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Influence of Vertical Eddy Diffusivity Parameterization on Daily and Monthly Mean Concentrations of O_3 and NO_y

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ABSTRACT

Two parameterization schemes for vertical eddy diffusivity were utilized to investigate their impacts on both the daily and monthly mean concentrations of ozone and NO_y, which are the major fractions of the sum of all reactive nitrogen species, i.e., NO_y=NO+NO_2+HNO_3+PAN. Simulations indicate that great changes in the vertical diffusivity usually occur within the planetary boundary layer (PBL). Daily and monthly mean concentrations of NO_y are much more sensitive to changes in the vertical diffusivity than those of ozone and ozone and NO_y levels only at or in (relatively) clean sites and areas, where long-range transport plays a crucial role, display roughly equivalent sensitivity. The results strongly suggest that a widely-accepted parameterization scheme be selected and the refinement of the model's vertical resolution in the PBL be required, even for regional and long-term studies, and ozone only being examined in an effort to judge the model's performance be unreliable, and NO_y be included for model evaluations.

Key words: Planetary boundary layer，vertical eddy diffusivity parameterization，NO_y, O_3, Acid Deposition and Monitoring Network in East Asia (EANET)

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1. Introduction

For long-term (monthly, seasonal, annual, interannual) and regional (one degree by one degree) studies, horizontal eddy diffusion can be neglected as suggested by Chang et al. (1987). Studies of the impacts of the vertical eddy diffusivity (K_z) parameterization on three-dimensional model results are limited (Russell and Dennis, 2000; Mangia et al., 2002). To investigate the changes in the daily and monthly mean concentrations of O_3 and NO_y due to changes of the K_z parameterization, two parameterization schemes were included in the regional air quality model (RAQM) (An et al., 2002) and the model was run each time with only one scheme, but using the same remaining conditions, e.g., emissions, meteorology, initial and boundary conditions. The two schemes were named A and B. Scheme A utilized the RADM2.6 parameterization scheme (Byun and Dennis, 1995). Specifically, K_z was calculated according to the Monin-Obukhov similarity theory (Businger et al., 1971; Louis, 1979) in the surface layer and computed using the Brost and Wyngaard (1978) method above the surface layer, but within the planetary boundary layer (PBL), the calculations were performed according to the critical Richardson Number and the wind shear in the free troposphere (Chang et al., 1987). An et al. (2002) used Scheme A to simulate the influence of seasonal changes in the precipitation on the distribution patterns of nitrate concentrations over East Asia. Scheme B assumes K_z was equal to 10 m^2 s^{-1} in the entire PBL and 1 m^2 s^{-1} in the free troposphere. The height of the PBL for Scheme B was estimated using Scheme A. The simulation period was defined over the months of January, April, July, and October of 2000. All results were similar, so the simulations for April are presented in this paper. The RAQM model is briefly introduced in section 2. Results and discussion are presented in section 3 and conclusions are given in the final section.

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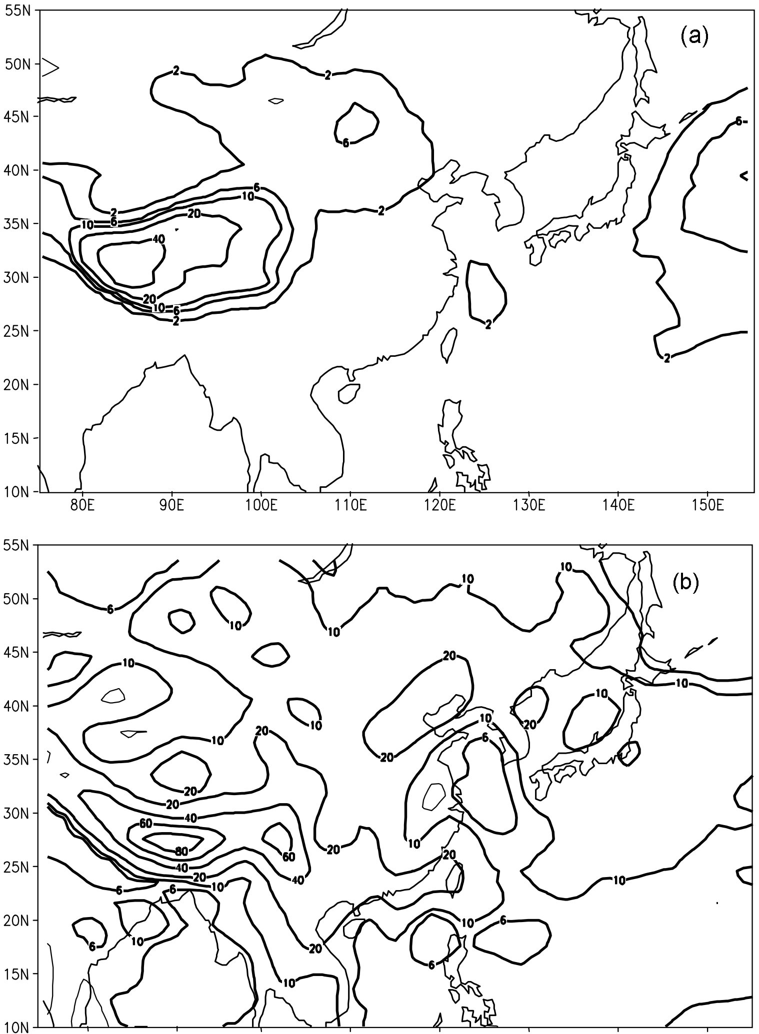

Fig. 1. The simulated distributions in the monthly-mean vertical eddy diffusivity (m^2 s^{-1}) in the (a) first and (b) second model layers above the ground in East Asia in April, 2000.

2. Model description

The RAQM model utilizes a simple but very accurate mass-conserving, peak-preserving algorithm to solve a three-dimensional mass conservation equation via a time-splitting method (Carmichael et al., 1991; Walcek and Aleksic, 1998). The gas chemistry chosen a condensed Carbon-Bond IV mechanism (An et al., 2002). The solution scheme for the chemical mechanism was an appropriate pseudo steady-state approximation (Chang et al., 1987; Carmichael et al., 1991; Odman et al., 1992). The cloud scale was parameterized according to the critical relative humidity (Langmann and Graf, 1997). Dry deposition was calculated by using a modified Wesely's parameterization scheme (Wesely, 1989; Walmsley and Wesely, 1996). Calculated dry deposition velocities for all gas species were bracketed into possible measured ranges (Brook et al., 1999; Wesely and Hicks, 2000). Wet removal processes were simplified by the scavenging ratios (Brodzinsky et al., 1984; Okita et al., 1996). The current model domain covered most of the areas of East Asia (10°–55°N, 75°–155°E), with horizontal grids at 1° × 1° resolution. The vertical extent consisted of 8 layers (0.05, 0.30, 0.75, 1.50, 2.75, 4.50, 6.50, and 8.75 km) with a terrain-following height coordinate. Precipitation, which was corrected via observations, and other meteorological fields (2.5° × 2.5°) four times per day, were taken from National Centers for Environmental Prediction (NCEP, http://www.cdc.noaa.gov/). All NCEP data were interpolated into the 1° × 1° grids and associated vertical layers.

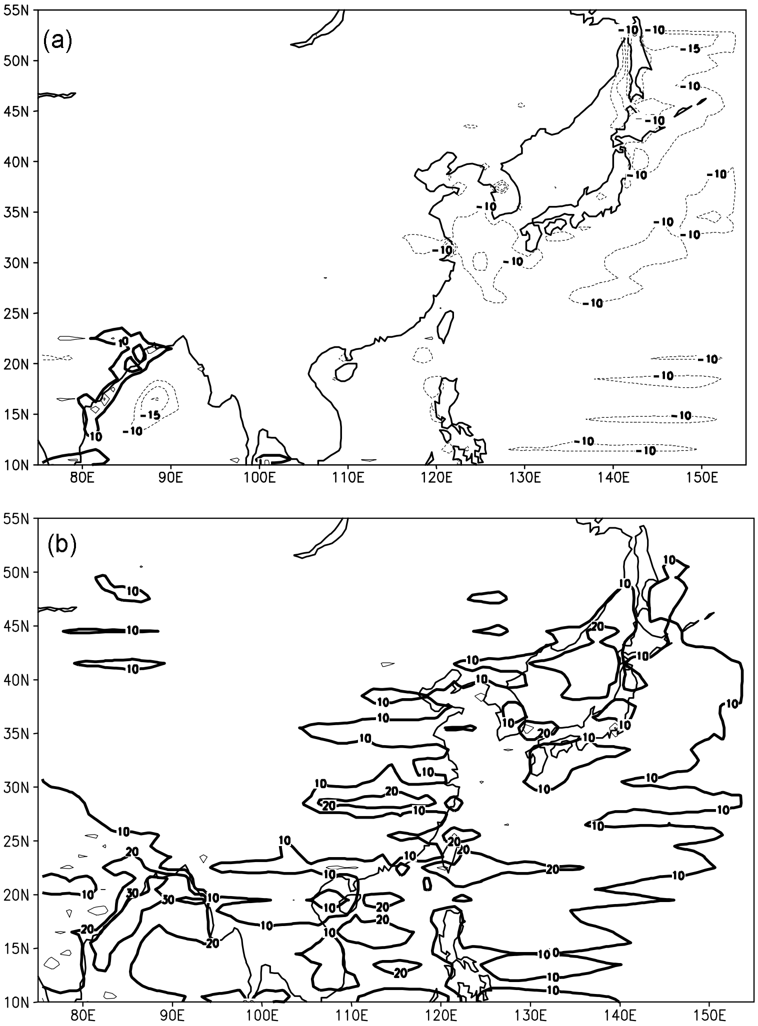

Fig. 2. The relative O_3 deviation (%) between Schemes A and B in the (a) first and (b) second model layers above the ground for the simulations in April 2000.

The initial ozone concentrations (ppb) from the first model layer above land and over sea to the top model layer were set from 40 to 90 and 20 to 90, respectively, and those above the top model layer were set to 100. For the northern and southern boundaries, the ozone values were specified from the suggestions of Carmichael et al. (1998). Other chemical species were set to clean conditions (An et al., 2002). Emissions of NO_x(=NO+NO_2) and volatile organic compounds (VOC) in 2000 were obtained from Klimont et al. (2001). All emissions were released in the first model layer above the ground. Mass-splitting factors for VOC were taken from Carmichael et al. (1998). The other related data were given in An et al. (2002). Three days prior to the simulation period, an initialization run was started with horizontally-uniform, vertically-varying clean conditions (An et al., 2002) and realistic meteorology and emissions.

3. Results and discussion

3.1 *Spatial distribution of monthly mean vertical diffusivity*

The vertical diffusivity showed a remarkable spatial variability within the surface layer (~50 m) (Fig.1a), second layer (~300 m) (Fig. 1b), and third layer (~750 m). The highest eddy diffusivities (~80 m^2 s^{-1}) were found in western China due to the large effects of the high and steep mountains that are found there (Fig. 1). Significant changes in K_z among the three model layers suggest that the vertical resolutions were too coarse (only one or two layers within the PBL) and are unable to fully depict the vertical eddy diffusion processes.

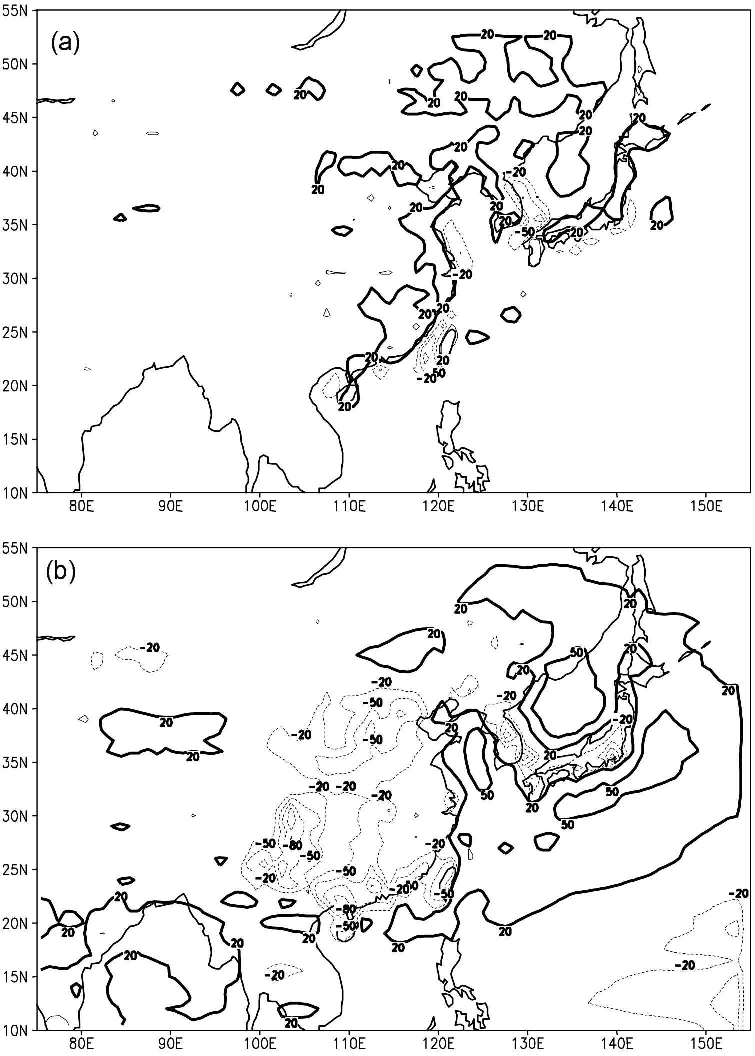

Fig. 3. The relative NO_y deviation (%) between Schemes A and B in the (a) first and (b) second model layers above the ground for the simulations in April 2000.

3.2 *Spatial distribution of monthly averaged concentration deviations of* O_3 *and* NO_y

The deviation in the pollutant concentrations between Schemes A (C_A) and B (C_B) are defined as $(C_A - C_B) \times 100\%/C_A$. The O_3 deviations were usually less than 15% in most areas of the model domain in the surface layer (Fig. 2a). Substantial changes in K_z in the high and steep mountainous areas of Western China (Fig. 1a) did not cause large changes in the ozone levels (Fig. 2a) because the upwind areas were situated far away from the industrialized coastal regions of the mainland of China. Ozone concentrations in the second layer showed an increase (Fig. 2b) with increasing K_z (comparing Figs. 1a and 1b). Similar to those in the surface layer, relative concentration changes in ozone in the third layer were not sensitive to changes in K_z. This was also true under convective meteorological conditions (Nowacki et al., 1996). Reduced vertical diffusion was found to inhibit the vertical mixing of NO_x and VOC and resulted in increases in the surface NO_y concentrations in industrialized regions, i.e., the coastal area of the mainland of China, Korea, and southern Japan and decreases in the NO_y levels (from -20% to 80%) in the neighboring areas that were downwind of these regions (northerly or northwesterly winds were prevalent in April), e.g., the Taiwan Strait and the downwind area near the Korean Peninsula (Fig. 3a). Contrarily, increased vertical diffusion led to substantial decreases (from -20% to -110%) in the NO_y concentrations in the second layer over emission areas, particularly high NO_x emission areas, e.g., Beijing, China, Seoul and Pusan in South

Korea, and Tokyo, Japan and noticeable increases in the NO_y levels (from 20% to 50%) were found in the large downwind areas (Fig. 3b). For the third layer, the value of K_z was less than 2 m^2 s^{-1} and O_3 deviation was less than 5% in most areas in the studied domain (not shown), however, more than 20% of NO_y deviation covered almost the entire domain and more than 50% of that occurred in the coastal region of the Guangdong and Fujian provinces of China and Taiwan (not shown). This demonstrated that NO_y concentrations are much more sensitive to K_z changes than the ozone levels.

3.3 *Variation of daily mean concentration deviations of* O_3 *and* NO_y

The relative concentration changes in NO_y were much more significant than changes in the ozone concentrations in all three model layers, particularly in the second, corresponding to the remarkable K_z changes (comparing Figs. 1a–b) observed at all of the selected sites. An example of this is the NO_y deviation at Zhuxian Cavern Site of Zhuhai, which fluctuates within a large range of 0 to 200% (Fig. 4a). Compared to the other selected sites, e.g., the Zhuxian Cavern of Zhuhai, the Hedo site exhibits a roughly equivalent amplitude in ozone and NO_y concentration deviations (Fig. 4b). Very low local emissions of NO_x at this site (An et al., 2002) suggest that long-range transport plays a central role in the changes in both the ozone and NO_y concentrations.

3.4 *Comparison of observations and simulations*

3.4.1 *Monitoring sites of EANET used for model comparison*

The Acid Deposition Monitoring Network in East Asia (EANET, http://www.adorc.gr.jp) has collected observation data from all participating countries since 1999. The ten participating countries are China, Indonesia, Japan, Malaysia, Mongolia, the Philippines, South Korea, Russia, Thailand, and Vietnam. They have carried out this monitoring on wet deposition, dry deposition, soil and vegetation, and inland aquatic environments based on their own national monitoring plans. Though the monitoring methods followed the Monitoring Guidelines and the Technical Manuals of the Network, quality control of the data is one of the most important issues of the EANET. The Quality Assurance/Quality Control (QA/QC) programs were therefore developed. The Inter-laboratory Comparison (a round-robin analysis survey of uniformly prepared artificial rainwater samples) has been conducted among the analytical laboratories of EANET, as one of the primary QA/QC activities. The major purpose of the inter-laboratory comparison was to recognize the analytical precision and accuracy of the data from each participating laboratory and give an opportunity to improve the quality of the analysis (Otoshi et al., 2001). Artificial rainwater samples that contained major ions were prepared and distributed by the network center of EANET. Most of the participating laboratories submitted their analytical data and the obtained data for pH, electrical conductivity and SO_4^{2-}, NO_3^-, Cl^-, NH_4^+, Ca^{2+}, Mg^{2+}, Na^+, and K^+ concentrations were compared with prepared values and treated statistically. Others can be seen from the web site of EANET. Most of the sites are remote (Table 1), which may provide a good representation of the regional air pollution.

3.4.2 *Comparison of the daily mean concentrations of* O_3 *and* NO_2 *in the air and monthly mean nitrate concentrations in rainwater*

For comparison with observations, Scheme A was adopted in the RAQM. Figure 5a indicates that the ozone concentration fluctuations at the Sado-seki and Oki sites in Japan were well captured, while the amplitude of the simulated ozone levels was substantially

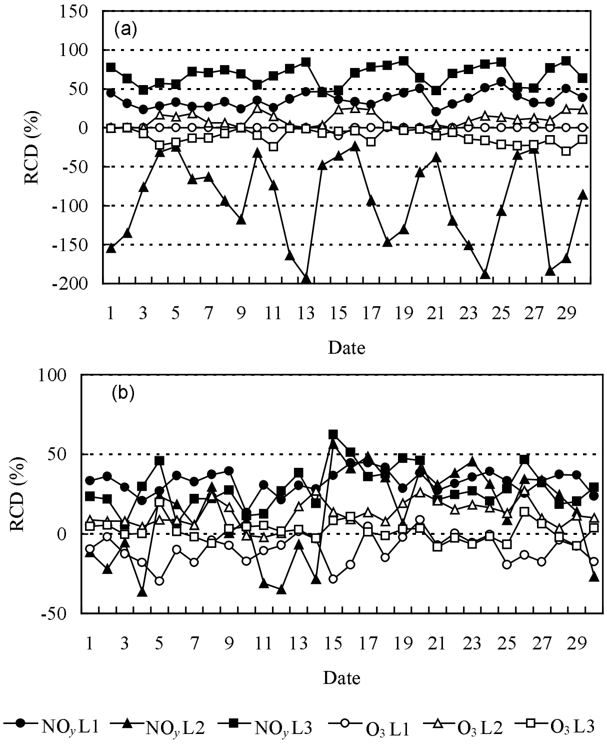

Fig. 4. The daily variations in the relative concentration deviations (RCD) of O_3 and NO_y between Schemes A and B in the first three model layers (L1, L2, and L3) above the ground at (a) Zhuxian Cavern of Zhuhai and (b) Hedo sites in April 2000.

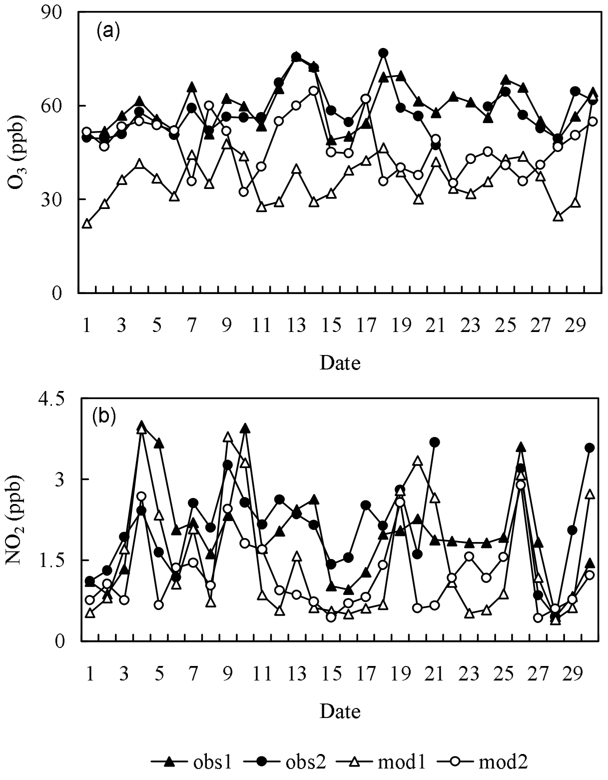

Fig. 5. Time-series comparison of the observed and simulated concentrations of (a) O_3 and (b) NO_2 at Sado-seki (1) and the Oki (2) Islands of Japan in April 2000.

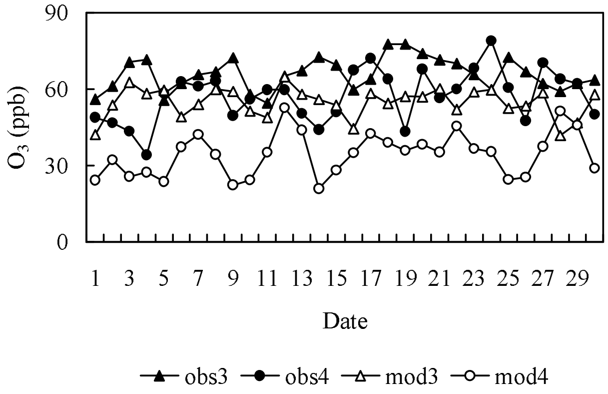

Fig. 6. Time series comparison of the observed and simulated concentrations of O_3 at the Happo (3) and Hedo (4) sites in Japan in April 2000.

underestimated at the Sado-seki site. This was the result of a combination of the coarse horizontal reslutions (1° × 1°), uncertainty in the emission, e.g., exclusions of natural emissions and the uncertainty of the initial chemical species concentrations. The spatial variations in the ozone concentrations were large and the ozone observations were generally limited for a large studied domain, so the initial ozone concentrations are usually assumed to be horizontally uniform and vertically varying. This may influence the ozone simulations at some of the other sites (An et al., 2002). NO_2 simulations at Sado-seki followed observations quite well (Fig. 5b). For the Oki site, the timing of the peaks in the NO_2 concentration was accurately captured and the amplitude was simulated quite well (Fig. 5b). The O_3 concentrations at the Happo site was well predicted, and those at the Hedo site were underestimated, although the monitored daily variation patterns were well captured (Fig. 6). NO_x emissions at the Hedo site were very low (An et al., 2002) and long-range transport contributed much to the variations in the ozone concentrations. The monthly-averaged nitrate concentrations in the rainwater at the Happo and Yusuhara sites, which are situated in the neighboring industrialized areas of Japan (An et al., 2002), showed noticeable overestimation when compared to the observations (Fig. 7) due to the coarse horizontal resolution (1° × 1°). The uncertainty in the NO_x and VOC emissions at sites 2 (Dabagou of Xi'an) and 14 (Hoa Binh), as mentioned above, were the major reasons for the considerable under-prediction of the nitrate concentrations there (Fig. 7). In most cases, the simulations of the nitrate concentrations fit the observations quite well with a discrepancy of less than a factor of 2 (Fig. 7).

4. Conclusions

The choice of widely accepted parameterization schemes for the simulation of the vertical eddy diffusivity (K_z) was strongly suggested even for regional and long-term studies. The great changes in K_z usually occurred within the PBL, so the refinement of the model vertical resolutions in the PBL was needed.

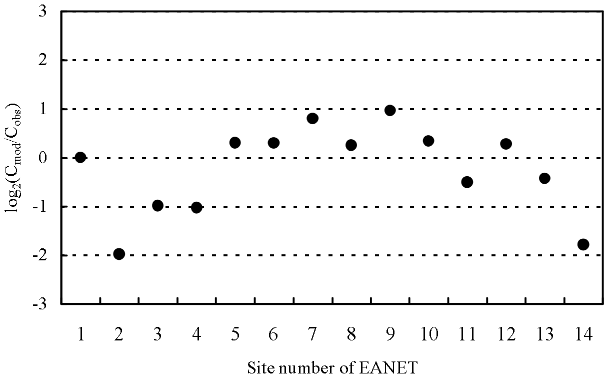

Fig. 7. A logarithmic plot of the ratios between the volume-averaged calculated (C_{mod}) and observed (C_{obs}) nitrate concentrations in the rainwater at the monitoring sites in April 2000.

Table 1. 14 monitoring sites of EANET used for model comparison.

Site	Name of sites	Latitude(N)	Longitude(E)	Characteristics	Country
1	Nanshan of Chongqing	29°49′	106°22′	Rural	China
2	Dabagou of Xi'an	33°50′	108°48′	Remote	China
3	Xiaoping of Xiamen	24°51′	118°02′	Remote	China
4	Zhuxian Cavern of Zhuhai	22°12′	113°31′	Urban	China
5	Tappi	41°15′	141°21′	Remote	Japan
6	Sado/Sado-seki	38°15′	138°24′	Remote	Japan
7	Happo	36°41′	137°48′	Remote	Japan
8	Oki	36°17′	133°11′	Remote	Japan
9	Yusuhara	32°44′	132°59′	Remote	Japan
10	Ogasawara	27°05′	142°13′	Remote	Japan
11	Hedo	26°47′	128°14′	Remote	Japan
12	Lake Ijira	35°34′	136°42′	Rural	Japan
13	Kosan	33°17′	126°10′	Remote	South Korea
14	Hoa Binh	20°49′	105°20′	Rural	Vietnam

Steep and high mountains were found to have a significant impact on K_z variations. Daily and monthly mean concentrations of NO_y depended significantly on the changes in K_z. Only at relatively clean sites, where long-range transport contributed much to the changes in the ozone and NO_y concentrations, exhibited ozone and NO_y levels roughly similar sensitivity to changes in K_z. This implies that by examining the ozone concentration alone as a means of judging a model's performance, is at least partially unreliable and that NO_y concentrations should be included for the model evaluations. The daily-averaged levels of the ozone or NO_2 concentrations at several selected sites were well simulated and the synoptic-scale changes were reasonably captured. The monthly-mean nitrate concentrations generally agreed well with the observations, with the differences falling within a factor of 2.

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