Application of WRF/Chem over East Asia:

Part I. Model Evaluation and Intercomparison with MM5/CMAQ

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Abstract

In this work, the application of the online-coupled Weather Research and Forecasting model with chemistry(WRF/Chem) version 3.3.1 is evaluated over East Asia for January, April, July, and October 2005 and compared with results from a previous application of an offline model system, i.e., the Mesoscale Model and Community Multiple Air Quality modeling system (MM5/CMAQ). The evaluation of WRF/Chem is performed using multiple observational datasets from satellites and surface networks in mainland China, Hong Kong, Taiwan, and Japan. WRF/Chem simulates well specific humidity (Q2) and downward longwave and shortwave radiation (GLW and GSW) with normalized mean biases (NMBs) within 24%, but shows moderate to large biases for temperature at 2-m (T2) (NMBs of -9.8% to 75.6%) and precipitation (NMBs of 11.4-92.7%) for some months, and wind speed at 10-m (WS10) (NMBs of 66.5-101%), for all months, indicating some limitations in the YSU planetary boundary layer scheme, the Purdue Lin cloud microphysics, and the Grell-Devenyi ensemble scheme.

WRF/Chem can simulate the column abundances of gases reasonably well with NMBs within 30% for most months but moderately to significantly underpredicts the surface concentrations

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of major species at all sites in nearly all months with NMBs of -72% to -53.8% for CO, -99.4% to -61.7% for NO_x, -84.2% to -44.5% for SO₂, -63.9% to -25.2% for PM_{2.5}, and -68.9% to 33.3% for PM₁₀, and aerosol optical depth in all months except for October with NMBs of -38.7% to -16.2%. The model significantly overpredicts surface concentrations of O₃ at most sites in nearly all months with NMBs of -11% to 160.3% and NO₃⁻ at the Tsinghua site in all months. Possible reasons for large underpredictions include underestimations in the anthropogenic emissions of CO, SO₂, and primary aerosol, inappropriate vertical distributions of emissions of SO₂ and NO₂, uncertainties in upper boundary conditions (e.g., for O₃ and CO), missing or inaccurate model representations (e.g., secondary organic aerosol formation, gas/particle partitioning, dust emissions, dry and wet deposition), and inaccurate meteorological fields (e.g., overpredictions in WS10 and precipitation, but underpredictions in T2), as well as the large uncertainties in satellite retrievals (e.g., for column SO₂). Comparing to MM5, WRF generally gives worse performance in meteorological predictions, in particular, T2, WS10, GSW, GLW, and cloud fraction in all months, Q2 and precipitation in January and October, due to limitations in the above physics schemes or parameterizations. Comparing to CMAQ, WRF/Chem performs better for surface CO, O₃, and PM₁₀ concentrations at most sites in most months, column CO and SO₂ abundances, and AOD. It, however, gives poorer performance for surface NO_x concentrations at most sites in most months, surface SO₂ concentrations at all sites in all months, and column NO₂ abundances in January and April. WRF/Chem also gives lower concentrations of most secondary PM and black carbon. Those differences in results are attributed to differences in simulated meteorology, gas-phase chemistry, aerosol thermodynamic and dynamic treatments, dust and sea salt emissions, and wet and dry deposition treatments in both models.

Key words: WRF/Chem, MM5/CMAQ, East Asia, Model Evaluation, Model intercomparison

1. Introduction

Three-dimensional (3-D) atmospheric models provide a powerful tool in simulating atmospheric processes. A number of 3-D air quality and climate models have been developed in the past decades. Prior to 2000, most of these models are offline-coupled meteorology-chemistry models in which the hourly outputs of simulated meteorological fields from a meteorological model are used to drive a chemical transport model. Examples of the offline-coupled models include STEM-2K3 and its predecessors (Tang et al., 2004), the Community Multiple Air Quality (CMAQ) modeling system (Binkowski and Roselle, 2003; Byun and Schere, 2006; Eder and Yu, 2006; Yu et al., 2012)), CMAQ with the Model of Aerosol Dynamics, Reaction, Ionization, and Dissolution MADRID (Zhang et al., 2004, 2010a), and the Comprehensive Air quality Model with extensions (CAMx) (Gaydos et al., 2007). Those models have shown overall good skills in reproducing past pollution episodes. Comprehensive reviews of those offline models can be found in the literature (e.g., Peters et al., 1995; Russell and Dennis, 2000; Seigneur, 2001). The development of the online-coupled models has been recently gained extensive research attentions because they represent more realistically the real atmosphere and can simulate various climate-chemistry interactions and feedback processes. The tradeoff of the online-coupled models is that they are much more complicated in model treatments, and also more computationally-expensive comparing to offline-coupled models. Examples of online-coupled models include a gas, aerosol, transport, and radiation air quality model/a mesoscale meteorological and tracer dispersion model (GATOR/MMTD) (Jacobson, 2001); the multiscale climate chemistry model (MCCM) (Grell et al., 2000), the mesoscale Weather Research and Forecast model with Chemistry (WRF/Chem) (Grell et al., 2005), and the two-way coupled WRF-CMAQ (Wong et al., 2012; Yu et al., 2014). Detailed reviews of

recently developed online-coupled models along with their advantages and limitations can be found in several review papers (e.g., Zhang, 2008; Kukkonen et al., 2012; Baklanov et al., 2014).

At present, both offline and online models are actively used in current regional and global models, because of their relative merits for a variety of applications with different purposes. While offline-coupled models have been applied and evaluated extensively in the past decades, the evaluations of online-coupled models are limited. Such evaluations have been instrumental in identifying the limitations and deficiencies of 3-D models and inaccuracies and uncertainties in the model inputs for model improvements. While the chemistry and aerosol treatments in the offline-coupled models have been tested and improved over several decades, those in the online-coupled models are being tested and improved. Intercomparison of newly developed online-coupled models with more established offline-coupled models can thus provide insightful information regarding the strengths and limitations associated with model treatments in current online-coupled models as well as the appropriateness of the model inputs such as emissions and boundary conditions, and model configurations such as grid resolutions and nesting. The intercomparison between online and offline coupled models should ideally be set up within the same online-coupled model with two different application modes, one with online-coupled and one with offline-coupled. However, such intercomparison is rarely performed because of the unavailability of the offline-coupled mode within the online-coupled models that are not designed for such intercomparisons. Comparison between an online-coupled model and an offline-coupled model, on the other hand, can be performed more easily because most applications have been previously performed using an offline-coupled model, and all the model inputs can be set up for applications using an online-coupled model and intercomparison with the results from the offline-coupled model. For example, Herwehe and

Kang (2008) compared online-coupled WRF/Chem and offline-coupled WRF/CMAQ for their applications for a summer episode in eastern U.S. in 2006. They found that both models overpredicted the maximum 8-hour average ground-level ozone (O_3) by 5-10 ppb (or by 5-20%), using the same gas-phase mechanism of the 2005 Carbon bond mechanisms (CB05) and CMAQ gives a greater range of values and correlates better with observations than WRF/Chem. Lin and Holloway (2009) applied online-coupled WRF/Chem and offline-coupled WRF/CMAQ to East Asia. They reported that both models can reproduce the variations of observed ground-level ozone from the Acid Deposition Monitoring Network in East Asia Data (EANET) but WRF-Chem can better capture vertical profiles of major species from aircraft measurements. Zhang et al. (2013) intercompared the online-coupled WRF/Chem-MADRID with the offline-coupled WRF/Polyphemus over western Europe and found that WRF/Polyphemus gives more accurate concentrations of $PM_{2.5}$, and WRF/Chem-MADRID reproduces better the observations of PM_{10} concentrations at all sites.

In this work, WRF/Chem is applied to East Asia to evaluate its capability in simulating meteorology, air quality, and their interactions. To assess the capability of WRF/Chem, the results from an initial application of WRF/Chem are first evaluated using observations and compared with those from MM5/CMAQ using the same model inputs. Major limitations/deficiencies identified through such intercomparison and evaluation are then addressed by improving the model inputs and representations of several processes and by performing sensitivity simulations with improved inputs and model treatments. The first objective of this study is to identify limitations and uncertainties in model inputs and process representations for the online-coupled WRF/Chem through a comprehensive model evaluation using available observations and intercomparison with results from an offline-coupled MM5/CMAQ described in Wang et al. (2010 a, b). WRF/Chem is an online-coupled model that

contains more advanced features that are not included in the offline coupled MM5/CMAQ such as the two-way feedbacks between meteorology and chemistry. However, the history of development and application of WRF/Chem is much shorter than that of most other established 3-D air quality models such as MM5/CMAQ that have been systematically developed and refined, extensively tested, and routinely applied for research and regulatory modeling over numerous countries and regions for several decades. In particular, the chemistry and aerosol treatments in WRF/Chem may not be as complete and mature as those in the more established models, and there have been limited number of applications and evaluations of WRF/Chem over limited regions. Using MM5/CMAQ results as benchmark, the intercomparison will help identify any significant discrepancies between the results using the two model systems, thus providing a basis for further improvement. The second objective is to address major limitations and uncertainties of WRF/Chem identified from model evaluation and intercomparison by improving model inputs and representations of several processes and performing sensitivity simulations to assess the effectiveness of the model improvement. The third objective is to accurately estimate the impacts of anthropogenic aerosols on air quality and climate through direct and indirect effects in East Asia using the improved WRF/Chem. The results are presented in a sequence of two papers. Part I describes the model configurations, evaluation protocols and databases used, the operational evaluation using available observations, and comparison with MM5/CMAQ. Part II (Zhang et al., 2015) describes improvements in model inputs and process representations, sensitivity simulation design, re-evaluation using observations, as well as the recommendations for additional model improvements. The estimated impacts of anthropogenic aerosols on air quality and climate will also be presented.

2. Model Configurations and Evaluation Protocols

2.1 Description of the Testbed and Model Setup

WRF/Chem version 3.3.1 is applied to simulate meteorology and air quality over East Asia including entire China, Northeast Asian Countries such as Japan, North Korea and South Korea, parts of Southeast Asian countries, such as Vietnam, and Thailand, and Northern part of India (see Figure 1). at a horizontal grid resolution of 36-km (163×97 horizontal grid cells) and a vertical resolution of 23 layers from 1000 to 100 mb, with 8 layers in the planetary boundary layer (PBL). The simulation domain is centered in China. As a developing country, China has experienced a rapid growth of economy and associated increases in pollutant emissions since 1980's, emerging as one of the largest contributors to global climate change. Increased emissions, coupled with complicated weather system in China, make China an ideal testbed for coupled meteorology-chemistry model applications. Four months in 2005, i.e., January, April, July, and October, which represent the four seasons are selected for the model simulations. 2005 is selected for two main reasons. First, it is the end year of the 10th National Five Year Plan for emission control policies in China (Wang et al., 2010a) for which an assessment of the impact of the reduced emissions due to emission control policies on air quality is particularly useful. Second, the observed precipitation from the National Climatic Data Center (NCDC) shows a strong seasonal variation with the highest amount in July, followed by October, April, and January. 2005. This strong seasonality allows an assessment of the model's capability in capturing seasonal variations of regional climate and its sensitivity to changes in model inputs and representations of various processes.

Table 1 summarizes the selected physical and chemical options for WRF/Chem, which are the same or similar to those used in Zhang et al. (2010b, 2012). To achieve the objectives of an assessment of the fully-coupled WRF/Chem, the options that allow the simulation of aerosol direct and indirect effects are needed. The only combination available in WRF/Chem version 3.3.1 to simulate aerosol direct and indirect effects is to use the gas-phase chemistry of the

Carbon Bond Mechanism-Z (CBM-Z) (Zaveri and Peters, 1999), the Carnegie Mellon University (CMU) aqueous-phase mechanism (CMU_AQ) of Fahey and Pandis (2001), and the Model for Simulating Aerosol Interactions and Chemistry (MOSAIC) (Zaveri et al., 2008). The combination of CBM-Z, CMU_AQ, and MOSAIC is therefore selected in this study. This combination requires the use of the Goddard shortwave radiation scheme (Chou et al., 1998), the Fast-J photolysis scheme (Wild et al., 2000), and the Purdue Lin microphysics (Lin et al., 1983; Chen and Sun, 2002). Other selected physics options include the rapid radiative transfer model (RRTM) (Mlawer et al., 1997) for longwave radiation, the Community National Centers for Environmental Prediction (NCEP), Oregon State University, Air Force, and Hydrologic Research Lab-NWS Land Surface Model (NOAH) for land surface model, the Monin-Obukhov (Janjić, 2001) for surface layer model, the Yonsei University (YSU) PBL scheme (Hong et al., 2006) for PBL scheme, the Grell-Devenyi ensemble (Grell and Devenyi, 2002) for cumulus parameterization, and the Abdul-Razzak and Ghan (Abdul-Razzak and Ghan, 2002) for aerosol activation into warm and mix-phased clouds.

In MOSAIC, the aerosol size distribution is represented using eight sectional aerosol bins in the size range of 0.0390625 to 10 μm with the first six bins for particulate matter with diameter less or equal to 2.5 μm ($\text{PM}_{2.5}$) and the 7th and 8th bins for coarse particles ($\text{PM}_{2.5-10}$). MOSAIC simulates sulfate (SO_4^{2-}), nitrate (NO_3^-), chloride (Cl^-), ammonium (NH_4^+), sodium (Na^+), black carbon (BC), primary organic mass (OC), other inorganic mass (OIN), and liquid water on the surface of aerosol particles. It simulates major aerosol processes including binary nucleation, coagulation, condensation, inorganic aerosol thermodynamic equilibrium, PM formation due to aqueous-phase chemistry, aerosol scavenged by cloud droplets, and dry and wet deposition. For the formation of secondary organic aerosols (SOA), MOSAIC with 4 bins is coupled with the SAPRC99 chemistry and includes volatility basis set (VBS) for SOA

formation in WRF/Chem version 3.3.1. However, this MOSAIC (4-bin)- SAPRC99/VBS option does not simulate aerosol direct and indirect effects, which are one of the main foci for this work. On the other hand, the 8-bin option of MOSAIC coupled with CBM-Z in WRF/Chem v3.3.1 does not simulate SOA. In this work, the default 8-bin option of MOSAIC coupled with CBM-Z is used in an initial application of WRF/Chem (i.e., the baseline simulation). A simple treatment of SOA formation is thus added in the CBM-Z and MOSAIC chemistry option, which will be described in Part II paper.

Meteorological initial and boundary conditions (ICs and BCs, respectively) are based on the National Centers for Environmental Predictions Final Analysis (NCEP-FNL) reanalysis data. In the baseline simulation, WRF/Chem is run freely with only grid nudging for wind vectors in the PBL using a nudging coefficient of 3×10^{-4} . In the sensitivity simulations, meteorology is reinitialized every day to construct a better meteorological field. The chemical ICs are based on the results from CMAQ (Byun and Schere, 2006) described by Wang et al. (2010a, b). The chemical BCs are based on the results from Goddard Earth Observing System Atmospheric Chemistry Transport Model (GEOS-Chem) (<http://acmg.seas.harvard.edu/geos/>). The anthropogenic emissions used in the baseline simulation are based on Wang et al. (2010a, b), which uses the 2005 Carbon Bond Mechanism (CB05). The CB05 volatile organic compounds (VOCs) speciation is mapped into the CBM-Z VOCs speciation. Adjustments are applied to the anthropogenic emissions based on the evaluation of the baseline and sensitivity simulation results, which will be further discussed in Part II paper. Biogenic, dust, and sea-salt emissions are treated using online modules. The model of Emissions of Gases and Aerosols from Nature (MEGAN) version 2 (Guenther et al., 2006) is used for biogenic emissions for both baseline and sensitivity simulations. The original Shaw (2008) dust emission scheme is used in the baseline simulation. It is replaced by the modified Shaw (2008) as implemented in Zhang et

al. (2012) and by Zender et al. (2003) as implemented by Wang et al. (2012) in the sensitivity simulations to be described in Part II paper. Gong et al. (2002) is used for the generation of sea-salt emissions for both baseline and sensitivity simulations.

Since the predictions of MM5/CMAQ of Wang et al. (2010a, b) will be used as a benchmark for WRF/Chem predictions, a brief description of the inputs and configurations for MM5/CMAQ is provided below. More detailed descriptions can be found in Wang et al. (2010a, b). MM5/CMAQ simulations of Wang et al. (2010 a, b) use the same meteorological ICs and BCs and chemical BCs for MM5/CMAQ as those used for WRF/Chem baseline simulations in this work. The chemical ICs for MM5/CMAQ are from GEOS-Chem. Table 1 also includes major physics and chemistry options used in MM5/CMAQ. While both model systems use the same RRTM for longwave radiation and the same NOAH land surface model for land surface modeling, they use different schemes/methods for other physical and chemical processes. For example, MM5 simulations use the Kain-Fritsch 2 cumulus scheme (Kain, 2002), the high resolution Blackadar PBL scheme (Zhang and Anthes, 1982), the mixed-phase (Reisner 1) explicit moisture scheme for cloud microphysics (Reisner et al., 1998), the cloud-radiation shortwave radiation scheme (also known as Dudhia shortwave radiation scheme), and the force/restore (Blackadar) surface scheme (Blackadar, 1976). For air quality simulation, CMAQ version 4.6 was used with a vertical resolution of 14 layers from the surface to the tropopause (1000 mb to 100 mb) and 10 layers at lower altitudes to resolve the PBL. CMAQ uses the CB05 of Yarwood et al. (2005) for gas-phase chemistry. Similar to CBM-Z used in WRF/Chem, CB05 is a variant of CBM-IV of Gery et al. (1989) that is based on the lumped structure method. While CBM-Z is designed for regional and global scale applications (Zaveri and Peters, 1999), CB05 is designed for better simulations under pristine, wintertime, and high altitude conditions (Yarwood et al., 2005); they thus differ in several aspects. For example,

CBM-Z has more detailed isoprene chemistry than CB05, but does not treat terpene chemistry that is treated in CB05. Comparing to CBM-Z, CB05 includes one more hydrogen reaction, a few more odd-oxygen reactions, NO_3 radical reactions, and NO_x recycling reactions, which may be important under very dry conditions in upper troposphere, pristine conditions, nighttime conditions, and very cold conditions, respectively (Sarwar et al., 2008). CB05 does not treat acetone, but treats lumped species including high aldehydes (ALDX) and its corresponding peroxyacyl radicals, peroxy nitrates, carboxylic acids, and peroxy carboxylic acids. CMAQ uses the modified RADM (Walcek and Taylor, 1986) for aqueous-phase chemistry, and the Aero 4 for aerosol module. Aero 4 uses a modal approach with three lognormally-distributed modes for PM size distribution: Aitken, accumulation, and coarse modes. Comparing to the sectional approach with 8-section used in MOSAIC in WRF/Chem, the modal approach with 3-mode used in CMAQ is less accurate but computationally more efficient. Aero 4 treats all major aerosol thermodynamic and dynamic processes such as inorganic aerosol equilibrium, SOA formation, nucleation, condensation, and coagulation, but it uses different modules from those used in MOSAIC. The aforementioned differences in gas- and aqueous-phase chemistry, and aerosol treatments between WRF/Chem and CMAQ would contribute to differences in their chemical predictions.

2.2 Observational Datasets and Model Evaluation Protocols

Table S1 in the supplementary material summarizes the ground-based observational datasets that are collected and used in this study. Figure 1 shows the locations of these observational sites in the modeling domain. The NCDC global hourly dataset is used to evaluate the surface meteorological variables, including temperature at 2-m (T2), water vapor mixing ratio at 2-m (Q2), wind speed at 10-m (WS10), and daily precipitation (Precip). Sites that are located outside of the modeling domain are filtered out. Several surface observational datasets

are collected for the chemical evaluation. PM₁₀ and SO₂ concentrations are retrieved for 84 major cities in mainland China through the Air Pollution Index (API). Observations of PM_{2.5} and its composition are available from Duan et al. (2006) at a suburban site (i.e., Tsinghua University (THU)) and a rural site (i.e., Miyun (MY)) in Beijing, China. Concentrations of major pollutants including particulate matters with diameter less than or equal to 10 µm (PM₁₀), carbon monoxide (CO), nitrogen monoxide (NO), nitrogen dioxide (NO₂), sulfur dioxide (SO₂), and ozone (O₃) at eleven general sites and three roadside sites in Hong Kong are available. The three roadsides are not used since road features cannot be resolved at a coarse resolution of 36-km. Similar concentration data available in Taiwan include PM₁₀, PM_{2.5}, CO, NO, NO₂, SO₂, and O₃. Data in Japan include monthly mean concentrations of suspended particulate matter (SPM) (approximated as PM₁₀), O_x (photochemical oxidants, approximated as O₃), CO, NO, NO₂, and SO₂. In addition, the concentrations and wet deposition fluxes of SO₄²⁻, NO₃⁻, and NH₄⁺ from the EANET network are used for model evaluation of CMAQ and improved WRF/Chem with improved inputs at 27 sites that fall into the simulation domain in Part II paper.

Table S2 summarizes satellite datasets along with meteorological, radiative, optical variables as well as total column mass abundances of gases evaluated in this study. The meteorological/radiative/optical variables and datasets include Precip from the Tropical Rainfall Measuring Mission (TRMM), aerosol optical depth (AOD) from the Moderate Resolution Imaging Spectroradiometer (MODIS), and cloud fraction (CF), liquid water path (LWP), downward longwave radiation GLW, and downward shortwave radiation (GSW) from the Clouds and Earth's Radiant Energy System (CERES). The total column abundances include CO column from the Measurements Of Pollution In The Troposphere (MOPITT)/Terra, NO₂ and SO₂ columns from the SCanning Imaging Absorption SpectroMeter for Atmospheric

ChartographY (SCIAMACHY), tropospheric ozone column (TOC) from the Ozone Monitoring Instrument (OMI)/Aura, and tropospheric ozone residue (TOR) from the Total Ozone Mapping Spectrometer/the Solar Backscatter Ultraviolet (TOMS/SBUV). Low air mass factors that represent passive degassing of volcanoes and anthropogenic activities are used to retrieve SO₂ vertical column from slant column. Also, only model outputs that are close to the satellite local overpassing time (within 2 hours) are averaged for comparison to avoid errors due to diurnal cycles.

Model evaluation is performed following Zhang et al. (2006). The evaluation protocol includes spatial distribution, temporal variation, column abundances, vertical profiles, and overall statistical trends. The performance statistics are calculated separately for different networks, due to the inherent differences in methods of observation, data collection, and data processing across different networks, as well as differences in data collection frequency. For surface observations from Hong Kong, Taiwan, and Japan, a grid mean observed value is calculated when more than one observational sites fall into the same model grid. The statistics analyzed based on paired observational and simulated data in this study include mean bias (MB), normalized mean bias (NMB), root mean square error (RMSE), normalized mean gross error (NME), and correlation coefficient (R). The definitions and formulations for these performance statistics can be found in Yu et al. (2006) and Zhang et al. (2006).

3. Model Evaluation of the WRF/Chem Simulation

Table 2 compares the performance statistics of surface meteorological variables against NCDC data for WRF/Chem and MM5/CMAQ for all four months. Figure 2 shows the spatial distributions of MBs for those variables in January and July, 2005. The performance of WRF/Chem is discussed in this section. Comparison of WRF/Chem and MM5/CMAQ will be discussed along with the performance of MM5/CMAQ in Section 4. The WRF/Chem baseline

simulation shows moderate to large biases for all major meteorological variables except for Q2 for most months. For T2, the MBs range from -1.5 to 1°C, NMBs range from -9.8 to 75.6%, and RMSEs range from 14.1-20.9 °C. As shown in Figure 2, the largest domain mean warm bias occurs in January because the high warm biases over North and South Korea, Japan, and northwestern part of the domain dominate over the large cold biases in most of the western China and northern Vietnam, Laos, and Thailand. The largest domain mean cold bias occurs in July because the large cold biases over North and South Korea, Japan, Sichuan basin in China and southern China, and northern Laos and Thailand dominate over the warm biases in central and northern China. For Q2, WRF/Chem performs well with MBs of 0.1-1.1 g kg⁻¹, NMBs of 0.4-23.4%, and RMSEs of 2.8-7.6 g kg⁻¹. The largest domain mean bias occurs in January, due to the dominances of large positive biases over North and South Korea, and Japan. For WS10, significant overpredictions occur in all months with the MBs of 1.9-3.1 m s⁻¹, NMBs of 66.5-101.0%, and RMSEs of 11.3-20.5 m s⁻¹. The largest overpredictions also occur over North and South Korea, and Japan, Sichuan basin in China and southern China in January. For Precip, the MBs, NMBs, and RMESs are 0.2-1.7 mm day⁻¹, 11.4-92.7%, and 49.9-441.4 mm day⁻¹, respectively. Large overpredictions occur over North and South Korea, and Japan in January and October, and over additional regions such as the southern China and northern Vietnam, Laos, and Thailand in July. These results indicate certain limitations in the YSU PBL and the Monin-Obukhov schemes used in resolving main features of the PBL meteorology, particularly over complex terrain with uneven surface topography such as Sichuan basin, and hills or mountainous regions over North Korea, Japan, Vietnam, and Laos. For example, the significant overpredictions in WS10 are mainly caused by an inaccurate representation of the surface roughness (Mass and Owens, 2010) in the PBL scheme. The evaluation also indicates limitations in the Purdue Lin cloud microphysics and the Grell-Devenyi ensemble schemes in

simulating cloud and precipitation formation. As reported by Zhang et al. (2010b), the Grell-Devenyi ensemble cumulus parameterization has a tendency to predict too frequent afternoon convective rainfall and/or to overestimate the intensity of the rainfall. The Purdue Lin cloud microphysics also has a tendency to overpredict cloud ice, graupel, and surface rainfall. Those limitations explain the predicted excessive convection and non-convection rain over the eastern oceanic area in January and excessive non-convection rain over the southwestern oceanic area in July, as shown in Figure S1 in the supplementary material.

Figure 3 compares the observed and simulated column meteorological variables by WRF/Chem and MM5/CMAQ in January and July, 2005. The performance of MM5/CMAQ will be discussed in Section 4. WRF/Chem captures the general pattern of CF in January and July, although it underpredicts CF in southern China and overpredicts CF over the Pacific oceanic area in the southeastern corner of the domain in January and overpredicts CF over most of the domain except for the northwestern part of the domain in July. LWP is better predicted in July than in January in terms of both spatial distribution and magnitude. Large underpredictions in LWP occur over land areas, particularly in northern domain. While the model simulates GLW well, it overpredicts GLW over southeastern part of the domain in January and most of the domain in July. The model also simulates well GSW but underpredicts GSW in western China and southeastern part of the domain in January, and in northwestern and southeastern parts of the domain in July. While the model can generally capture the spatial distributions of Precip, overpredictions occur in eastern part of domain in January and in southwestern part of the domain, northeastern China, and Japan in July, which are consistent with areas having excessive clouds and LWP from WRF/Chem simulations. The evaluation of CF and Precip against satellite derived products is consistent with the evaluation of Precip using NCDC data,

both indicating the limited capabilities of the Purdue Lin cloud microphysics and the Grell-Devenyi ensemble schemes in accurately simulating cloud and precipitation formation.

Tables 3 and 4 summarize the performance statistics of surface concentrations and column variables, respectively. The concentrations of all surface chemical species except for surface O₃ are underpredicted significantly by WRF/Chem. The simulated concentrations or mixing ratios of CO are lower than the surface observations at Hong Kong, Taiwan, and Japan, with NMBs ranging from -72.0% to -53.8%. Such large underpredictions indicate a possible underestimation in local CO emissions in terms of emission rates and the vertical distributions over those monitoring sites. The simulated domain CO column abundance agrees reasonably well with satellite observations, with the largest NMB of -24.2% in April 2005 and smaller NMBs of -3.5% to 4.0% in other months. The annual mean contribution of biomass burning to the total CO emissions over Asia could be as high as 24% (Streets et al., 2003). Streets et al. (2003) investigated the seasonal trend of biomass burning in Asia and reported that there are significant biomass burning activities in spring over South and Southeast Asia, indicating a large contribution of CO emissions from biomass burning. CO is a slowly-reacting species and its fate is mainly determined by atmospheric transport and mixing. CO emissions from biomass burning in April over Southeast Asia (which is outside the simulation domain) could result in a high background CO concentration in the simulation domain, which is not well represented in the WRF/Chem simulation. Biomass burning also occurs frequently over North and South Korea and Japan, its emissions are not well represented in the emission inventories used in this study. Figure 4 shows clearly the impacts of biomass burning on the satellite-derived column CO abundance in January over North and South Korea, Japan, and northern Burma, Vietnam, and Laos where the underpredictions occur. Improved BCs of CO are needed to improve the performance of the CO column abundance in spring in future studies.

The simulated concentrations or mixing ratios of NO and NO₂ are much lower than those from surface observations in all months over Hong Kong, Taiwan, and Japan, with NMBs ranging from -99.4% to -91.8% for NO and from -61.7% to -88.1% for NO₂. The simulated column abundances of NO₂ are also underpredicted, but not as significant as the NO₂ mixing ratio at surface level, with NMBs ranging from -30.6% to -0.01 %, indicating that there may be some problems in simulating NO₂ vertical distribution, particularly in January during which the largest underprediction occurs. Figure 4 clearly shows such underpredictions over eastern China in January, although the model simulates well the spatial distributions and the seasonal variations of the column abundance of NO₂ in both months.

The simulated concentrations or mixing ratios of SO₂ are lower than those from surface observations in all months over mainland China, Hong Kong, Taiwan, and Japan, with NMBs ranging from -84.2% to -44.5%. As shown in Figure 4, the data quality of satellite-derived SO₂ column abundance is poor, which contains a large fraction of missing values. The NMBs of the simulated SO₂ column abundance against satellite observations are 21.4%, -31.7%, -40.0%, and 26.1% for January, April, July, and October 2005, respectively. The moderate overpredictions in the SO₂ column abundance in January and October are not consistent with the evaluation results against surface observations. Also, the spatial maps in Figure 4 suggest that the underpredictions of SO₂ column abundance in July (and April, see Figure 5 in Part II paper) mainly occur over the Sea of Japan and west Pacific Ocean. Such underpredictions are likely because the volcanic emissions of SO₂ over those regions are not represented in the emission inventories used in the simulation. This inconsistency between surface and column evaluations suggests that there might be a similar problem in simulating the vertical distributions of SO₂ to that for NO₂ due to uncertainties in total emissions and/or vertical allocations of their emissions, which will be further discussed in Part II paper. X. Wang et al. (2010) reported similar problems

caused by inaccurate temporal and vertical allocations of emissions of pollutants in East Asia and showed improved performance with diurnally- and vertically-adjusted emissions. Another reason for underpredictions in SO₂ concentrations is the possible overpredictions in dry deposition fluxes of SO₂, which will be discussed further in Part II paper.

Contrasting to other species, the simulated concentrations or mixing ratios of O₃ are mostly higher than those from surface observations over Hong Kong (with NMBs of 88.0-160.3%), Taiwan (with NMBs of 13.6-83.8%), and Japan (with NMBs of -11.0% to 33.2%). The overprediction of O₃ and underprediction of NO_x at all sites in all months except for Japan in April indicate an insufficient titration of O₃ by NO_x, which will be further discussed in Part II paper. The column abundances of tropospheric O₃ are simulated well for April and October 2005, but overpredicted for January 2005 (with an NMB of 45.4% against TOMS data, and 27.3% against OMI data) and underpredicted for July 2005 (with an NMB of -32.3 % against TOMS data, and -19.4% against OMI data), due likely to the incorrect representation of the seasonal variations of stratospheric O₃ intrusions to the upper troposphere. Figure 4 shows clearly the overpredictions in January 2005 and underpredictions in July in the column abundances of tropospheric O₃ over most of the domain. Since stratosphere is not included in this study, the source of O₃ in upper layers is reflected in the upper BCs. The impact of the BCs of O₃ on the model performance will be discussed in Part II paper.

The model tends to underpredict the PM concentrations over mainland China (with NMBs of -37.8% to -2.9% for PM₁₀), Hong Kong (with NMBs of -47.4% to -6.9% for PM₁₀), Taiwan (with NMBs of -68.9% to -49.3% for PM₁₀, and NMBs of -63.9% to -25.2% for PM_{2.5}), and Japan (with NMBs of -51.2% to 33.3%). Figure 5 shows the simulated spatial distributions of PM_{2.5} and PM₁₀ overlaid with observed concentrations of PM_{2.5} over Taiwan, and derived PM₁₀ concentrations over mainland China, Hong Kong, Taiwan, and Japan, respectively, during

the four months. Consistent with the emissions of primary PM and the precursors of secondary PM, the simulated PM_{2.5} concentrations are the highest in central and eastern China in all months. The highest PM_{2.5} concentrations occur in January, followed by October, April, and July. The underpredictions of PM_{2.5} concentrations over Taiwan (possibly over other sites, though observations are not available) may be caused by underestimations in the emissions of primary PM species such as OC and EC, and a lack of SOA module in the version of WRF/Chem used, which will be discussed further in Part II paper. For PM₁₀ concentrations, the largest underpredictions occur over most sites in January, and the best agreement between observations and simulated PM₁₀ concentrations occurs in October. PM concentrations are affected not only by anthropogenic emissions, but also natural emissions such as mineral dust. The default Shaw (2008) dust module used in the WRF/Chem baseline simulation generates very high dust emissions over northern China and Mongolia (where the land type is primarily grassland), which is not consistent with the known dust source regions in the northwestern China. Due to the long range transport, dust emissions from the north could affect the entire northeastern domain, leading to higher PM₁₀ concentrations. Part II paper will discuss results from sensitivity simulations with adjusted OC emissions, a simple SOA module, the modified Shaw (2008) dust emission scheme, and a new dust emission scheme based on Zender et al. (2003), as well as their impacts on model performance. As shown in Figure 4, the simulated AODs are mostly lower than those from Terra/MODIS with NMBs of -16.2%, -38.7%, -28.0%, and 5.6% for January, April, July, and October 2005, respectively, particularly over eastern China in January and southwestern Pacific ocean in July. The underpredictions of AOD are related due to underpredictions in PM_{2.5} concentrations in those regions. Overpredictions in AOD occur in northeastern China, North and South Korea, and Japan in all months, due mainly

to possible overpredictions in PM_{10} concentrations throughout the atmosphere because of unrealistically high dust emissions in those regions.

Figure 5 shows simulated $PM_{2.5}$ and PM_{10} concentrations by WRF/Chem overlaid with available $PM_{2.5}$ observations in Taiwan and PM_{10} observations over mainland China, Hong Kong, Taiwan, and Japan, respectively. Moderate to large underpredictions in $PM_{2.5}$ and PM_{10} occur at all surface sites in all months (except for mainland China and Hong Kong in October where PM_{10} concentrations are well reproduced with NMBs of -2.9% and -6.9%, respectively). Figure 6 compares observed and simulated concentrations of $PM_{2.5}$ and its composition at the Tsinghua site in Beijing, China during the four months. WRF/Chem underpredicts $PM_{2.5}$ concentrations in all months, particularly in January when large underpredictions occur. The underpredictions in $PM_{2.5}$ in January, April, and July are caused by underpredictions in SO_4^{2-} , NO_3^- , and NH_4^+ in January, April, and October, underpredictions in OIN in January and July, and underpredictions in OC in all months. Higher first layer thickness used (thus possible underestimation of emissions) and higher PBLH simulated in WRF/Chem lead to possible underpredictions of precursors of those aerosol species, which explain most of the underpredictions in OIN and OC. Lack of a SOA module and underestimates of primary OC emissions in WRF/Chem also contribute to the underpredictions in OC. Different from most other PM composition, EC concentrations are overpredicted in all months. OIN concentrations are underpredicted in January and July but overpredicted in April and October. Figure 7 compares observed and simulated concentrations of O_3 and PM_{10} at six cities in Japan during the four months. WRF/Chem overpredicts O_3 concentrations in all cities in Japan in January and April, and in Nagasaki in April, and in Sapporo, Nagoya, and Nagasaki in July. Such overpredictions are caused by insufficient titration of NO_x resulted from significant underpredictions of NO_x concentrations in Japan as shown in Table 3. For PM_{10} ,

underpredictions occur in all cities except for Tsukuba in January and July and except for Sapporo and Tsukuba in October, and overpredictions occur in all cities in April. The underpredictions in PM₁₀ are mainly caused by underpredictions in the precursor gases such as SO₂ and NO_x (see Table 3). The overpredictions in April may be related to the unrealistically high dust concentrations due to the use of Shaw (2008). The simulated very high PM₁₀ concentrations in Tsukuba are caused by the long range transport of the unrealistically high dust concentrations from sources in China.

4. Intercomparison of the WRF/Chem and MM5/CMAQ Simulations

As shown in Table 1 and Figures 2 and S1, MM5 performs similarly to WRF/Chem for Q2 and P. For T2, MM5 gives smaller MBs in January, April, and July (with -0.8, -1.1, and -0.6 °C, respectively) but a much larger MB in October (-1.2 °C in MM5 vs. 0.2 °C in WRF/Chem), despite similar spatial distributions of T2. Figure 2 also shows better agreement of T2 simulated by MM5 than by WRF/Chem in term of spatial distributions, particularly over North and South Korea and Japan in January and over central China in July. For WS10, MM5 gives much smaller MBs and better spatial agreement. Better performance of MM5 for T2 and WS10 can be attributed to several reasons. First, MM5 and WRF/Chem simulations use different nudging methods for different variables. The four dimensional data assimilation (FDDA) with analysis nudging of T2 and Q2 above the PBL and also WS10 in the PBL is used in the MM5 simulations but the grid nudging of wind vectors in the PBL is used in WRF/Chem simulations. Second, MM5 uses an established PBL scheme, i.e., the high resolution Blackadar PBL scheme (Zhang and Anthes, 1982), whereas WRF/Chem uses relatively new YSU scheme. As indicated by Mass and Owens (2010), the surface drag exerted by the unresolved topography such as hills and valleys and other smaller scale terrain features is not well represented in the YSU scheme in WRF, leading to a high bias for WS10 in WRF simulations. As a result of different PBL and

surface layer schemes, PBLH simulated in WRF/Chem is much higher than that simulated in MM5 (see Figure S1), which will affect their chemical predictions, as discussed below. Third, although MM5 and WRF/Chem use a different shortwave radiation scheme, i.e., the cloud-radiation shortwave radiation scheme for MM5 and the Goddard shortwave radiation scheme for WRF/Chem. As shown in Figure 3, MM5 performs better in GSW and GLW in terms of both magnitudes and spatial distributions.

For Precip, MM5 performs similarly to WRF/Chem in April and July but much better in January and October in terms of performance statistics and performs better in terms of spatial distributions for all months (see January and July in Figure 3). While convective rain dominates over western Pacific in all months and over land in April and July, non-convective rain may also be important over land in all months and over ocean in January and April. Comparing to MM5, WRF/Chem predicts much stronger convective rain and non-convective rain over western Pacific in January (see Figure S1) and less convective rain in most of the domain but much stronger non-convective rain over Japan, western Pacific, western China, northern Bay of Bengal, northern Burma, and eastern India in October (Figure not shown). This indicates the excessive convective and non-convective precipitation predicted by both the Purdue Lin microphysics scheme and the Grell-Devenyi ensemble cumulus scheme in January and the excessive non-convective precipitation predicted by the Purdue Lin microphysics scheme in October. For comparison, the mixed phase (Reisner 1) explicit moisture scheme and the Kain-Fritsch 2 cumulus scheme used in MM5 perform very well for precipitation in terms of both spatial distributions and intensities in all months (see Figure 2 for January and July). The differences in the cloud microphysics scheme and cumulus cloud scheme also explain the differences in simulated CF and LWP by the two models, as shown in Figure 3. WRF/Chem

gives closer agreement for CF in terms of both magnitudes and spatial distributions, but both models overpredict LWP and fail to reproduce its spatial distributions.

As shown Table 3, comparing to CMAQ, WRF/Chem gives less underpredictions in surface CO mixing ratios in Taiwan in all months, in Hong Kong for all months except for January, and in Japan in April and July. WRF/Chem also gives lower biases in column CO abundance predictions and better spatial distributions than CMAQ (see Figure 4). For surface NO_x concentrations, both models give similar large underpredictions at the surface sites (see Table 3), and WRF/Chem gives lower NO_x concentrations over most of the domain (see NO₂ plots in Figure S2). For column NO₂ abundance, WRF/Chem gives larger underpredictions in January and April but less underprediction in July and October, with similar spatial distributions in all months (see Table 3 and Figure 4). Figure S2 and Table 3 show that comparing to CMAQ, WRF/Chem gives much lower SO₂ concentrations over most of the domain and thus larger underpredictions at all surface sites in mainland China, Hong Kong, Taiwan, and Japan in all months. WRF/Chem also gives lower OH, HO₂, and O₃ concentrations than CMAQ in all months (see Figure S2). These results indicate that the larger underpredictions for surface SO₂ concentrations by WRF/Chem are mainly caused by much higher PBLH and higher surface layer thickness (see Figure S1), higher aqueous-phase oxidation of SO₂ to SO₄²⁻ due to greater Precip than MM5 in all months, and higher dry deposition fluxes (see further discussions in Part II paper), rather than by differences in the gas-phase chemistry between CB05 used in WRF/Chem and CBM-Z used in CMAQ. By contrast, WRF/Chem performs better than CMAQ for column SO₂ abundances, particularly in January, with NMBs of 21.4% and 104.1%, respectively. WRF/Chem gives the spatial distributions of column SO₂ abundances that agree better than CMAQ (see Figure 4). For surface O₃, WRF/Chem performs similarly to CMAQ but with less overpredictions in Hong Kong, Taiwan in January and April and in Japan in all

months except in April during which surface O₃ mixing ratios are underpredicted by WRF/Chem with an NMB of -11.0% but overpredicted by CMAQ with an NMB of 21.6%. In July, WRF/Chem moderately overpredicts surface O₃ mixing ratios at Taiwan with an NMB of 14.5% whereas CMAQ underpredicts them with an NMB of -12.0%. The chemistry differences between CB05 in WRF/Chem and CBM-Z in CMAQ lead to lower concentrations of OH, HO₂, NO_x, and HCHO over most of the domain (see their plots in January and July in Figure S2), which may help explain in part the lower O₃ predictions than CMAQ. However, the differences in surface O₃ mixing ratios simulated by CBM-Z in WRF/Chem and CB05 in CMAQ are much larger than those simulated by CBM-Z and CB05 in WRF/Chem reported in Zhang et al. (2012). Therefore, the much lower O₃ mixing ratios by WRF/Chem over most of the domain are mainly caused by other possible reasons, e.g., higher dry deposition fluxes (see further discussions in Part II paper), higher PBLH and surface layer thickness, which in turn lead to lower mixing ratios of O₃ precursors and O₃, and to a much less extent by gas-phase chemistry differences between CB05 and CBM-Z. On the other hand, WRF/Chem gives higher surface O₃ in Hong Kong and Taiwan in July and October due mainly to higher isoprene and HCHO mixing ratios than CMAQ in those regions during the two months. Such an impact on O₃ formation dominates over the impact of higher PBLH, leading to opposite results in Hong Kong and Taiwan comparing to most of the domain in July and October. Despite large differences in surface O₃ predictions, WRF/Chem and CMAQ perform similarly for column O₃ abundances in terms of magnitude comparing to TOMS and OMI data, because the column O₃ is mainly determined by O₃ concentrations in upper troposphere. Although the spatial distributions of column O₃ abundances simulated by CMAQ show better agreement with observations than those by WRF/Chem, the underpredictions of column O₃ abundances remain, particularly in

July (see Figure 4), indicating the inappropriateness of the upper layer BCs of O_3 in both CMAQ and WRF/Chem simulations.

Figure 5 shows simulated $PM_{2.5}$ and PM_{10} concentrations by CMAQ and WRF/Chem overlaid with available $PM_{2.5}$ observations in Taiwan and PM_{10} observations over mainland China, Hong Kong, Taiwan, and Japan, respectively, in all months. Comparing to CMAQ, WRF/Chem gives much higher PM_{10} over most of the domain in all months and higher $PM_{2.5}$ in northern and western parts of the domain in all months. Such higher PM concentrations lead to much less underpredictions in PM_{10} over mainland China in all months except for January, and over Hong Kong, Taiwan, and Japan in all months. However, the simulated spatial distributions of $PM_{2.5}$ and PM_{10} by WRF/Chem are quite different from those by CMAQ in northern and western parts of the domain, because of unrealistically high dust concentrations (as shown in the OIN concentrations in Figure S3) predicted by the default Shaw dust emission scheme. For central China and southern part of the domain, both models give similar spatial distributions of $PM_{2.5}$ and PM_{10} because the PM concentrations are mainly from anthropogenic sources. However, the simulated concentrations of PM composition by both models are quite different. Comparing to CMAQ, WRF/Chem gives lower concentrations of secondary inorganic (i.e., SO_4^{2-} , NO_3^- , NH_4^+) and carbonaceous (i.e., EC and OC) PM, but higher OIN concentrations over land and higher Na^+ and Cl^- concentrations over oceanic areas (see Figure S3). Those differences can be attributed to differences in simulated meteorology, gas-phase chemistry, aerosol thermodynamic and dynamic treatments, dust and sea salt emissions, and dry deposition in both models. For example, as a consequence of higher aqueous-phase oxidation of SO_2 to SO_4^{2-} due to greater Precip in all months, the simulated concentrations of H_2SO_4 (see Figure S2) by WRF/Chem are higher than those by CMAQ. However, WRF/Chem gives lower SO_4^{2-} (see Figure S3) than those by CMAQ, indicating that differences in the dry and wet deposition

treatments between the two models may be responsible for large differences in simulated SO_4^{2-} . Comparing to CB05 in CMAQ, CBM-Z in WRF/Chem gives lower mixing ratios of HNO_3 over most of the domain and in terms of the domain mean in all months (except for July when WRF/Chem gives higher HNO_3 mixing ratios over Beijing, Hebei, and Shandong areas) (see HNO_3 plots in January and July in Figure S2) due mainly to a much higher PBL height rather than a different reaction rate for conversion of N_2O_5 to HNO_3 used in CBM-Z and CB05 mechanisms (note that the reaction rate constant used in CBM-Z is about 7.5 times greater than that used in CB05, as indicated by Zhang et al., (2012)). The lower mixing ratios of HNO_3 by WRF/Chem lead to lower NO_3^- concentrations. Higher SO_4^{2-} and NO_3^- concentrations by CMAQ neutralize more NH_3 in the gas-phase to form more NH_4^+ than WRF/Chem. As discussed by Yu et al. (2005), SO_4^{2-} , NO_3^- , and NH_4^+ are closely related through aerosol thermodynamics, in particular, the partitioning of total ($\text{HNO}_3 + \text{NO}_3^-$) between gas and particulate phases depends on the concentrations of SO_4^{2-} and NH_4^+ . Therefore, different predictions of SO_4^{2-} and NH_4^+ by WRF/Chem and CMAQ can also help explain different partitioning of total nitrate in the gas- and particulate phases from both models. While higher PBLH and surface layer thickness in WRF/Chem explain the lower concentrations of EC and OC, neglecting SOA formation is another reason for lower OC. In the CMAQ simulation of Wang et al. (2010a, b), mineral dust emissions are not included, leading to much lower OIN concentrations than WRF/Chem. Comparing to CMAQ, WRF/Chem predicts much higher NaCl concentrations, because of much higher NaCl emissions resulted from much higher wind speeds. On the other hand, the concentrations of NO_3^- , EC, OC, and OIN simulated by WRF/Chem in Taiwan are higher than those by CMAQ, leading to higher $\text{PM}_{2.5}$ concentrations thus much less underpredictions in $\text{PM}_{2.5}$ in all months as shown in Table 3. Comparing to

CMAQ, WRF/Chem gives more accurate AOD in all months except for April due to higher PM_{10} concentrations at surface and throughout the atmosphere.

Figure 6 compares simulated concentrations of $\text{PM}_{2.5}$ and its composition by both models at the THU site against observations. Comparing to WRF/Chem, CMAQ gives better agreement for $\text{PM}_{2.5}$ in January, July, and October, SO_4^{2-} , NO_3^- , and NH_4^+ in all months except for July, and OC in all months. Although CMAQ and WRF/Chem use the same emissions, they differ in their PBLH and surface layer thickness, which lead to generally higher concentrations predicted by CMAQ than by WRF/Chem in most months. CMAQ simulates SOA formation, which also helps explain its better OC agreement. However, even with a SOA module, CMAQ significantly underpredicts the OC concentrations in April, July, and October, further supporting possible underestimates in primary OC emissions. Figure 7 compares simulated concentrations of O_3 and PM_{10} by the two models and against observations in six cities in Japan during the four months. CMAQ gives higher O_3 at all sites in April, and July at most sites (except for Nagoya and Nagasaki) in January, only at two sites (Sapporo and Nagoya) in October. As discussed before, this is mainly attributed to higher PBLH and surface layer thickness in WRF/Chem and to a much less extent to chemistry differences between CB05 and CBM-Z. CMAQ gives lower PM_{10} concentrations at Nagasaki and Tsukuba in January, all sites in April and July, and three sites (i.e., Sapporo, Nagasaki, and Tsukuba) in October. This is mainly attributed to the higher dust concentrations simulated by WRF/Chem, particularly at Nagasaki and Tsukuba in all months, Sapporo in all months except for January, and at other sites in April and July.

5. Conclusions

WRF/Chem v. 3.3.1 is applied at a 36-km grid resolution to East Asia for January, April, July, and October 2005 using released default model treatments and the model inputs based on a previous application of CMAQ. The simulation results are comprehensively evaluated against

multiple surface and satellite observational datasets. The WRF/Chem baseline simulation shows moderate to large biases for all major meteorological variables except for Q2 for most months. For T2, the MBs range from -1.5 to 1°C, and NMBs range from -9.8% to 75.6%. For WS10, the MBs range from 1.9 to 3.1 m s⁻¹ and NMBs range from 66.5 to 101.0%. For Precip, WRF/Chem can generally capture its spatial distributions but tends to overpredict in some regions, with MBs of 0.2-1.7 mm day⁻¹ and NMBs of 11.4-92.7%. WRF/Chem captures the general pattern of CF in January and July but with underpredictions over southern and northwestern China, and overpredictions over the Pacific oceanic areas. It simulates GLW and GSW well in terms of both spatial distributions and magnitudes but underpredicts LWP over northern domain. These results indicate some limitations in the YSU PBL and the Monin-Obukhov schemes used in resolving main features of complex terrain with uneven surface topography, and in the Purdue Lin cloud microphysics and the Grell-Devenyi ensemble schemes in simulating cloud and precipitation formation.

WRF/Chem significantly underpredicts the surface concentrations of all chemical species and overpredicts those of O₃. The seasonal mean NMBs are -72.0% to -53.8% for CO, -99.4% to -91.8% for NO, -61.7% to -88.1% for NO₂, -84.2% to -44.5% for SO₂, -11.0% to 160.3% for O₃, -63.9% to -25.2% for PM_{2.5} (at the Taiwan sites only), and -68.9% to -2.9% for PM₁₀ at all surface sites. The model simulates reasonably well PM_{2.5} concentrations in all months except for January at the THU site in Beijing. Possible reasons for such large underpredictions in all species except for O₃ include possible underestimations in anthropogenic emission rates (e.g., local and biomass burning emissions for CO, the volcanic and surface emissions for SO₂, surface emissions for primary PM), vertical distributions of emissions (e.g., for SO₂ and NO₂), missing or inaccurate model representations (e.g., a lack of SOA module, the uncertainty in the dust emission scheme, and overpredicted dry deposition of SO₂), and

inaccurate meteorological fields (e.g., overpredicted WS10 and Precip, possibly higher PBLH than observations, and underpredicted T2). The overpredictions of O₃ are closely related to the underpredictions of NO_x because of an insufficient titration of O₃ by NO_x and possible underpredictions in dry deposition fluxes of O₃.

Comparing to surface concentrations, WRF/Chem can better simulate the column abundances of gases, with NMBs of -24.2% to 4.0% for column CO, -30.6% to -0.01 % for column NO₂, -40.0%, to 26.1% for column SO₂, and -32.3% to 45.4% against TOMS and -22.4% to 27.2% against OMI for column O₃. Possible reasons for moderate biases include some problems in the vertical allocations of emissions (e.g., for NO₂ and SO₂), large uncertainties in satellite retrievals (e.g., for SO₂), uncertainties in upper BCs (e.g., for O₃ and CO), and overpredictions in dry deposition fluxes (e.g., for SO₂). Moderate underpredictions with NMBs of -38.7% to -16.2% in AOD occur in all months except for October, due mainly to underpredictions in PM_{2.5} concentrations over eastern China in January and southwestern Pacific ocean in July.

Comparing to MM5, WRF generally gives worse meteorological predictions, in particular, T2, WS10, GSW, GLW, and CF in all months, and Q2 and Precip in January and October. Better performance of MM5 can be attributed to the use of FDDA with analysis nudging, the high resolution Blackadar PBL scheme, the cloud-radiation shortwave radiation scheme, the mixed phase (Reisner 1) explicit moisture scheme, and the Kain-Fritsch 2 cumulus scheme used in the MM5 simulations. Comparing to CMAQ, WRF/Chem gives less underpredictions in surface CO mixing ratios and PM₁₀ concentrations, less overpredictions in surface O₃ mixing ratios at most sites in most months, and lower biases in column CO and SO₂ abundances. It, however, gives poorer performance for surface NO_x at most sites in most months, surface SO₂ at all sites in all months, and column NO₂ abundances in January and

April. Both models perform similarly for column O₃ abundances in terms of magnitudes but the spatial distributions from CMAQ agree better with observations. Those differences can be attributed to several reasons including much higher PBLH, surface layer thickness, precipitation, dry deposition of SO₂ and O₃, aqueous-phase oxidation of SO₂ to SO₄²⁻, but lower concentrations of OH, HO₂, NO_x, and HCHO in the WRF/Chem simulations. WRF/Chem gives quite different spatial distributions of PM_{2.5} and PM₁₀ in northern and western parts of the domain, because of unrealistically high dust concentrations. It gives lower concentrations of secondary inorganic (i.e., SO₄²⁻, NO₃⁻, NH₄⁺) and carbonaceous PM (i.e., EC and OC), but higher OIN concentrations over land and higher Na⁺ and Cl⁻ concentrations over oceanic areas. WRF/Chem gives more accurate AOD in all months except for April due to higher PM₁₀ concentrations at surface and throughout the atmosphere. Those differences can be attributed to differences in simulated meteorology (MM5 vs. WRF), gas-phase chemistry (i.e., CB05 in CMAQ vs. CBMZ in WRF/Chem), dry and wet deposition treatments (e.g., for SO₂ and SO₄²⁻), aerosol thermodynamic and dynamic treatments including SOA formation (e.g., no SOA formation in WRF/Chem), and dust and sea salt emissions (e.g., unrealistically high dust emissions due to the use of default Shaw (2008) dust emission scheme, and higher NaCl emissions due to higher WS10 by WRF/Chem).

The comprehensive evaluations of WRF/Chem and the intercomparison with MM5/CMAQ indicate that with the original inputs based on a previous CMAQ application and the default model treatments of WRF/Chem v3.3.1, the skills of WRF/Chem are generally not as good as MM5/CMAQ with model configurations that have been tested extensively. This work also identifies several areas of improvements for WRF/Chem including the emissions in terms of both magnitudes and vertical distributions, upper BCs for O₃, inappropriateness of the default Shaw (2008) dust emission scheme, inaccurate representations of surface roughness in

the PBL scheme, and a lack of SOA formation. These major limitations will be addressed through improvement of WRF/Chem inputs and treatments in Part II paper.

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List of Figures

Figure 1. Map of locations of observational sites. (a) NCDC sites (blue dots), (b) China-API (blue dots), Japan-NIES (green dots), Taiwan-PSI (yellow dots), Hong Kong-API (purple pentagram), and THU-PM (red pentagram).

Figure 2. The spatial distributions of major meteorological variables simulated by MM5/CMAQ and WRF/Chem in January and July, 2005.

Figure 3. The observed and simulated column meteorological variables by MM5/CMAQ and WRF/Chem in January and July, 2005. The observed CF, LWP, GLW, and GSW are from CERES observations and the observed Precip is from TRMM observations.

Figure 4. The spatial distributions of observed and simulated column chemical variables by MM5/CMAQ and WRF/Chem in January and July, 2005.

Figure 5. The surface concentrations of $PM_{2.5}$ and PM_{10} simulated by MM5/CMAQ and WRF/Chem in January, April, July, and October, 2005.

Figure 6. Comparison of observed surface concentrations of $PM_{2.5}$ and its composition and those simulated by MM5/CMAQ and WRF/Chem at the Tsinghua site, Beijing, China in Jan., Apr., Jul., and Oct., 2005.

Figure 7. Comparison of observed surface concentrations of Ox and PM_{10} and those simulated by MM5/CMAQ and WRF/Chem at the six city sites, Japan in Jan., Apr., Jul., and Oct., 2005.

Table 1. Configurations of MM5/CMAQ and WRF/Chem

Process	MM5/CMAQ	WRF/Chem
Shortwave radiation	The cloud-radiation shortwave radiation scheme	The Goddard shortwave radiation scheme (Chou et al., 1998)
Longwave radiation	The rapid radiative transfer model (RRTM) longwave radiation scheme (Mlawer et al., 1997)	RRTM
Land surface	Community National Centers for Environmental Prediction (NCEP), Oregon State University, Air Force, and Hydrologic Research Lab-NWS Land Surface Model (NOAH) (Chen and Dudhia, 2001; Ek et al., 2003)	NOAH
Surface layer	The force/restore (Blackadar) surface scheme (Blackadar, 1976)	The Monin-Obukhov (Janjić, 2001)
PBL	The high resolution Blackadar PBL scheme (Zhang and Anthes, 1982)	The Yonsei University Scheme (YSU) (Hong et al., 2006)
Cumulus	The Kain-Fritsch 2 cumulus scheme (Kain, 2002)	The Grell-Devenyi ensemble (Grell and Devenyi, 2002)
Microphysics	The mixed phase (Reisner 1) explicit moisture scheme for cloud microphysics (Reisner et al., 1998)	The Purdue Lin (Lin et al., 1983; Chen and Sun, 2002)
Gas-phase chemistry	The 2005 Carbon Bond Mechanism (CB05) (Yarwood et al., 2005)	CBM-Z (Zaveri and Peters, 1999)
Photolysis	Precalculated rates using the total ozone column data from the Total Ozone Mapping Spectrometer (TOMS) and the photolysis rates processor (JPROC)	Fast-J (Wild et al., 2000)
Aerosol module	Aero4 aerosol module	Model for Simulating Aerosol Interactions and Chemistry (MOSAIC) (Zaveri et al., 2008)
Aqueous-phase chemistry	Modified RADM (Walcek and Taylor, 1986)	Carnegie Mellon University (CMU) mechanism of Fahey and Pandis (2001)
Aerosol activation	None	Abdul-Razzak and Ghan (Abdul-Razzak and Ghan, 2002)

Table 2. Performance statistics for meteorological variables for MM5 and WRF/Chem

Variable /Data Source [Unit]	Time Period	Run ID	Data Point	Mean Obs	Mean Sim	MB	NMB (%)	NME (%)	RMSE	R
T2 /NCDC (°C)	Jan.	MM5	341262	1.3	0.5	-0.8	-62.3	2.0	11.9	0.95
		WRF/Chem			2.3	1.0	75.6	270.2	20.9	0.91
	Apr.	MM5	333109	14.0	12.9	-1.1	-7.6	0.2	12.7	0.91
		WRF/Chem			12.6	-1.4	-9.8	22.3	16.7	0.88
	Jul.	MM5	345581	24.5	23.9	-0.6	-2.4	0.1	9.5	0.84
		WRF/Chem			23.0	-1.5	-6.0	12.5	15.6	0.76
	Oct.	MM5	335051	16.3	15.1	-1.2	-7.1	0.2	9.8	0.93
		WRF/Chem			16.5	0.2	1.5	17.6	14.1	0.88
Q2 /NCDC (g kg ⁻¹)	Jan.	MM5	206380	3.4	3.6	0.2	6.2	0.2	0.5	0.96
		WRF/Chem			4.2	0.8	23.4	36.0	2.8	0.86
	Apr.	MM5	184416	6.3	6.6	0.3	5.1	0.2	2.2	0.93
		WRF/Chem			6.4	0.1	1.5	19.7	2.9	0.90
	Jul.	MM5	214619	14.6	14.1	-0.5	-3.5	0.1	4.8	0.87
		WRF/Chem			14.7	0.1	0.4	11.5	4.9	0.85
	Oct.	CMAQ	218732	8.6	8.6	0.0	0.3	0.1	2.2	0.94
		WRF/Chem			9.7	1.1	13.1	24.9	7.6	0.86
WS10 /NCDC (m s ⁻¹)	Jan.	MM5	341349	3.1	3.9	0.9	27.8	0.6	6.1	0.61
		WRF/Chem			6.2	3.1	101.0	115.4	20.5	0.51
	Apr.	MM5	332437	3.3	3.6	0.3	8.5	0.5	5.2	0.59
		WRF/Chem			5.6	2.2	66.5	86.9	13.5	0.45
	Jul.	MM5	344863	2.6	3.0	0.3	11.8	0.6	3.8	0.58
		WRF/Chem			4.5	1.9	70.9	97.3	11.3	0.36
	Oct.	MM5	334380	2.7	3.2	0.5	18.8	0.6	4.0	0.62
		WRF/Chem			5.0	2.3	84.5	104.4	13.1	0.43
Precip /NCDC (mm day ⁻¹)	Jan.	MM5	24107	1.0	0.9	-0.1	-13.0	1.2	18.4	0.33
		WRF/Chem			2.0	0.9	92.7	207.8	49.9	0.23
	Apr.	MM5	24319	1.7	1.4	-0.2	-13.5	1.3	41.6	0.32
		WRF/Chem			1.9	0.2	13.6	159.2	61.1	0.20
	Jul.	MM5	24701	5.3	4.5	-0.7	-14.0	1.2	240.1	0.37
		WRF/Chem			5.9	0.6	11.4	155.8	441.4	0.13
	Oct.	MM5	24695	1.9	1.6	-0.3	-17.3	1.2	65.0	0.36
		WRF/Chem			3.6	1.7	89.8	233.4	216.7	0.16

Table 3. Performance statistics for surface CO, NO, NO₂, SO₂, O₃, PM_{2.5}, and PM₁₀ from 2005 WRF/Chem simulations

Dataset [Unit]	Time Period	Model	CO		NO		NO ₂		SO ₂		O ₃		PM _{2.5}		PM ₁₀	
			NMB (%)	R	NMB (%)	R	NMB (%)	R	NMB (%)	R	NMB (%)	R	NMB (%)	R	NMB (%)	R
China-API	Jan.	CMAQ	--	--	--	--	--	--	-54.7	0.10	--	--	--	--	-36.2	0.14
		WRF/Chem	--	--	--	--	--	--	-71.6	0.11	--	--	--	--	-37.8	0.07
	Apr.	CMAQ	--	--	--	--	--	--	-54.9	0.20	--	--	--	--	-48.5	0.16
		WRF/Chem	--	--	--	--	--	--	-80.4	0.22	--	--	--	--	-17.2	0.28
	Jul.	CMAQ	--	--	--	--	--	--	-61.3	0.30	--	--	--	--	-47.2	0.30
		WRF/Chem	--	--	--	--	--	--	-80.1	0.18	--	--	--	--	-35.5	0.16
	Oct.	CMAQ	--	--	--	--	--	--	-53.1	0.21	--	--	--	--	-26.5	0.41
		WRF/Chem	--	--	--	--	--	--	-78.0	0.22	--	--	--	--	-2.9	0.28
Hong Kong-API	Jan.	CMAQ	-63.0	0.31	-99.4	-0.10	-82.0	0.43	-41.1	0.52	197.2	0.57	--	--	-28.1	0.42
		WRF/Chem	-64.0	0.28	-99.4	-0.08	-88.1	0.27	-79.6	0.19	160.3	0.19	--	--	-15.8	0.12
	Apr.	CMAQ	-75.6	0.60	-99.2	0.34	-84.8	0.40	-62.8	0.43	113.6	0.72	--	--	-53.3	0.59
		WRF/Chem	-70.6	0.61	-98.6	0.14	-86.1	0.45	-84.2	0.27	88.0	0.58	--	--	-47.4	0.69
	Jul.	CMAQ	-80.0	0.36	-98.9	0.38	-85.3	0.32	-78.4	0.65	106.5	0.78	--	--	-68.3	0.73
		WRF/Chem	-72.0	0.58	-98.7	0.23	-83.7	0.35	-81.6	0.38	125.0	0.76	--	--	-31.3	0.59
	Oct.	CMAQ	-64.1	0.54	-98.6	0.26	-80.0	0.12	-24.6	0.23	56.7	0.61	--	--	-25.6	0.47
		WRF/Chem	-55.3	0.00	-98.7	0.20	-82.8	0.21	-59.1	0.52	94.4	0.42	--	--	-6.9	0.29
Taiwan-PSI	Jan.	CMAQ	-64.4	0.11	-95.8	0.05	-63.6	0.25	-30.3	0.25	93.8	0.47	-52.8	0.35	-63.8	0.35
		WRF/Chem	-62.4	0.08	-96.8	0.01	-75.5	0.24	-65.5	0.15	83.8	0.43	-61.0	0.08	-60.7	0.17
	Apr.	CMAQ	-72.8	0.13	-93.6	0.04	-70.9	0.14	-40.5	0.10	24.9	0.53	-57.9	0.44	-72.7	0.48
		WRF/Chem	-67.2	0.09	-92.2	-0.01	-67.5	0.13	-44.5	0.04	13.6	0.59	-41.1	0.19	-49.7	0.27
	Jul.	CMAQ	-70.0	0.13	-84.1	0.02	-64.2	0.18	-41.7	0.04	-12.0	0.61	-73.6	0.27	-81.7	0.17
		WRF/Chem	-62.6	0.09	-91.8	-0.01	-61.7	0.14	-49.6	0.01	14.5	0.66	-63.9	0.29	-68.9	0.18
	Oct.	CMAQ	-62.9	0.14	-87.2	0.05	-59.2	0.27	-20.7	0.22	0.0	0.53	-59.3	0.49	-74.5	0.43
		WRF/Chem	-53.8	0.14	-93.8	0.03	-68.0	0.15	-45.9	0.18	23.7	0.52	-25.2	0.15	-49.3	0.26
Japan-NIES	Jan.	CMAQ	-67.7	0.25	-94.6	0.28	-63.2	0.47	-53.4	0.24	35.1	0.37	--	--	-53.8	0.59
		WRF/Chem	-69.7	0.27	-96.9	0.29	-80.2	0.42	-81.6	0.18	33.2	0.33	--	--	-46.0	0.36
	Apr.	CMAQ	-62.9	0.19	-95.5	0.33	-69.8	0.52	-64.6	0.32	21.6	0.36	--	--	-50.0	0.59
		WRF/Chem	-61.4	0.24	-92.9	0.19	-76.4	0.48	-79.5	0.23	-11.0	0.24	--	--	33.3	0.56
	Jul.	CMAQ	-66.6	0.19	-95.9	0.23	-68.2	0.57	-70.0	0.41	34.2	0.33	--	--	-72.5	0.60
		WRF/Chem	-59.5	0.20	-93.2	0.18	-64.4	0.58	-78.0	0.38	16.3	0.37	--	--	-51.2	0.50
	Oct.	CMAQ	-62.6	0.17	-95.5	0.19	-57.8	0.56	-49.1	0.34	39.4	0.33	--	--	-52.2	0.47
		WRF/Chem	-65.4	0.22	-97.4	0.25	-74.9	0.54	-79.0	0.28	28.5	0.44	--	--	-15.5	0.32

“--” no observations are available

Table 4. Performance statistics for column variables

Variable /Data Source [Unit]	Time Period	Run ID	Data Point	Mean Obs	Mean Sim	MB	NMB (%)	NME (%)	RMSE	R
CO /MOPITT [1×10^{17} molecules cm^{-2}]	Jan.	CMAQ	15903	20.1	18.7	-1.3	-6.7	20.1	5.1	0.70
		WRF/Chem			20.8	0.8	3.9	17.4	5.2	0.69
	Apr.	CMAQ	15908	24.9	--	--	--	--	--	--
		WRF/Chem			18.9	-6.0	-24.2	25.7	7.1	0.85
	Jul.	CMAQ	15862	16.7	13.7	-3.0	-17.9	28.3	5.1	0.68
		WRF/Chem			16.1	-0.6	-3.5	21.8	4.6	0.59
	Oct.	CMAQ	15908	19.6	--	--	--	--	--	--
		WRF/Chem			19.6	0.0	0.2	9.7	2.8	0.86
NO ₂ /SCIA-MACHY [1×10^{15} molecules cm^{-2}]	Jan.	CMAQ	11275	3.7	3.0	-0.7	-18.7	56.1	5.1	0.77
		WRF/Chem			2.6	-1.1	-30.6	60.3	5.7	0.75
	Apr.	CMAQ	14257	2.1	1.7	-0.4	-17.2	55.7	2.7	0.73
		WRF/Chem			1.7	-0.4	-19.1	56.2	2.8	0.75
	Jul.	CMAQ	12981	1.5	1.1	-0.4	-28.4	61.1	2.4	0.51
		WRF/Chem			1.4	-0.2	-11.3	57.7	2.1	0.61
	Oct.	CMAQ	13203	2.1	2.3	0.2	-0.9	66.7	3.0	0.74
		WRF/Chem			2.1	0.0	-0.0	67.6	3.1	0.74
SO ₂ /SCIA-MACHY [DU]	Jan.	CMAQ	9320	0.2	0.5	0.3	104.1	140.9	0.6	0.64
		WRF/Chem			0.3	0.1	21.4	76.8	0.3	0.64
	Apr.	CMAQ	14477	0.2	--	--	--	--	--	--
		WRF/Chem			0.2	-0.1	-31.7	56.0	0.2	0.61
	Jul.	CMAQ	13347	0.2	0.1	-0.1	-41.3	84.1	0.3	0.15
		WRF/Chem			0.1	-0.1	-40.0	82.2	0.3	0.15
	Oct.	CMAQ	9824	0.2	--	--	--	--	--	--
		WRF/Chem			0.2	0.0	26.1	90.9	0.2	0.54
TOR/TOMS [DU]	Jan.	CMAQ	15908	24.5	35.4	10.9	44.5	44.9	12.9	0.06
		WRF/Chem			35.7	11.1	45.4	46.0	13.1	0.11
	Apr.	CMAQ	15908	41.3	--	--	--	--	--	--
		WRF/Chem			41.1	-0.2	-0.5	12.9	6.8	0.19
	Jul.	CMAQ	15908	45.3	29.5	-15.8	-34.9	34.9	16.9	0.72
		WRF/Chem			30.7	-14.6	-32.3	32.6	16.6	0.21
	Oct.	CMAQ	15908	30.7	--	--	--	--	--	--
		WRF/Chem			32.4	1.7	5.6	12.9	4.6	0.60
TOC/OMI [DU]	Jan.	CMAQ	15899	28.0	35.4	7.4	26.4	27.3	9.3	0.64
		WRF/Chem			35.7	7.6	27.3	28.2	8.9	0.78
	Apr.	CMAQ	15904	36.0	--	--	--	--	--	--
		WRF/Chem			41.1	5.1	14.2	18.3	8.0	0.54
	Jul.	CMAQ	15897	38.0	29.5	-8.5	-22.4	23.0	9.6	0.86
		WRF/Chem			30.7	-7.4	-19.4	21.1	9.5	0.65
	Oct.	CMAQ	15908	30.2	--	--	--	--	--	--
		WRF/Chem			32.4	2.2	7.4	12.6	4.6	0.70
AOD /MODIS	Jan.	CMAQ	11012	0.3	0.3	0.1	19.0	43.4	0.2	0.72
		WRF/Chem			0.2	-0.0	-16.2	44.1	0.2	0.53
	Apr.	CMAQ	13425	0.4	0.3	-0.1	-31.2	38.9	0.2	0.66
		WRF/Chem			0.3	-0.2	-38.7	45.2	0.3	0.51
	Jul.	CMAQ	15039	0.3	0.2	-0.1	-38.7	47.0	0.2	0.62
		WRF/Chem			0.3	-0.1	-28.0	46.7	0.2	0.52
	Oct.	CMAQ	14544	0.2	0.3	0.0	14.6	51.0	0.2	0.73
		WRF/Chem			0.2	0.0	5.6	47.4	0.2	0.57

-- no observations are available. Note that the simulated results for column CO, SO₂, and O₃ are not available because of the loss of upper layer model outputs from CMAQ simulations of Wang et al. (2010a, b).

Figure 1. Map of locations of observational sites. (a) NCDC sites (blue dots), (b) China-API (blue dots), Japan-NIES (green dots), Taiwan-PSI (yellow dots), Hong Kong-API (purple pentagram), and THU-PM (red pentagram).

Figure 2. The spatial distributions of major meteorological variables simulated by MM5/CMAQ and WRF/Chem in January and July, 2005.

Figure 3. The observed and simulated column meteorological variables by MM5/CMAQ and WRF/Chem in January and July, 2005. The observed CF, LWP, GLW, and GSW are from CERES observations and the observed Precip is from TRMM observations.

Figure 4. The spatial distributions of observed and simulated column chemical variables by MM5/CMAQ and WRF/Chem in January and July, 2005.

Figure 5. The surface concentrations of PM_{2.5} and PM₁₀ simulated by MM5/CMAQ and WRF/Chem in January, April, July, and October, 2005.

Figure 6. Comparison of observed surface concentrations of PM_{2.5} and its composition and those simulated by MM5/CMAQ and WRF/Chem at the Tsinghua site, Beijing, China in Jan., Apr., Jul., and Oct., 2005.

Figure 7. Comparison of observed surface concentrations of O_x and PM₁₀ and those simulated by MM5/CMAQ and WRF/Chem at the six city sites, Japan in Jan., Apr., Jul., and Oct., 2005.