

CHAPTER 8: ATMOSPHERIC MODELING

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Air quality models (also referred to as atmospheric chemical transport models and, in the case of ozone and PM, photochemical models) simulate the atmospheric concentrations and deposition fluxes to the Earth's surface of air pollutants by solving the mass conservation equations that represent the emissions, transport, dispersion, transformations and removal of those air pollutants and associated chemical species. Figure 8.1 presents a schematic overview of the major components of a multipollutant air quality model. Contemporary air quality models can be grouped into two major categories: 1) models that calculate the concentrations of air pollutants near a source (source-specific models) and 2) models that calculate concentrations of air pollutants over large areas ranging from an urban area, to a region, a continent and the globe (grid-based models).¹ A few models combine both modeling approaches in a hybrid formulation suitable for Level 1 and 2 applications, and perhaps to Level 3 as described in Chapter 2.

Air quality models can be applied to a variety of spatial and temporal scales. Source-specific models such as plume and puff models are typically applied up to 50 to 150 km from the source,² whereas grid-based air quality models range from the urban scale (>4 km) to regional, continental, hemispheric, and global scales (see Chapter 10 for a discussion of hemispheric and global scale modeling). Inputs to air quality models include the emission rates of primary air pollutants and precursors of secondary air pollutants, meteorology (three-dimensional fields of winds, turbulence, temperature, pressure, boundary layer height, relative humidity, clouds and solar radiation), and boundary conditions (baseline or background conditions in the case of source-specific models; see Figure 8.1). For grid-based models, an emission model is used to translate an emission inventory into a spatially distributed and temporally resolved grid structure.

¹ Source-specific models are Lagrangian models, which treat atmospheric dispersion as a source-specific process (i.e., the dispersion coefficients are a function of distance from the sources) whereas grid-based models are Eulerian models, which treat atmospheric dispersion as a characteristic of the ambient environment (i.e., dispersion coefficients are not related to any source characteristics). Source-specific Lagrangian models include steady-state Gaussian plume models such as AERMOD and non-steady-state puff dispersion models such as CALPUFF and SCICHEM.

² Neighborhood scale calculations < 1 km² are much smaller than the resolution of grid-based models. Estimation of concentrations in this range require merging of plume models with the larger scale calculations.

Inventories identify point sources and area sources within grid-geographic locations. For example, on-road mobile source emissions must account for vehicle fleet composition, vehicle speed, and ambient temperature as a function of time and road type. Biogenic emissions are a function of land use, season, ambient temperature and solar radiation. Emission inventories and models are discussed in Chapter 7. Meteorological conditions are obtained from observational data or from the output of a model (or a combination of both). In advanced research-grade models, both meteorology and air quality are simulated jointly so that the chemical composition of the atmosphere can influence the meteorology (e.g., the effect of particulate matter on atmospheric radiation); examples include the Multiscale Climate and Chemistry Model (MCCM; Grell et al., 2000) and the Weather Research and Forecast model with chemistry (WRF-Chem; Grell et al., 2005). When models are simulating a combination of several spatial scales, the calculations need to downscale meteorology from global to synoptic scale or to regional/urban-neighborhood scale. Such downscaling can be challenging when forecasting future climatology, which is needed to address the effect of climate change on future air quality and atmospheric deposition due to changes in air concentrations, precipitation and possibly also land use (see Chapter 10). The effect of future climate change also will need to be reflected in the emissions (see Chapter 7). Boundary conditions for downscaling to regional-scale models (~10-40 km resolution) are now typically generated from larger-scale models. Such approaches, although ultimately dependent on the quality of the global emission inventory, reduce the uncertainty in the estimation of boundary conditions for finer scale resolution, particularly those above the planetary boundary layer (e.g., Appel et al., 2007).

Although air quality models have been applied historically to address issues specific to ambient air quality standards (i.e., one criteria pollutant at a time) or welfare (e.g., acid deposition or visibility impairment), they are inherently multipollutant based. Therefore, in principle air quality models can be applied in the context of integrated emissions control programs that are designed to optimally address all of the above air quality issues simultaneously. Limitations arise, however, as additional chemical species of concern are identified that are not currently treated in air quality models. Such cases require the compilation of emission inventories and boundary conditions for these new chemical species and the addition of chemical and physical mechanisms in the model to treat their transformation and deposition.

8.1 ATMOSPHERIC MODELING FOR EXPOSURE ASSESSMENT

8.1.1 NEEDS FOR EXPOSURE MODELING AND HEALTH EFFECTS

The estimation of the health effects of air pollution requires knowledge of the concentrations of air pollutants to which an individual or a population cohort is exposed (see Chapter 4). These concentrations can be measured or calculated with an atmospheric model. Because individuals are exposed to different air pollutant levels as they move through different environments during their daily activities (e.g., home, vehicle, office, school, outdoor), one would ideally want to have high spatial and temporal resolutions of the air pollutant concentrations. The needs for exposure characterization and health effects estimation may be categorized as follows.

Spatial resolution: Some health effects studies, such as time-series mortality studies, do not necessarily require fine spatial information on air pollutant concentrations because they deal with information at the urban area or sub-urban/neighborhood level. However, a statistically based estimate of individual-level health effects requires fine spatial information on the air pollutant concentrations. The spatial resolution provided by an air quality model then needs to be sufficient to resolve the spatial variability of outdoor air pollutant concentrations so that 1) outdoor exposure of individuals and population cohorts can be assessed with sufficient spatial resolution and 2) micro-environmental models for indoor exposure have the needed outdoor concentration inputs (Isakov and Ozkaynak, 2007).³ The requirement for fine spatial resolution is greatest near sources of pollutants because the concentration gradients are strongest near those sources (e.g., near an industrial site, near a roadway). The entrainment of fresh emissions into the ambient air affects the emitted as well as the ambient pollutants through chemical reactions. For example, ozone concentrations are depleted near power plants and roadways because of the rapid reaction of the emitted NO with ambient ozone.

Temporal resolution: The requirement for temporal resolution for exposure calculations may be very fine (e.g., minutes to an hour for acute exposures), but such resolution is typically provided by the micro-environmental models. The temporal resolution needed from the air quality model therefore must be sufficient to provide the needed inputs to the micro-environmental

³ The spatial resolution of the model output is typically coarser than the grid spacing because a grid model resolves horizontal features only at about four times the grid spacing.

calculations. Such temporal resolution must be able to capture the temporal variability of the air pollutant concentrations. Continuous measurements of gaseous and particulate chemical species provide indications of the temporal evolution of the concentrations of primary and secondary air pollutants. For example, fluctuations in the wind (i.e., turbulence) and in the source activity (e.g., vehicular traffic) near a source lead to strong temporal variability in chemical species concentrations at a given location (Thoma et al., 2008; Baldauf et al., 2008). It is generally considered that hourly concentrations provide the desired temporal resolution for air pollutant concentrations in the ambient atmosphere. However, in some instances temporal resolution of 1, 5, 10 or 15 minutes may be desirable for special studies of acute exposure. In those cases, the temporal resolution of the emissions and local meteorology needs to be compatible with the selected temporal resolution of the air quality and exposure models. Alternatively, the sub-hourly variability in air pollutant concentrations due to meteorological and source variability can be treated in a statistically based uncertainty analysis (see below) rather than in deterministic calculations. Some exposure models require probability distributions of the exposure concentrations; there is then a requirement to translate deterministic output, even on fine scales, to probabilities. The development of probabilistic air quality model outputs is discussed in Section 8.4.

Temporal duration: Longitudinal epidemiological studies require exposure information on the relevant air pollutant concentrations over long time periods (multi-years). Time-series epidemiological studies address acute effects and may also require information on air pollutant concentrations over multi-year periods to have sufficient statistical power.

Chemical species and particle size: Chemical species of interest to the exposure and health effects community include the regulated species (i.e., criteria pollutants and hazardous air pollutants) as well as other chemical species considered as potentially harmful to human health. Consequently, they are investigated in terms of exposure, epidemiological and toxicological studies. Ultrafine particles (i.e., those particles less than 0.1 μm in aerodynamic diameter) are one example of a non-regulated fraction of PM that is being investigated as a potential cause of adverse health effects. Exposure to particles depends on size and chemical composition as a function of size; therefore, quantitative information from an air quality model incorporating these

PM properties will lead to more complete exposure estimation. Since the indoor component of PM exposure depends on size dependent infiltration into buildings, the outdoor estimates can be used as a component of micro-environmental models as well..

8.1.2 CURRENT STATUS OF ATMOSPHERIC MODELS

Current atmospheric models calculate the outdoor concentrations of air pollutants as a surrogate for exposure. Human exposure is known to depend not only on outdoor conditions but also indoor conditions as well, including residents, office and commercial buildings and transportation elements. If indoor sources of pollutants are known or negligible, concentrations of air pollutants in indoor environments can be calculated from outdoor concentrations using micro-environmental models. We discuss below whether current atmospheric models are suitable to address the needs of the exposure and health sciences communities.

Spatial resolution: Regional models can cover large areas but their grid spacing is constrained to 1 km or more and, therefore, they provide spatially averaged concentrations that may not be representative of the actual concentrations that may occur, for example, in the vicinity of emission sources (the formulation of some parameterizations must be modified as the spatial resolution of the model increases, e.g., convection, turbulent diffusion). Source-specific models offer a spatial resolution of a few meters if needed but they are typically limited to about 50 km from point sources and a few hundred meters from line sources. However, a few source-specific models can provide very fine spatial resolution near the source and also apply to long distances. Nevertheless, it is not practical to use source-specific models for an area with a large number of emission sources as the treatment of many sources with such models become computationally prohibitive. Therefore, a combination of a grid-based model that provides air pollutant concentrations over a large domain with a relatively coarse grid spacing (1 km or more) and source-specific models that provide information on the spatial gradients in the vicinity of major emission sources is needed to address the needs articulated above.

Touma et al. (2006) addressed the issue of representing air pollutant concentrations with fine spatial resolution over large areas. They identified three major approaches for estimating air

pollutant concentrations at the sub-grid scale level within a grid-based air quality model. Figure 8.2 depicts the general features of those approaches.

The first approach (Ching et al., 2006) is solely based on a grid model but it uses finer grid resolution than generally used (e.g., down to 1 km, whereas minimum grid size in urban areas is typically 4 to 5 km). Then, the concentrations calculated by the fine grid model are used to construct a distribution of concentrations over a larger grid cell (e.g., a set of 16 concentrations for a 4 km x 4 km grid cell). This concentration distribution represents the variability of the chemical species concentrations within that grid cell (actually, it may still under-represent the full variability because concentrations may not be homogeneous at scales below 1 km). Such concentration distributions can be used to construct generic concentration distributions that would be a function of the chemical species, the land use category (e.g., urban, suburban, non-urban) and time (e.g., season, day of the week, hour of the day). Those generic distributions are then available to complement the results of a grid-based simulation of chemical concentrations by providing for each grid cell a probability distribution function that characterizes the variability of the modeled concentration.

The second approach uses a grid-based model and a source-specific model separately for the simulations of different sources and combines the results of the two models to construct chemical concentration fields due to all sources (e.g., Isakov and Venkatram, 2006). This approach is theoretically correct for chemical species that are chemically inert or undergo first-order chemical reactions (i.e., linear chemistry). However, it is not strictly correct for chemical species that undergo non-linear chemistry and the uncertainty associated with this approach cannot be estimated a priori.

The third approach combines a grid-based model and a source-specific model into a single hybrid model (Karamchandani et al., 2007). The hybrid model is formulated so that interactions of emitted species treated by the grid-based model and those treated by the source-specific model are treated explicitly to take into account the non-linear chemical reactions. Thus, the modeled concentrations are theoretically correct for chemically inert species as well as for chemically reactive species with linear or non-linear chemistry. This approach is currently operational for

point sources (e.g., stacks) and undergoing preliminary applications for line sources (e.g., roadways).

Applications of these different modeling approaches have been limited to date and there is a need to evaluate each approach against measurements as well as to compare those different approaches to assess their relative strengths and weaknesses.

Temporal resolution: The temporal resolution provided by air quality models (both grid-based and source-specific) is one hour because meteorological and emission inputs are typically available on an hourly basis. This resolution has typically been considered appropriate for the simulation of outdoor concentrations, which are used either as input to outdoor calculation exposure or to micro-environmental models. Finer temporal resolution is currently limited by the availability of sub-hourly emission and meteorological inputs.

Temporal duration: As discussed in Section 8.3.3, air quality model simulations are now routinely conducted for one-year periods, but not for multi-year periods. Multi-year emission inventories are currently under development at EPA; once these inventories become available, multi-year air quality simulations will be feasible.

Chemical species and particle size: Air quality models currently treat all major criteria pollutants (ozone, NO_x, SO₂, CO and PM), except lead, and some air toxics (VOCs, and trace metals). Air quality models typically treat VOCs via carbon-bond representations (e.g., CB IV and CB05 mechanisms) or representative molecules that correspond to a large group of molecules (e.g., SAPRC99 and RACM mechanisms). Only a few air toxic organic molecules (e.g., formaldehyde) are treated explicitly in the chemical mechanisms. To address air toxics VOC, some air quality models have been modified to include explicit treatments of VOC air toxics of interest such as aldehydes (formaldehyde, acetaldehyde), benzene and butadiene (Seigneur et al., 2003; Luecken et al., 2006). Table 8.1 presents the list of the air toxics treated by the EPA Community Multiscale Air Quality (CMAQ) model (Byun and Schere, 2006).

Mercury is an air toxic of current interest that is currently treated in air quality models; it is of concern for atmospheric deposition and subsequent bioaccumulation (see Chapter 5; see also Section 8.3) rather than for population exposure via inhalation. Other trace metals treated in air quality models are assumed to be chemically inert. This assumption is appropriate for trace metals that have potential adverse health effects that do not depend on their chemical state. It is not appropriate for chromium (Cr) because chromium has health effects that depend on the oxidation state (Cr[VI]) is considered carcinogenic whereas Cr[III] is not) and it undergoes reduction-oxidation transformations in the atmosphere (Seigneur and Constantinou, 1995; Lin, 2004). One major limitation for the treatment of trace metals other than mercury and lead is the paucity of trace metal emission inventories that have received the scrutiny needed to ensure that they are reliable and accurate.

Persistent organic pollutants (POPs) are currently not treated by air quality models. POPs are of interest mostly for atmospheric deposition (see Section 5.1.6) rather than for population exposure via inhalation.

Air quality models currently calculate PM mass concentrations in two main size fractions: fine PM (PM_{2.5}) and coarse PM (PM_{10-2.5}), using either modal or sectional representations of the size distributions (finer size resolution is actually provided by the modal representation and by sectional representations that use more than two size sections). PM chemical speciation includes sulfate, nitrate, ammonium, black carbon, organic compounds and “other” primary species (those “other” species include for example fly ash and other PM emissions from anthropogenic sources, crustal species such as soil dusts, and sea salt). In some areas (e.g., Mexico City), soil erosion leads to a significant fraction of PM₁₀ concentrations and algorithms have been developed to quantify such crustal PM emissions as a function of wind velocity, surface roughness, soil characteristics and soil moisture. This representation of PM in two speciated size ranges (PM_{2.5} and PM_{10-2.5}) is consistent with the current U.S. or Canadian air quality standards for PM. Other characteristics of PM are of potential interest for adverse health effects; for example, the number concentration of ultrafine particles, the particle surface area, the acidity of particles, the concentrations of individual elements (e.g., metals), and gaseous co-pollutant interactions. PM

air quality models currently are not suited to address these characteristics (McMurry et al., 2004).

8.1.3 EVALUATION OF AIR QUALITY MODELS

Air quality models are generally evaluated with ambient measurements of concentrations of gaseous and particulate chemical species and PM mass concentrations. This type of performance evaluation, generally referred to as operational performance evaluation, does not necessarily provide information on the ability of a model to simulate the relative contributions of various source categories or source areas (i.e., source apportionment) or to simulate the response of ambient concentrations to changes in emissions (generally referred to as dynamic evaluation). To that end, other modes of evaluation are conducted. First, we summarize the current status of air quality model operational performance for various chemical species, spatial scales and temporal scales. Then, we discuss some examples of source apportionment and dynamic evaluations.

Ozone: Grid-based air quality models have been applied to simulate ozone concentrations for over three decades and there is considerable experience available for this chemical species. An assessment of our ability to address ozone air pollution was conducted by NARSTO (2000). Russell and Dennis (2000) reported a summary of model performance for ozone in the United States.. The Canadian air quality models have recently been evaluated for eastern North America (Tarasick et al., 2007). McKeen et al. (2005) have described some recent ozone forecast evaluations for U.S. and Canadian models.. Performance of air quality models for ozone has also been evaluated for the Mexico City area (e.g., Jazcilevich et al., 2003, 2005; Lei et al., 2007; Tie et al., 2007; see for example Figure 8.3). Although there are still some uncertainties in our knowledge of the atmospheric chemistry leading to ozone formation (e.g., oxidation of aromatics, free radical chemistry, and odd nitrogen budget), ozone modeling is a mature field, which is unlikely to evolve significantly from its current status over the next few years, given a focus on a range of multiple pollutants. Overall, we can consider the ability of models to simulate ozone concentrations to be adequate for most regulatory applications. The error and bias of air quality models for 1-hr average ozone concentrations are typically within 35 percent and 15 percent, respectively. However, some caution is advised when applying ozone models to

predict the effect of precursor emission reductions (see also the discussion of dynamic model evaluations below).

Other gaseous criteria pollutants (NO₂, CO and SO₂): Air quality models simulate NO, NO₂, CO and SO₂ as part of the atmospheric chemistry of ozone and PM formation. These chemical species are primary species (i.e., directly emitted into the atmosphere) with the exception of NO₂, which is both emitted into the atmosphere and formed in the atmosphere by the oxidation of NO (CO is also formed in the atmosphere via VOC photo-oxidation; however, the primary form dominates in urban areas where concentrations are highest). Air quality models generally perform more poorly for these primary species than for secondary species such as ozone because primary species exhibit strong concentration gradients, which are not captured by grid-based air quality models. Nevertheless, Lei et al. (2007) obtained satisfactory model performance for CO in Mexico City. Concentrations of SO₂ near point sources are typically simulated using source-specific models (point source models); thus, the spatial concentration gradients can be captured by using a fine array of receptor points where the SO₂ concentrations are calculated.

The performance of point source models has been evaluated with a variety of field data where gaseous tracers were released from a point source and measured downwind at a large number of receptor sites. The error metric used was the robust highest concentration (RHC) statistic, where the RHC represents a smoothed estimate of the highest concentrations based on an exponential fit to the upper end of the concentration distribution. For the AERMOD model (i.e., the model currently recommended by EPA for local impacts of point sources) applied to point sources with no significant downwash, the ratio of modeled to observed RHC ranged from 0.77 to 1.18 for 1-hour average concentrations (four studies), from 1.00 to 1.35 for 3-hour average concentrations (six studies), from 0.73 to 1.65 for 24-hour average concentrations (six studies), from 0.31 to 1.65 for annual concentrations (six studies); a ratio of 1 would mean perfect agreement (Perry et al., 2005). Similarly, NO, NO₂ and CO concentrations near roadways typically are simulated with source-specific models (line source models), which can reproduce the sharp concentration gradients away from the roadway. The performance of line source models has been evaluated in several studies by comparison with measurements from five different field studies at a number of receptor sites in the vicinity of roadways. The correlation coefficients (r) ranged from 0.51 to

0.87 with 85 percent of the model results overall being within a factor of two of the measured concentrations (Benson, 1992).

The photochemically-based models also can estimate concentration fields for VOC, including some speciation, as well as other oxidant species, including nitric acid, organo-nitrates, hydrogen peroxides and organic peroxides. The fidelity of these estimates is largely unknown, because of the rarity of ambient measurements for testing.

Particulate matter: Applications of grid-based air quality models to PM have taken place over the past two decades but most of the major model development and evaluation efforts have occurred over the past decade. An assessment of the ability of air quality models to simulate PM air pollution levels was conducted by NARSTO (McMurry et al., 2004). Seigneur (2001) has summarized early model performance evaluations for PM. More recent performance evaluation results for annual PM_{2.5} are reported by Eder and Yu (2006) and Appel et al. (2008) for the CMAQ model over the contiguous United States; by Tesche et al. (2006) for CMAQ and the Comprehensive Air Quality Model with extensions (CAMx) over the southeastern United States; and by Gong et al. (2006) and Park et al. (2007) for A Unified Regional Air Quality Modeling System (AURAMS) of the Meteorological Service of Canada. McKeen et al. (2007) has reported performance characteristics for several U.S. and Canadian models applied in forecasting mode. Russell (2008) has reported results for CMAQ and CAMx evaluations compared with data from the EPA Supersites Program.

Particulate matter consists of several chemical species and model performance is typically conducted for PM_{2.5} mass and the major PM_{2.5} chemical components: sulfate, nitrate, ammonium, black carbon and organic compounds. Figure 8.4 illustrates results for annual average concentrations of PM_{2.5} and its major components simulated with AURAMS over Canada and the contiguous United States. Model performance was evaluated against measurements available from the National Air Pollution Surveillance (NAPS) network of Environment Canada, the Speciated Trends Network (STN), and the Interagency Monitoring of Protected Visual Environments (IMPROVE) network. For this specific AURAMS 2002 annual simulation, the normalized mean errors were 37 percent for PM_{2.5}, 27 percent for sulfate, 44 percent for nitrate,

27 percent for ammonium, 66 percent for black carbon, and 85 percent for organics; the carbonaceous species were under-predicted compared with the measurements. The performance of CMAQ was recently evaluated against measurements available from STN (mostly urban and suburban sites) and IMPROVE (mostly remote sites) for a 2001 simulation of the eastern United States using a 12 km horizontal grid (Appel et al., 2008). For this specific CMAQ 2001 annual simulation, the normalized mean errors were 44 percent (STN) and 39 percent (IMPROVE) for PM_{2.5}, 40 percent (STN) and 34 percent (IMPROVE) for sulfate, 72 percent (STN) and 95 percent (IMPROVE) for nitrate, 59 percent (STN) for ammonium, 46 percent (IMPROVE) for black carbon and 49 percent for organics (IMPROVE). Major differences between the AURAMS and CMAQ performance results occur for nitrate (AURAMS shows better performance) and organics (CMAQ shows better performance).

In general, modeling errors for PM_{2.5} mass and sulfate are typically on the order of 50 percent or less. SO₂ emissions are fairly well characterized, the chemistry of SO₂ oxidation to sulfate is well known and sulfate is non-volatile. Thus, sulfate PM formation is well simulated by air quality models relative to the other PM components (uncertainties in cloud and precipitation fields are the largest source of uncertainty for sulfate, as discussed further in Section 8.2). Performance is worse typically for nitrate and organic compounds. Although NO_x emission inventories are not as well characterized as those of SO₂, they are reasonably accurate; however, the oxidation of NO₂ to nitric acid (HNO₃) includes some heterogeneous pathways that are still highly uncertain (No₃ and N₂O₅ reactions on particles and droplets; Davis et al., 2007) and the partitioning of HNO₃ between the gas phase and the condensed phase involves temperature and humidity, as well as the reaction with NH₃, which in turn involves uncertainties in the NH₃ emission inventories (Yu et al., 2005). Particulate organic compounds result from primary emissions of VOCs and SVOCs and the formation of secondary organic aerosols (SOA) via VOC and SVOC oxidation. The organic compounds can be of either anthropogenic or biogenic origin. Uncertainties in the emissions of primary organic PM and SOA precursors, the chemistry of SOA formation, and the partitioning of organic compounds between the gas and the condensed phase lead to large uncertainties in organic PM concentrations. Performance for ammonium (which is associated with sulfate and nitrate) and black carbon (which is a primary PM species) tend to lie between those of sulfate and those of nitrate and organic PM.

Air toxics: Air toxics (HAPs) include a large variety of chemical compounds including principally VOC, metals, POPs and diesel particles. POPs and some metals (e.g., mercury) are mostly of concern for atmospheric deposition rather than for health effects via inhalation (see Chapter 5 and Section 8.2). Some model performance evaluations have been conducted for VOC simulated with grid-based models (Seigneur et al., 2003; Luecken et al., 2006; MATES-II, 2000), as well as with source-specific models (Pratt et al., 2004; MATES-II, 2000). Using a 4-km grid resolution, a grid-based model showed an error of 64 percent and a coefficient of determination of 0.25 for benzene concentrations in New York (Seigneur et al., 2003). Using a 36-km resolution over the continental United States, a grid-based model reproduced episodic and seasonal behavior of the pollutant concentrations at many measurement sites satisfactorily but the model showed a slight tendency to underestimate (mean normalized bias for 30-day average concentrations over all sites and seasons in the range of 20 to 40 percent; Luecken et al., 2006). In MATES-II (2000), annual concentrations of most VOC were within 15 percent of the measurements at ten sites on average, although some species were significantly underestimated (e.g., 1, 3-butadiene by a factor of 2) or overestimated (e.g., acetaldehyde by a factor of 1.6). Pratt et al. (2004) concluded that their source-specific model simulation results were within a factor of two of the measurements (matched in space and time) on average. Model performance was best for pollutants emitted mostly from mobile sources and poorest for pollutants emitted mostly from area sources. Pratt et al. listed improving the emission inventory (better localization of the sources and better quantification of the emissions) as the best way to improve model performance.

Model performance evaluation was conducted for simulation of a pesticide, atrazine, with a grid-based model (Cooter and Hutzell, 2002; Cooter et al., 2002). Performance of grid-based models has not been evaluated for metals, except mercury (which is discussed below for atmospheric deposition). Some evaluations of source-specific models have been conducted for metals (e.g., MATES-II, 2000). No direct evaluation has been conducted for diesel particles because of lack of measurements specific to this type of particle. Black carbon has been used as a surrogate in some studies because diesel particles typically contain about 50 percent of black carbon.

However, this approach assumes that no other major sources of black carbon exist (Seigneur et al., 2003).

The treatment of meteorology is also very important to be able to correctly predict air pollutant concentrations in complex flow situations characteristic of neighborhood scale. For example, pollutant concentrations near roadways are particularly sensitive to the vertical dispersion characteristics of the atmosphere (Venkatram et al., 2007) and the presence of noise barriers (Bowker et al., 2007). Air pollutant concentrations in street canyons are difficult to simulate because of the complex air flows rarely measured (Kastner-Klein et al., 2004; Britter and Hanna, 2003).

Source apportionment: EPA (2007) in its guidelines for the performance evaluation of models for PM and regional haze recommends that receptor models be used to corroborate the results of air quality models. Receptor models use statistical analyses of ambient chemical concentration measurements to estimate the contribution of various source categories to PM concentrations (Hopke, 1985; McMurry et al., 2004). They can be used without consideration of air mass transport, or can be combined with back-trajectories analyses of winds to identify the corresponding upwind source areas. One example of the application of receptor modeling techniques to corroborate the results of air quality models is the Big Bend Regional Aerosol and Visibility Observational (BRAVO) study. The BRAVO study addressed the contribution of U.S. and Mexican source areas to sulfate concentrations in Big Bend National Park, Texas. Sulfate is the major contributor to regional haze surrounding Big Bend during summer months. After reconciliation of the modeling results and correction for model bias, the air quality models and receptor models led to similar relative contributions of the Mexico Texas, eastern U.S. and western U.S. source areas to sulfate concentrations around Big Bend, thereby providing confidence in the predicted source area contributions (Schichtel et al., 2005). Both air quality models and receptor models have pros and cons and their combined use helps improve our understanding of source contributions. For example, Marmur et al. (2006) showed that for $PM_{2.5}$ in the southeastern United States air quality models lack temporal representativeness (because of limited temporal information in emission inventories) whereas a receptor model such as the Chemical Mass Balance (CMB) lacks spatial representativeness (unless a dense speciation

monitoring network is available). Another example of receptor modeling is the source apportionment of VOC in Mexico City (Vega et al., 2000; Mugica et al., 2002; Wörnschimmel et al., 2006).

Perhaps the best applications of receptor modeling have been obtained for source apportionment of PM₁₀ in cases where the secondary fraction is a minor component. Although receptor modeling techniques are based on ambient monitoring data, many uncertainties are associated with their use and caution is advised when interpreting their results. Engel-Cox and Weber (2007) present a summary of recent applications of two receptor modeling techniques based on factor analysis; Reff et al. (2007) present a discussion of one quantitative method based on factor analysis (the Positive Matrix Factorization) and highlight the sensitivity of the results to the choice of the method parameters (species selected in the analysis, number of factors, etc.). Watson et al. (2008) provide an overview of recent receptor modeling applications in the context of the EPA Supersite Program. Lee et al. (2008) offer a critical comparison of two standard receptor modeling techniques (Chemical Mass Balance and Positive Matrix Factorization) and discuss their limitations. One of the more critical of these is the lack of capability to directly assign sources for secondary particles.

Dynamic evaluation: The prediction of the response of ambient concentrations to changes in emissions can be challenging because of the non-linearity of secondary pollutant formation pathways. Figure 8.5 depicts the response of PM_{2.5} components to 50 percent changes in precursor emissions for a summer episode in the southeastern United States; some of those responses are complex and non-intuitive. Pun et al. (2007) showed that poor operational performance is very likely to lead to a poor ability to predict model response to emission changes. However, satisfactory operational model performance does not necessarily guarantee that an air quality model will predict the correct response to an emission change. To evaluate model skill, it is necessary to conduct a dynamic evaluation where the model is evaluated for at least two different emission scenarios. Gilliland et al. (2008) conducted such an evaluation for the regional response of ozone concentrations to changes in NO_x emissions in the northeastern United States (see also Godowitch et al., 2007). Such dynamic evaluations require detailed emission inventories for the years of interest. Differences in emissions between weekdays and

weekends can also be used to that end. For example, Yarwood et al. (2003) showed that an air quality model could reproduce the day-of-the-week variability of ozone concentrations in the Los Angeles Basin.

Another approach to evaluating the ability of models to predict the response to emission changes is using measurements of chemical species that provide information on the chemical regime of the atmosphere (e.g., NO_x vs. VOC sensitive for ozone, HNO₃ vs. NH₃ sensitive for ammonium nitrate; see McMurry et al., 2004 and Pinder et al., 2008 for more details).

8.1.4 AREAS FOR FUTURE IMPROVEMENT

Areas for future improvement in air quality modeling as applied to population exposure and health effects studies, for advancing to Levels 3 and 4, include all areas where the current needs of the exposure and health communities are not met by existing air quality models.

Spatial resolution: A major area for improvement is the representation of the sharp concentration gradients that occur near emission sources, mostly near roadways as population exposure is very sensitive to those spatial concentration gradients (Jarrett et al., 2005). Some modeling techniques were described above that approach this problem. Each of those techniques needs to be evaluated against ambient data to assess their accuracy, to compare those techniques using a common data set to determine their relative strengths and weaknesses, and to further develop the most promising techniques.

Temporal extent, trends and accountability: Meteorological and air quality model simulations should be conducted over multi-year periods given the appropriate inputs. The availability of emission inventories is the limiting factor at the moment, because a North American emission inventory that covers a multi-year period with a consistent methodology for emission estimates does not exist and is unlikely to become available in the near future. Clearly, such emission inventories are needed if one wants to apply models to analyze or interpret trends in air pollutant concentrations and to check the effect of an emission changes on air quality over a period of several years.

Chemical species and particle size: Air quality models need to be improved for some aspects of their treatment of criteria pollutants. For example, the simulation of photochemical production using new in situ measurements of free radicals needs to be assessed. Considerable uncertainties remain in the simulation of primary gaseous pollutants such as CO, NO₂ and VOC species, as well as in the simulation of primary and secondary organic aerosols. PM characteristics are of interest to the health community and are not currently well treated by air quality models. These are formulated to address air quality regulations rather than multipollutant health research topics. Some air toxics of interest for exposure and health effects studies are not treated in standard air quality models (major VOCs are now treated explicitly but most trace metals are not). Following their improvements, air quality models need to be evaluated against ambient measurements; in many cases these measurements are not available to be compatible with modeling requirements. To the extent possible, diagnostic (e.g., by process, region, and season) and dynamic evaluations will need to be performed.

Emissions: Emission inputs are essential for air quality simulations. In particular, the uncertainties associated with emissions typically dominate the uncertainties associated with the simulation results of source-specific models (Sax and Isakov, 2003; Hanna et al., 2007). As finer spatial and temporal resolution becomes critical for exposure assessments, the need for reliable emission inventories at finer spatial and temporal scales will increase. There obviously is a practical limit to acquisition of emission information, but it is not known what this limit is.

Meteorology: Obtaining more accurate predictions of pollutant concentrations at finer spatial resolution in urban areas implies obtaining reliable meteorological fields (winds and turbulence) within areas with complex building settings (e.g., street canyons; noise barriers near roadways). Meteorological models need to be developed and evaluated to address such complex situations. Some initial efforts are underway in the United States (e.g., Otte et al., 2004) and in Mexico. UNAM-CCA is implementing, in collaboration with San Jose State University, an urbanized version of MM5 that will allow 500-meter resolution; finer temporal resolution may be desirable as the spatial resolution increases.

8.2 ATMOSPHERIC MODELING FOR ECOSYSTEM MANAGEMENT

8.2.1 NEEDS FROM ECOSYSTEM MODELING

Ecosystem models obtain inputs of atmospheric stressors in terms of air concentrations or deposition load to calculate changes in ecosystem processes, structure, and/or function. (Ecosystem models are described in Chapter 5.) The current models are generally suitable for calculations for Level 1 and 2 approaches. For Level 3 and 4, ecosystem exposure models may require further advancement to account for multipollutant interactions including cation-anion balances, and bidirectional flux calculations. Calculation of atmospheric deposition of chemical species to ecosystems requires knowledge of deposition fluxes of atmospheric chemical species to the Earth's surface. Wet deposition processes include the removal of chemical species from the atmosphere by precipitation (rain, snow, etc.), settling of fog droplets, and impaction of cloud hydrometeors. Dry deposition processes include the removal of chemical species from the atmosphere as they adsorb to, absorb into or react with surfaces such as soil, water, vegetation or man-made structures. Atmospheric species contact surfaces following two major transport steps: 1) turbulent transport, which brings gaseous species or particles near the surface and 2) molecular or Brownian diffusion within the thin air layer that is in contact with the surface. Both wet and dry deposition fluxes are needed as input to ecosystem models. The needs of ecosystem modelers may be further categorized as follows.

Spatial resolution: The spatial resolution provided by an air quality model must be compatible with the spatial variability of the atmospheric fluxes to the ecosystem of interest. Atmospheric fluxes may vary because of changes in air pollutant concentrations (e.g., near a source), precipitation patterns (precipitation may vary significantly with location in mountainous and coastal areas) and land use patterns (which affect dry deposition). Ecosystem models are not constrained to rectangular grids and most follow land use, terrain and the boundaries of water bodies using a grid of irregular polygons. The polygons are typically designed to resolve sub-components of watersheds. Explicit recognition of different land use types includes water bodies and topography.

Temporal resolution: The temporal resolution needed for atmospheric fluxes to ecosystems is highly variable, from daily to annual, to match ecosystem time scales. For stream chemistry

models, current temporal resolution required of the atmospheric fluxes is monthly. The required resolution is expected to increase to daily in the future. For rivers and estuaries, the simpler models operate with annual to monthly time steps, but the more refined, process-oriented models operate with a daily to hourly time steps to treat tidal influences. Providing a daily budget of accumulated dry fluxes is most important. A fine temporal resolution to resolve the diurnal pattern of the atmospheric flux is not required at this time, but could be in the future. At a minimum, seasonal or monthly variations must be provided as the ecosystem will govern the evolution of chemical species differently as the ambient conditions vary (e.g., surface temperature, soil moisture).

Temporal extent: Ecosystems typically react over long time scales, and sulfur, nitrogen, and mercury have a legacy effect. Therefore, soil chemistry, surface water chemistry and mercury models spin up for about 100 years, starting about 1850 to 1900. The spin up period, until contemporary data are encountered, uses annual time steps and fairly rough estimates of wet and dry deposition, temperature and rainfall. For contemporary data, around 1980 to 1990 onward, ecosystem modelers prefer monthly deposition data. Some watershed and estuarine models only calibrate against contemporary chemical, hydrologic and temperature data. They may use 5 to 20 years as a calibration period, because precipitation (hydrology) may vary significantly from year to year. For these models it is important to obtain atmospheric fluxes over several years to capture the inter-annual temporal variability of precipitation patterns, and there is a preference for the atmospheric flux inputs to be monthly or daily. For some models, climatological atmospheric fluxes are acceptable as long as no significant changes in air emissions occur during the period being averaged. Long-term projections into the future tend not to consider changes in meteorology and, hence, repeat a multi-year contemporary period. Thus, there is little accounting for the impact of climate change on the chemical and physical input variables.

Accuracy: Because water chemistry models are typically calibrated or spun up against a time series of inputs, high accuracy of the inputs is desirable. Ecosystem modelers would prefer the input accuracy supplied by atmospheric models be on the order of the analytical accuracy of the within watershed observations used for inputs. Thus, the lack of accuracy between modeled meteorology and observed hydrology is of concern. A related concern is the incompatibilities

introduced in the transition from measurements for hindcasts to atmospheric model predictions for forecasts and a concern about lack of cross-consistency when data come from different sources of measurements and models.

Chemical and physical variables: The chemical species of most interest to the ecosystem community include ozone; the acidic species (mostly, sulfate and nitrate, but also sulfur dioxide and ammonia [ammonium]) plus the neutralizing species for the more advanced water chemistry models (calcium, magnesium, sodium, potassium, and chloride), which can lead to acidification of water bodies; nitrogenous species (nitrogen oxides, nitric and nitrous acids, organic nitrogen, ammonia, particulate ammonium and nitrate, etc.), which can lead to lake, bay and estuary eutrophication; mercury species (divalent gaseous mercury, elemental gaseous mercury and particulate mercury), which can be methylated in water bodies and lead to high concentrations of methylmercury in aquatic biota via bioaccumulation. Persistent organic pollutants are of interest, which can bioaccumulate in the food chain, as discussed in Chapter 5. Ecosystem models also require meteorological variables, including temperature, precipitation and photosynthesizing radiation.

Atmosphere/ecosystem interface: Some chemical species deposit from the atmosphere to surfaces irreversibly; that is, they are not transferred back to the atmosphere. This is the case, for example, for sulfate. Other species may be emitted back to the atmosphere either in their original form or in a different oxidation state. For example, nitrogenous species may be emitted back to the atmosphere as nitric oxide or ammonia, and mercury species may be emitted back to the atmosphere as elemental mercury. Such processes need to be simulated via an interface that accounts for the deposition from the atmosphere to an ecosystem, the possible chemical transformation in the ecosystem (e.g., vegetation, top soil layer, wetland or water column), and the emission of some chemical species back to the atmosphere. The atmospheric fluxes to different land use types within a grid cell also need to be associated with the corresponding land use types within the spatial polygons used by the ecological model.

8.2.2 NEEDS FROM ECOSYSTEM CRITICAL LOAD ANALYSIS

The critical load concept is an effect-based approach that attempts to estimate the pollutant concentration level or atmospheric deposition load that would be likely to cause environmental harm (see also Chapter 5). A critical load is specifically defined as a quantitative estimate of an exposure (concentration level or atmospheric deposition) to one or more pollutants below which significant harmful effects on specified sensitive elements of the environment or on ecosystem structure and function do not occur according to present knowledge. A sensitive element can constitute a part of, or the whole of an ecosystem. While it is deposition or air concentration itself that is of interest, the needs of critical load assessments similarly may be categorized as above.

Spatial resolution: Critical loads are directly related to atmospheric fluxes to local/regional natural ecosystems. Critical load values may vary considerably between different ecological zones of North America. Critical load mapping is now being performed at high resolution (30 m to a few km) across North America. The spatial variation of atmospheric deposition to underlying soils and vegetation types and vegetation/ soil/ bedrock gradients determine the degree of sensitivity of ecosystem functioning. Therefore, critical loads are defined at a high spatial resolution and may be highly variable spatially. The spatial resolution of an air quality model must address variations in atmospheric fluxes due to changes in air pollutant concentrations (resulting from topography), precipitation patterns (precipitation may vary significantly with location in mountainous and coastal areas) and land use and soil patterns (affecting estimation of dry deposition). The air quality model should also be able to distinguish fluxes to different land use types within a grid.

Temporal resolution: Dynamic and steady state ecosystem models are used to calculate a critical load associated with a particular degree of ecosystem protection. These models typically calculate a critical load at a scale of an average annual deposition many decades into the future. Thus, a fine temporal resolution, such as hourly inputs, is not required for projections of future atmospheric fluxes. However, these models may have the same temporal requirements for historical and contemporary flux inputs as those listed in Section 8.2.1 for purposes of calibration.

Accuracy: Different from the NAAQS, critical loads require chemical components of the atmospheric loading to be measured and combined (e.g., total sulfur and total nitrogen), creating a more complicated set of accuracy expectations to support the use of critical loads to protect ecosystems. The latter also affect critical loading in terms of media chemistry and vulnerability.

Temporal extent: For critical loads modeling using steady state models, the temporal extent involves multi-year averages to smooth out inter-annual meteorological and deposition variability. For critical load calculations using dynamic models, it is desirable to provide deposition simulations spanning multiple years to account for emission changes as well as inter-annual variability. For both types of models, long-term projections and, potentially, an accounting for the impact of climate change on the input variables may be needed. Emission projections are essential for estimating long term effects. This is a particularly challenging aspect of studies of atmospheric-ecological stress.

Chemical species: The chemical species of most interest to the critical loads community at this time include: ozone and the combined effects of total sulfur (sulfate and sulfur dioxide), total nitrogen, (oxidized and reduced inorganic nitrogen and dissolved organic nitrogen) and mercury. Ozone affects vegetation on direct contact. Deposition of the combined acidic sulfur and nitrogen species can lead to acidification of soils and vulnerable water bodies and the release of aluminum (an important causal agent of ecosystem damage and degradation), as discussed in Chapter 5.

Atmosphere/ecosystem interface: The atmospheric fluxes to different land use and vegetation types within a grid cell need to be linked to the parallel land use types within the polygons used by critical load mapping. Addressing the potential bi-directionality of the atmospheric flux in the air-surface interface may be less important for natural systems than for anthropogenically impacted systems, such as agricultural practices. However, the transport of pollutants to natural systems will be affected by bi-directional fluxes occurring in the intervening landscape.

8.2.3 CURRENT STATUS OF ATMOSPHERIC DEPOSITION MODELS

Current deposition models calculate the wet and dry deposition fluxes of several major chemical species. Calculation of wet deposition fluxes requires knowledge of the concentrations of the species of interest within the cloud droplets, raindrops, snowflakes, ice crystals and fog droplets, as well as the precipitation rate (see Figure 8.6 as an example of precipitation and wet deposition of sulfate, nitrate and ammonium simulated over Canada and the United States with the Environment Canada model AURAMS). Calculation of dry deposition fluxes requires knowledge of the atmospheric characteristics (turbulence, temperature), chemical species properties (molecular or Brownian diffusion coefficient, ability to adsorb, absorb or react) and surface properties (ability to retain gaseous species). We discuss below whether current atmospheric models are suitable to address the specific needs of the ecosystem modelers.

Spatial resolution: Regional models calculate atmospheric deposition fluxes on a rectangular-type horizontal grid. The most common geographical projections are Lambert conformal, Universal Transverse Mercator, and latitude-longitude, with a spatial resolution that ranges from a few kilometers to several tens of kilometers. Therefore, the gridded atmospheric deposition fluxes may not correspond to the areas relevant to the ecosystem model. For example, a given grid cell may cover a combination of some land areas and some water areas. Thus, the atmospheric flux calculated by the model represents an average over a mixture of water and land areas within the grid, and may differ from both the atmospheric fluxes to the water area and to the land area. Furthermore, the land area may include different land use types (e.g., bare soil, vegetation) that may lead to significantly different atmospheric dry deposition fluxes. For example, the mercury deposition flux is significantly greater to a deciduous forest than to bare soil (Lindberg and Stratton, 1998). Also, topographic effects in complex terrain are not well represented at current grid resolutions.

Temporal resolution: The temporal resolution provided by air quality models is one hour because meteorological and emission inputs are typically available on an hourly basis. This resolution is much finer than needed for input to ecosystem models and is, therefore, quite sufficient.

Temporal extent, trends and accountability: Air quality model simulations are now routinely conducted for one-year periods. However, there are very few examples of multi-year air quality simulations at regional scales, and none yet in which all emissions are truly varied by year of interest. Such multi-year simulations require geographically specific emission inventories for each year of a simulation period. To date, emission inventories have only been available for a given year of interest. These are available every few years but with changes in methodology (see Chapter 7), which has limited the possibility of multi-year simulations. Modeling tools are available for the development of emission inventories for future years (prospective modeling); however, significant effort is required to develop such inventories, particularly in terms of data collection. Moreover, the application of modeling tools for the development of emission inventories for past years is limited by the availability of pertinent data. The need for multi-year emission inventories that are internally consistent in terms of methodology was identified by NARSTO (2005). EPA is currently setting up such an approach. Once those multi-year emission inventories become available, multi-year air quality simulations that account for emission changes will be feasible.

Accuracy: The meteorological variables are provided by the meteorological models, such as temperature and precipitation, may differ significantly from actual values available from local measurements. Current models, for example, do not provide sufficiently precise estimates of precipitation and chemical deposition, and therefore are not used in water chemistry/hydrology model calibration. Observed precipitation and deposition with some type of spatial interpolation is used instead. This leads to some inconsistencies in addressing the effects of change in deposition loading between current conditions (measurement determined) and future (calculated from meteorological/air quality models).

Chemical and physical variables: Air quality models currently calculate deposition of ozone (see Figure 8.7 for deposition of ozone over the continental United States simulated with the CMAQ model), sulfate, sulfur dioxide, oxidized-nitrogen and reduced-nitrogen compounds (see Figure 8.8 for total deposition of oxidized-and reduced-nitrogen over the continental United States simulated with the CMAQ model), and mercury. Two important categories relevant to acidification and critical loads that are not treated are deposition of base cations and deposition of

dissolved organic nitrogen (DON). Another major category of chemical species relevant to atmospheric deposition, which is not currently treated by air quality models, is organic toxins listed in Chapter 5, such as polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), polybrominated biphenyls, dioxins, furans, some pesticides, and chlorophenols; this group of chemicals is generally referred to as POPs. POPs have been modeled mostly in North America using multi-media compartmental models that include major assumptions on the spatial resolution of concentrations (i.e., the atmosphere is often represented by a single well-mixed compartment). Limited attempts have been made to treat POPs in air quality models in North America. The simulation of POPs by air quality models is limited at the moment by a) the availability of reliable emission inventories (Breivik et al., 2003) and b) knowledge of their atmospheric chemistry (Franklin et al., 2000).

Meteorological variables needed by ecosystem models (temperature, precipitation and photosynthesizing radiation) are provided by meteorological models; however, these may differ significantly from actual values available from local measurements, particularly in the case of precipitation. This potential discrepancy raises the question of how to integrate different sources of chemical and physical information (model calibration, data assimilation, data fusion, etc.; see Text Box 8.1).

Atmosphere/ecosystem interface: Most air quality models do not currently account for the possible transformation of chemical species in an ecosystem and the emission of derivative species back to the atmosphere. Some interfacial algorithms have been developed for mercury (e.g., Lin et al., 2005), but they have not yet been incorporated into standard air quality models. Most air quality models do not yet treat the bi-directional exchange of nitrogenous species, controlled by chemical and physical conditions at the plant/soil level, especially ammonia. But some algorithms are being developed for North American conditions at NOAA/EPA.

8.2.4 EVALUATION OF ATMOSPHERIC DEPOSITION MODELS

Air quality models are evaluated for ambient concentrations, wet deposition fluxes and, in rare cases, total or dry deposition fluxes. As discussed above, an operational evaluation is not sufficient to guarantee the ability of an air quality model to quantitatively predict the response of atmospheric deposition fluxes to changes in emissions. Source apportionment and dynamic

evaluations are, therefore, recommended to complement the operational evaluation. We summarize the current status of air quality model operational performance for major chemical species.

Ozone: Measurements of hourly ozone ambient concentrations near the surface are conducted in remote areas by the Clean Air Status and Trends Network (CASTNET) at 80 sites in the United States and in urban areas by various federal and state networks integrated into the Air Quality System (AQS) database. Model performance for ozone concentrations has been evaluated for regional scales over the contiguous United States (Eder and Yu, 2006; Appel et al., 2007), and was found overall to be commensurate with model performance at urban scales (see Section 8.2.3), though models with coarse grid spacing (> 10 km) have difficulties reproducing urban ozone concentrations in areas with complex meteorology (e.g., Los Angeles basin) and steep emission gradients.

Acid deposition: The National Atmospheric Deposition Network (NADP) and CAPMoN provide weekly measurements of the wet deposition fluxes of sulfate, nitrate, chloride, ammonium, other base cations (calcium, magnesium, potassium and sodium) and hydrogen ions at over 250 sites in the United States and a number of sites in Canada.. The Atmospheric Integrated Research Monitoring Network (AIRMoN) provides similar measurements, but with finer temporal resolution (daily), at seven eastern sites. CASTNET provides weekly measurements of ambient surface concentrations of sulfur dioxide, particulate sulfate, nitric acid, particulate nitrate, and particulate ammonium.. The ambient concentrations are then combined with estimates of dry deposition velocities to obtain estimates of dry deposition fluxes. The evaluation of wet deposition fluxes for sulfate, nitrate and ammonium have shown that model performance is satisfactory for sulfate (Dennis et al., 1990) but larger uncertainties are associated with nitrate and ammonium (Mathur and Dennis, 2003). Nitrate fluxes are reasonable for the cold season but are biased low in the warm season. Evaluation of ammonium fluxes has been tied to inverse modeling to establish estimates of ammonia emission seasonality (Gilliland et al., 2006).

Uncertainties in wet deposition fluxes are compounded by errors in local precipitation predictions of the meteorological models. There continues to be significant spatial variability in errors even when the regional deposition pattern is relatively unbiased. The evaluation of dry deposition fluxes with routine network data is not a direct evaluation because a) the deposition velocity is estimated for the measurement network using meteorological data taken in cleared areas which are generally not representative of deposition in varied land use, and b) the dry deposition velocity differs from that calculated by the air quality model, in part, because the parameterization used to infer dry deposition from observed data differs from the dry deposition algorithm imbedded in the air quality model. Furthermore, the measurements of gaseous nitric acid, particulate nitrate, and particulate ammonium are approximate because of sampling artifacts and, in addition, gaseous ammonia data are generally missing.

Nitrogenous compounds: Atmospheric deposition of nitrogenous compounds encompasses a large number of nitrogen-containing species; however, a few of these species tend to dominate the nitrogen deposition budget. Typically, nitric acid (and its associated particulate nitrate), ammonia (and its associated particulate ammonium) dominate in rural areas, with nitrogen oxides (NO and NO₂) and organic nitrates contributing less but significantly. Therefore, the evaluation of inorganic nitrate and ammonia/ammonium for acid deposition is directly pertinent to the evaluation of models for the atmospheric deposition of nitrogenous compounds since it covers the largest fraction of the nitrogen deposition budget.

Mercury: The Mercury Deposition Network (MDN) measures the wet deposition flux of mercury species on a weekly basis at over 90 sites in the United States and Canada. No North America-wide network measures either ambient concentrations of the major mercury species groups (i.e., elemental mercury, gaseous oxidized mercury and particulate mercury) or the dry deposition of mercury, although there have been some proposals to establish such a network in the United States (Lyman et al., 2007). The Southeastern Aerosol Research and Characterization study (SEARCH) includes several stations in the southeastern United States that measure ambient concentrations of speciated mercury and mercury wet deposition. Model performance for mercury deposition depends significantly on the model formulation, simulated precipitation fields and boundary conditions (because mercury is a global pollutant). The evaluation of

mercury wet deposition is conducted routinely using the MDN data; recent results have shown differences among models due to, in order of decreasing importance, model formulation, boundary conditions, and simulated precipitation (Bullock et al., 2009). As there are currently no dry deposition data for model evaluation, models have been evaluated instead using the few mercury speciated concentrations available. Although models tend to reproduce the global-scale gradients in total mercury concentrations and elemental mercury concentrations (most atmospheric mercury is elemental; e.g., Selin et al., 2007; Lohman et al., 2008), model performance for gaseous and particulate divalent mercury is more variable due to the shorter lifetime of those species in the atmosphere and the interactions between gaseous divalent mercury species and particulate matter (e.g., Seigneur et al., 2004; Selin et al., 2007).

Source apportionment and dynamic evaluations: The ability of an air quality model to properly attribute atmospheric deposition fluxes to various source categories and/or upwind source areas should be investigated. As for ambient concentrations, receptor modeling techniques can be used to that end. Dynamic evaluations would also be necessary to complement source apportionment evaluations for cases where the atmospheric deposition/precursor emission relationship is non-linear (e.g., nitrogen deposition). In the case of nitrogen deposition, a possible option is the use of nitrogen isotopes in wet deposition (Elliott et al., 2007). As another example, Keeler et al. (2006) applied two receptor modeling techniques (Positive Matrix Factorization, PMF, and UNMIX) to wet deposition data collected at Steubenville, OH, to estimate the relative contribution of coal combustion sources to mercury wet deposition, which was 70 percent \pm 15 percent. A chemical transport model for atmospheric mercury (Seigneur et al., 2004) estimated a contribution of U.S. coal-fired power plants (a subset of coal combustion sources) to mercury deposition in the Steubenville area of 62 percent, i.e., a value well within the range of 55 to 85 percent obtained with the receptor modeling techniques. (Note: This community is in an area where many large coal-fired power plants are located.)

8.2.5 AREAS FOR FUTURE IMPROVEMENT

Several improvements of atmospheric models and their interface with ecosystem models can lead to significant advances in our ability to provide the needed inputs to ecosystem models.

Spatial resolution: It is desirable to calculate dry deposition fluxes at a scale compatible with that of the ecosystem model using sub-grid scale land use information for dry deposition fluxes. It is also desirable to improve the meteorological model parameterizations to provide better quality precipitation estimates at spatial scales down to 1 km and terrain effects on air concentrations and dry deposition fluxes at grid sizes of 1-4 km.

Accuracy: It is desirable to reduce the error in precipitation simulations and air-surface flux estimates for daily to monthly temporal averages to provide more accurate data that can be input to the water quality models, potentially as data for accountability analyses. The adaptation of chemical data assimilation techniques or development of methods to combine measured and modeled data (data fusion) are worth investigating to help reduce error in the precipitation and deposition fields and reduce disparities with calibration data.

Temporal extent, trends and accountability: Development of a consistent, continuous time series of physical parameters (especially temperature and precipitation amount) and air-surface flux from the meteorological and chemical transport models is becoming a necessity for trend analysis. For practical purposes, this series could effectively start around 2001 which marks the beginning of the period for which consistent methodologies for estimating emissions across multiple years, from sources other than power plants, are being developed and when NO_x emissions begin to change noticeably. Meteorological and air quality model simulations could be conducted over multi-year periods given the appropriate inputs and compared with measurements (see, e.g., Chapter 11). The availability of emission inventories is the limiting factor at the moment. A continuous, historical time series of physical parameters and air-surface flux, starting around 1900, could be developed for the ecosystem models as collaboration between the air quality and ecosystem modeling communities. Such a historical time series needs to smoothly transition to current empirically-based and model-based time series. Looking to the future, guidance on the inclusion of climate change impacts on hydrology and chemistry for long-term projections of deposition (50 years in the future) needs to be developed.

Chemical species: The major chemical species of interest for atmospheric deposition are simulated routinely by atmospheric models (i.e., ozone, sulfate, nitrate, ammonium, other

nitrogenous compounds with the exception of dissolved organic nitrogen (DON), and mercury). But there are still significant uncertainties in our ability to correctly simulate the atmospheric deposition of nitrogenous compounds and mercury and we lack the necessary information (emissions inventories and model formulations) to simulate DON. However, base cation assimilation is needed by the more advanced soil and surface water chemistry models and base cations are not simulated by current atmospheric models; there is enormous uncertainty regarding emissions that would have to be overcome through inventory development. POPs are not currently treated in most atmospheric models; emission inventories and model representations of their atmospheric fate and transport need to be developed, incorporated into atmospheric models and evaluated with ambient measurements of air concentrations and deposition fluxes.

Atmosphere/ecosystem interface: Air-surface exchange algorithms in the air quality models need continued evaluation and improvement. These algorithms also need to calculate dry deposition fluxes for specific sub-grid scale land use categories compatible with that of the ecosystem models. Most air quality models do not currently account for the possible transformation of chemical species within an ecosystem and emission of chemical species back to the atmosphere. This is particularly important for nitrogenous species (nitric oxide and ammonia), mercury and POPs. Some interface algorithms have been developed that need to be incorporated and tested in atmospheric models and new algorithms need to be developed, evaluated and incorporated into the models.

8.3 ATMOSPHERIC MODELING FOR RISK ASSESSMENT

Risk assessments are conducted to address both human health and ecological impacts as noted in Chapter 3. The issues addressed above are for exposure and health effects studies and for atmospheric deposition to ecosystems. Therefore, they are pertinent to the application of atmospheric models in risk assessment. Guidelines for risk assessment generally require an uncertainty analysis to be conducted in addition to the deterministic analysis for representative individuals or the general population (NRC, 1994). Therefore, one aspect of atmospheric modeling that needs to be considered when using atmospheric models in the context of risk assessment is the treatment of uncertainties. There have been limited attempts to account for uncertainties in air quality modeling.

Because taking into account uncertainties requires sampling various values from the probability distribution functions (pdf) of model inputs and parameters, a large number of simulations is generally required. However, grid-based air quality models are computationally demanding and conducting a large number of simulations (e.g., >10000) may not be feasible. Three major approaches have been used:

The effect of the uncertainties in model inputs and parameters is simulated by conducting a moderate number of simulations (on the order of 100) based on the optimistic assumption that a large number of simulations is not required to cover the full range of uncertainties if the values of the inputs and parameters being sampled are carefully selected (Hanna et al., 2001, 2002). The effect of uncertainties in model inputs and parameters is simulated by conducting a large number of simulations with a simple air quality model, such as a one-dimensional trajectory model, instead of a three-dimensional model (Bergin et al., 1999; Bergin and Milford, 2000; Martien et al., 2003).

The effect of uncertainties in model inputs and parameters is simulated by conducting a large number of simulations with a reduced form of the three-dimensional air quality model; i.e., using a response-surface methodology (Seigneur et al., 1999; Lohman et al., 2000; Phillips et al., 2006).

Reduced-form models are versions of the model that reproduce the major characteristics of the model with a computationally simpler version of the model. A standard approach consists in using a response surface model (Box and Wilson, 1951). The first step consists in identifying the inputs and parameters that are the most influential for the model output of interest (typically by conducting a sensitivity analysis). Then, the model output is expressed as some mathematical function of those model inputs and parameters. A response-surface model is, therefore, a parameterization of the actual model results, and it may only be valid for the set of conditions under which it was developed. Since process-specific information may not be explicitly included in the response-surface model, one must be aware of the limitations of the response-surface model. The advantage of the response-surface model over the original model is that its

simplicity leads to greater computational speed, which is of particular interest for probabilistic analyses that involve a large number of model simulations.

A major component of an uncertainty analysis is to define the probability distribution functions of the influential model inputs and parameters to properly characterize their epistemic uncertainties (i.e., those uncertainties that can be reduced with more information) and aleatory uncertainties (i.e., variability, those uncertainties that originate from natural randomness and cannot be reduced, even with more information).

8.4 SYNTHESIS

8.4.1 SUMMARY OF THE CURRENT STATUS OF AIR QUALITY MODELS FOR EXPOSURE ASSESSMENTS, HEALTH EFFECTS STUDIES, AND ECOSYSTEM MODELING

We have reviewed the needs of exposure characterization for the health and ecosystem sciences. We have assessed whether current air quality models can address these needs in a satisfactory manner at least within Level 1 and 2 of regulatory requirements.. Our assessment is summarized in terms of what air quality models can do now, what they could do if input data currently missing were to become available, and what they could do after some pertinent model improvements were to be implemented. Except for obtaining accurate precipitation predictions, most improvements are realizable within the next ten years and several are possible in the next few years.

What atmospheric models can do:

- They treat criteria pollutants, acidic species, nitrogen species, mercury and some other inorganic and organic air toxics; however, there are uncertainties associated with the atmospheric modeling of those pollutants which, to be addressed, will require improvements in some model inputs (in particular, emissions and meteorology) and model formulation (e.g., better understanding of organic PM).
- They provide good temporal resolution (1 hour) for the afore-mentioned chemical species, which is suitable for exposure modeling and ecosystem modeling.
- They provide good spatial resolution for atmospheric concentrations of secondary pollutants and deposition (with nested grid and plume-in-grid treatments if needed for finer resolution in urban areas and near point sources, respectively).
- They can be applied for long-term (seasonal to annual) simulations of the afore-mentioned chemical species.

- Models and measurements can be used together to create optimal concentration “surfaces” for air pollutants through data fusion (as a model post-processing step) or data assimilation (as an optimized modeling approach).

What atmospheric models could do but input data are currently missing:

- Multiple year simulations can be conducted but internally consistent multi-year emission inventories are not readily available yet for periods >5 years; there is, however, an ongoing effort at EPA to develop such nationwide emission inventories.
- Air toxic metals are treated in a model such as CMAQ but the corresponding emission inventories are not currently available.
- The lack of compositional information and emission inventories currently precludes the simulation of the deposition of dissolved organic nitrogen.

What atmospheric models could do but some improvements are needed:

- Fine spatial resolution for near-source population exposure, in particular, near roadways (the plume-in-grid technology already exists for point sources). Various techniques are currently under development but more testing and development are needed before they become operational.
- The treatment of several air toxics (e.g., POPs, atmospheric chemistry of hexavalent and trivalent chromium) and some PM characteristics (acidity, ultrafine number) is currently missing in air quality models and the corresponding emission inventories are not available (e.g., ultrafine PM, POPs)
- Two-way surface exchange, which is needed for a correct representation of the atmospheric deposition of nitrogenous and mercury compounds, is not currently treated in air quality models; some two-way surface exchange modules exist but they need to be incorporated into air quality models and evaluated with experimental field data.
- Enhanced spatial resolution down to 1 km, particularly in complex terrain, to account for topographic effects on deposition fluxes and air concentrations.
- The allocation of dry deposition to land-use classes within a model grid is desirable to provide proper dry deposition inputs to ecosystem models; it cannot currently be performed by air quality models, which only provide a grid-average atmospheric deposition flux. There is, however, an ongoing effort to address this issue.
- Models and measurements can, in theory, be used together to create optimal “surfaces” of atmospheric deposition through data fusion; however, discrepancies between modeled and measured precipitation amounts and between dry deposition algorithms need to be resolved satisfactorily before such data fusion techniques can be used routinely. Also, some critical species data are missing for deposition pathways.
- Models do not currently treat the deposition of alkaline species that act to neutralize acid deposition (potassium, calcium, magnesium and sodium). Emission methodologies for those species are currently missing and, as a result, emission inventories are not available (except for sea salt sodium).
- Accurate precipitation estimates are needed at all scales, particularly for the prediction of atmospheric deposition. They also required for PM and regional haze modeling; although

there will always be some uncertainty associated with local precipitation fields, some effort must be made to reduce such uncertainties.

- Improvements to models could be checked via diagnostic and dynamic evaluations. Diagnostic evaluations could address individual processes to the extent possible as well as model performance by spatial region and time periods (e.g., by season). Dynamic evaluations (which require robust multi-year emission inventories) are essential to build credibility for the application of air quality models to the design of emission control strategies.

8.4.2 USE OF AIR QUALITY MODELS FOR ACCOUNTABILITY

Air quality models can play an important role in ensuring that emission strategies lead to the desired or projected results. Because they incorporate key chemical and physical processes and potential nonlinear interactions, air quality models can play an important role in explaining and interpreting trends or the lack thereof. Air quality models are ideally suited to separate out the role of meteorology from the role of emissions and chemistry to characterize emissions/exposure relationships or emissions/deposition relationships independently of the meteorological variability (however, the models must first be subject to diagnostic and dynamic evaluations to ensure that they can realistically represent the influence of meteorology and emissions on air pollutant concentrations and deposition fluxes). Air quality models provide more detailed information (spatially, temporally and chemically) than monitoring networks can ever provide in practice. Consequently, air quality models can be used to complement monitoring networks to provide more complete information on the air pollutant concentrations and deposition fluxes and can assist monitoring design, including future designs that take into account anticipated changes in concentrations and/or deposition fluxes. The link between human exposure and ambient concentrations needs to be quantified using parametrization of indoor-outdoor relationships for multipollutants estimated for buildings and vehicles, taking into different geographical climate regimes, building practices and personal activity. These steps are considered a priority to realize regulatory support in Levels 3 and 4 discussed in Chapter 2.

Data fusion, where model simulation outputs and measurements are combined to create continuous concentration and deposition fields that are consistent with the available measurements, will be a step in this process. Then, the resulting concentration and deposition fields can be used to track their long-term temporal evolution and to assess whether the changes in emissions over a given time period led to the anticipated changes in atmospheric concentrations and/or atmospheric deposition fluxes. Retrospective analyses of initial modeling

calculations of the future need to be designed into major regulatory actions as a feedback mechanism to determine if the projections and their methods were and are reliable.

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Table 8.1. Air toxics (HAPs) Treated Explicitly in CMAQ. (See the List of Terms for a complete list of HAPs.)

Volatile organic compounds	Metals
Acetaldehyde ^{a, b}	Beryllium compounds ^{a, b}
Acrolein ^{a, b}	Cadmium compounds ^{a, b}
Acrylonitrile ^{a, b}	Chromium (hexavalent and trivalent) ^{a, b}
Benzene ^{a, b}	Lead ^{a, b}
1, 3-Butadiene ^{a, b}	Manganese ^{a, b}
Carbon tetrachloride ^{a, b}	Mercury (elemental, gaseous divalent and particulate divalent) ^{a, b}
Chloroform ^{a, b}	Nickel compounds ^{a, b}
p-Dichlorobenzene ^a	
1,3-Dichloropropene ^{a, b}	
Ethylene dibromide (1,2-dibromoethane) ^{a, b}	Volatile inorganic compounds
Ethylene dichloride (1,2-dichloroethane) ^{a, b}	
Ethylene oxide ^{a, b}	Chlorine ^a
Formaldehyde ^{a, b}	Hydrochloric acid ^a
Hexamethylene 1,6-diisocyanate ^a	
Hydrazine ^{a, b}	Other compounds
Maleic anhydride ^a	
Methanol ^a	Diesel particles ^b
Methylene chloride (dichloromethane) ^{a, b}	
Naphthalene ^a	
Propylene dichloride (1,2-dichloropropane) ^{a, b}	
Quinoline ^{a, b}	
1, 1,2,2-Tetrachloroethane ^{a, b}	
Tetrachloroethylene (perchloroethylene) ^{a, b}	
Toluene ^a	
2,4-Toluene diisocyanate ^a	
Trichloroethylene ^{a, b}	
Triethylamine ^a	
Vinyl chloride ^{a, b}	
Xylene ^a	

^aOne of the 187 hazardous air pollutants (<http://www.epa.gov/ttn/atw/188polls.html>).

^bOne of the 33 urban pollutants listed as air toxins by EPA (<http://www.epa.gov/ttn/atw/nata/34poll.html>).

Text Box 8.1. Elements of Model Calibration

Model calibration consists in the adjustment of model inputs or model parameters/algorithms to obtain better operational performance. *Data assimilation* forces the air quality model predictions toward observations using various mathematical techniques such as a variational analysis, a sequential analysis (e.g., Kalman filter) or an additional “nudging” term in the model equations; although this is now done routinely in meteorology to assimilate wind and temperature observations, the assimilation of air quality observations in air quality modeling has been limited to date (e.g., Chai et al., 2006, 2007). *Data fusion* combines the results of an air quality simulation with data to develop fields of air concentrations or atmospheric deposition fluxes that leverage the best aspects of model results and data; standard interpolation techniques, kriging techniques and hierarchical Bayesian approaches have been used for data fusion (e.g., Fuentes and Raftery, 2005). Data assimilation is a dynamic process because the data affect the model simulation as it progresses (on-line procedure), whereas data fusion can be seen as a static assimilation process because the assimilation step does not feed back into the model simulation (post-processing step). Note that in the case of both data assimilation and data fusion, the result is a combination of the model and observations, therefore, it does not correspond to a solution of the original model. Also, these techniques focus on creating a better representation of current conditions.

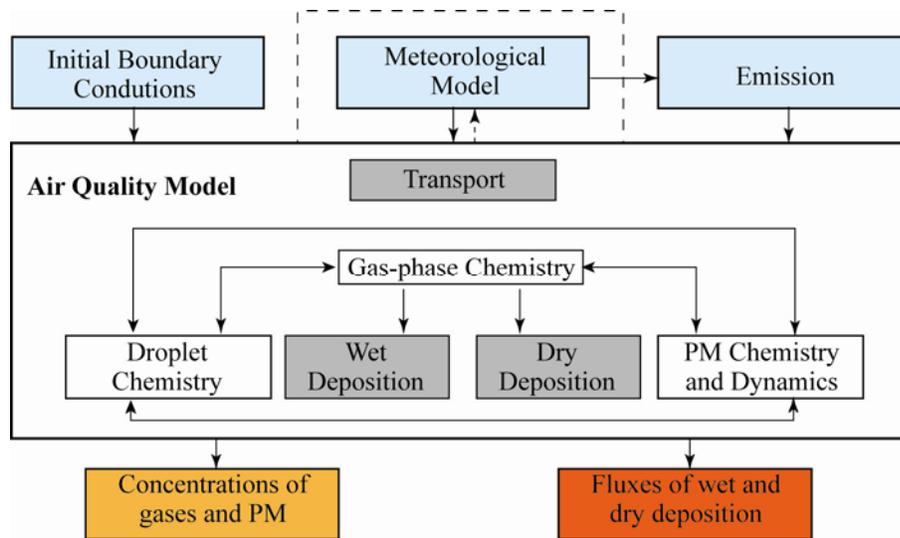


Figure 8.1. Schematic Description of an Air Quality Model; the dotted line and arrow correspond to the case where both meteorology and air quality are simulated jointly.

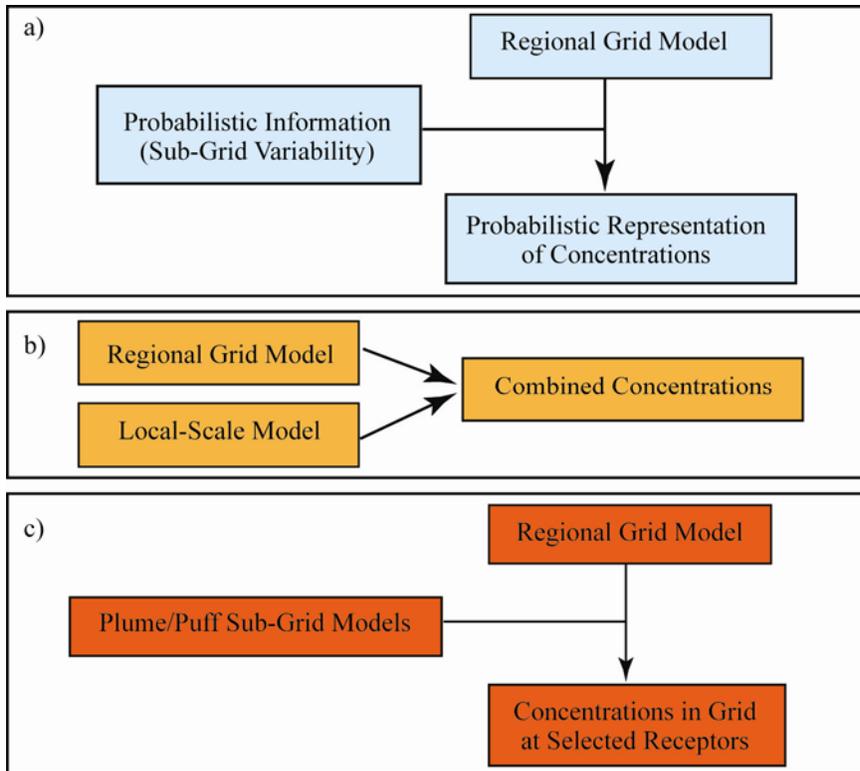


Figure 8.2. Schematic Representation of Three Major Approaches to Modeling Air Pollutant Concentrations at the Sub-Grid Scale Within a Grid-Based Air Quality Model (Source: Touma et al., 2006).

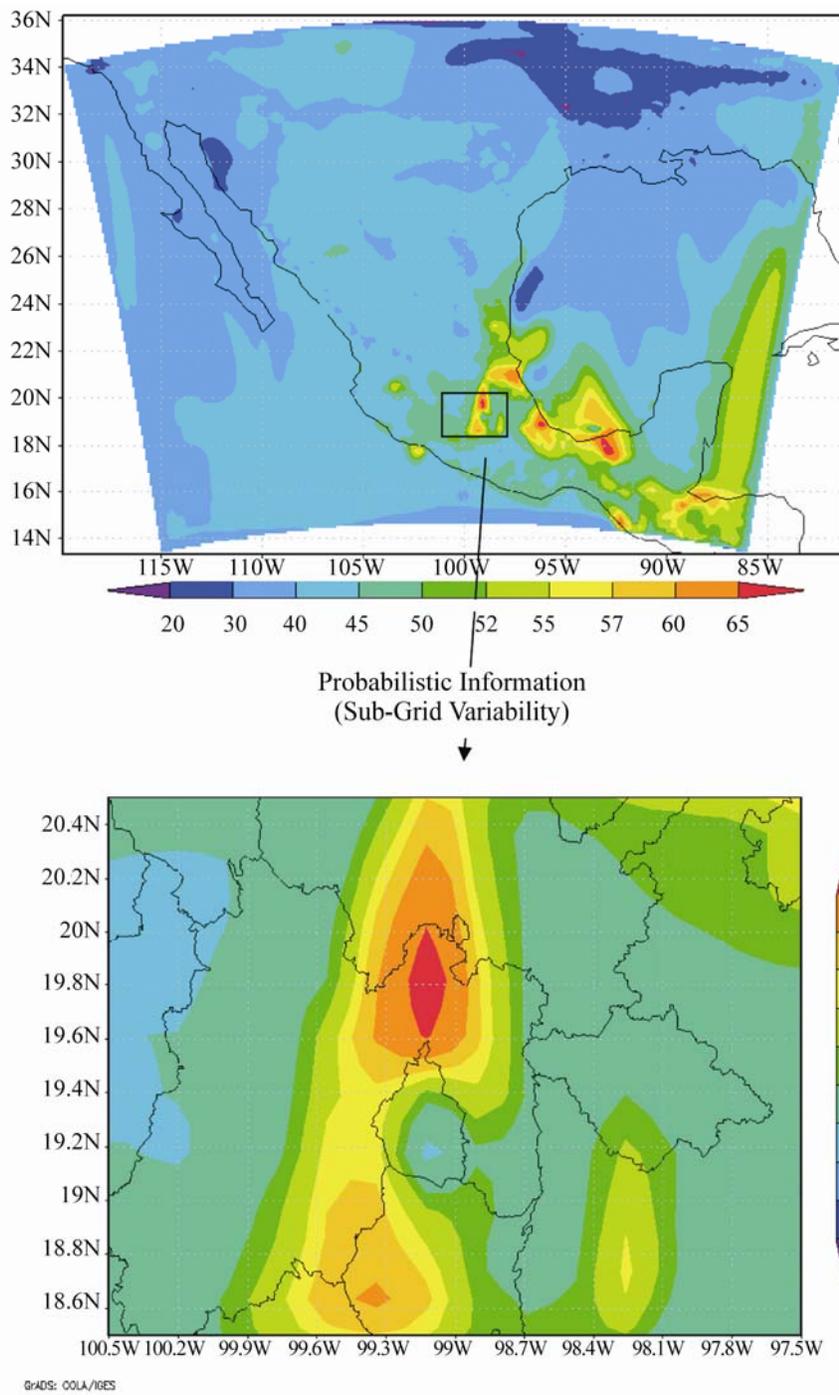


Figure 8.3. Surface Ozone Concentrations Simulated with MCCM for 20 March 2006 at Noon over Mexico (top) and over Mexico City (bottom).

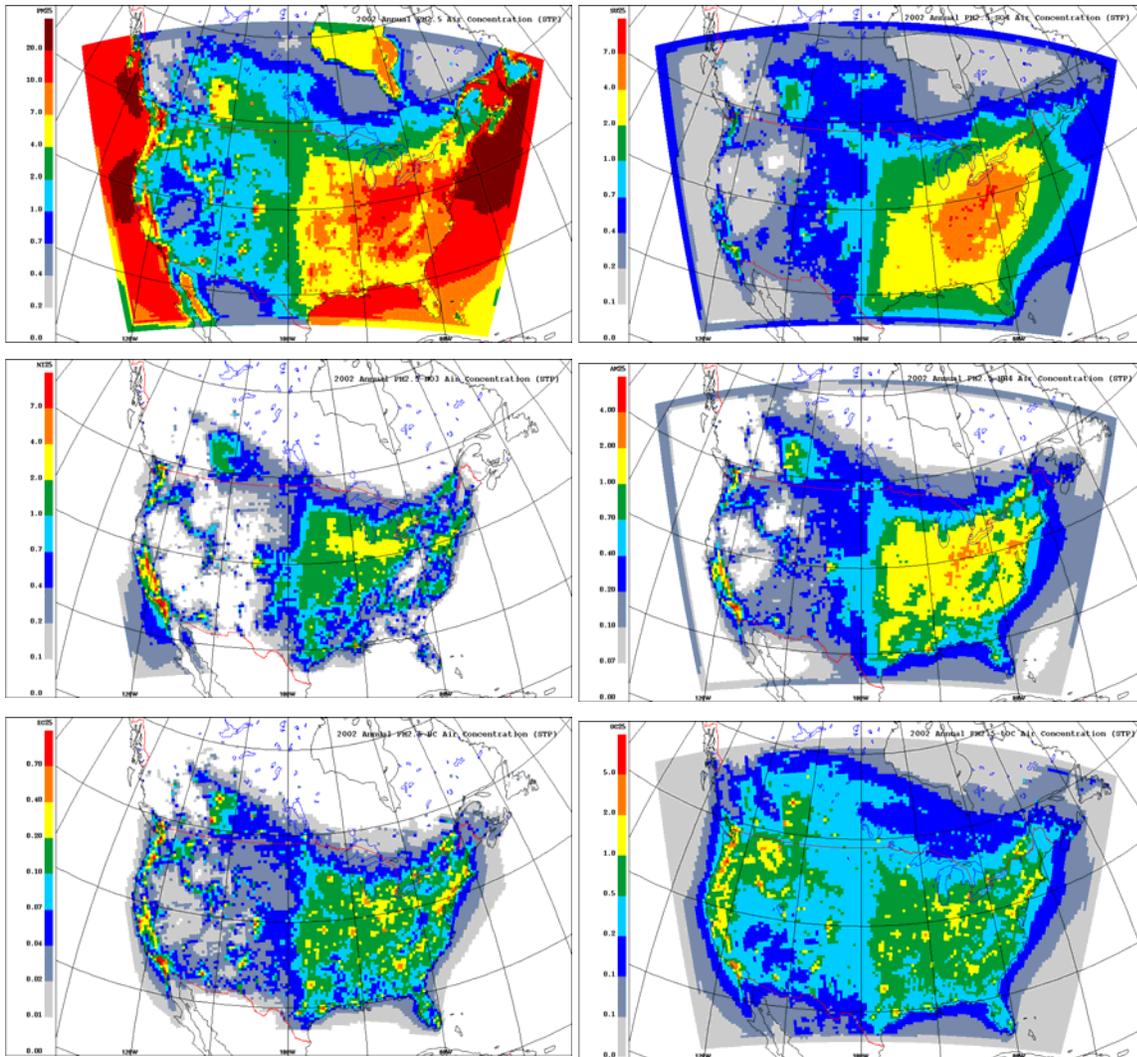


Figure 8.4. Annual Surface Concentrations ($\mu\text{g}/\text{m}^3$ at STP, 0°C) of $\text{PM}_{2.5}$ and Major Components over Canada and the United States Simulated for 2002 with AURAMS: $\text{PM}_{2.5}$ (top left), sulfate (top right), nitrate (middle left), ammonium (middle right), black carbon (bottom left), and organics (bottom right) (Moran et al., 2008). $\text{PM}_{2.5}$ concentrations over the ocean are affected by sea salt (which is not shown as a separate component in the figure).

50 Percent Reduction in emissions of

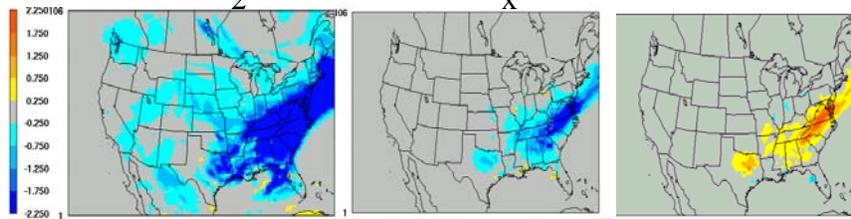
Percent
Change in

SO₂

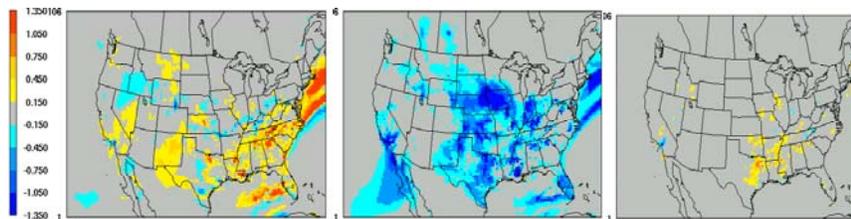
NO_x

VOC

Sulfate



Nitrate



Organics

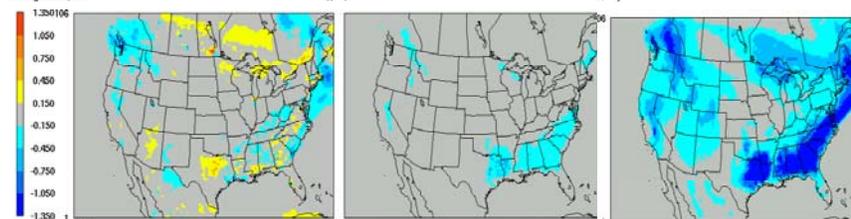


Figure 8.5. Response of the Concentrations of PM_{2.5} Components (sulfate, nitrate and organics) to 50 Percent Reductions in SO₂, NO_x and VOC Emissions Simulated over the Contiguous United States for the 1-10 July 1999 Period (Source: Seigneur, 2005).

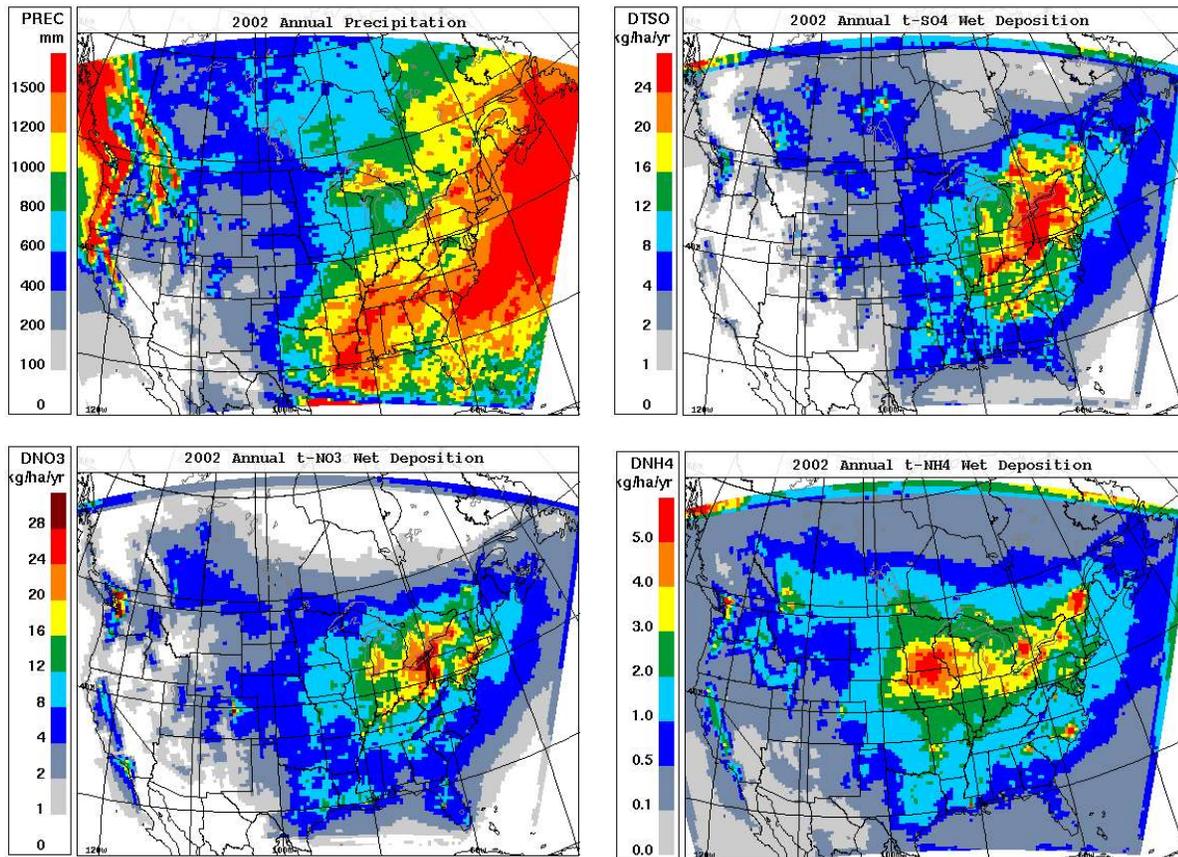


Figure 8.6. Simulation of a) Annual Precipitation (mm), b) Sulfate, c) Nitrate, and d) Ammonium Wet Deposition Fluxes ($\text{kg ha}^{-1} \text{y}^{-1}$) over Canada and the United States for 2002 with the Environment Canada Chemical Transport Model AURAMS (Source: Moran et al., 2008).

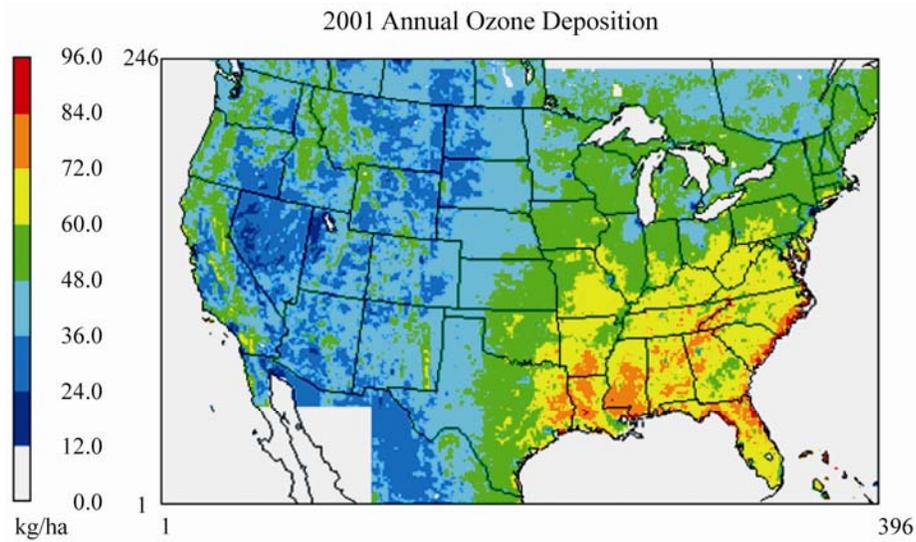


Figure 8.7. Total Wet + Dry Ozone Deposition Simulated for 2001 Emissions over the Continental United States with CMAQ. The total deposition of ozone is essentially all dry deposition.

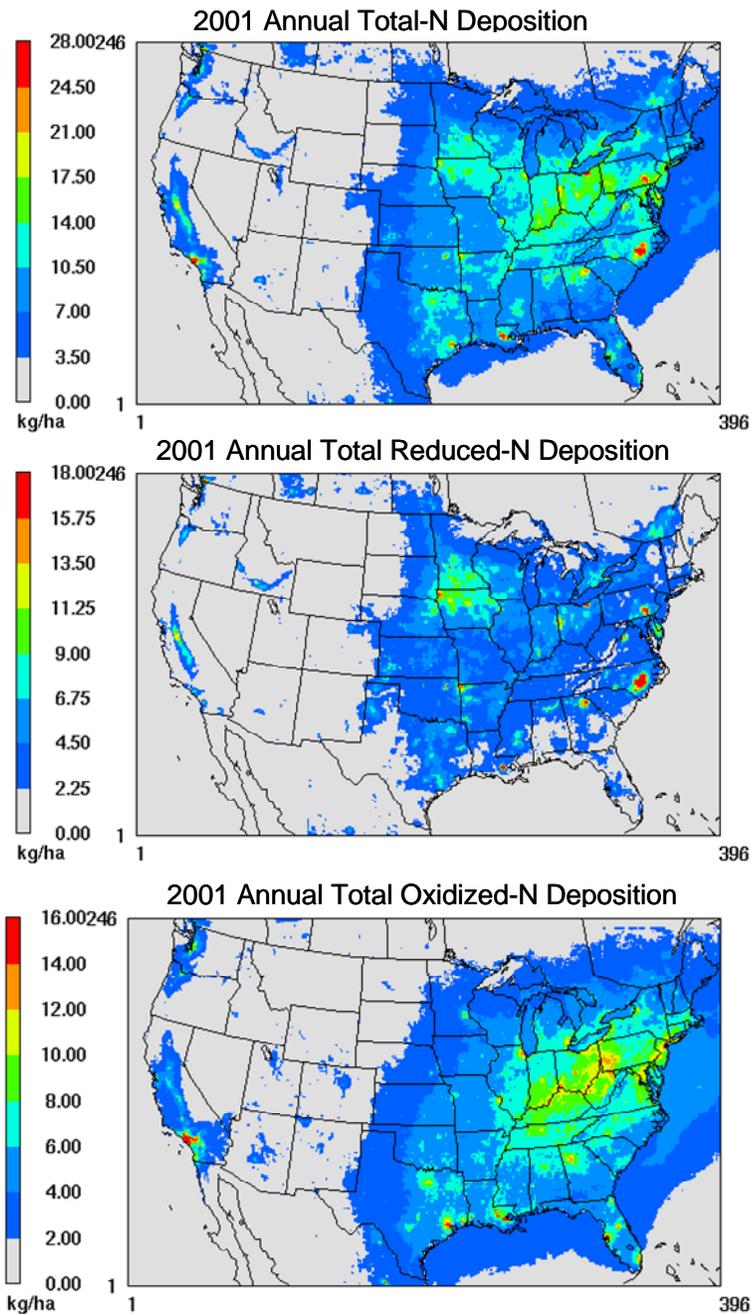


Figure 8.8. Total Wet + Dry Nitrogen Deposition Simulated for 2001 Emissions over the Continental United States with the CMAQ. The influence of power plants and transportation corridors is evident in the oxidized-nitrogen deposition pattern, and the influence of confined animal feeding operations is evident in the reduced-nitrogen deposition pattern.