

Air Pollution Meteorology

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Synopsis

Meteorological conditions play important roles in modulating the ambient concentrations of pollutants through different ways. For example, meteorological variables exert important influences on the formation and fate of pollutants such as ozone and aerosols; meteorological processes (e.g., advection and vertical mixing) dictate the dispersion of pollutants. Thus, accurately simulating meteorological conditions is critical for correctly simulating pollution events. Uncertainties are associated with model treatments for various processes in air quality models. Methods such as ensemble simulation and parameter estimation could potentially improve air quality simulations.

Description of Pollutants in the Air

The United States Environmental Protection Agency (U.S. EPA) set National Ambient Air Quality Standards (NAAQS) for six principal pollutants in 1990s to provide protection for public health and the environment. These six principal pollutants are called 'criteria' pollutants, which include carbon monoxide (CO), lead, nitrogen dioxide (NO₂), ozone (O₃), sulfur dioxide (SO₂), and particles (or aerosols). The NAAQS are periodically reviewed and revised to be in line with the updated science. Among the six criteria air pollutants, the formation of O₃ and aerosols involves the most complicated processes. Ozone is a secondary pollutant, produced from oxides of nitrogen and reactive organic gases in the presence of sunlight. When O₃ reaches critical levels, adverse environmental effects are expected for human health, crops, and natural vegetation. The adverse environmental effects of O₃ were first reported in Los Angeles during 1940s. Now it is realized that O₃ pollution is no longer confined to Los Angeles and it affects major urban locations in the world. Elevated O₃ concentrations were also reported in rural and even remote regions. Aerosols range from nanometers to hundreds of micrometers (μm), coming from both primary and secondary sources. Elevated concentrations of aerosols can cause or enhance respiratory, cardiovascular, infectious, and allergic diseases. The primary parameters that determine the environmental and health effects of aerosols are their concentration, size, structure, and chemical composition, which are spatially and temporally highly variable. The formation and fate of O₃ and aerosols have received extensive attention by the research community.

Structure of the Atmospheric Boundary Layer and Its Relationship with Plume Behaviors

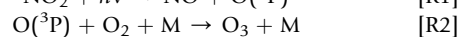
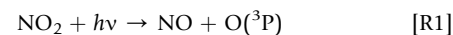
The atmospheric boundary layer is defined as the lowest part of the troposphere that is directly influenced by the presence of the earth's surface, and responds to surface forcing within a timescale of about an hour or less. The variation of the boundary layer plays a critical role for dictating the dispersion of pollutants since most pollutants are emitted or formed in the boundary layer. The boundary layer depth may vary from hundreds of meters to a few kilometers. Over oceans, the

boundary layer depth varies relatively slowly in space and time due to little change of ocean water temperature. The boundary layer depth varies dramatically over the land. During the daytime, due to the surface heating from shortwave radiation, turbulence is generated in the lower 1–2 km above the ground, which is called the mixed layer. The turbulence tends to mix heat, momentum, moisture, and pollutants uniformly in the mixed layer. A stable layer at the top of the mixed layer restrains the vertical extent of turbulence. This layer is called the entrainment zone because entrainment into the mixed layer occurs at this layer. After sunset, turbulence decays in the formerly mixed layer. The upper portion of the formerly mixed layer becomes the residual layer, in which the state variables and concentrations of pollutants remain mostly invariant. The lower portion of the formerly mixed layer is transformed into a stable boundary layer, which is characterized by statically stable air with weaker, sporadic turbulence. After sunrise of the following day, the mixed layer starts to grow again.

A large portion of anthropogenic emissions is released in the form of plumes. Due to higher temperatures compared with the ambient air, these plumes are typically highly buoyant. Depending on the thermal conditions of plume itself and the ambient atmosphere, the plumes can rise to different heights. Different characteristics of the atmospheric boundary layer dictate the way the plumes are dispersed. Plumes released in the mixed layer may loop up and down initially and become uniformly distributed vertically eventually. Plumes released in the stable boundary layer fan out in the horizontal with little vertical dispersion. Plumes in the residual layer spread with an almost equal rate in the vertical and horizontal, exhibiting a conelike shape.

Tropospheric O₃ Chemistry and Aerosol Processes

The overall tropospheric photochemical O₃ formation mechanism is well known. In the troposphere, O₃ is produced from the photolysis of nitrogen dioxide ([R1]) and the subsequent reaction of the ground state oxygen atoms, O(³P), with molecular oxygen ([R2]).



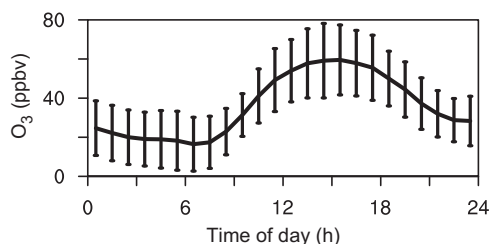
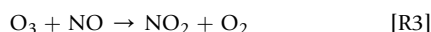


Figure 1 Mean diurnal variation of O_3 and its standard deviation in Beltsville, Maryland, United States, during August 2010.

Once formed, O_3 may be removed from the atmosphere through dry deposition process and NO titration reaction [R3].



Ozone has different variability in different regions. In the continental atmospheric boundary layer, where the concentration of nitrogen oxides (NO_x) is relatively high, local photochemical production of O_3 will contribute to the O_3 maximum in the afternoon in the presence of sunlight and high temperature. Figure 1 shows the diurnal variation of O_3 in Beltsville, Maryland, United States, during August 2010. During the night, O_3 mixing ratios decreased due to NO titration ([R3]) and dry deposition. Photochemical reactions contributed to the O_3 formation during daytime. In the marine boundary layer, where the concentration of NO_x is relatively low, air chemistry can lead to the destruction of O_3 . Figure 2 shows the diurnal variation of O_3 mixing ratio at Kwajalein Atoll situated in the equatorial Pacific Ocean in summer 1999. During the daytime, O_3 photolysis, hydroperoxyl radicals (HO_2), hydroxyl radicals (OH), and bromine atoms (Br) contributed to the destruction of O_3 , which led to the observed minimum O_3 levels in the afternoon. The entrainment of O_3 -rich air from the free troposphere to the local marine boundary layer provided a recovery mechanism of surface O_3 during nighttime.

Aerosol particles are ubiquitous in the atmosphere with diameters ranging from a few nanometers to around hundred micrometers. The ambient aerosol particles are characterized by two modes, the fine mode (with a diameter $\leq 2.5 \mu m$) and the coarse mode (with a diameter $> 2.5 \mu m$). Fine mode aerosol particulate mass is referred to as $PM_{2.5}$, which is believed to pose the largest health risks. The aerosol particulate matter may

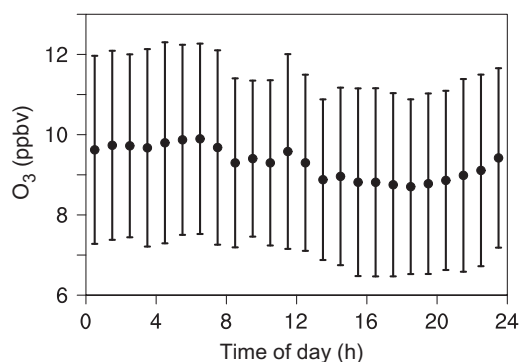


Figure 2 Mean diurnal variation of O_3 mixing ratio and its standard deviation at Kwajalein during July, August, and September 1999.

be either directly emitted or formed in the atmosphere, which are referred to as primary and secondary sources, respectively. Primary sources of aerosol include combustion, windblown dust, pollen, plant fragments, and sea salt. Secondary aerosols are produced in the atmosphere by photochemical processes and added to the preexisting particles through the gas/particle mass transfer process. Most of the mass of $PM_{2.5}$ is composed of secondary aerosol. In some cases more than 90% of the $PM_{2.5}$ mass may be attributed to secondary aerosol.

Effects of Meteorology on Air Pollution

Effects of Meteorology on Biogenic Emissions

Biogenic emissions play an important role in regional air quality and global atmospheric chemistry. Isoprene (C_5H_8) is the predominant volatile organic compound (VOC) emitted by vegetation. It plays a key role in contributing to the formation of O_3 and affecting the lifetime of other species. Biogenic emissions are controlled by ambient environmental variables, most notably temperature and light. Increases in temperature normally lead to increased isoprene emissions. Future climate change (e.g., temperature increase) is expected to increase biogenic emissions, which will likely influence regional air quality.

Effects of Meteorological Variables on the Formation of O_3 and Aerosol

Episodes of high concentrations of surface O_3 usually occur during the summertime in stagnant air under dry, sunny weather conditions. On a local scale, intense solar radiation favors photochemical O_3 production. Ozone generally increases with increasing temperature and decreases with increasing relative humidity. Warmer temperature enhances O_3 production through affecting photochemical rate constants and biogenic emissions. Water vapor affects O_3 abundance through its consumption of $O(^1D)$ via the reaction $O(^1D) + H_2O \rightarrow 2OH$.

Meteorological variables affect the formation of precursors of aerosols through modulating the reaction efficiency. Once the semivolatile precursors of aerosols are formed, meteorological variables also affect the partitioning of those species between the gas phase and aerosols. The partitioning of semivolatile species depends highly on temperature and relative humidity. Low temperature and high relative humidity favor the partitioning of semivolatile species into the aerosol phase while high temperature and low relative humidity favor the partitioning of semivolatile species into the gas phase.

Effects of Meteorology on Dispersion of Pollutants

Meteorological processes (e.g., advection and vertical mixing) dictate the dispersion of pollutants. A good example of a favorable meteorological condition for heavy pollution is the horizontal advection induced by the coastal breeze in Los Angeles, California. The highly populated Los Angeles is surrounded by mountains on three sides and opens to the Pacific Ocean to the west and southwest. Pollutants accumulated over the urban areas in the stagnant morning air are regularly

transported downwind with the onset of the westerly sea breeze in the morning. The air mass is moved back after the onset of land breeze in the evening. The back and forth flow of the air is constrained by the surrounding mountains which allows the air to become highly enriched with pollutants, which likely leads to pollution episodes. Land/sea breezes are also reported to contribute to the elevated O_3 events in other regions such as Houston, Texas and Hampton, Virginia.

Vertical mixing events are reported to affect the variation of O_3 . Figure 3 shows observed O_3 , NO_x , wind vector, and temperature at Beltsville, Maryland, on 11 August 2010. During the period from 1:00 to 4:00 local time (LT), surface O_3 mixing ratio increased by about 30 parts per billion on a volume basis (ppbv) while NO_x mixing ratio decreased by ~ 25 ppbv (Figure 3). During the night of 10–11 August and most of 11 August 2010 the air mass came from the north. A cold front passed the research site, traveling from north to south on 11 August 2010. If O_3 increases resulted from the advection of an upstream polluted plume then mixing ratios of other pollutants such as CO, NO_x would be likely higher. However, NO_x level decreased as O_3 increased. The duration of this nocturnal O_3 increase (several hours) was similar to the 'leaky inversion' event, which was caused by the vertical exchange of air between the surface stable boundary layer and the residual layer above it. Since the residual layer had higher O_3 and lower concentrations of other pollutants, the vertical exchange of trace gases allowed decreases in surface NO_x and increases in surface O_3 .

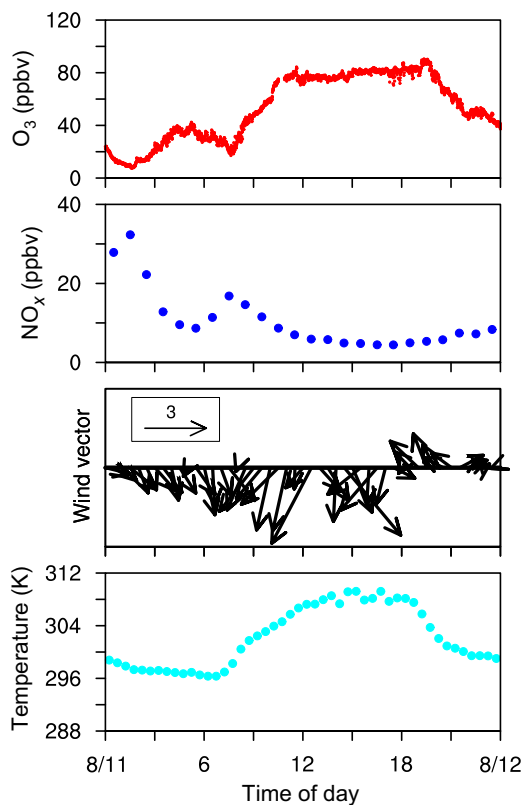


Figure 3 Observed (top to bottom) O_3 , NO_x , wind vector, and temperature at Beltsville, Maryland, on 11 August 2010.

Vertical mixing could be also induced from wind shear and impair air quality near the surface. Nighttime low-level jets (LLJs) occur frequently in the Great Plains. The strong wind shear associated with LLJs was observed to affect the vertical redistribution of O_3 . On the night of 24–25 July 2003, nocturnal O_3 maxima were noticed in the presence of an LLJ (Figure 4). Such phenomenon occurred in Oklahoma quite frequently. Under a calm condition, surface O_3 normally decreased to very low levels (< 10 ppbv) between 20:00 and 22:00 LT due to dry deposition and NO titration. However, on the night of 24–25 July 2003, surface O_3 around Oklahoma city (OKC) increased after 20:00 LT and O_3 concentration stayed at elevated levels (> 40 ppbv) during most of the night. Such nocturnal O_3 maxima (or elevated O_3 concentration) were unlikely due to advection. On the nights of 24–25 July 2003 southerly wind persisted. If the nocturnal surface O_3 maxima were due to southerly advection of O_3 -rich air mass, the upwind site, Goldsby would have experienced higher O_3 maxima than the other downwind sites, which was clearly not the case (Figure 4). Instead, turbulence can be induced by the wind shear associated with the LLJs; the resulted vertical mixing can transport O_3 -rich air mass downward to the surface, thus explaining the frequently observed nocturnal O_3 maxima associated with the LLJs.

Vertical mixing could be also induced from cloud-top radiative cooling and affect the variation of pollutants in the boundary layer. During the springtime, anomalously low O_3 mixing ratios are frequently observed in the Arctic region. Such phenomena are called O_3 depletion events (ODEs). A few mechanisms are proposed to be responsible for the termination of the ODEs. One of the mechanisms is related to the vertical mixing induced from cloud-top radiative cooling. Downdrafts and compensating updrafts induced by the cloud-top radiative cooling can be sufficiently strong to reach the surface. The averaged vertical velocity in the presence of clouds may be as large as 0.6 m s^{-1} in the mixing layer. The vertical mixing associated with cloud updrafts and downdrafts

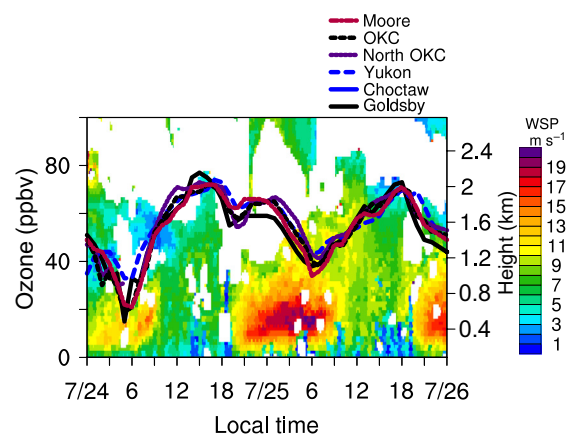


Figure 4 Time–height diagram of wind speed (WSP) in the atmospheric boundary layer and time series of surface O_3 observed on 24–25 July 2003 in the OKC metropolitan area. The left y-axis is O_3 mixing ratio while the right y-axis is the height for wind speed. The six EPA sites in the OKC metropolitan area where O_3 is observed are Moore, OKC, North OKC, Yukon, Choctaw, and Goldsby.

triggered by the clouds can mix the free tropospheric O_3 -rich air downward to replenish the O_3 near the surface, thereby terminating the ODEs.

Air Pollution Modeling

Review of Three-Dimensional Air Quality Models

Air quality models (AQMs) integrate our knowledge on how physical and chemical processes affect pollutant concentrations and serve as a numerical laboratory. AQMs could be divided into two categories based on their reference frame: Lagrangian and grid-based Eulerian models. The Lagrangian models have simple structures and low requirements for computational resources, but have limitations in their formulation. The grid-based Eulerian models involve the least restrictive assumptions and are potentially the most powerful.

The grid-based Eulerian models can be further divided into two types based on the coupling between the meteorology (or dynamics) and chemistry in the model: offline vs online. In the off-line models, the meteorology representation/simulation is conducted prior to the simulation of chemistry. The off-line models use either prescribed observation-based or model-based meteorological fields at discrete times (normally hourly) to drive the chemistry models. The meteorological fields are interpolated to the appropriate transport time and coordinate frame for the use of the chemistry simulation in the off-line models. The off-line models are computationally efficient, and one set of meteorological data can be used to drive multiple chemistry simulations; however, they are incapable of simulating chemistry feedback to meteorology. In the real atmosphere, chemical and meteorological processes closely interact through climate–chemistry–aerosol–cloud–radiation feedbacks. Such feedbacks include: (1) aerosols may warm or cool the atmosphere by directly absorbing and scattering solar and terrestrial radiation; (2) aerosols may also indirectly affect cloud microphysics such as formation, albedo, lifetime, and precipitation through serving as cloud condensation nuclei. Those feedbacks are important; however, they cannot be simulated in the off-line models because of the decoupled treatments of meteorology and chemistry. The off-line models are traditionally used for air quality modeling due to the historical separation of meteorology and air quality communities, as well as our limited understanding of the climate–chemistry–aerosol–cloud–radiation feedbacks. In the online models, the meteorology and chemistry are simulated simultaneously in one coordinate frame. The online models make it possible to simulate the complex climate–chemistry–aerosol–cloud–radiation feedbacks given their closely coupled structure and treatments. In addition, the online models can utilize the detail meteorological process to drive chemistry simulation without interpolation.

Eulerian AQMs developed thus far can be categorized into three generations. The first-generation models are relatively simple models, in which dry deposition processes are not included. The second-generation models include deposition processes and have expanded chemical mechanisms in terms of both chemical species and reactions, and use improved numerical integration schemes. Both the first-generation and second-generation AQMs are off-line models. The off-line models

developed in the United States include the Sulfur Transport Eulerian Model, the Regional Oxidant Model (ROM), the Urban Airshed Model with Carbon Bond IV (UAM-IV), the Urban Airshed Model with Variable Grid (UAM-V), the Acid Deposition and Oxidant Model, the Regional Acid Deposition Model, the Community Multiscale Air Quality (CMAQ) Modeling System, SJVAQS/AUSPEX Regional Model Adaptation Project air quality model, the Multiscale Air Quality Simulation Program, and the Urban-to-Regional Multiscale model. ROM, UAM-IV, UAM-V, and CMAQ have been recommended by the U.S. EPA for regulatory applications. Several European regional AQMs are also off-line models, including the European Monitoring and Evaluation Programme model, the European Air Pollution Dispersion model, the Long-Term Ozone Simulation model, and the Regional Eulerian Model with three different chemistry schemes. It was envisioned that the third-generation models should be online models, in which the interactions among chemistry and meteorology will be treated.

Some simple online models were developed since 1960s; however, in most of those, the coupling between meteorology and chemistry was largely incomplete and only limited to a very few prognostic gaseous species. The first online fully coupled meteorology–air quality model is the Gas Aerosol, Transport, and Radiation AQM with a Mesoscale Meteorological and Tracer Dispersion model (referred to as GATOR/MMTD), which solves meteorological and chemical processes simultaneously and considers the two-way feedback between air quality and meteorological parameters. The first community online coupled meteorology–air quality model in the United States, Weather Research and Forecasting Model with Chemistry (WRF/Chem), is developed through the collaborative effort of several research institutes, agencies, and universities. In WRF/Chem, the air quality component is fully consistent with the meteorology component, both of which use the same transport scheme, same gridding, and same physics. The coupling between meteorology and chemistry components in WRF/Chem is relatively comprehensive. Various applications of online AQMs have shown their advantages over the off-line AQMs in many ways. For example, significant model errors of off-line AQMs for chemistry prediction may come from the low updating frequency of meteorological inputs, since some meteorological processes occur in a short timescale (<1 h). Such model errors are found rectified in online AQMs.

Since most of the $PM_{2.5}$ is composed of secondary aerosol, simulating gas/particle mass transfer is essential for accurately predicting aerosol size/composition distributions. The treatment of gas/particle mass transfer in three-dimensional (3-D) AQMs, however, represents one of the major challenges for air quality simulations. Three approaches, equilibrium, kinetic (or dynamic), and hybrid, have been used to simulate gas/particle mass transfer in AQMs. The equilibrium approach assumes equilibrium between gas and aerosol. An aerosol thermodynamic model is used alone to determine the partitioning of semivolatile species between gas phase and aerosol phase. The kinetic approach does not rely on the equilibrium assumption. In this approach, the gas/particle mass transfer due to the difference between the ambient gas concentration and equilibrium gas concentration is explicitly simulated for each size section. The kinetic approach provides the most accurate solution when an appropriate numerical solver and a sufficiently fine

size resolution are used. However, its computational demands hinder its wide applications in 3-D AQMs. The hybrid approach provides a compromise between accuracy and efficiency by using the equilibrium approach for fine particles and the kinetic approach for coarse particles. The hybrid and kinetic gas/particle mass transfer approaches have been implemented in the Model of Aerosol Dynamics, Reaction, Ionization, and Dissolution (MADRID). The improved MADRID has been incorporated into WRF/Chem. The resulted modeling system, WRF/Chem-MADRID, will be used for the following case study.

Case Study of Air Pollution Modeling

Testbed, model configurations, and simulation design

WRF/Chem-MADRID is applied to a 5-day (28 August–2 September) episode from the 2000 Texas Air Quality Study (TexAQS-2000). During this episode more than twenty 1-h O_3 exceedances were observed in the Houston–Galveston–Brazoria area, among which six of them exceeded 150 ppbv. TexAQS-2000 was an intensive field study for air quality issues in the Houston–Galveston area. Houston is the fourth most populous city in the United States with a population of 4 million. Traffic and other anthropogenic activities result in high emission rates of NO_x and VOCs in this area. The biogenic emissions from the forested regions in the northeast of Houston also contribute to the total VOC emissions in the Houston area, depending on the wind direction. Another distinct characteristic of Houston as compared with other large cities in the United States is the numerous petrochemical industries in its surrounding area. Forty percent of the world's production capacity for low molecular weight alkenes is found in the Houston–Galveston area. The O_3 mixing ratios in Houston often exceed the former 1-h NAAQS of 120 ppbv (Note: As of 15 June 2005, EPA revoked the 1-h O_3 standard in all areas except the 8-h O_3 nonattainment Early Action Compact Areas). Under favorable meteorology conditions, the O_3 formation in Houston is rather rapid and some high O_3 events are observed even when the background O_3 mixing ratio is modest, making the O_3 problem in Houston quite unique. Annual mean $PM_{2.5}$ in southeastern Texas is close to the NAAQS of $15 \mu g m^{-3}$ and tends to be higher near urban and industrial areas of Houston. In this area direct emissions contribute approximately 40–50% of $PM_{2.5}$ while secondary sources account for 50–60% of $PM_{2.5}$ and inorganic species dominate the secondary PM. The southeastern Texas is affected by sea-salt emissions from the Gulf of Mexico as well as the anthropogenic emissions. Certain gas/particle mass transfer approaches may fail to predict the distribution of semi-volatile species for the areas where anthropogenic emissions are mixed with sea-salt emission.

The TexAQS-2000 was conducted to improve the understanding of the formation and transport of the pollutants along the Gulf Coast of the southeastern Texas. Intensive measurements of gaseous, particulate, and other hazardous air pollutants were made in the eastern Texas. Significant research efforts are devoted to investigate the pollution issues around the Houston–Galveston area. The modeling study in this work will focus on the effects of different gas/particle mass transfer approaches on the performance of 3-D air quality predictions over the eastern Texas.

The model inputs are set up for a region of $1056 \times 1056 km^2$ with a 12-km horizontal grid spacing and 56 layers vertically

from surface to 100 millibar (mb). Physics options used for the WRF/Chem-MADRID simulations include the Goddard short-wave radiation scheme, the rapid and accurate radiative transfer model for longwave radiation, the Yonsei University (YSU) boundary layer scheme, and the National Center for Environmental Prediction, Oregon State University, Air Force, and Hydrologic Research Lab's land surface scheme. Microphysics is turned off since there was no precipitation around Houston–Galveston area during this episode. The emissions of gas phase species were provided by the Texas Commission on Environmental Quality. The particulate matter emission was obtained from the EPA's 1999 National Emissions Inventory version 3. Eight size sections are used to represent the aerosol size distribution. To test the effects from the improvements of gas/particle mass transfer approaches, simulations are conducted with three mass transfer approaches, i.e., equilibrium, hybrid, and kinetic approaches.

Evaluation of meteorological predictions

Meteorological processes (e.g., sea breeze, low-level jets) play a vital role in O_3 events in Houston. Without properly capturing these meteorological processes, it is unlikely for the model to accurately predict the O_3 events in terms of time of occurrence, location, and peak values. The meteorological predictions are therefore first evaluated before the presentation of the chemical predictions.

Simulated temperature at 2 m (T_2) is evaluated at 32 observational sites. The observed mean temperature during the simulation period is as high as $31.2^\circ C$. Maximum surface temperature exceeded $40^\circ C$ on several days at certain sites during this episode. High temperatures accelerate chemical reactions and favor rapid production of secondary pollutants such as O_3 . WRF/Chem-MADRID captures the diurnal variation of temperature quite well for most sites (with a high correlation of 0.92 with the observation) and only overpredicts T_2 by $0.15^\circ C$.

On the average, wind speed is overpredicted by 8.7%. The mean observed wind direction is south-southwestly while the simulated mean wind is biased by 25° to be more westly. WRF/Chem-MADRID captures the diurnal variations of the wind fairly well at most sites. In addition to the overall statistics, the statistics for wind speed are calculated for nighttime and daytime separately. The performance of wind speed at night (with a correlation coefficient of 0.374, and a Normalized Mean Bias (NMB) of 39.8%) is worse than that during daytime (with a correlation coefficient of 0.492, and an NMB of -10.9%). The worse performance during nighttime may be due to the well-known model deficiency in accurately simulating nocturnal turbulent mixing near the surface, which is a common problem for all numerical weather prediction models.

Planetary boundary layer (PBL) height determines the vertical extent of dilution of pollutants and significant uncertainties are associated with the estimation of PBL height in current AQMs. Evaluation of PBL height at five radar wind profiler sites shows that overall the PBL height is overpredicted by 72.1%.

The high O_3 mixing ratios in the Houston–Galveston area are at times associated with the occurrence of sea breezes. Sea breeze circulations were clearly observed on 29–31 August 2000 over this area. WRF/Chem-MADRID reproduced the observed sea breeze development sequence fairly well even

though there is underestimation of the strength of the sea breeze (Figure 5). Large-scale offshore flow (westerly wind) near the surface persists for most of the morning in the Houston–Galveston area. A sea breeze develops around

noontime. The front of the sea breeze reaches around Houston at 12:00 LT and a confluence line forms there, when the wind field is nearly stagnant around Houston. Such stalled sea breeze favors the buildup of high pollutant concentrations in this

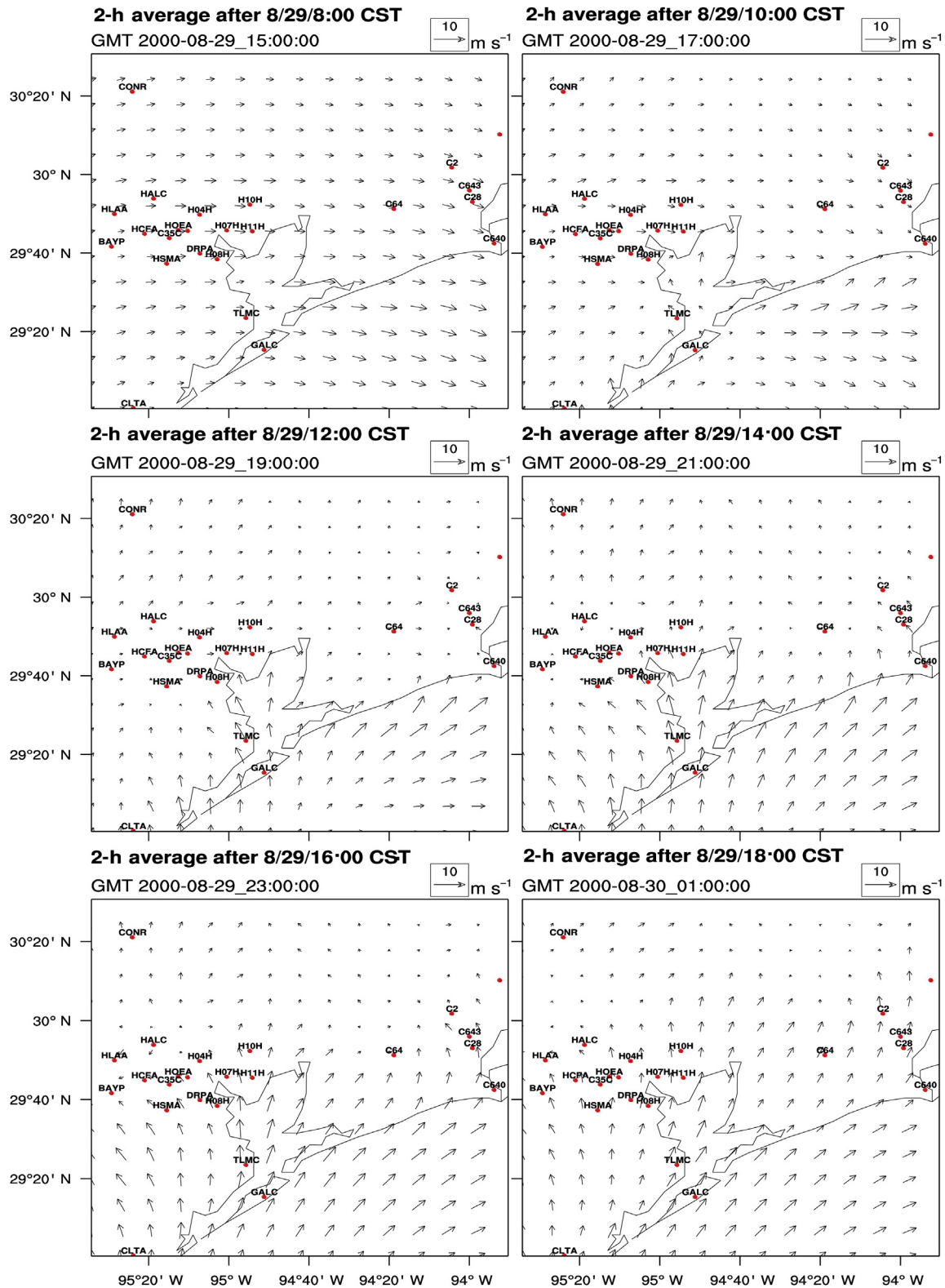


Figure 5 Predicted wind fields on 29 August 2000 by WRF/Chem-MADRID.

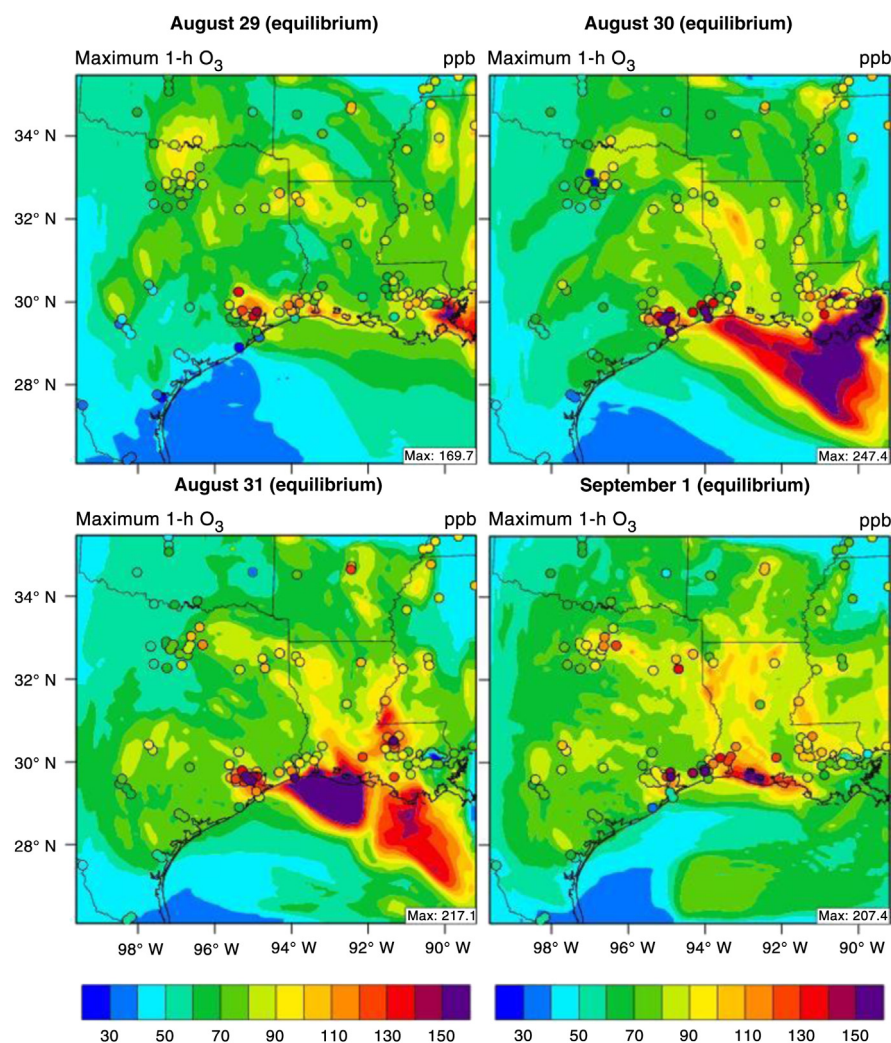


Figure 6 Spatial distributions of maximum 1-h O_3 on 29, 30, 31 August, and 1 September 2000 predicted by WRF/Chem-MADRID with the equilibrium mass transfer approach. The observed values are indicated by shaded circles.

region. The sea breeze continues in the afternoon and the sea breeze front reaches more inland until 18:00 LT.

Results of chemical predictions

Figure 6 shows the spatial distributions of daily maximum 1-h O_3 . There is a cluster of sites experiencing high O_3 mixing ratios around Houston on all 4 days. Substantial photochemical production of O_3 following the emission of precursors (e.g., VOCs and NO_x) from the Houston area leads to prominent O_3 -rich plumes on 30 and 31 August. Driven by the large-scale westerly wind, the O_3 -rich plumes are eastward moving. South part of Louisiana is affected by the O_3 -rich plumes. Such a regional transport pattern was reported to impair the air quality in Louisiana at times.

WRF/Chem-MADRID captures the diurnal variations of surface O_3 at 60 observational sites quite well (Figure not shown). The hourly O_3 throughout the simulation period is underpredicted by 4.6% (1.8 ppbv) from WRF/Chem-MADRID with the equilibrium mass transfer approach (Note: Different mass transfer approaches had negligible effects on O_3

predictions). The daytime hourly O_3 is only underpredicted by 0.4% (0.2 ppbv). This indicates that WRF/Chem-MADRID captures the O_3 formation mechanisms reasonably well.

The differences of daily average $PM_{2.5}$ predicted by WRF/Chem-MADRID with the three different mass transfer approaches are trivial over the inland area while the differences are more prominent over the sea and some coastal areas (Figure 7). The $PM_{2.5}$ concentrations in the plume originating from Houston predicted by the equilibrium approach are much higher than those predicted by the hybrid and kinetic approaches, and the differences are mainly due to nitrate (NO_3^-). The equilibrium approach predicts more fine nitrate (NO_3^- in particles with diameter less than 2.5 μm) and less coarse nitrate (NO_3^- in particles with diameter larger than 2.5 μm) than the hybrid and kinetic approaches (Figure 8). The spatial distribution of simulated nitrate plume matches that of the sodium (Na^+) plume quite well (Figure not shown). Sodium is a tracer of sea-salt aerosol and it is emitted together with chloride (Cl^-) from the ocean. Most sodium chloride is emitted in the coarse mode. Sodium stays in the aerosol phase

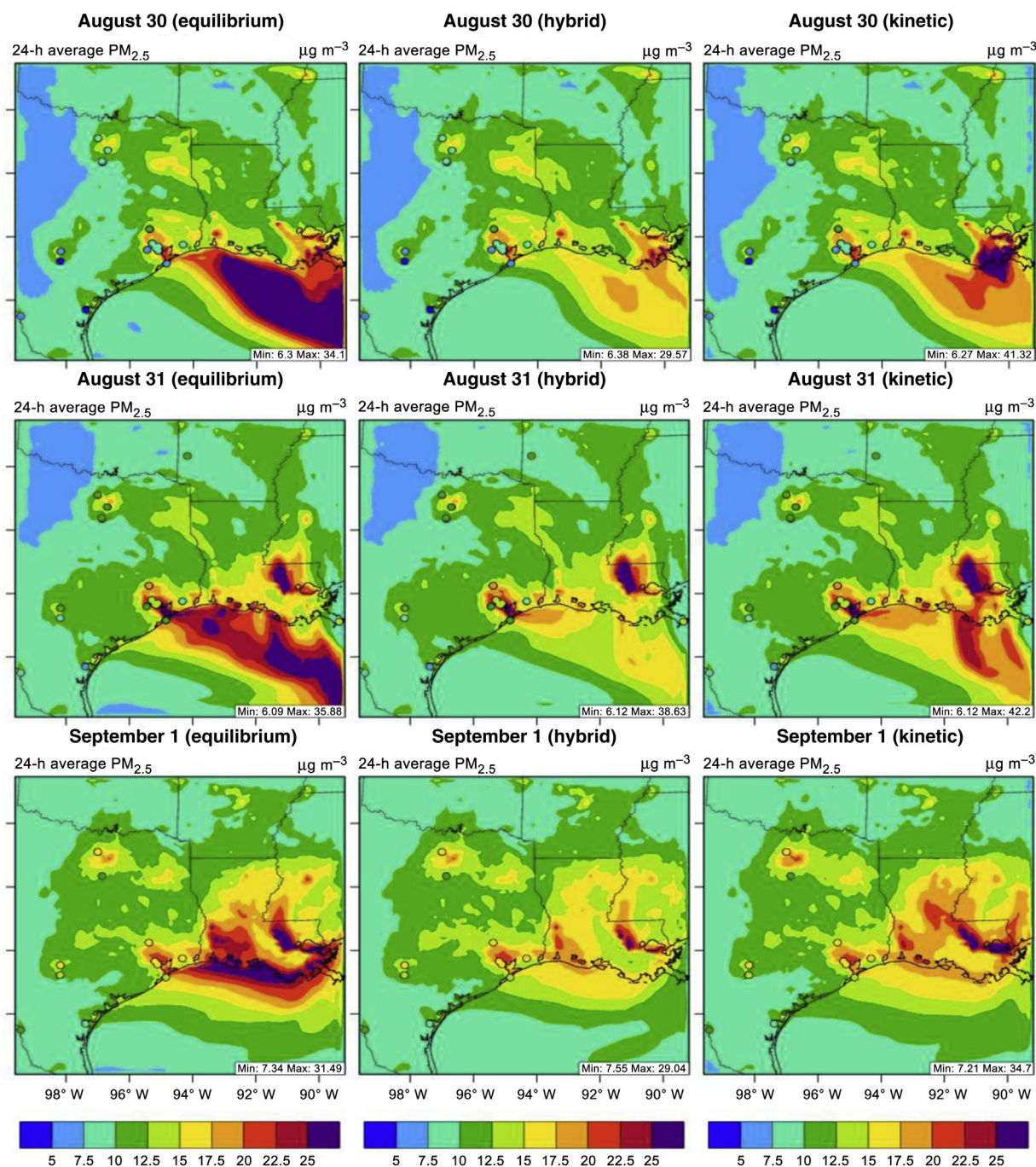
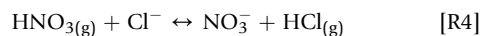


Figure 7 Spatial distributions of daily average $\text{PM}_{2.5}$ mass concentrations simulated with (left to right) the equilibrium, hybrid, and kinetic mass transfer approaches on (top to bottom) 30, 31 August, and 1 September 2000. The measured values are indicated by shaded circles.

since it is nonvolatile, while chloride may exchange between aerosol and gas phase. Nitrate enters aerosol phase through the chloride depletion process ([R4]):



Since the hybrid and kinetic mass transfer approaches both solve the mass transfer for coarse particles kinetically, the chloride depletion process is correctly simulated when anthropogenic pollutant plumes (which contain plenty of

nitric acid, HNO_3) mix with sea salt (which contains sodium chloride). However in the equilibrium approach, the aerosol phase is treated together to equilibrate with gas phase. Even though [R4] can still be simulated by the equilibrium approach, the transferred mass into aerosol phase is redistributed among each section based on initial sulfate (SO_4^{2-}) distribution. Since most sulfates are in the fine mode, the transferred nitrate from the chloride depletion process is erroneously redistributed mostly to the fine mode by the

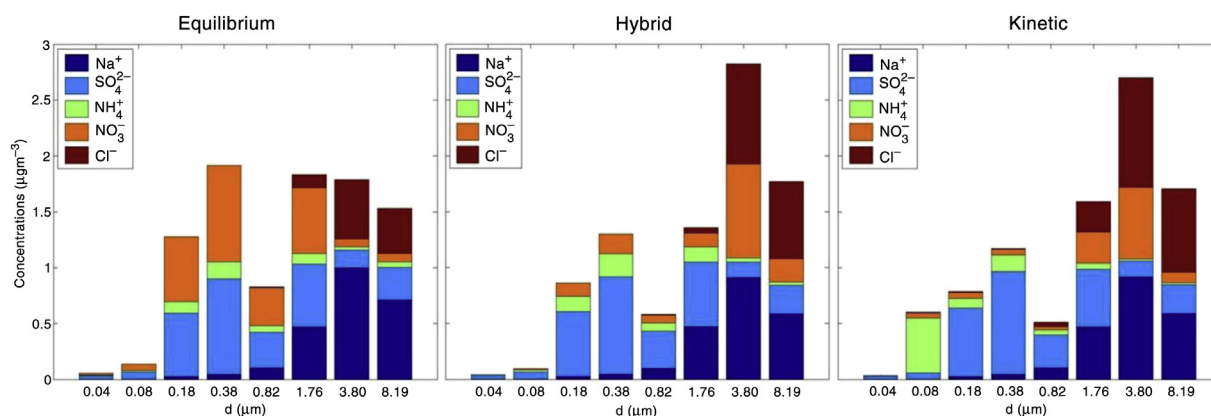


Figure 8 Aerosol size/composition distributions at a coastal site, i.e., Galveston (GALC) on 30 August 2000 predicted by WRF/Chem-MADRID with (left to right) the equilibrium, hybrid, and kinetic gas/particle mass transfer approaches. The x -axis is the diameter of aerosol.

equilibrium approach. Thus WRF/Chem-MADRID with the equilibrium approach predicted higher $PM_{2.5}$ in the coastal area. Due to the prevailing large-scale westerly wind, the $PM_{2.5}$ concentrations in southern Louisiana are enhanced by the pollution plumes originated from Houston (Figure 7).

Improvement of Simulation of Air Pollution Meteorology

Uncertainties of current AQMs

The accuracy of air quality simulations is affected by the uncertainties associated with the model treatments for various processes, including vertical mixing, dry deposition, and chemical mechanisms. Vertical mixing is handled by the PBL scheme in the models. The uncertainties associated with the PBL schemes remain one of the main sources of inaccuracies in air quality simulations. Three PBL schemes in the WRF model, i.e., the YSU scheme, the asymmetric convective model, version 2, (ACM2) scheme, and the Mellor–Yamada–Janjic (MYJ) scheme were evaluated in a modeling study covering the domain of the South Central United States. In that study, the WRF simulations underpredict temperature and overpredict moisture near the surface. Use of the local-closure MYJ scheme produces the largest bias. The YSU and ACM2 schemes both lead to predictions of higher temperature and lower moisture, and thus smaller biases, than the MYJ scheme in the lower atmosphere during daytime because of their stronger vertical mixing. Stronger vertical mixing causes stronger entrainment at the top of PBL, which helps warm and dry the PBL. In the local-closure MYJ scheme, the only entrainment that develops must come from local mixing. Entrainment from penetrating plumes or large eddies is not accounted for. Underestimated entrainment is shown to at least partially cause the colder PBL predicted by the WRF model with the MYJ scheme. During nighttime the WRF model with the YSU PBL scheme produces higher temperatures and lower moisture than with the other two schemes in the lower atmosphere because of its enhanced mixing during nighttime.

Parameter estimation

The accuracy of model simulations is dictated by the uncertainties associated with model treatments for various processes.

Parameter estimation offers a way to improve the accuracy of those model treatments. Parameter estimation is a technique for determining the best value of certain model parameters through data assimilation or similar techniques. When applied to parameterizations of meteorological processes, one hopes to identify optimal parameter values within a given parameterization, with ‘optimal’ defined over some appropriate domain in space and time.

Advanced data assimilation methods, e.g., variational approaches and the ensemble Kalman filter (EnKF), are capable of extracting from observations significant information about the model parameters in addition to the model state. They have been used to counter model errors due to incorrect parameters by calibrating those parameters simultaneously with the model state during the analysis process. The EnKF was applied to estimate the flow-dependent optimal values of two parameters fundamental to the performance of a PBL scheme in the WRF model. Parameter estimation EnKF results in a significant reduction in the model biases of both wind and temperature. Also, deterministic forecasts with updated parameters outperform forecasts with standard parameter settings.

Ensemble simulation

There are dramatic uncertainties in the air quality simulations due to uncertainties in the initial meteorological/chemical conditions and model treatments of physical and chemical processes. Even with plentiful observations, analysis inaccuracies are unavoidable, so a single-minded pursuit of improved initial conditions is inadvisable. Given the uncertainties associated with various model treatments under various conditions, improving model performance in a single deterministic simulation through pursuing perfect model treatments for all the conditions is also unlikely. Instead, ensemble simulations should be utilized to span the range of possible outcomes on a given day, and that uncertainty should be incorporated into the regulatory analysis. As with simulations, deterministic photochemical forecasts are similarly unlikely to be successful. An ensemble forecasting system, incorporating as many sources of error as possible, can provide guidance on not only the most likely evolution of pollutants but also the range of possibilities.

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Further Reading

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