissions over different spatial and temporal scales. Comparison studies to estimate monthly average of maximum 8-h ozone contributions from anthropogenic and biogenic sources showed a generally similar but slightly different contribution for each receptor region. The other total, which included boundary inflows and domain-wide emissions without predefined source regions, was ranked as the biggest contributor but represented different contribution rates for each method. HDDM tends to estimate the other total contributions lower than OPTM and BF in China, whereas OPTM tends to overestimate the other total compared with HDDM and BF. For the July period, most of the receptor regions were substantially influenced by Region 2 emissions, which is the largest anthropogenic emissions source region in East Asia. Nevertheless, local emissions are still major contributors, especially Region 4 (South Korea) and Region 5 (Japan) emissions. On the other hand, a case study of maximum 8-h ozone concentrations on April 9 in South Korea shows that the NOx and VOC emissions from China contributed approximately 82% and 91%, respectively, to maximum 8-h ozone over region 4 without BC, which indicates that Chinese emissions are the dominant contributor in this episode. The comparison results between CMAQ–HDDM and CMAQ–OPTM for the July period show that HDDM tends to estimate the biogenic source contributions lower than OPTM in China but similarly in South Korea and Japan.

Comparison of the sensitivity results of the BF method and HDDM showed reasonably good agreement during the same period. The location- and time-dependent maximum 8-h ozone isopleths in the South Korea receptor region created by HDDM suggest that most ozone was transported from central China, whereas almost no ozone was formed locally during April 2009. When local NOx emissions increase results in a substantial ozone decrease, the local conditions are heavily VOC-limited. On the other hand, local emissions were the dominant contributor during July 2009, and every source region showed a NOx-limited regime, which indicates that ozone concentrations in South Korea strongly depend on NOx emissions during this month.

This study is the first attempt to estimate source contributions and sensitivity for tropospheric ozone in East Asia by using the CMAQ chemical transport model with multiple approaches. Model boundary inflow and domain resolution may act as a limitation of our study, which will be focused on in the next phase of this research. Although the results have limitations, such as meteorological variability and uncertainties in model and emissions, our results can provide quantitative information for environmental policies and research purposes, as well as suggest possible methodologies to evaluate source–receptor relationships in East Asia.

Acknowledgments

This work was funded by the Korea Meteorological Administration Research and Development Program under Grant CATER 2012-6123.