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ScienceDirect
Journal of Environmental Sciences 2011, 23(7) 1150–1157

JOURNAL OF ENVIRONMENTAL SCIENCES
ISSN 1001-0742
CN 11-2629/X
www.jesc.ac.cn

Ozone sensitivity analysis with the MM5-CMAQ modeling system for Shanghai

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Received 15 August 2010; revised 12 April 2011; accepted 25 April 2011

Abstract

Ozone has become one of the most important air pollution issues around the world. This article applied both O_3/(NO*y*-NO*x*) and H_2O_2/HNO_3 indicators to analyze the ozone sensitivity in urban and rural areas of Shanghai, with implementation of the MM5-CMAQ modeling system in July, 2007. The meteorological parameters were obtained by using the MM5 model. A regional emission inventory with spatial and temporal allocation based on the statistical data has been developed to provide input emission data to the MM5-CMAQ modeling system. Results showed that the ozone concentrations in Shanghai show clear regional differences. The ozone concentration in rural areas was much higher than that in the urban area. Two indicators showed that ozone was more sensitive to VOCs in urban areas, while it tended to be NO*x* sensitive in rural areas of Shanghai.

Key words: ozone sensitivity; indicators; Shanghai

DOI: 10.1016/S1001-0742(10)60527-X

Citation: Li L, Chen C H, Huang C, Huang H Y, Zhang G F, Wang Y J et al., 2011. Ozone sensitivity analysis with the MM5-CMAQ modeling system for Shanghai. Journal of Environmental Sciences, 23(7): 1150–1157

Introduction

Shanghai is the most important economic center in China. It hosts around 19 million residents and occupies 6340 km^2. The GDP and per capita GDP of Shanghai reached 1505 billion CNY and 78,989 CNY, respectively, in 2009 (Shanghai Statistical Yearbook, 2010). This represents an increase of almost 2.5 times during the period 2000–2009 (Shanghai Statistical Yearbook, 2001). Such a fast pace of economic growth drives high growth in energy consumption, and thus huge air pollutant emissions (Zhang et al., 2009), which causes the secondary air pollution becoming worse. Regional visibility is decreasing and ozone concentration is increasing, especially in summer. Ozone is considered to be one of the most serious air pollutants of concern in the United States, as well as in most metropolitan areas around the world (Streets et al., 2007), and it has attracted much interest for its impact on people's health. Many observations (Shan et al., 2008; Wang et al., 2001, 2005) show that high ozone concentrations have begun to appear in eastern China. Wang et al. (2003) found that the occurrence frequency of ozone concentration higher than 160 $\mu g/m^3$ reached 20% in some sites of the Yangtze River Delta (YRD). Tang et al. (2008) found that 167 high ozone days with daily one hour ozone concentrations higher than 104 $\mu g/m^3$ occurred in 2006 in Shanghai.

Ozone is formed through a serious of complex chemical reactions from the mixture of reactive volatile organic compounds (VOCs) and nitrogen oxides (NO*x*). The ratio of these two ingredients determines how much ozone is formed. Ozone increases rapidly between 9:00 am and 3:00 pm related to the average lifetime of the most reactive VOC compounds, which dominate the reactivity of hydroxyl radical (OH·), and start to decrease in the late afternoon, when its loss processes catch up with formation. During the nighttime, continuous nitrogen monoxide (NO) emissions gradually titrate ozone, forming high NO_2 mixing ratios. Under significant ozone and NO_2 abundances, these species slowly react to form NO_3· radicals, which serves as equivalent to daytime OH· at night, oxidizing hydrocarbons. In this way, NO*x* can be oxidized to NO*z* at night. Once the sun comes up, NO_3 is rapidly photolyzed. Thus, the control of O_3 is a complicated problem due to the nature of the non-linear formation of O_3 (Seinfeld and Pandis, 1998). Due to different emission characteristics of the precursors, the control of ozone may differ with regions. Many studies on the complex formation processes of ozone have been made (Geng et al., 2007; Ran et al., 2011; Tang, 2004; Tie et al., 2006; Wang and Li, 2002; Xu et al., 2006;

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Xu and Zhang, 2006; Zhao et al., 2004;). However, since Shanghai occupies a large area, the emissions rates, emission characteristics of the ozone precursors vary greatly. This means that the ozone formation mechanism differs with areas in Shanghai. Studies on the ozone sensitivity at different sites in Shanghai are quite limited up to now. With development of the numerical air quality models, using indicators to study the ozone sensitivity in different regions becomes more possible. In this study, we chose two sites representing the rural and urban areas of Shanghai respectively, and applied H_2O_2/HNO_3 and $O_3/(NOy\text{-}NOx)$ ratios to study the ozone sensitivity characteristics. The results are helpful for guiding the development of ozone control strategies to be made in Shanghai.

1 Materials and methods

The methodology used in this article is to simulate the atmospheric processes over both Shanghai and its surrounding areas using the Models-3/Community Multiscale Air Quality (CMAQ) modeling system (Version 4.4), developed by the US EPA (Byun and Ching, 1999). The CMAQ model is used for regional- and urban-scale air quality simulations, integrating a number of air quality issues (particulate matter, ozone, acid deposition, visibility, etc.) into a so-called "one-atmosphere" approach. The driving meteorological inputs for this work are provided by the fifth-generation NCAR/Penn State Mesoscale Model (MM5), version 3.6.2, and the meteorology-chemistry interface processor (MCIP) was used to transfer MM5 output into gridded meteorological field data as the input to CMAQ. The Carbon Bond – IV chemical mechanism (CB-IV) was used in the CMAQ model, which consists of 36 chemical species, 93 chemical reactions, and 11 photochemical reactions (Lamb, 1982). Geographic Information System (GIS) technology is applied in gridding the regional emission inventory to the model domain.

1.1 Model domain and simulation episodes

The model domain is based on a Lambert Conformal map projection, using a one-way nested mode with 81 km (covering all China, Japan, Korea, parts of India and Southeast Asia); 27 km (covering eastern China); 9 km (covering major city-clusters including Shandong Province, the Yangtze River Delta (YRD) and the Pearl River Delta (PRD)) and 3 km (covering most of the YRD area, with Shanghai in the center) grid resolutions respectively. The large domain is centered at (118°E, 32°N). The YRD domain has 99 × 102 horizontal grid cells. The model domain is shown in Fig. 1.

The pollution episode is from July 21–30, 2007, when the photochemical reaction is very active and regional air pollution is significant. The initial conditions were prepared by running the model five days ahead of the period starting with a clean initial condition. The model employs 14 vertical layers of varying thickness with denser layers in the lower atmosphere to better resolve the mixing height.

1.2 Regional emission inventory

Since one-way nested modeling is used in this study, emission inventories for different simulation domains need to be prepared. In this work, the anthropogenic emissions in Shanghai in 2007 are based on the pollution source survey launched in China in 2007, which was a national scale anthropogenic pollution source investigation, including major air pollution sources like power plants, industry, vehicles and residential sources. The regional emission inventory in the YRD is built using emission factors and local statistics (Jiangsu Statistical Yearbook, 2008;

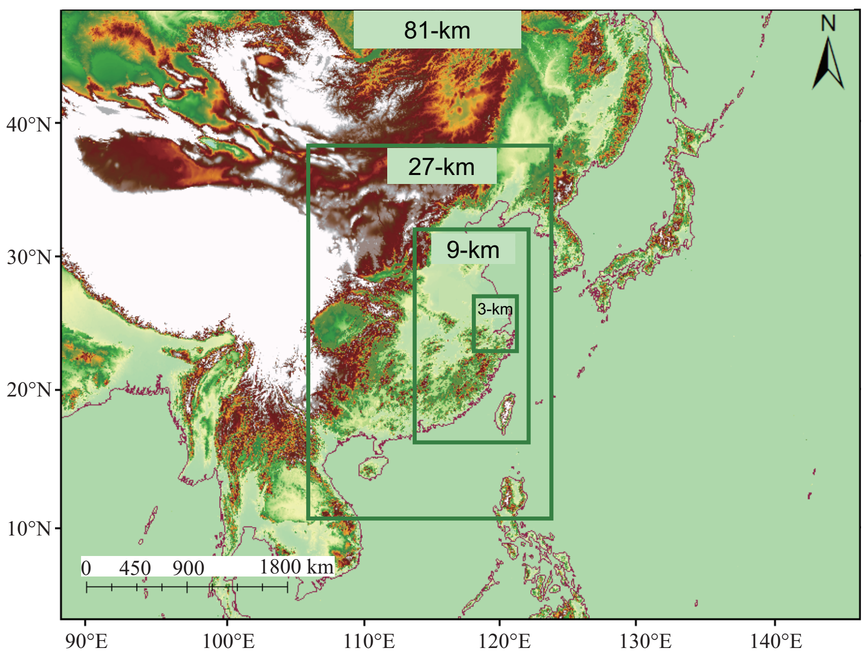

Fig. 1 One-way nested model domain.

Zhejiang Statistical Yearbook, 2008). Supporting data on emission factors and related activity data were assembled from related studies (Streets et al., 2001, 2003a, 2003b; US EPA, 2006; MEP, 1996). The main sources considered in the anthropogenic emission inventory in the YRD in 2007 include industry, transportation, residential and agriculture sectors. The emission sources of the industry sector include the emissions from fuel combustion processes of power plants, boilers, furnaces, kilns, and non-combustion processes such as iron and steel manufacturing, oil refining, cement producing. Transport emission sources mainly consist of vehicle exhaust and road dust emissions. The residential emission sources cover residential fuel combustion emissions, domestic paint and solvent use, gas evaporation in the service stations, etc. The agriculture emission sources include the emissions from livestock feeding, fertilizer application and biomass burning. Huang et al. (2011) has reported detailed information about development of the emission inventory in the Yangtze River Delta.

Emissions of the area outside the YRD are taken from the INTEX-B emission inventory (Zhang et al., 2009). This emission inventory is the latest one that can be found for China. The energy consumption has increased from 2006 to 2007, and thus emissions may also be different between the two years. However, we do not have an updated emission inventory that could be used. The previous version of the INTEX-B emission inventory has been described and demonstrated to be reliable for China in previous studies (Carmichael et al., 2003; Streets et al., 2003a, 2003b).

Table 1 summarizes the emissions used in the modeling for 16 major cities in the YRD. The total anthropogenic VOCs emissions in the YRD in 2007 were around 2767 kilo tons, which mainly comes from non-combustion sources, including oil refining, chemical producing, and fugitive emissions from paint and solvent use in industry, sharing 9%, 30%, and 20% of the total, respectively. In addition, vehicle emission and fugitive emissions from domestic paint and solvent use contribute 15% and 14% of total VOCs emission, respectively. For biogenic VOCs emissions, this paper used the natural VOCs emission inventory of GEIA Global Emissions Inventory Activity 1990 (http://geiacenter.org). In July, total biogenic VOCs emissions in Shanghai were 3286 tons, taking a share of 23% of the total biogenic emissions in the YRD.

1.3 Volatile organic compounds (VOCs) speciation

The VOCs speciation is one of the most important factors that influence the ozone simulation results. The VOCs sources include refinery process, chemical process, industrial use of paint and solvent, vehicle exhaust, domestic use of paint and solvent, gas evaporation, biomass burning and biogenic emissions. Some local experimental results of coking industry and vehicle exhaust were adopted to determine the source profiles, and parts of the studies have been published previously (Jia et al., 2009; Lu et al., 2010). The VOCs speciation for other sources without local measurement in the modeling work is mainly compiled based on a literature survey (Liu et al., 2008; Wang et al., 2008; Yuan et al., 2010). The VOCs species are then inserted into the CB-IV mechanism in the CMAQ model.

1.4 Model verification

Figure 2 shows comparisons between observed and modeled meteorological parameters including temperature, wind speed, wind direction and relative humidity during the period of July 21–30, 2007. The figure gives average data of six meteorology monitoring sites, including Xujiahui, Nanhui, Qingpu, Baoshan, Jinshan and Minhang. The average bias of temperature, humidity, wind speed and wind direction are 0%, –12%, 15% and –5% respectively. Hourly comparisons of the meteorological parameters show that MM5 can reflect the variation trends of the major meteorological conditions. The selected parameters adopted in MM5 can be used in the pollutant concentration simulation.

Figure 3 shows a comparison between observed and modeled NO_2 concentrations at four national observational sites including Putuo, Xuhui, Luwan and Weifang

Table 1 Emissions of major anthropogenic species in the YRD in 2007

Province	City	Area (km^2)	Total anthropogenic emissions (kilo ton)				
			SO_2	NO_x	PM_{10}	$PM_{2.5}$	VOCs
Jiangsu	Suzhou	1650	174.0	368.6	389.2	208.1	483.3
	Nantong	355	73.0	90.5	111.6	56.8	87.7
	Wuxi	1623	217.0	183.7	347.5	167.8	191.7
	Changzhou	1872	108.0	90.7	211.6	98.8	73.2
	Taizhou	444	20.0	52.5	64.9	31.2	62.8
	Zhenjiang	1082	60.0	103.3	208.3	96.4	45.9
	Yangzhou	980	32.0	110.4	81.8	48.3	58.1
	Nanjing	4723	148.0	144.2	255.9	129.7	153.2
Zhejiang	Jiaxing	3915	116.0	114.3	219.7	97.4	58.0
	Huzhou	5818	78.0	71.5	190.0	83.2	53.7
	Ningbo	9816	158.0	211.0	211.6	111.6	150.3
	Zhoushan	1440	4.0	15.7	10.4	6.1	17.9
	Shaoxing	8256	120.0	105.0	196.8	88.2	287.3
	Hangzhou	16596	131.0	134.5	282.0	129.3	391.6
	Taizhou	9411	29.0	117.1	69.1	38.5	66.0
Shanghai		6340	208.0	380.0	265.5	119.2	586.9
16 cities in the YRD		74321	1676.0	2293.0	3115.9	1510.6	2767.6

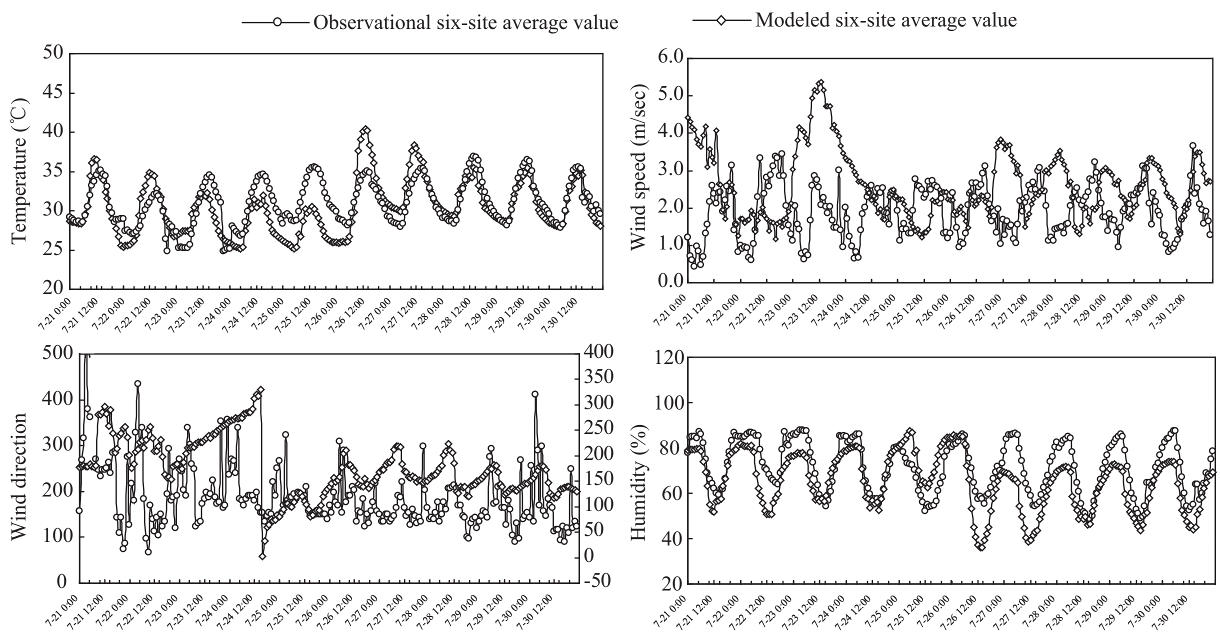

Fig. 2 Comparisons of meteorological parameters between model and observational data during July 21–30, 2007.

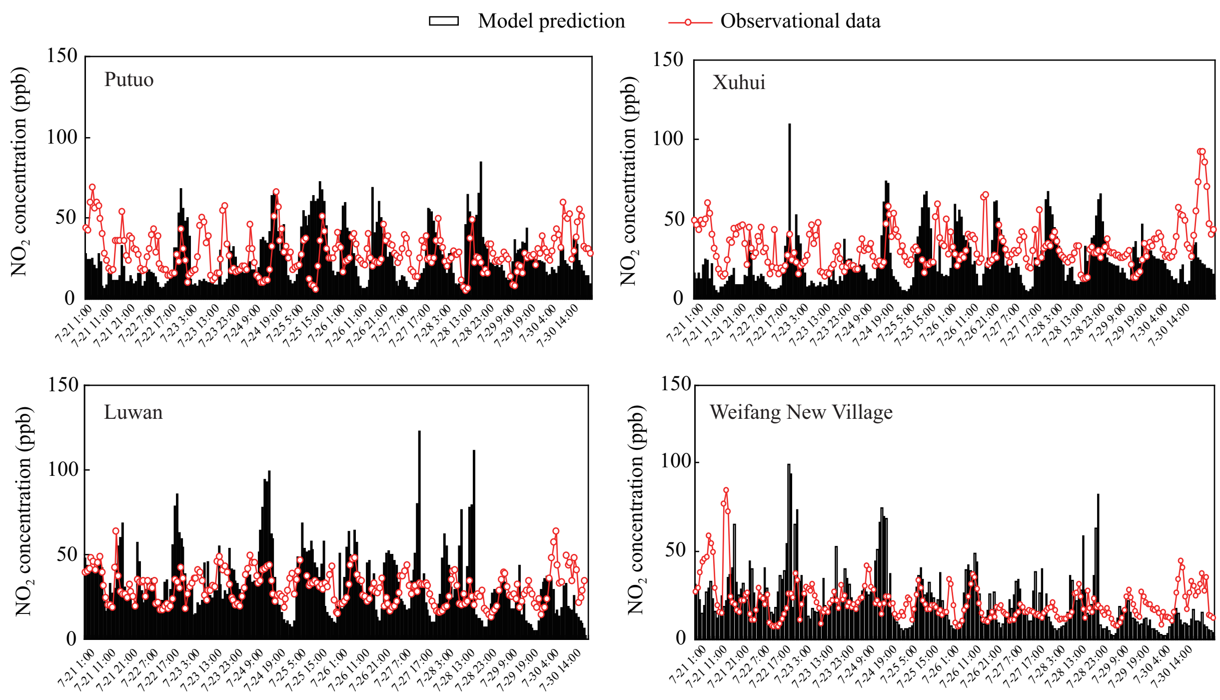

Fig. 3 Comparison of CMAQ model simulations for NO_2 concentrations against observations.

New Village Sites during July 21–30 in 2007. Generally speaking, the modeled data of CMAQ are similar to the observational pollutant trends. The emission inventory of NO_2 in the YRD in 2007, the meteorological field and the modeling results of CMAQ could reflect the NO_2 pollution situation in the YRD.

Figure 4 shows the comparisons between the calculated and observed data of O_3 hourly concentrations at the four national observational sites during July 21–30 in 2007. The results show that the model can well reflect the daily changes of O_3 concentration. With increase of radiation, O_3 concentration rises; while in the afternoon, with decrease of radiation, O_3 concentration gradually declines. The O_3 concentration gradually decreases and even disappears in the evening. As is shown in the figure, there is still discrepancy between the observed and computed values of ozone concentrations, which might be caused by the out-of-dated biogenic VOCs emissions. As is known, biogenic VOCs contribute significantly to the ozone formation, since the ISOP and TERPB are very active in atmospheric chemistry reactions. However, the biogenic VOCs emissions are based on GEIA, which uses emission data for 1990, possibly quite different from the current situation. The update of biogenic VOCs emissions will be done in a future study. In addition, the calculated O_3 concentrations at midnight are not as low as expected,

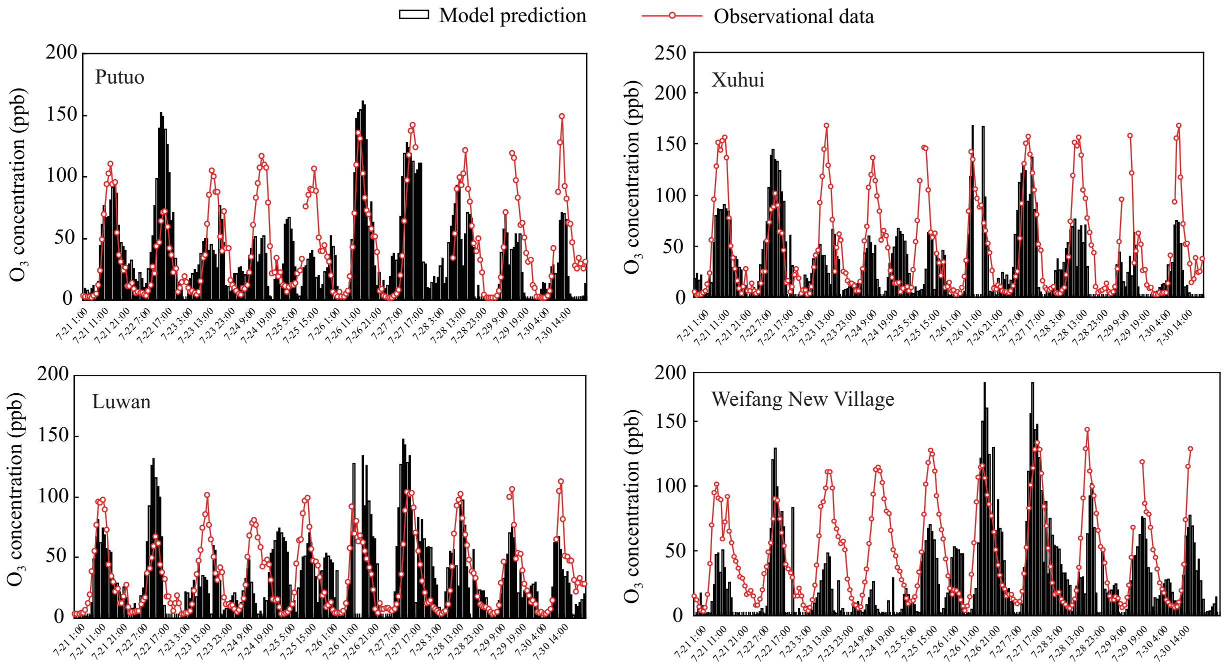

Fig. 4 Comparison of CMAQ model simulations for O_3 concentrations against observations.

which is due to the PBL height simulation by MM5. In this work, the MRF parameters are adopted in MM5 modeling, which gives high PBL height in daytime and low PBL at night. This systematic error causes that the ozone concentration at daytime to be too low while is higher than the observations at night time.

1.5 Ozone sensitivity analysis

The photochemical reactions producing ozone are propagated by cycling of HO*x* radicals. The pathway for HO*x* loss is determined by the relative abundance of HO*x* and NO*x*. Ozone production tends to be either NO*x*-sensitive if HO*x*-loss occurs primarily by self reaction of peroxy radicals, or NO*x*-saturated if the primary HO*x*-loss pathway is via reaction of NO and OH (Sillman et al., 1990). Three indicators for ozone formation sensitivity, including O_3/(NO*y*-NO*x*), HCHO/NO*y* and H_2O_2/HNO_3 have been developed (Sillman and Samson, 1995; Sillman and He, 2002). Related ozone sensitivity studies show that the ratios are good indicators for regions that are sensitive to either NO*x* or VOCs emissions changes (Chen, 2002). In addition, the ratios indicate the degree of ozone response to changes in precursor emissions.

To understand the ozone formation mechanism in different areas of Shanghai, this study applied O_3/(NO*y*-NO*x*) and H_2O_2/HNO_3 indicators to study the sensitivity of ozone. Regions with a higher ratio have a higher degree of NO*x* emission sensitivity, while regions with a lower ratio have a higher degree of VOCs emission sensitivity. In buffer areas, the O_3/(NO*y*-NO*x*) is between 8–10 and H_2O_2/HNO_3 is between 0.35–0.6. To obtain the difference of ozone sensitivity at urban and rural sites in Shanghai, this study chooses Dianshan Lake (DSL) as a representative site of rural areas and Jiang'an (JA) as a representative site of urban areas. Locations of the two representative sites are shown in Fig. 5.

Fig. 5 Locations of the two representative sites in Shanghai.

2 Results and discussions

2.1 Difference of ozone concentrations at rural and urban sites

The modelling system indicates that the ozone concentration in Shanghai shows great difference between rural and urban areas. Figure 6 shows the modeled hourly ozone concentrations at Dianshan Lake and Jing'an sites during July 21–30, 2007. It is obvious that the ozone concentration at Dianshan Lake is higher than that at Jing'an. The average ozone hourly concentrations at Dianshan Lake and Jing'an during the modelling episode are 65.25 and 35.40 ppb, respectively. The average ozone hourly concentration at Dianshan Lake is 46% higher than that at Jing'an. The average concentration of ozone at 14:00 on each day

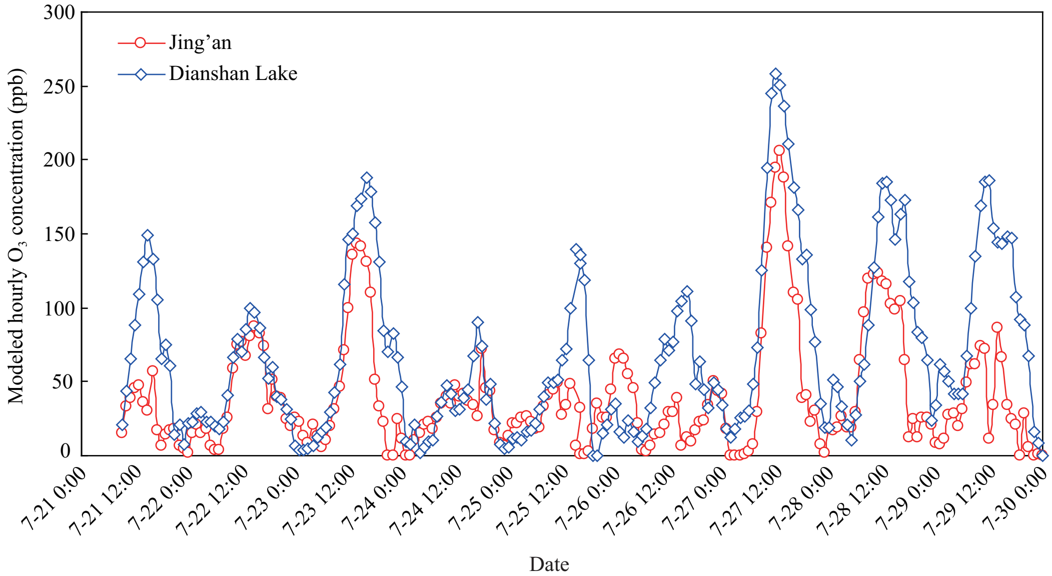

Fig. 6 Modeled hourly ozone concentrations at two sites in Shanghai during Jul 21–30, 2007.

during July 21–30, 2007 at Dianshan Lake is 129.72 ppb, which is 28% higher than the Grade II National Ambient Air Quality Standard. The average concentration of ozone at 14:00 on each day during July 21–30, 2007 at Jing'an is 79.58 ppb, which is 39% lower than that at Dianshan Lake. Results show that the ozone concentrations in rural areas are generally higher than those in urban areas, and the exceedance rate of ozone concentration in rural areas should be paid more attention to. The main reason causing this ozone distribution characteristic is that the ozone is a secondary air pollutant, which is produced through photochemical reactions of NO*x*, VOCs, and CO in the presence of sunlight. The formation of ozone is influenced by the emissions of precursors like NO*x*, VOCs, and the solar radiation intensity. In the urban area of Shanghai, the emissions of NO*x* and VOCs are significant, which produces high ozone concentration in daytime and it is then transported to the rural area. During the night time, the high NO emissions in the urban area gradually titrate ozone, which causes the ozone concentration becoming lower. However, the NO emissions in the rural area are much lower, which preserves the high ozone concentration.

2.2 Ozone sensitivity distribution in Shanghai areas

Figure 7 shows distributions of the average value of O_3/(NO*y*-NO*x*) and H_2O_2/HNO_3 at 14:00 during July 21–30, 2007 in Shanghai, modeled by MM5-CMAQ modeling system. As is shown in the figure, the average O_3/(NO*y*-NO*x*) and H_2O_2/HNO_3 values during the modeling period within the inner-ring road region is generally lower than 8 and 0.6 respectively, which indicates that in the urban area, the ozone is more sensitive to VOCs. However, in the southeast of Shanghai, the area surrounding Dianshan Lake, and East Chongming District, which represents sub-urban areas, the average O_3/(NO*y*-NO*x*) and H_2O_2/HNO_3 values are higher than 10 and 0.6 respectively, showing that ozone is more sensitive to NO*x* emissions. Thus, to control ozone pollution in Shanghai, different emission control strategies should be made with consideration of the characteristics of different regions.

2.3 Ozone sensitivity at rural and urban sites

The formation mechanism of ozone indicates that the ozone sensitivity in a specific region depends on both the

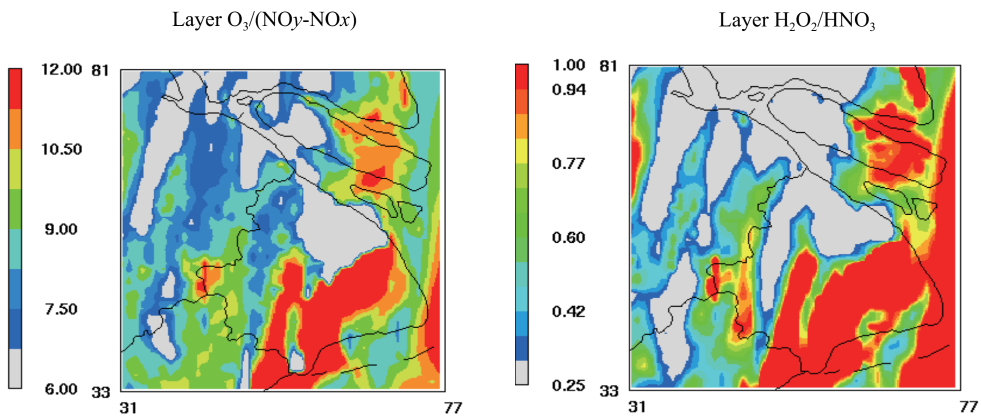

Fig. 7 Modeled distribution of two ozone formation sensitivity indicators in July, 2007.

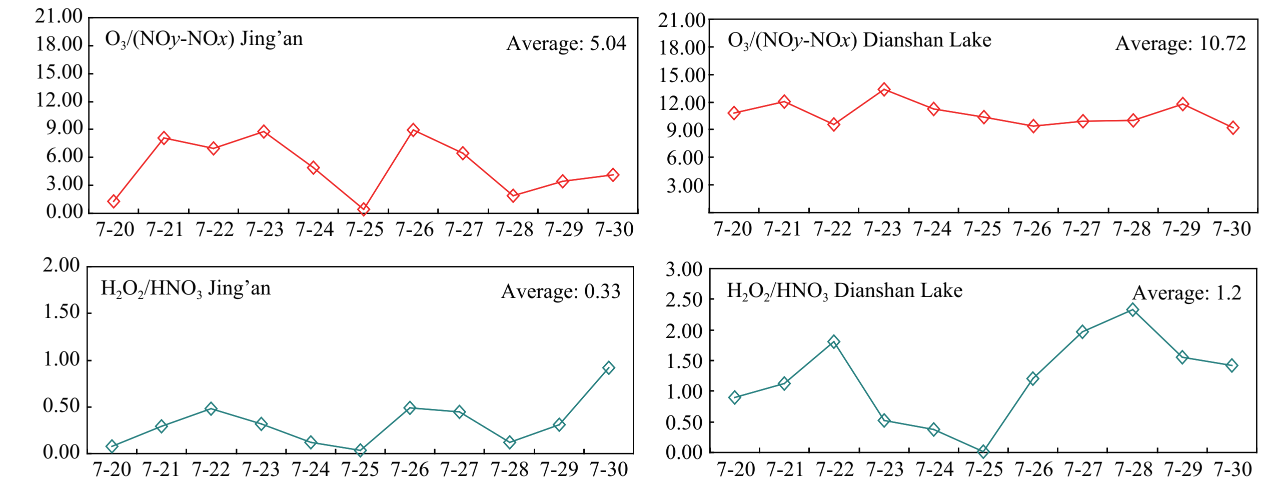

Fig. 8 Modeled indicators at Dianshan Lake and Jing'an sites at 14:00 during July 20–30, 2007.

NO*x*, VOCs concentrations, and the reactivity characterization of each VOC compound. Quantifying the ozone sensitivity with the O_3/(NO*y*-NO*x*) and H_2O_2/HNO_3 ratios takes both factors into consideration. High ratio of both the indictors represents that the VOCs catalyst is over abundant, and the control strategy favors NO*x* control. However, low ratio of the indicators shows that the NO*x* is higher than the optimum ozone production level, and the control strategy favors VOCs control.

Both O_3/(NO*y*-NO*x*) and H_2O_2/HNO_3 ratios for the two representative locations in Shanghai were calculated during high ozone concentration episodes. Figure 8 gives the O_3/(NO*y*-NO*x*) and H_2O_2/HNO_3 indicators at Dianshan Lake and Jing'an sites at 14:00 from July 21–30, 2007. From this figure, it can be seen that the O_3/(NO*y*-NO*x*) value at Jing'an site varies from 0 to 9, with an average value of 5.04, where O_3 is obviously sensitive to VOCs according to Sillman's measure. On the other hand, most of the H_2O_2/HNO_3 values at the Jing'an site are between 0–0.5, with the average value of 0.33, which also shows that the Jing'an site belongs to VOCs control areas. However, the Dianshan Lake site is quite different from Jing'an. The O_3/(NO*y*-NO*x*) values at Dianshan Lake are between 9–13, with the average of 10.72, where O_3 is significantly sensitive to NO*x*. And most of the H_2O_2/HNO_3 values at the Dianshan Lake site are between 0.5–2.5, with the average value of 1.2, which also indicates that the Dianshan Lake site belongs to NO*x*-sensitive areas. From the modeling results, it can be concluded that the urban area in Shanghai belongs to VOCs control areas, while the rural area tends to be NO*x*-sensitive.

The ozone sensitivity analysis with application of O_3/(NO*y*-NO*x*) and H_2O_2/HNO_3 ratio in this study compared well with other studies in the literature. This result agrees with the work of Geng et al. (2008), who applied a chemical mechanism model (NCAR-MM) to assess the ozone sensitivity in Shanghai, and found that the ozone formation is clearly under VOC-sensitive regime in the urban city of Shanghai, where the O_3 production is strongly depressed by high NO*x* concentrations, resulting in lower O_3 concentration in center of the city than in rural areas.

3 Conclusions

This article applies the MM5-CMAQ modeling system to a regional air pollution study in the Yangtze River Delta with Shanghai in the center. The model performance study shows that the system can well reflect the air pollution situation in this region. Modeling results indicate that the ozone concentration shows an obvious regional difference. The ozone concentration in rural areas (taking Dianshan Lake site as the example) is higher than that in the urban area (taking Jing′an site as the example).

The design of control strategies for surface ozone has been impeded by limited observations of O_3-NO*x*-VOC sensitivity (Sillman, 1999). This article uses a model-based indicator method to characterized O_3-NO*x*-VOC sensitivity in Shanghai. Two indicators including O_3/(NO*y*-NO*x*) and H_2O_2/HNO_3 show that ozone is more sensitive to VOCs in urban areas like Jiang'an, and tends to be NO*x* sensitive in rural areas like Dianshan Lake.

Shanghai and the Yangtze River Delta are presently undergoing tremendous economic growth, and the threats of high regional pollutant emissions and high ozone pollution are very real. However, the ozone pollution issue may have different characteristics in different regions. Thus, measures to reduce the ozone concentrations should be carefully made.

Acknowledgments

This work was supported by the Chinese National Key Technology R&D Program (No. 2009BAK43B33). The authors would like to thank US EPA for providing the CMAQ model code, full model documentation, and assistance with model set-up and running.

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