1   **CHAPTER 8: ATMOSPHERIC MODELING**

2   Air quality models (also referred to as atmospheric chemical transport models and, in the case of

3   ozone and PM, photochemical models) simulate the atmospheric concentrations and deposition

4   fluxes to the Earth's surface of air pollutants by solving the mass conservation equations that

5   represent the emissions, transport, dispersion, transformations and removal of those air pollutants

6   and associated chemical species. Figure 8.1 presents a schematic overview of the major

7   components of a multipollutant air quality model. Air quality models can be grouped into two

8   major categories: 1) models that calculate the concentrations of air pollutants near a source

9   (source-specific models) and 2) models that calculate concentrations of air pollutants over large

10   areas ranging from an urban area, to a region, a continent and the globe (grid-based models).[1] A

11   few models combine both modeling approaches in a hybrid formulation.

12

13   Air quality models can be applied to a variety of spatial and temporal scales. Source-specific

14   models such as plume and puff models are typically applied up to 50 to 150 km from the source,

15   whereas grid-based air quality models range from the urban scale to regional, continental,

16   hemispheric and global scales (see Chapter 10 for a discussion of hemispheric and global scale

17   modeling). Inputs to air quality models include the emission rates of primary air pollutants and

18   precursors of secondary air pollutants,[2] meteorology (three-dimensional fields of winds,

19   turbulence, temperature, pressure, boundary layer height, relative humidity, clouds and solar

20   radiation) and boundary conditions (or background conditions in the case of source-specific

21   models; see Figure 8.1). For grid-based models, an emission model is used to translate an

22   emissions inventory into a spatially distributed and temporally resolved grid structure. For

23   example, on-road mobile source emissions must account for the vehicle fleet composition,

24   vehicle speed and ambient temperature as a function of time and road type. Also biogenic

25   emissions are a function of land use, season, ambient temperature and solar radiation. Emissions

26   were discussed in Chapter 7. Meteorology is obtained from observational data or from the

---

[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] Primary air pollutants are those that are emitted to the atmosphere; secondary pollutants are those that are formed by chemical processes in the atmosphere.

1   output of a meteorological model (or a combination of both). In a few research-grade models,

2   both meteorology and air quality are simulated jointly so that the chemical composition of the

3   atmosphere can influence the meteorology (e.g., the effect of particulate matter on atmospheric

4   radiation); examples include the Multiscale Climate and Chemistry Model (MCCM, Grell et al.,

5   2000) and the Weather Research and Forecast model with chemistry (WRF-Chem, Grell et al.,

6   2005). When simulating a combination of several spatial scales, downscaling of meteorology

7   from global to synoptic scale or to regional/urban scale is needed. Such downscaling can be

8   challenging when forecasting future climatology, which is needed to address the effect of climate

9   change on future air quality and atmospheric deposition due to changes in air concentrations,

10 precipitation and possibly also land use (see Chapter 10). The effect of future climate change

11 will need also to be reflected in the emissions (see Chapter 7). Boundary conditions for

12 downscaling to regional-scale models are now typically generated from larger-scale models.

13 Such approaches, although ultimately dependent on the quality of the global emissions inventory,

14 reduce the uncertainty in the estimation of boundary conditions, particularly those above the

15 planetary boundary layer (e.g., Appel et al., 2007).

16

17 It should be noted that, although air quality models have historically been applied to address

18 issues specific to ambient air quality standards (i.e., one criteria pollutant at a time) or welfare

19 (e.g., acid deposition or visibility impairment), they are inherently multipollutant based.

20 Therefore, it seems that air quality models can be applied in the context of integrated emissions

21 control programs that are designed to optimally address all of the above air quality issues

22 simultaneously. Limitations arise, however, as additional chemical species of concern are

23 identified that are not currently treated in air quality models. Such cases require the compilation

24 of emissions inventories and boundary conditions for these new chemical species and the

25 addition of chemical and physical mechanisms in the model to treat their transformation and

26 deposition.

27

28 **8.1   ATMOSPHERIC MODELING FOR EXPOSURE ASSESSMENT**

29 **8.1.1 NEEDS FROM EXPOSURE MODELERS AND HEALTH EFFECTS SCIENTISTS**

30 The estimation of the health effects of air pollution requires knowledge of the concentrations of

31 air pollutants to which an individual or a population cohort is exposed (see Health Effects

32 Chapter). These concentrations can be measured or calculated with an atmospheric model.

1   Because individuals are exposed to different air pollutant levels as they move through different

2   environments during their daily activities (e.g., home, vehicle, office, school, outdoor), one

3   would ideally want to have high spatial and temporal resolutions of the air pollutant

4   concentrations. The needs of exposure modelers and health effects scientists may be categorized

5   as follows.

6

7   *Spatial resolution*: Some health effects studies, such as time-series mortality studies, do not

8   necessarily require fine spatial information on air pollutant concentrations because they deal with

9   information at the urban area or neighborhood level. However, the individual-level health effect

10   analyses require fine spatial information on the air pollutant concentrations. The spatial

11   resolution provided by an air quality model must then be sufficient to resolve the spatial

12   variability of outdoor air pollutant concentrations so that (1) outdoor exposure of individuals and

13   population cohorts can be assessed with sufficient spatial resolution and (2) micro-environmental

14   models for indoor exposure have the needed outdoor concentration inputs (Isakov and Ozkaynak,

15   2007).[3] The need for fine spatial resolution is greatest near sources of pollutants because the

16   concentration gradients are strongest near those sources (e.g., near an industrial site, near a

17   roadway). The entrainment of fresh emissions into the ambient air affects the emitted as well as

18   the ambient pollutants through chemical reactions. For example, O_3 concentrations are depleted

19   near power plants and roadways because of the rapid reaction of the emitted NO with O_3.

20

21   *Temporal resolution*: The temporal resolution needed for exposure calculations may be very fine

22   (e.g., minutes) but such resolution is typically provided by the micro-environmental models. The

23   temporal resolution needed from the air quality model must, therefore, be sufficient to provide

24   the needed inputs to the micro-environmental models. Such temporal resolution must be able to

25   capture the temporal variability of the air pollutant concentrations. Continuous measurements of

26   various gaseous and particulate chemical species provide indications of the temporal evolution of

27   the concentrations of primary and secondary air pollutants. There are some instances, e.g., near a

28   source, where fluctuations in the wind (i.e., turbulence) and in the source activity (e.g., vehicular

29   traffic) lead to strong temporal variability in chemical species concentrations at a given location

---

[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.

1   (Thoma et al., in press 2007; Baldauf et al., in press 2007). It is generally considered that hourly

2   concentrations provide the desired temporal resolution for air pollutant concentrations in the

3   ambient atmosphere. However, there may be instances where finer temporal resolution (e.g., 1,

4   5, 10 or 15 min) is desirable. In those cases, the temporal resolution of the emissions and local

5   meteorology must be compatible with the selected temporal resolution of the air quality and

6   exposure models. Alternatively, the sub-hourly variability in air pollutant concentrations due to

7   meteorological and source variability can be treated in an uncertainty analysis (see below) rather

8   than in deterministic calculations. Some exposure models require probability distributions of the

9   exposure concentrations; there is then a need to translate deterministic output, even on fine

10   scales, to probabilities. The development of probabilistic air quality model outputs is discussed

11   in Section 4.

12

13   *Temporal extent*: Longitudinal epidemiological studies require exposure information on the

14   relevant air pollutant concentrations over long time periods (multi-years). Time-series

15   epidemiological studies address acute effects and may also require information on air pollutant

16   concentrations over multi-year periods to have sufficient statistical power.

17

18   *Chemical species and particle sizes*: Chemical species of interest to the exposure and health

19   effects community include the regulated species (i.e., criteria pollutants and hazardous air

20   pollutants, a.k.a. air toxics) as well as other chemical species that are being considered as

21   potentially harmful to human health and, consequently, are being investigated in exposure,

22   epidemiological and toxicological studies. Ultra-fine particles (i.e., those particles less than 100

23   nm in aerodynamic diameter) are one example of a non-regulated fraction of PM that is being

24   investigated in various studies as a potential cause of adverse health effects. Also, the infiltration

25   of particles from outdoors to indoors depends on size and chemical composition; therefore,

26   quantitative information from an air quality model on the PM size distribution and chemical

27   composition will lead to more reliable exposure modeling.

28

29   **8.1.2 CURRENT STATUS OF ATMOSPHERIC MODELS**

30   Current atmospheric models calculate the outdoor concentrations of air pollutants.

31   Concentrations of air pollutants in indoor environments can then be calculated from the outdoor

1   concentrations by means of micro-environmental models (see Chapter 4). We discuss below

2   whether current atmospheric models are suitable to address the needs of the exposure and health

3   sciences communities.

4

5   *Spatial resolution*: Regional models can cover large areas but their grid spacing is constrained to

6   about 1 km or more and, therefore, they provide spatially averaged concentrations that may not

7   be representative of the actual concentrations that may occur, for example, in the vicinity of

8   emission sources (the formulation of some parameterizations must be modified as the spatial

9   resolution of the model increases, e.g., convection, turbulent diffusion). Source-specific models

10   offer a spatial resolution of a few meters if needed but they are typically limited to about 50 km

11   from point sources and a few hundred meters from line sources. There are, however, a few

12   source-specific models that can provide very fine spatial resolution near the source and also

13   apply to long distances. Nevertheless, it is not practical to use source-specific models for an area

14   with a large number of emission sources as the treatment of many sources with such models

15   become computationally prohibitive. Therefore, a combination of a grid-based model that

16   provides air pollutant concentrations over a large domain with a relatively coarse grid spacing (1

17   km or more) and source-specific models that provide information on the spatial gradients in the

18   vicinity of major emission sources is needed to address the needs articulated above.

19

20   Touma et al. (2006) addressed the issue of representing air pollutant concentrations with fine

21   spatial resolution over large areas and they identified three major approaches for modeling air

22   pollutant concentrations at the sub-grid scale level within a grid-based air quality model. Figure

23   8.2 depicts the general features of those approaches.

24

25   The first approach (Ching et al., 2006) is solely based on a grid model but it uses finer grid

26   resolution than generally used (e.g., down to 1 km, whereas minimum grid size in urban areas is

27   typically 4 to 5 km). Then, the concentrations calculated by the fine grid model are used to

28   construct a distribution of concentrations over a large grid cell (e.g., a set of 16 concentrations

29   for a 4 km x 4 km grid cell). This concentration distribution represents the variability of the

30   chemical species concentrations within that grid cell (actually, it may still under-represent the

31   full variability because concentrations may not be homogeneous at scales below 1 km). Such

1   concentration distributions can be used to construct generic concentration distributions that

2   would be a function of the chemical species, the land use category (e.g., urban, suburban, non-

3   urban) and time (e.g., season, day of the week, hour of the day). Those generic distributions are

4   then available to complement the results of a grid-based simulation of chemical concentrations

5   by providing for each grid cell a probability distribution function that characterizes the

6   variability of the modeled concentration.

7

8   The second approach uses a grid-based model and a source-specific model separately for the

9   simulations of different sources and combines the results of the two models to construct chemical

10 concentration fields due to all sources (e.g., Isakov and Venkatram, 2006). This approach is

11 theoretically correct for chemical species that are chemically inert or undergo first-order

12 chemical reactions (i.e., linear chemistry). However, it is not strictly correct for chemical species

13 that undergo non-linear chemistry and the uncertainty associated with this approach cannot be

14 estimated a priori.

15

16 The third approach combines a grid-based model and a source-specific model into a single

17 hybrid model (Karamchandani et al., 2006, 2007). The hybrid model is formulated so that

18 interactions of emitted species treated by the grid-based model and those treated by the source-

19 specific model are treated explicitly to take into account the non-linear chemical reactions. Thus,

20 the modeled concentrations are theoretically correct for chemically inert species as well as for

21 chemically reactive species with linear or non-linear chemistry. This approach is currently

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

23 sources (e.g., roadways).

24

25 Applications of these different modeling approaches have been limited to date and there is a need

26 to evaluate each approach against measurements as well as to compare those different

27 approaches to assess their relative strengths and weaknesses.

28

29 *Temporal resolution*: The temporal resolution provided by air quality models (both grid-based

30 and source-specific) is one hour because meteorological and emission inputs are typically

31 available on an hourly basis. This resolution has typically been considered appropriate for the

1   simulation of outdoor concentrations, which are used either as input to outdoor calculation

2   exposure or to micro-environmental models. Finer temporal resolution is currently limited by

3   the availability of sub-hourly emission and meteorological inputs.

4

5   *Temporal extent*: As discussed in Section 3.3 below, air quality model simulations are now

6   routinely conducted for one-year periods, but not for multi-year periods. Multi-year emission

7   inventories are currently under development at EPA; once these inventories become available,

8   multi-year air quality simulations will be feasible.

9

10 *Chemical species and particle sizes*: Air quality models currently treat all major criteria

11 pollutants (O_3, NO_x, SO_2, CO and PM), except lead (Pb), and some air toxics (VOC and trace

12 metals).[4] Air quality models typically treat VOC via the use of carbon-bond representations

13 (e.g., CB IV and CB05 mechanisms) or the use of representative molecules that represent a large

14 group of molecules (e.g., SAPRC99 and RACM mechanisms). Therefore, only a few air toxic

15 organic molecules (e.g., formaldehyde) are treated explicitly in those chemical mechanisms. To

16 address air toxics VOC, some air quality models have been modified to include explicit

17 treatments of VOC air toxics of interest such as aldehydes (formaldehyde, acetaldehyde),

18 benzene and butadiene (Seigneur et al., 2003; Luecken et al., 2006). Table 8.1 presents the list

19 of the air toxics treated by the U.S. EPA Community Multiscale Air Quality (CMAQ) model.

20

21 Mercury is a major air toxic that is currently treated in air quality models; it is of interest for

22 atmospheric deposition (see Section 7.3) rather than for population exposure via inhalation.

23 Other trace metals treated in air quality models are assumed to be chemically inert. This

24 assumption is appropriate for trace metals that have potential adverse health effects that do not

25 depend on their chemical state. It is not appropriate for chromium (Cr) because it has health

26 effects that depend on the oxidation state (Cr(VI) is considered carcinogenic whereas Cr(III) is

27 not) and it undergoes reduction-oxidation transformations in the atmosphere (Seigneur and

28 Constantinou, 1995; Lin et al., 2004). One major limitation for the treatment of trace metals

29 other than mercury and lead is the paucity of trace metal emission inventories that have received

30 the scrutiny needed to ensure that they are reliable and accurate.

---

[4] Note that lead (Pb) is listed in the United States as both a criteria pollutant and an air toxic

1

2   Persistent organic pollutants (POPs) are a major category of air toxics, which is currently not

3   treated by air quality models. POPs are of interest mostly for atmospheric deposition (see

4   Section 3.4) rather than for population exposure via inhalation.

5

6   Air quality models currently calculate PM mass concentrations in two main size fractions, fine

7   PM ($PM_{2.5}$) and coarse PM ($PM_{10-2.5}$), using either modal or sectional representations of the size

8   distributions (finer size resolution is actually provided by the modal representation and by

9   sectional representations that use more than two size sections). PM chemical speciation includes

10   sulfate, nitrate, ammonium, black carbon, organic compounds and "other" primary species (those

11   "other" species include for example fly ash and other PM emissions from anthropogenic sources,

12   crustal species and sea salt). In some areas (e.g., Mexico City), soil erosion leads to a significant

13   fraction of PM_{10} concentrations and algorithms have been developed to quantify such crustal PM

14   emissions as a function of wind velocity, surface roughness, soil characteristics and soil

15   moisture. This representation of PM in two speciated size ranges ($PM_{2.5}$ and $PM_{10-2.5}$) is

16   consistent with the current U.S. air quality standards for PM. Other characteristics of PM are of

17   potential interest for adverse health effects, for example, the number concentration of ultrafine

18   particles, the particle surface area, the acidity of particles, the concentrations of individual

19   elements (e.g., metals), and gaseous co-pollutant interactions. PM air quality models are not

20   currently suited to address those characteristics (NARSTO, 2004).

21

22   **8.1.3   EVALUATION OF AIR QUALITY MODELS**

23   Air quality models are generally evaluated with ambient measurements of concentrations of

24   gaseous and particulate chemical species and PM mass concentrations. This type of performance

25   evaluation (generally referred to as operational performance evaluation) does not necessarily

26   provide information on the ability of a model to simulate the relative contributions of various

27   source categories or source areas (i.e., source apportionment) or to simulate the response of

28   ambient concentrations to changes in emissions (generally referred to as dynamic evaluation).

29   To that end, other modes of evaluation need to be conducted. First, we summarize the current

30   status of air quality model operational performance for various chemical species, spatial scales

1   and temporal scales. Then, we discuss some examples of source apportionment and dynamic

2   evaluations.

3

4   *Ozone*: Grid-based air quality models have been applied to simulate ozone concentrations for

5   over three decades and there is considerable experience available for this chemical species. An

6   assessment of our ability to address ozone air pollution was conducted by NARSTO (2000). A

7   summary of model performance for ozone in the United States was presented by Russell and

8   Dennis (2000). The Canadian air quality models have recently been evaluated for eastern North

9   America (Tarasick et al., 2007). Some recent ozone forecast evaluations for United States and

10 Canadian models are presented by McKeen et al. (2005). Performance of air quality models for

11 ozone has also been evaluated for the Mexico City area (e.g., Jazcilevich et al., 2003, 2005; Lei

12 et al., 2007; Tie et al., 2007; see Figure 8.3). Although there are still some uncertainties in our

13 knowledge of the atmospheric chemistry leading to ozone formation (e.g., oxidation of

14 aromatics, radical chemistry), ozone modeling is a mature field, which is unlikely to evolve

15 significantly from its current status over the next few years. Overall, we can consider the ability

16 of models to simulate ozone concentrations to be adequate and the error and bias of air quality

17 models for 1-hour average ozone concentrations are typically within 35 percent and 15 percent,

18 respectively. However, some caution is advised when applying ozone models to predict the

19 effect of precursor emission reductions (see discussion of dynamic model evaluations below).

20

21 *Other gaseous criteria pollutants (NO_2, CO and SO_2)*: Air quality models simulate NO, NO_2,

22 CO and SO_2 as part of the atmospheric chemistry of ozone and PM formation. These chemical

23 species are primary species (i.e., directly emitted into the atmosphere) with the exception of NO_2,

24 which is both emitted into the atmosphere and formed in the atmosphere by the oxidation of NO

25 (CO is also formed in the atmosphere via VOC photo-oxidation, however, the primary form

26 dominates in urban areas where concentrations are highest). Air quality models generally

27 perform more poorly for these primary species than for a secondary species such as ozone

28 because primary species exhibit strong concentration spatial gradients, which are not captured by

29 grid-based air quality models. Nevertheless, Lei et al. (2007) obtained good model performance

30 for CO in Mexico City. Concentrations of SO_2 near point sources are typically simulated using

31 source-specific models (point source models); thus, the spatial concentration gradients can be

1 captured by using a fine array of receptor points where the SO_2 concentrations are calculated.

2 The performance of point source models has been evaluated with a variety of field data where

3 gaseous tracers were released from a point source and measured downwind at a large number of

4 receptor sites. The error metric used was the robust highest concentration (RHC) statistic, where

5 the RHC represents a smoothed estimate of the highest concentrations based on an exponential

6 fit to the upper end of the concentration distribution. For the AERMOD model (i.e., the model

7 currently recommended by EPA for local impacts of point sources) applied to point sources with

8 no significant downwash, the ratio of modeled to observed RHC ranged from 0.77 to 1.18 for 1-

9 hour average concentrations (four studies), from 1.00 to 1.35 for 3-hour average concentrations

10 (six studies), from 0.73 to 1.65 for 24-hour average concentrations (six studies), from 0.31 to

11 1.65 for annual concentrations (six studies); a ratio of 1 would mean perfect agreement (Perry et

12 al., 2005). Similarly, NO, NO_2 and CO concentrations near roadways are typically simulated

13 with source-specific models (line source models), which can reproduce the sharp concentration

14 gradients away from the roadway. The performance of line source models has been evaluated in

15 several studies by comparison with measurements from five different field studies at a number of

16 receptor sites in the vicinity of roadways. The correlation coefficients (r) ranged from 0.51 to

17 0.87 with 85% of the model results overall being within a factor of two of the measured

18 concentrations (Benson, 1992).

19

20 *Particulate Matter*: Applications of grid-based air quality models to PM have taken place over

21 the past two decades but most of the major model development and evaluation efforts have

22 occurred over the past decade. An assessment of the ability of air quality models to simulate PM

23 air pollution levels was conducted by NARSTO (2004). A summary of early model performance

24 evaluations for PM has been presented by Seigneur (2001). More recent performance evaluation

25 results for annual $PM_{2.5}$ are provided by Eder and Yu (2006) and Appel et al. (in press) for the

26 CMAQ model over the contiguous United States, by Tesche et al. (2006) for CMAQ and the

27 Comprehensive Air quality Model with extensions (CAMx) over the southeastern United States,

28 by Gong et al. (2006) and Park et al. (2007) for A Unified Regional Air quality Modelling

29 System (AURAMS) of the Meteorological Service of Canada, by McKeen et al. (2007) for

30 several U.S. and Canadian models applied in forecasting mode and by Russell (2008) for CMAQ

31 and CAMx evaluations against data from the EPA Supersites Program.   PM consists of several

1 chemical species and model performance is typically conducted for $PM_{2.5}$ mass and the major

2 $PM_{2.5}$ chemical components: sulfate, nitrate, ammonium, black carbon and organic compounds.

3 Figure 8.4 depicts annual concentrations of $PM_{2.5}$ and its major components simulated with

4 AURAMS over Canada and the contiguous United States. Model performance was evaluated

5 against measurements available from the National Air Pollution Surveillance (NAPS) network of

6 Environment Canada, the Speciated Trends Network (STN) of the U.S. EPA and the U.S.

7 Interagency Monitoring of Protected Visual Environments (IMPROVE) network. For this

8 specific AURAMS 2002 annual simulation, the normalized mean errors were 37% for $PM_{2.5}$,

9 27% for sulfate, 44% for nitrate, 27% for ammonium, 66% for black carbon and 85% for

10 organics; the carbonaceous species were underpredicted. The performance of the U.S. EPA

11 CMAQ model was recently evaluated against measurements available from STN (mostly urban

12 and suburban sites) and IMPROVE (mostly remote sites) for a 2001 simulation of the eastern

13 United States using a 12 km horizontal grid (Appel et al, in press). For this specific CMAQ 2001

14 annual simulation, the normalized mean errors were 44% (STN) and 39% (IMPROVE) for

15 $PM_{2.5}$, 40% (STN) and 34% (IMPROVE) for sulfate, 72% (STN) and 95% (IMPROVE) for

16 nitrate, 59% (STN) for ammonium, 46% (IMPROVE) for black carbon and 49% for organics

17 (IMPROVE). Major differences between the AURAMS and CMAQ performance results occur

18 for nitrate (AURAMS shows better performance) and organics (CMAQ shows better

19 performance). In general, modeling errors for $PM_{2.5}$ mass and sulfate are typically on the order

20 of 50% or less. SO_2 emissions are fairly well characterized, the chemistry of SO_2 oxidation to

21 sulfate is well known and sulfate is non-volatile (i.e., it is completely present in the particulate

22 phase); thus, sulfate PM formation is well simulated by air quality models relative to the other

23 PM components (uncertainties in cloud and precipitation fields are the largest source of

24 uncertainty for sulfate, as discussed further in Section 8.2). Performance is worse typically for

25 nitrate and organic compounds. Although NO_x emission inventories are not as well

26 characterized as those of SO_2, they are reasonably accurate; however, the oxidation of NO_2 to

27 nitric acid (HNO_3) includes some heterogeneous pathways that are still highly uncertain (NO_3

28 and N_2O_5 reactions on particles and droplets) (Davis et al., 2007) and the partitioning of HNO_3

29 between the gas phase and the particulate phase occurs via reaction with ammonia (NH_3), which

30 involves uncertainties in the ammonia emission inventories (Yu et al., 2005). Particulate organic

31 compounds result from primary emissions of non-volatile and semi-volatile organic compounds

1   and the formation of secondary organic aerosols via the oxidation of semi-volatile and volatile

2   organic compounds (SVOC and VOC). All those organic compounds can be of either

3   anthropogenic or biogenic origin. Uncertainties in the emissions of primary organic PM and

4   secondary organic aerosol (SOA) precursors, the chemistry of SOA formation and the

5   partitioning of organic compounds between the gas and the particulate phases lead to large

6   uncertainties in organic PM concentrations. Performance for ammonium (which is associated

7   with sulfate and nitrate) and black carbon (which is a primary PM species) tend to lie between

8   those of sulfate and those of nitrate and organic PM.

9

10 *Air toxics*: Air toxics include a large variety of chemical compounds including principally VOC,

11 metals, POPs and diesel particles. POPs and some metals (e.g., mercury) are mostly of concern

12 for atmospheric deposition rather than for health effects via inhalation (see Section 8.2). There

13 have been some model performance evaluations conducted for VOC simulated with grid-based

14 models (Seigneur et al., 2003; Luecken et al., 2006; MATES-II, 2000), as well as with source-

15 specific models (Pratt et al., 2004; MATES-II, 2000). Using a 4-km grid resolution, a grid-based

16 model showed an error of 64% and a coefficient of determination of 0.25 for benzene

17 concentrations in New York (Seigneur et al., 2003). Using a 36 km resolution over the

18 continental United States, a grid-based model reproduced episodic and seasonal behavior of the

19 pollutant concentrations at many measurement sites satisfactorily but the model showed a slight

20 tendency to underestimate (mean normalized bias for 30-day average concentrations over all

21 sites and seasons in the range of 20 to 40%) (Luecken et al., 2006). In MATES-II (2000), annual

22 concentrations of most VOC were within 15% of the measurements at ten sites on average,

23 although some species were significantly underestimated (e.g., 1,3-butadiene by a factor of 2) or

24 overestimated (e.g., acetaldehyde by a factor of 1.6). Pratt et al. (2004) concluded that their

25 source-specific model simulation results were within a factor of two of the measurements

26 (matched in space and time) on average and that model performance was best for pollutants

27 emitted mostly from mobile sources and poorest for pollutants emitted mostly from area sources.

28 They listed improving the emission inventory (better localization of the sources and better

29 quantification of the emissions) as the best way to improve model performance. Model

30 performance evaluation was conducted for simulation of a pesticide, atrazine, with a grid-based

31 model (Cooter and Hutzell, 2002; Cooter et al., 2002). Performance of grid-based models has

1   not been evaluated for metals, except mercury (which is discussed below for atmospheric

2   deposition). Some evaluations of source-specific models have been conducted for metals (e.g.,

3   MATES-II, 2000). No direct evaluation has been conducted for diesel particles because of lack

4   of measurements specific to this type of particles. Black carbon has been used as a surrogate in

5   some studies because diesel particles typically contain about 50% of black carbon. However,

6   this approach assumes that there are no other major sources of black carbon (Seigneur et al.,

7   2003). The treatment of meteorology is also very important to be able to correctly predict air

8   pollutant concentrations in complex flow situations. For example, air pollutant concentrations

9   near roadways are particularly sensitive to the vertical dispersion characteristics of the

10   atmosphere (Venkatram et al., 2007) and the presence of noise barriers (Bowker et al., 2007),

11   and air pollutant concentrations in street canyons are difficult to simulate because of the complex

12   wind flows (Kastner-Klein at al., 2004; Britter and Hanna, 2003).

13

14   *Source apportionment*: EPA (2007) in its guidelines for the performance evaluation of models

15   for PM and regional haze recommends that receptor models be used to corroborate the results of

16   air quality models. Receptor models use statistical analyses of ambient chemical concentration

17   measurements to estimate the contribution of various source categories to PM concentrations

18   (Hopke, 1985). They can be combined with back-trajectories analyses of winds to identify the

19   corresponding upwind source areas. One example of the application of receptor modeling

20   techniques to corroborate the results of air quality models is the Big Bend Regional Aerosol and

21   Visibility Observational (BRAVO) study. The BRAVO study addressed the contribution of U.S.

22   and Mexican source areas to sulfate concentrations in Big Bend National Park, Texas. Sulfate is

23   the major contributor to regional haze at Big Bend during summer months. After reconciliation

24   of the modeling results and correction for model bias, the air quality models and receptor models

25   led to similar relative contributions of the Mexican, Texas, eastern U.S. and western U.S. source

26   areas to sulfate concentrations at Big Bend, thereby providing confidence in the predicted source

27   area contributions (Schichtel et al., 2005). Both air quality models and receptor models have

28   pros and cons and their combined use helps improve our understanding of source contributions.

29   For example, Marmur et al. (2006) showed that for $PM_{2.5}$ in the southeastern United States air

30   quality models lack temporal representativeness (because of limited temporal information in

31   emission inventories) whereas a receptor model such as the Chemical Mass Balance (CMB)

1   lacks spatial representativeness (unless a dense monitoring network is available). Another

2   example of receptor modeling is the source apportionment of VOC in Mexico City (Vega et al.,

3   2000; Mugica et al., 2002; Wörnschimmel et al., 2006).

4

5   *Dynamic evaluation*: The prediction of the response of ambient concentrations to changes in

6   emissions can be challenging because of the non-linearity of secondary pollutant formation

7   pathways. Figure 8.5 depicts the response of $PM_{2.5}$ components to 50% changes in precursor

8   emissions for a summer episode in the southeastern United States; some of those responses are

9   complex and non-intuitive (see also Table 1.1 in Chapter 1). Pun et al. (2007) showed that poor

10   model operational performance is very likely to lead to a poor ability to predict model response

11   to emission changes; however, satisfactory operational model performance does not necessarily

12   guaranty that an air quality model will predict the correct response to an emission change. To

13   evaluate this model skill, it is necessary to conduct a dynamic evaluation where the model is

14   evaluated for two different emission scenarios. Gilliland et al. (2008) conducted such an

15   evaluation for the response of O_3 concentrations to changes in NO_x emissions in the northeastern

16   United States (see also Godowitch et al., 2007). Such dynamic evaluations require detailed

17   emission inventories for distinct years. Differences in emissions between weekdays and

18   weekends can also be used to that end; for example, Yarwood et al.,(2003) showed that an air

19   quality model was able to reproduce the day-of-the-week variability of O_3 concentrations in the

20   Los Angeles basin. Another approach to evaluate the ability of models to predict the response to

21   emission changes is the use of measurements of chemical species that provide information on the

22   chemical regime of the atmosphere (e.g., NO_x vs. VOC sensitive for O_3, HNO_3 vs. NH_3 sensitive

23   for ammonium nitrate; see NARSTO, 2004 and Pinder et al., 2007 for more details).

24

25   **8.1.4 AREAS FOR FUTURE IMPROVEMENT**

26   Areas for future improvement in air quality modeling for application to population exposure and

27   health effects studies include all areas where the current needs of the exposure and health

28   communities are not met by existing air quality models.

29

30   *Spatial resolution*: A major area for improvement is the representation of the sharp

31   concentration gradients that occur near emission sources, mostly near roadways as population

1   exposure is very sensitive to those spatial concentration gradients (Jarrett et al., 2005). Several

2   modeling techniques were described above that approach this problem from various angles.

3   There is a need to evaluate each of those techniques against ambient data to assess their

4   accuracy, to compare those techniques using a common data set to determine their relative

5   strengths and weaknesses, and to further develop the most promising techniques.

6

7   *Temporal extent*: Meteorological and air quality model simulations can be conducted over multi-

8   year periods given the appropriate inputs. The availability of emission inventories is the limiting

9   factor at the moment.

10

11 *Chemical species and particle sizes*: Air quality models need to be improved for some aspects of

12 their treatment of criteria pollutants. For example, there are still considerable uncertainties in the

13 simulation of primary gaseous pollutants such as CO, NO2 and toxic VOC, as well as in the

14 simulation of primary and secondary organic aerosols. PM characteristics that may be of interest

15 to the health community are not currently treated by air quality models, which are formulated to

16 address air quality regulations rather than health research topics. Some air toxics of interest for

17 exposure and health effects studies are not treated in standard air quality models (major VOC air

18 toxics are now treated explicitly but most trace metals are not).

19

20 *Emissions*: Emission inputs are essential for air quality simulations. In particular, the

21 uncertainties associated with the emissions typically dominate the uncertainties associated with

22 the simulation results of source-specific models (Sax and Isakov, 2003; Hanna et al., 2007). As

23 finer spatial and temporal resolution will be required for exposure assessments, the need for

24 reliable emission inventories at finer spatial and temporal scales will increase.

25

26 *Meteorology*: The need to obtain more accurate predictions of pollutant concentrations at finer

27 spatial resolution in urban areas implies obtaining reliable meteorological fields (winds and

28 turbulence) within areas with complex building settings (e.g., street canyons; noise barriers near

29 roadways). Meteorological models need to be developed and evaluated to address such complex

30 situations. Some initial efforts are underway at the U.S. EPA (e.g., Otte et al., 2004) and in

31 Mexico (UNAM-CCA is implementing in collaboration with San Jose State University an

1   urbanized version of MM5 that will allow 500 meters resolution; finer temporal resolution may

2   be desirable as the spatial resolution increases).

3

4   **8.2 ATMOSPHERIC MODELING FOR ECOSYSTEM MANAGEMENT**

5   **8.2.1 NEEDS FROM ECOSYSTEM MODELERS**

6   Ecosystem models expect to obtain inputs of atmospheric stressors in terms of air concentrations

7   or deposition load in order to calculate changes in ecosystem processes, structure, and/or

8   function. (Ecosystem models are described in Chapter 5.) The calculation of the atmospheric

9   deposition of chemical species to ecosystems requires knowledge of both the wet and dry

10 deposition fluxes of atmospheric chemical species to the Earth's surface. Wet deposition

11 processes include the removal of chemical species from the atmosphere by precipitation (rain,

12 snow, etc.), settling of fog droplets, and impaction of cloud droplets. Dry deposition processes

13 include the removal of chemical species from the atmosphere as they adsorb to, absorb into or

14 react with surfaces such as soil, water, vegetation or man-made structures. Atmospheric species

15 get into contact with surfaces following two major transport steps: 1) turbulent transport, which

16 brings the gaseous species or particle near the surface and 2) Brownian diffusion within the thin

17 air layer that is in contact with the surface. Both wet and dry deposition fluxes are needed as

18 input to ecosystem models. The needs of ecosystem modelers may be further categorized as

19 follows.

20

21 *Spatial resolution*: The spatial resolution provided by an air quality model must be compatible

22 with the spatial variability of the atmospheric fluxes to the ecosystem of interest. Atmospheric

23 fluxes may vary because of changes in air pollutant concentrations (e.g., near a source),

24 precipitation patterns (precipitation may vary significantly with location in mountainous and

25 coastal areas) and land use patterns (which affect dry deposition). Ecosystem models are not

26 constrained to rectangular grids and most follow land use, terrain and the boundaries of water

27 bodies using irregular polygons. The polygons are typically designed to resolve sub-components

28 of watersheds. Within these irregular polygons there is explicit recognition of different land use

29 types, including water bodies, and topography.

30

1   *Temporal resolution*: The temporal resolution needed for atmospheric fluxes to ecosystems is

2   highly variable, from daily to annual, to match ecosystem time scales. For stream chemistry

3   models current temporal resolution required of the atmospheric fluxes is monthly. The required

4   resolution is expected to increase to daily in the future. For rivers and estuaries the simpler

5   models operate with annual to monthly time steps, but the more refined, process-oriented models

6   operate with a daily to hourly time step in order to treat tidal influences. Providing a daily

7   budget of accumulated dry fluxes is most important. A fine temporal resolution to resolve the

8   diurnal pattern of the atmospheric flux is not required at this time, but could be in the future. At a

9   minimum, seasonal or monthly variations must be provided as the ecosystem will govern the

10   evolution of chemical species differently as the ambient conditions vary (e.g., surface

11   temperature, soil moisture).

12

13   *Temporal extent*: Ecosystems typically react over long time scales and for S, N and Hg there is a

14   legacy effect. Therefore, the soil chemistry, surface water chemistry and mercury models spin up

15   for about 100 years, starting about 1850 to 1900. The spin up period, until contemporary data is

16   encountered, uses annual time steps and fairly rough estimates of wet and dry deposition,

17   temperature and rainfall. For contemporary data, around 1980/1990 onward the ecosystem

18   modelers prefer monthly deposition data. Some watershed and estuarine models only calibrate

19   against contemporary chemical, hydrologic and temperature data. They may use 5-20 years as a

20   calibration period because precipitation (hydrology) may vary significantly from year to year.

21   For these models it is important to obtain atmospheric fluxes over several years to capture the

22   inter-annual temporal variability of precipitation patterns and there is a preference for the

23   atmospheric flux inputs to be monthly or daily. For some models climatological atmospheric

24   fluxes are acceptable as long as there are no significant trends in air emissions during the period

25   being averaged. Long projections into the future tend not to consider changes in meteorology

26   and, hence, repeat a multi-year contemporary period. Thus, there is little accounting for the

27   impact of climate change on the chemical and physical input variables.

28

29   *Accuracy*: Because the water chemistry models are typically calibrated or spun up against a time

30   series of inputs, the desire is for the accuracy of the inputs to be high. Ecosystem modelers

31   would prefer the input accuracy supplied by atmospheric models be on the order of the analytical

1 accuracy of the within watershed observations used for inputs. Thus, there is a concern about the

2 lack of accuracy between modeled meteorology and observed hydrology. There is also a related

3 concern about the incompatibilities introduced in the transition from measurements for hind casts

4 to atmospheric model predictions for forecasts and a concern about lack of cross-consistency

5 when data come from the two different sources of measurements and models.

6

7 *Chemical and physical variables*: The chemical species of most interest to the ecosystem

8 community include ozone; the acidic species (mostly, sulfate and nitrate, but also sulfur dioxide)

9 plus the neutralizing species for the more advanced water chemistry models (Ca, Mg, Na, K and

10 chloride), which can lead to acidification of water bodies; nitrogenous species (nitrogen oxides,

11 nitric and nitrous acids, organic nitrogen, ammonia, particulate ammonium and nitrate, etc.),

12 which can lead to lake, bay and estuary eutrophication; mercury species (divalent gaseous

13 mercury, elemental gaseous mercury and particulate mercury), which can be methylated in water

14 bodies and lead to high concentrations of methylmercury in aquatic biota via bioaccumulation;

15 and persistent organic pollutants (POPs), which can bioaccumulate in the food chain. The

16 ecosystem models also require meteorological variables, including temperature, precipitation and

17 photosynthesizing radiation.

18

19 *Atmosphere/ecosystem interface*: Some chemical species deposit from the atmosphere to

20 surfaces irreversibly, that is, they are not emitted back to the atmosphere. This is the case, for

21 example, for sulfate. Other species may be emitted back to the atmosphere either in their

22 original form or in a different oxidation state. For example, nitrogenous species may be emitted

23 back to the atmosphere as nitric oxide or ammonia, and mercury species may be emitted back to

24 the atmosphere as elemental mercury. Such processes need to be simulated via an interface that

25 accounts for the deposition from the atmosphere to an ecosystem, the possible chemical

26 transformation in the ecosystem (e.g., vegetation, top soil layer, wetland or water column), and

27 the emission of some chemical species back to the atmosphere. The atmospheric fluxes to

28 different land use types within a grid cell also need to be linked to the corresponding land use

29 types within the polygons used by the ecological model.

30

1　**8.2.2 NEEDS FROM ECOSYSTEM CRITICAL LOAD ANALYSIS**

2　The critical load concept is an effect-based approach that attempts to estimate the pollutant

3　concentration level or atmospheric deposition load that would be likely to cause environmental

4　harm. A critical load is specifically defined as a quantitative estimate of an exposure

5　(concentration level or atmospheric deposition) to one or more pollutants below which

6　significant harmful effects on specified sensitive elements of the environment or on ecosystem

7　structure and function do not occur according to present knowledge. A sensitive element can

8　constitute a part of, or the whole of, an ecosystem. While it is the deposition or air concentration

9　itself that is of interest, the needs of critical load assessments may similarly be categorized as

10　above.

11

12　*Spatial resolution*: Critical loads are directly related to atmospheric fluxes or deposition to

13　regional, natural ecosystems. Critical load values may vary quite considerably between different

14　ecological regions of North America. Critical load mapping is now being performed at high

15　resolution (30 m to a few km) across North America. The spatial variation in underlying soils

16　and vegetation types and vegetation/ soil/ bedrock gradients determine the degree of sensitivity

17　of ecosystem functioning to atmospheric deposition. Therefore, critical loads are defined at a

18　high spatial resolution and may be highly spatially variable. The spatial resolution provided by

19　an air quality model must address variations in atmospheric fluxes due to changes in air pollutant

20　concentrations (resulting from topography), precipitation patterns (precipitation may vary

21　significantly with location in mountainous and coastal areas) and land use and soil patterns

22　(which affect dry deposition). The air quality model should also be able to distinguish flux to

23　different land use types within a grid.

24

25　*Temporal resolution*: Dynamic and steady-state ecosystem models are used to calculate a critical

26　load associated with a particular degree of ecosystem protection. These models typically

27　calculate a critical load at the scale of an average annual deposition many decades into the future.

28　Thus, a fine temporal resolution, such as hourly inputs, is not required for projections of future

29　atmospheric fluxes. However, these models may have the same temporal requirements for

30　historical and contemporary flux inputs as those listed in Section 3.1 for purposes of calibration.

31

1   *Accuracy*: A critical load, as a defined level of deposition, has accuracy requirements that are

2   similar in nature to those of National Ambient Air Quality Standards (NAAQS). Different from

3   the U.S. NAAQS, critical loads will require several components of the atmospheric loading to be

4   measured and combined (e.g., total sulfur and total nitrogen), creating a more complicated set of

5   accuracy expectations to support the use of critical loads to protect ecosystems.

6

7   *Temporal extent*: For critical loads modeling the temporal extent involves multi-year averages to

8   smooth out inter-annual meteorological variability, long projections into the future and,

9   potentially, an accounting for the impact of climate change on the input variables.

10

11 *Chemical species*: The chemical species of most interest to the critical loads community at this

12 time include: ozone and the combined effects of total sulfur, S, (sulfate and sulfur dioxide), total

13 nitrogen, N, (oxidized-N and reduced-N) and mercury.   The deposition of the combined acidic S

14 and N species can lead to acidification of soils and water bodies and the release of aluminum (a

15 major causal agent of ecosystem damage and degradation).

16

17 *Atmosphere/ecosystem interface*: The atmospheric fluxes to different land use types within a grid

18 cell will need to be linked to the parallel land use types within the polygons used by the critical

19 loads mapping. Addressing the potential bi-directionality of the atmospheric flux in the air-

20 surface interface may be less important for natural systems than for anthropogenically impacted

21 systems, such as agriculture. However, the transport of pollutants to the natural systems will be

22 affected by any bi-directional flux occurring in the intervening landscape.

23

24 **8.2.3 CURRENT STATUS OF ATMOSPHERIC MODELS**

25 Current atmospheric models calculate the wet and dry deposition fluxes of several major

26 chemical species. Calculation of wet deposition fluxes requires knowledge of the concentrations

27 of the species of interest within the cloud droplets, raindrops, snowflakes, ice crystals and fog

28 droplets, as well as the precipitation rate (see Figure 8.6 for an example of precipitation and wet

29 deposition of sulfate, nitrate and ammonium simulated over Canada and the United States with

30 the Environment Canada model AURAMS). Calculation of dry deposition fluxes requires

31 knowledge of the atmospheric characteristics (turbulence, temperature), chemical species

1   properties (Brownian diffusion coefficient, ability to adsorb, absorb or react) and surface

2   properties (ability to retain gaseous species). We discuss below whether current atmospheric

3   models are suitable to address the specific needs of the ecosystem modelers.

4

5   *Spatial resolution*: Regional models calculate atmospheric deposition fluxes on a rectangular-

6   type horizontal grid (the most common geographical projections are Lambert conformal,

7   Universal Transverse Mercator, and latitude-longitude) with a spatial resolution that ranges from

8   a few kilometers to several tens of kilometers. Therefore, the gridded atmospheric deposition

9   fluxes may not correspond to the areas relevant to the ecosystem model. For example, a given

10   grid cell may cover some land area and some water area. Thus, the atmospheric flux calculated

11   by the atmospheric model represents an average over a mixture of water and land areas and may

12   differ from both the atmospheric fluxes to the water area and to the land area. Furthermore, the

13   land area may include very different land use types (e.g., bare soil, vegetation) that may lead to

14   significantly different atmospheric dry deposition fluxes. For example, the mercury deposition

15   flux is significantly greater to a deciduous forest than to bare soil (Lindberg and Stratton, 1998).

16

17   *Temporal resolution*: The temporal resolution provided by air quality models is one hour

18   because meteorological and emission inputs are typically available on an hourly basis. This

19   resolution is much finer that what is needed for input to ecosystem models and is, therefore, quite

20   sufficient.

21

22   *Temporal extent*: Air quality model simulations are now routinely conducted for one-year

23   periods. However, there are very few examples of multi-year air quality simulations at regional

24   scales and none yet in which emissions are varied by year. Such multi-year simulations will

25   require emission inventories for each year of the simulation period. To date, emission

26   inventories have only been available for a given year, which has limited the possibility of multi-

27   year simulations. Modeling tools are available for the development of emission inventories for

28   future years (prospective modeling); however, significant effort is required to develop such

29   inventories, particularly in terms of data collection. Moreover, the application of those modeling

30   tools for the development of emission inventories for past years is also limited by the availability

31   of pertinent data. The need for multi-year emission inventories that are internally consistent in

1   terms of methodology was identified by NARSTO (2005) and EPA is currently setting up such

2   an approach. Once those multi-year emission inventories become available, multi-year air

3   quality simulations will be feasible.

4

5   *Accuracy:* The meteorological variables provided by the meteorological models, such as

6   temperature and precipitation, may differ significantly from actual values available from local

7   measurements. Current models, for example, are not sufficiently accurate regarding precipitation

8   and chemical deposition, and therefore are not used in water chemistry/hydrology model

9   calibration. Observed precipitation and deposition with some type of spatial interpolation is used

10 instead. This leads to some inconsistency in addressing the effects of change in deposition

11 loading between current (based on measurements) and future (based on meteorological/air

12 quality modeling) conditions.

13

14 *Chemical and physical variables*: Air quality models currently treat atmospheric deposition of

15 ozone (see Figure 8.7 for deposition of ozone over the continental United States simulated with

16 the CMAQ model), sulfate, sulfur dioxide, oxidized-nitrogen and reduced-nitrogen compounds

17 (see Figure 8.8 for total deposition of oxidized- and reduced-nitrogen over the continental United

18 States simulated with the CMAQ model), and mercury. An important category relevant to

19 acidification and critical loads that is not treated is deposition of base cations. One major

20 category of chemical species relevant to atmospheric deposition, which is not currently treated

21 by air quality models, is organic compounds such as polycyclic aromatic hydrocarbons (PAH),

22 polychlorinated biphenyls (PCB), polybrominated biphenyls, dioxins, furans, some pesticides,

23 and chlorophenols; this group of chemicals is generally referred to as persistent organic

24 pollutants (POPs). POPs have been mostly modeled in North America using multi-media

25 compartmental models that include major assumptions on the spatial resolution of concentrations

26 (the atmosphere is often represented by a single well-mixed compartment). There have been

27 only limited attempts to treat POPs in air quality models in North America. It seems that the

28 simulation of POPs by air quality models is limited at the moment by (1) the availability of

29 reliable emission inventories (Breivik et al., 2003) and (2) knowledge of their atmospheric

30 chemistry (Franklin et al., 2000). Meteorological variables needed by ecosystem models

31 (temperature, precipitation and photosynthesizing radiation) are provided by meteorological

1   models; however, those may differ significantly from actual values available from local

2   measurements, particularly in the case of precipitation. This potential discrepancy raises the

3   question of how to integrate different sources of chemical and physical information (model

4   calibration, data assimilation, data fusion, etc.).[5]

5

6   *Atmosphere/ecosystem interface*: Most air quality models do not currently account for the

7   possible transformation of chemical species in an ecosystem and the emission of species back to

8   the atmosphere. Some interface algorithms have been developed, for example, for mercury (e.g.,

9   Lin et al., 2005) but they have not yet been incorporated into standard air quality models. Most

10   air quality models do not yet treat the bi-directional exchange of nitrogenous species, controlled

11   by chemical and physical conditions at the plant/soil level, especially ammonia. But some

12   algorithms are being developed for North American conditions at NOAA/US EPA.

13

14   **8.2.4 EVALUATION OF ATMOSPHERIC DEPOSITION MODELS**

15   Air quality models are evaluated for ambient concentrations, wet deposition fluxes and, in rare

16   cases, total or dry deposition fluxes. As discussed above, an operational evaluation is not

17   sufficient to guarantee the ability of an air quality model to predict the response of atmospheric

18   deposition fluxes to changes in emissions. Source apportionment and dynamic evaluations are,

---

[5] *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.]

1   therefore, recommended to complement the operational evaluation. We summarize the current

2   status of air quality model operational performance for major chemical species.

3

4   *Ozone*: Measurements of hourly ozone ambient concentrations near the surface are conducted in

5   remote areas by the Clean Air Status and Trends Network (CASTNET) at 80 sites in the United

6   States and in urban areas by various federal and state networks integrated into the Air Quality

7   System (AQS) database. Ozone performance has been evaluated for regional scales (e.g., the

8   contiguous United States; Eder and Yu, 2006; Appel et al., 2007) and was found overall to be

9   commensurate with model performance at urban scales (see Section 7.2.3) although models with

10   coarse grid spacing (> 10 km) may have difficulties reproducing urban ozone concentrations in

11   areas with complex meteorology (e.g., Los Angeles basin) and steep emission gradients.

12

13   *Acid deposition*: The National Atmospheric Deposition Network (NADP) provides weekly

14   measurements of the wet deposition fluxes of sulfate, nitrate, chloride, ammonium, other base

15   cations (calcium, magnesium, potassium and sodium) and hydrogen ions at over 250 sites in the

16   United States. The Atmospheric Integrated Research Monitoring Network (AIRMoN) provides

17   similar measurements, but with finer temporal resolution (daily), at seven eastern sites.

18   CASTNET provides weekly measurements of ambient surface concentrations of sulfur dioxide,

19   particulate sulfate, nitric acid, particulate nitrate, and particulate ammonium at 80 sites in the

20   United States. Those ambient concentrations are then combined with estimates of dry deposition

21   velocities to obtain estimates of dry deposition fluxes. The evaluation of wet deposition fluxes

22   for sulfate, nitrate and ammonium have shown that model performance is satisfactory for sulfate

23   (Dennis et al., 1990) but that there are larger uncertainties associated with nitrate and ammonium

24   (Mathur and Dennis, 2003) Nitrate fluxes are reasonable for the cold season but are biased low in

25   the warm season. Evaluation of ammonium fluxes has been tied to inverse modeling to establish

26   estimates of ammonia emission seasonality, leading to reasonable estimates (Gilliland et al.,

27   2006). The uncertainties in wet deposition fluxes are compounded by the errors in the

28   precipitation predictions of the meteorological models. There continues to be significant spatial

29   variability in errors even when the regional pattern is relatively unbiased. The evaluation of dry

30   deposition fluxes with routine network data is not a direct evaluation because (1) the dry

31   deposition velocity is estimated for the measurement network using meteorological data taken in

1   clearings and (2) this dry deposition velocity differs from that calculated by the air quality

2   model, in part, because the model used to infer the dry deposition from observed data is different

3   from the dry deposition model in CMAQ. Furthermore, the measurements of gaseous nitric acid,

4   particulate nitrate, and particulate ammonium are approximate because of sampling artifacts and,

5   in addition, gaseous ammonia is missing.

6

7   *Nitrogenous compounds*: The atmospheric deposition of nitrogenous compounds encompasses a

8   large number of nitrogen-containing species; however, a few of those species tend to dominate

9   the nitrogen deposition budget. Typically, nitric acid (and its associated particulate nitrate),

10 ammonia (and its associated particulate ammonium) dominate in rural areas, with nitrogen

11 oxides (NO and NO_2) and organic nitrates contributing less but significantly. Therefore, the

12 evaluation of inorganic nitrate and ammonia/ammonium described above for acid deposition is

13 directly pertinent to the evaluation of models for the atmospheric deposition of nitrogenous

14 compounds since it covers the largest fraction of the nitrogen deposition budget.

15

16 *Mercury*: The Mercury Deposition Network (MDN) measures the wet deposition flux of

17 mercury species on a weekly basis at over 90 sites in the United States and Canada. There is at

18 the moment no U.S. wide network that measures either the ambient concentrations of the major

19 mercury species groups (i.e., elemental mercury, gaseous oxidized mercury and particulate

20 mercury) or the dry deposition of mercury, although there have been some proposals for the set

21 up of such a network (Lyman et al., 2007). The Southeastern Aerosol Research and

22 Characterization study (SEARCH) includes several stations in the southeastern United States that

23 measure ambient concentrations of speciated mercury and mercury wet deposition.   Model

24 performance for mercury deposition depends significantly on the model formulation, simulated

25 precipitation fields and boundary conditions (because mercury is a global pollutant). The

26 evaluation of mercury wet deposition is conducted routinely using the MDN data; recent results

27 have shown differences among models due to, in order of decreasing importance, model

28 formulation, boundary conditions and simulated precipitation (Bullock et al., in preparation,

29 2007). As there are currently no dry deposition data for model evaluation, models have been

30 evaluated instead using the few mercury speciated concentrations available. Although models

31 tend to reproduce the global-scale gradients in total mercury concentrations and elemental

1   mercury concentrations (most mercury is elemental) (e.g., Selin et al., 2007; Lohman et al.,

2   2008), model performance for gaseous and particulate divalent mercury is more variable due to

3   the shorter lifetime of those species in the atmosphere and the interactions between gaseous

4   divalent mercury species and particulate matter (e.g., Seigneur et al., 2004; Selin et al., 2007).

5

6   *Source apportionment and dynamic evaluations*: The ability of an air quality model to properly

7   attribute an atmospheric deposition flux to various source categories and/or upwind source areas

8   should be evaluated. As for ambient concentrations, receptor modeling techniques can be used

9   to that end. For example, Keeler et al. (2006) applied two receptor modeling techniques

10   (Positive Matrix Factorization, PMF, and UNMIX) to wet deposition data collected at

11   Steubenville, OH, to estimate the relative contribution of coal combustion sources to mercury

12   wet deposition, which was 70% ± 15%. A chemical transport model for atmospheric mercury

13   (Seigneur et al., 2004) led to a contribution of U.S. coal-fired power plants (a subset of coal

14   combustion sources) to mercury deposition in the Steubenville area of 62%, i.e., a value, which

15   is well within the range of 55 to 85% obtained with the receptor modeling techniques.   (Note:

16   This site is in an area of many coal-fired power plants.) In the case of nitrogen deposition, a

17   possible direction is the use of nitrogen isotopes in wet deposition (Elliot et al., 2007). Dynamic

18   evaluations would also be necessary to complement source apportionment evaluations for cases

19   where the atmospheric deposition/precursor emission relationship is non-linear (e.g., nitrogen

20   deposition).

21

22   **8.2.5 AREAS FOR FUTURE IMPROVEMENT**
23   There are several areas where improvements of atmospheric models and their interface with

24   ecosystem models can lead to significant advances in our ability to provide the needed inputs to

25   ecosystem models.

26

27   *Spatial resolution*: It is desirable to calculate dry deposition fluxes at a scale compatible with

28   that of the ecosystem model using sub-grid scale land use information for dry deposition fluxes.

29   It is also desirable to improve the meteorological model parameterizations to provide better

30   quality precipitation estimates and terrain effects at grid sizes of 1-4 km.

31

1   *Accuracy*: It is desirable to reduce the error in precipitation simulations and air-surface flux

2   estimates for daily to monthly temporal averages to provide more accurate data that can be input

3   to the water quality models, potentially as model data, particularly for accountability analyses.

4   The adaptation of chemical data assimilation techniques or development of methods to combine

5   measured and modeled data (data fusion) are worth investigating to help reduce error in the

6   precipitation and deposition fields and reduce disparities with calibration data.

7

8   *Temporal extent*: Development of a consistent, continuous time series of physical parameters

9   (especially temperature and precipitation amount) and air-surface flux from the meteorological

10   and chemical transport models is becoming a necessity. This series could effectively start

11   around 2001 which marks the beginning of the period for which consistent methodologies for

12   estimating emissions across multiple years, from sources other than power plants, are being

13   developed and when NO_X emissions begin to change noticeably. Meteorological and air quality

14   model simulations can be conducted over multi-year periods given the appropriate inputs. The

15   availability of emission inventories is the limiting factor at the moment. A continuous, historical

16   time series of physical parameters and air-surface flux, starting around 1900, should be

17   developed for the ecosystem models as a collaboration between the air quality and ecosystem

18   modeling communities. Such a historical time series needs to smoothly transition to current

19   empirically-based and model-based time series. Looking to the future, guidance on the inclusion

20   of climate change impacts on hydrology and chemistry for long-term projections of deposition

21   (50 years in the future) needs to be developed.

22

23   *Chemical species*: The major chemical species of interest for atmospheric deposition are

24   simulated routinely by atmospheric models (i.e., ozone, sulfate, nitrate, ammonium, other

25   nitrogenous compounds, mercury) but there are still significant uncertainties in our ability to

26   correctly simulate the atmospheric deposition of nitrogenous compounds and mercury.

27   However, base cations are needed by the more advanced soil and surface water chemistry models

28   and are not simulated by current atmospheric models; there is enormous uncertainty regarding

29   emissions that would have to be overcome through inventory development. POPs are not

30   currently treated in most atmospheric models; emission inventories and model representations of

1 their atmospheric fate and transport need to be developed, incorporated into atmospheric models

2 and evaluated with ambient measurements of air concentrations and deposition fluxes.

3

4 *Atmosphere/ecosystem interface*: Air-surface exchange algorithms in the air quality models need

5 continued evaluation and improvement. These algorithms also need to calculate dry deposition

6 fluxes for specific sub-grid scale land use categories compatible with that of the ecosystem

7 models. Most air quality models do not currently account for the possible transformation of

8 chemical species in an ecosystem and the emission of chemical species back to the atmosphere.

9 This is particularly important for nitrogenous species (nitric oxide and ammonia), mercury and

10 POPs. Some interface algorithms have been developed that need to be incorporated and tested in

11 atmospheric models and new algorithms need to be developed, evaluated and incorporated into

12 atmospheric models.

13

14 **8.3 ATMOSPHERIC MODELING FOR RISK ASSESSMENT**

15 Risk assessments can be conducted to address both human health and ecological impacts. The

16 issues addressed above for atmospheric deposition to ecosystems and for exposure and health

17 effects studies are, therefore, pertinent to the application of atmospheric models in risk

18 assessment. Guidelines for risk assessment generally require an uncertainty analysis to be

19 conducted in addition to the deterministic analysis for representative individuals or the general

20 population (NRC, 1994). Therefore, one aspect of atmospheric modeling that needs to be

21 considered when using atmospheric models in the context of risk assessment is the treatment of

22 uncertainties. There have been limited attempts to account for uncertainties in air quality

23 modeling.

24

25 Because taking into account uncertainties requires sampling various values from the probability

26 distribution functions (pdf) of model inputs and parameters, a large number of simulations is

27 generally required. However, grid-based air quality models are computationally demanding and

28 conducting a large number of simulations (e.g., >10000) may not be feasible. Three major

29 approaches have been used:

30

1   The effect of the uncertainties in model inputs and parameters is simulated by conducting a

2   moderate number of simulations (on the order of 100) based on the optimistic assumption that a

3   large number of simulations is not required to cover the full range of uncertainties if the values

4   of the inputs and parameters being sampled are carefully selected (Hanna et al., 2001, 2002).

5   The effect of uncertainties in model inputs and parameters is simulated by conducting a large

6   number of simulations with a simple air quality model, such as a 1-D trajectory model, instead of

7   a 3-D model (Bergin et al., 1999; Bergin and Milford, 2000; Martien et al., 2003).

8   The effect of uncertainties in model inputs and parameters is simulated by conducting a large

9   number of simulations with a reduced form of the 3-D air quality model, i.e., using a response-

10   surface methodology (Seigneur et al., 1999; Lohman et al., 2000; Phillips et al., 2006).

11

12   Reduced-form models are versions of the model that reproduce the major characteristics of the

13   model with a computationally simpler version of the model. A standard approach consists in

14   using a response surface model (Box and Wilson, 1951). The first step consists in identifying the

15   model inputs and parameters that are the most influential for the model output of interest

16   (typically by conducting a sensitivity analysis). Then, the model output is expressed as some

17   mathematical function of those model inputs and parameters. A response-surface model is,

18   therefore, a parameterization of the actual model and it may only be valid for the set of

19   conditions under which it was developed. Since process-specific information may not be

20   explicitly included in the response-surface model, one must be aware of the limitations of the

21   response-surface model. The advantage of the response-surface model over the original model is

22   that its simplicity leads to greater computational speed, which is of particular interest for

23   probabilistic analyses that involve a large number of model simulations.

24

25   A major component of an uncertainty analysis is to define the probability distribution functions

26   of the influential model inputs and parameters to properly characterize their epistemic

27   uncertainties (i.e., those uncertainties that can be reduced with more information) and aleatory

28   uncertainties (a.k.a. variability, those uncertainties that originate from natural randomness and

29   cannot be reduced, even with more information).

30

1   **8.4 SYNTHESIS**

2   **8.4.1 SUMMARY OF THE CURRENT STATUS OF AIR QUALITY MODELS FOR APPLICATION TO**
3   **EXPOSURE ASSESSMENTS, HEALTH EFFECTS STUDIES AND ECOSYSTEM MODELING**

4

5   We have reviewed the needs of exposure modelers, health scientists and ecosystem modelers and

6   have assessed whether current air quality models can address those needs in a satisfactory

7   manner. We summarize our assessment in terms of what air quality models can do now, what

8   they could do if input data that are currently missing were to become available, and what they

9   could do after some pertinent model improvements were to be implemented. Except for

10   obtaining accurate precipitation predictions, most improvements are possible within the next 10

11   years and several are possible in the next few years.

12

13   *What atmospheric models can do*:

14

15   • They treat all relevant criteria pollutants, acidic species, nitrogen species, mercury and
16   some other inorganic and organic air toxics; however, there are uncertainties associated
17   with the atmospheric modeling of those pollutants which, to be addressed, will require
18   improvements in some model inputs (in particular, emissions and meteorology) and
19   model formulation (e.g., better understanding of organic PM).
20   • They provide good temporal resolution (1 hour) for the afore mentioned chemical
21   species, which is suitable for exposure modeling and ecosystem modeling.
22   • They provide good spatial resolution for atmospheric concentrations of secondary
23   pollutants and deposition (with nested grid and plume-in-grid treatments if needed for
24   finer resolution in urban areas and near point sources, respectively).
25   • They can be applied for long-term (seasonal to annual) simulations of the afore
26   mentioned chemical species.
27   • Models and measurements can be used together to create optimal "surfaces" of air
28   pollutant concentrations through data fusion (as a model post-processing step) or data
29   assimilation (as an optimized modeling approach).

30

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

32

33   • Multiple year simulations can be conducted but internally consistent multi-year emission
34   inventories are not readily available yet for periods >5 years; there is, however, an
35   ongoing effort at EPA to develop such nationwide emission inventories.
36   • Air toxic metals are treated in a model such as CMAQ but the corresponding emission
37   inventories are not currently available.

38

39   *What atmospheric models could do but some improvements are needed*:

40

41   • Fine spatial resolution for near-source population exposure, in particular, near roadways

1   (the plume-in-grid technology already exists for point sources). Various techniques are
2   currently under development but more testing and development are needed before they
3   become operational.
4   • The treatment of several air toxics (e.g., POPs, atmospheric chemistry of hexavalent and
5   trivalent chromium) and some PM characteristics (acidity, ultrafine number) is currently
6   missing in air quality models and the corresponding emission inventories are not
7   available (e.g., ultrafine PM, POPs)
8   • Two-way surface exchange, which is needed for a correct representation of the
9   atmospheric deposition of nitrogenous and mercury compounds, is not currently treated
10   in air quality models; some two-way surface exchange modules exist but they need to be
11   incorporated into air quality models and evaluated with experimental field data.
12   • The allocation of dry deposition to land-use classes within a model grid is desirable to
13   provide proper dry deposition inputs to ecosystem models; it cannot currently be
14   performed by air quality models, which only provide a grid-average atmospheric
15   deposition flux. There is, however, an ongoing effort to address this issue.
16   • Models and measurements can, in theory, be used together to create optimal "surfaces" of
17   atmospheric deposition through data fusion; however, discrepancies between modeled
18   and measured precipitation amounts and between dry deposition algorithms need to be
19   resolved satisfactorily before such data fusion techniques can be used routinely. Also,
20   some critical species data are missing for deposition pathways.
21   • Models do not currently treat the deposition of alkaline species that act to neutralize acid
22   deposition (potassium, calcium, magnesium and sodium). Emissions methodologies for
23   those species are currently missing and, as a result, emission inventories are not available
24   (except for sea salt sodium).
25   • Accurate precipitation estimates are needed, particularly for the prediction of atmospheric
26   deposition, but also for PM and regional haze modeling; although there will always be
27   some uncertainty associated with precipitation fields, some effort must be made to reduce
28   such uncertainties.
29
30   **8.4.2 USE OF AIR QUALITY MODELS FOR ACCOUNTABILITY**
31   Air quality models can play an important role in ensuring that emission strategies lead to the
32   desired results. Because they incorporate key chemical and physical processes and potential
33   nonlinear interactions, air quality models can play a very important role in explaining and
34   interpreting trends or the lack thereof. Air quality models are ideally suited to separate out the
35   role of meteorology from the role of emissions and chemistry to characterize emissions/exposure
36   relationships or emissions/deposition relationships independently of the meteorological
37   variability. Air quality models provide more detailed information (spatially, temporally and
38   chemically) than monitoring networks can ever provide. Consequently, air quality models can
39   be used to complement monitoring networks to provide more complete information on the air
40   pollutant concentrations and deposition fluxes and can assist monitoring design, including future
41   designs that take into account anticipated changes in concentrations and/or deposition fluxes.

1 Data fusion, where model simulation outputs and measurements are combined to create

2 continuous concentration and deposition fields that are consistent with the available

3 measurements, will be the first step in this process. Then, the resulting concentration and

4 deposition fields can be used to track their long-term temporal evolution and to assess whether

5 the changes in emissions over a given time period led to the anticipated changes in atmospheric

6 concentrations and/or atmospheric deposition fluxes.

7

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1   Table 8.1. Air toxics treated explicitly in CMAQ.

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Volatile organic compounds

Acetaldehyde[a, b]
Acrolein[a, b]
Acrylonitrile[a, b]
Benzene[a, b]
1, 3-Butadiene[a, b]
Carbon tetrachloride[a, b]
Chloroform[a, b]
p-Dichlorobenzene[a]
1,3-Dichloropropene[a, b]
Ethylene dibromide (1,2-dibromoethane) [a, b]
Ethylene dichloride (1,2-dichloroethane) [a, b]
Ethylene oxide[a, b]
Formaldehyde[a, b]
Hexamethylene 1,6-diisocyanate[a]
Hydrazine[a, b]
Maleic anhydride[a]
Methanol[a]
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]

Metals

Beryllium compounds[a, b]
Cadmium compounds[a, b]
Chromium (hexavalent and trivalent)[a, b]
Lead[a, b]
Manganese[a, b]
Mercury (elemental, gaseous divalent
          and particulate divalent)[a, b]
Nickel compounds[a, b]

Volatile inorganic compounds

Chlorine[a]
Hydrochloric acid[a]

Other compounds

Diesel particles[b]

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4   (a) One of the 188 hazardous air pollutants (http://www.epa.gov/ttn/atw/188polls.html).
5   (b) One of the 33 urban air toxics listed by the U.S. EPA (http://www.epa.gov/ttn/atw/nata/34poll.html).
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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.

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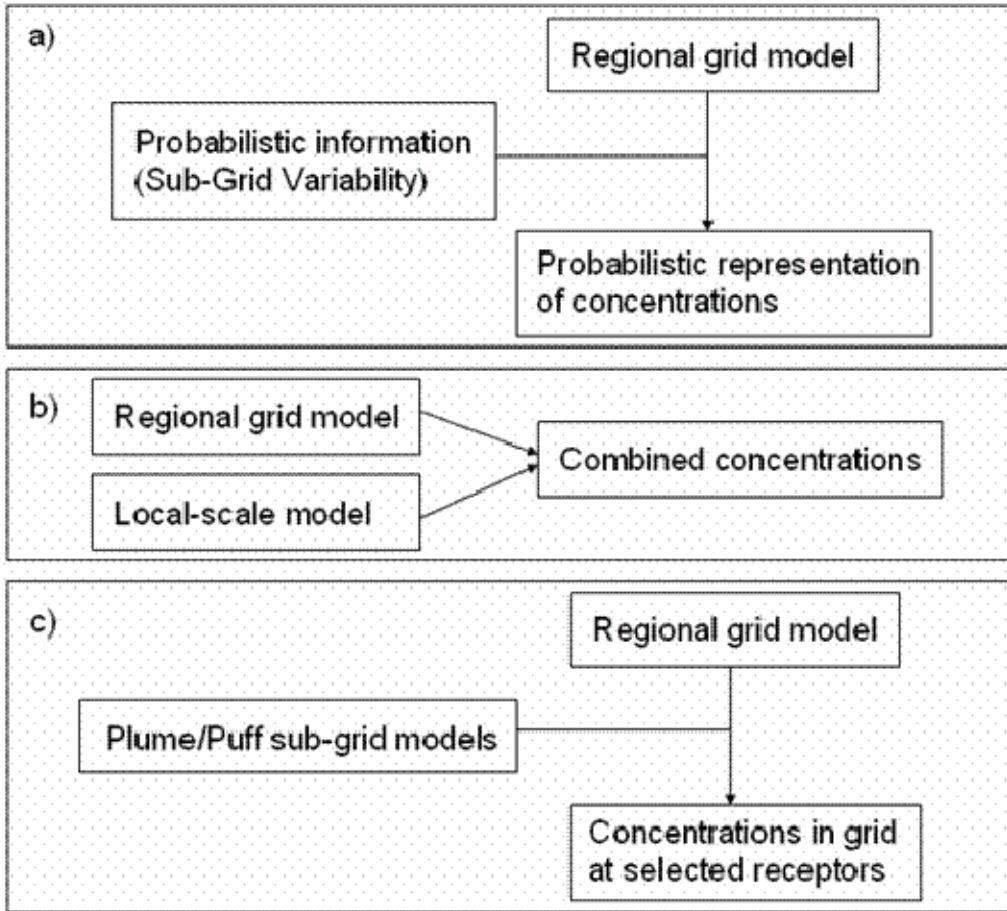
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13 Figure 8.2. Schematic representation of three major approaches to modeling air pollutant
14 concentrations at the sub-grid scale within a grid-based air quality model (Source: Touma et al.,
15 2006).
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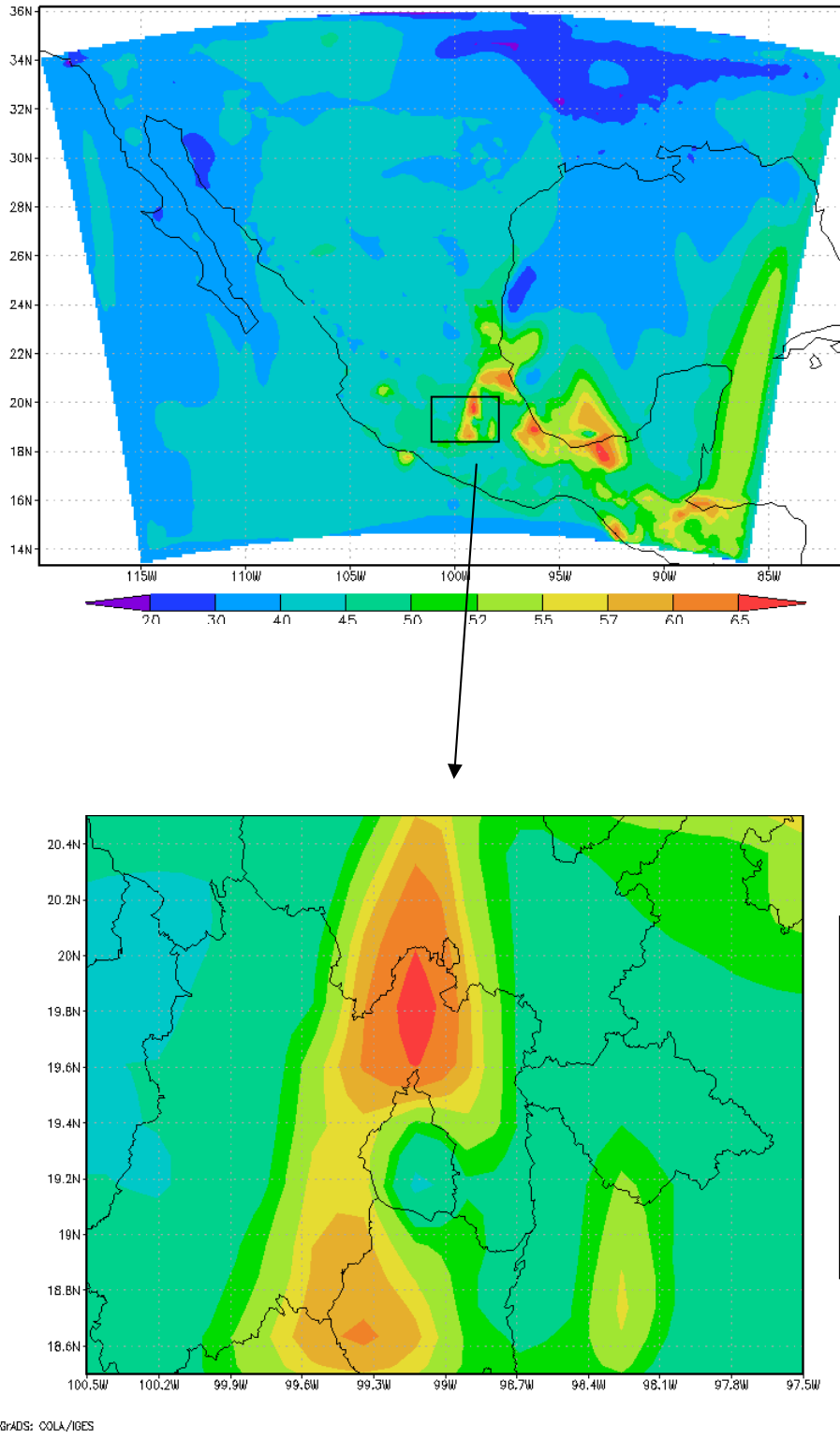
Figure 8.3. Surface ozone concentrations simulated with MCCM for 20 March 2006 at noon over Mexico (top) and over Mexico City (bottom).

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40 Figure 8.4. Annual surface concentrations (μg/m^3 at STP, 0°C) of PM$_{2.5}$ and major components
41 over Canada and the United States simulated for 2002 with AURAMS: PM$_{2.5}$ (top left), sulfate
42 (top right), nitrate (middle left), ammonium (middle right), black carbon (bottom left) and
43 organics (bottom right) (Moran et al., 2008). PM$_{2.5}$ concentrations over the ocean are affected by
44 sea salt (which is not shown as a separate component in the figure).
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50% Reduction in emissions of

% Change in   SO$_2$ NO$_x$ VOC

Sulfate
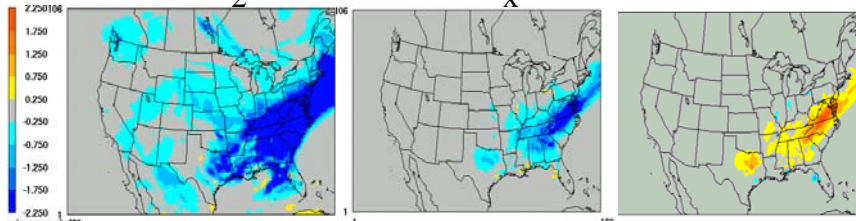
Nitrate
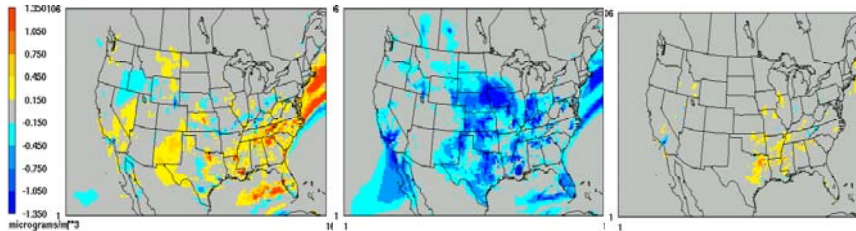
Organics
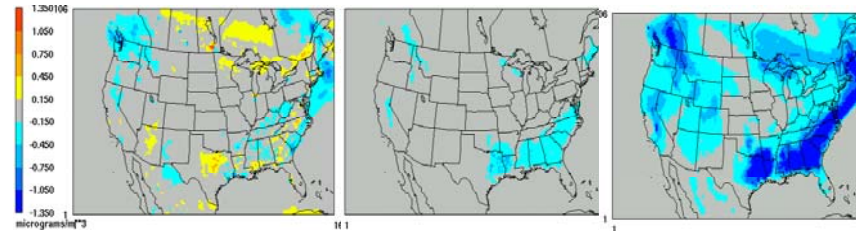
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13   Figure 8.5.   Response of the concentrations of PM$_{2.5}$ components (sulfate, nitrate and
14   ammonium) to 50% reductions in SO$_2$, NO$_x$ and VOC emissions simulated over the contiguous
15   United States for the 1-10 July 1999 period (Source: Seigneur, 2005).
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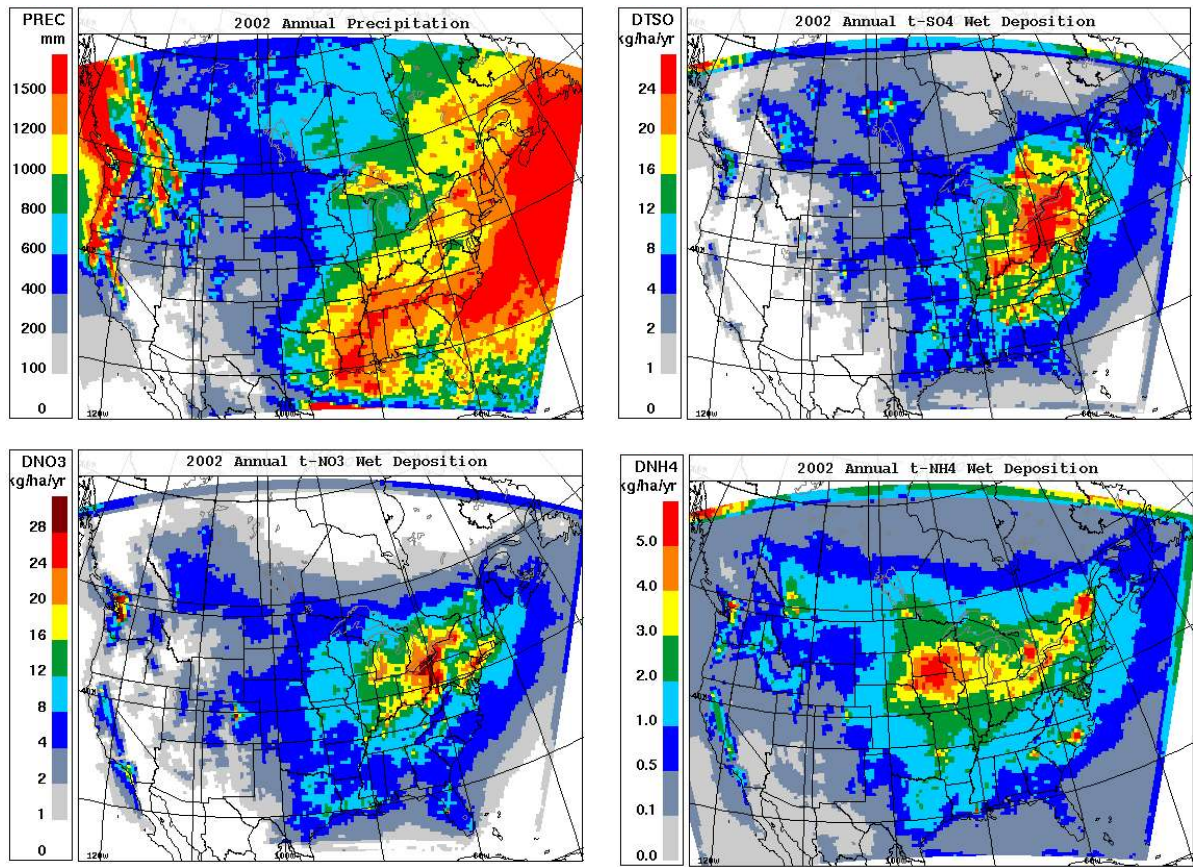
39 Figure 8.6.   Simulation of (a) annual precipitation (mm) and (b) sulfate, (c) nitrate and (d)
40 ammonium wet deposition fluxes (kg ha^{-1} y^{-1}) over Canada and the United States for 2002 with
41 the Environment Canada chemical transport model AURAMS (Source: Moran et al., 2008).

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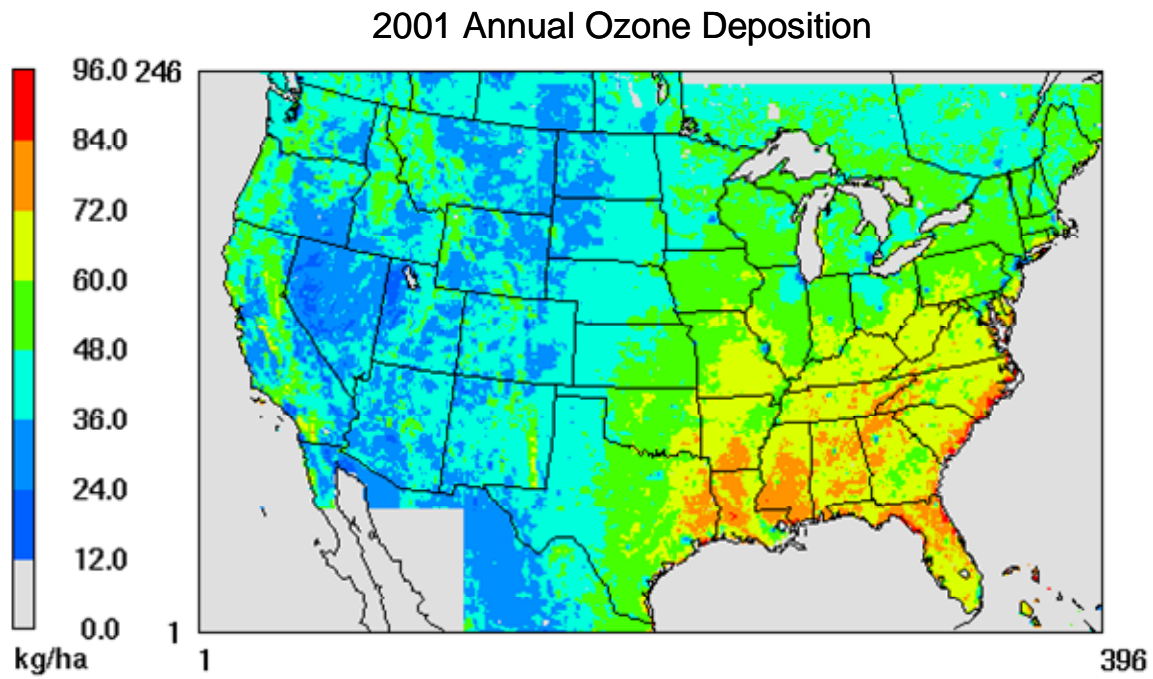5
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Figure 8.7. Total wet + dry ozone deposition simulated for 2001 emissions over the continental United States with the U.S. EPA Community Multiscale Air Quality model (CMAQ). The total deposition of ozone is essentially all dry deposition.

2001 Annual Total-N Deposition

2001 Annual Total Reduced-N Deposition
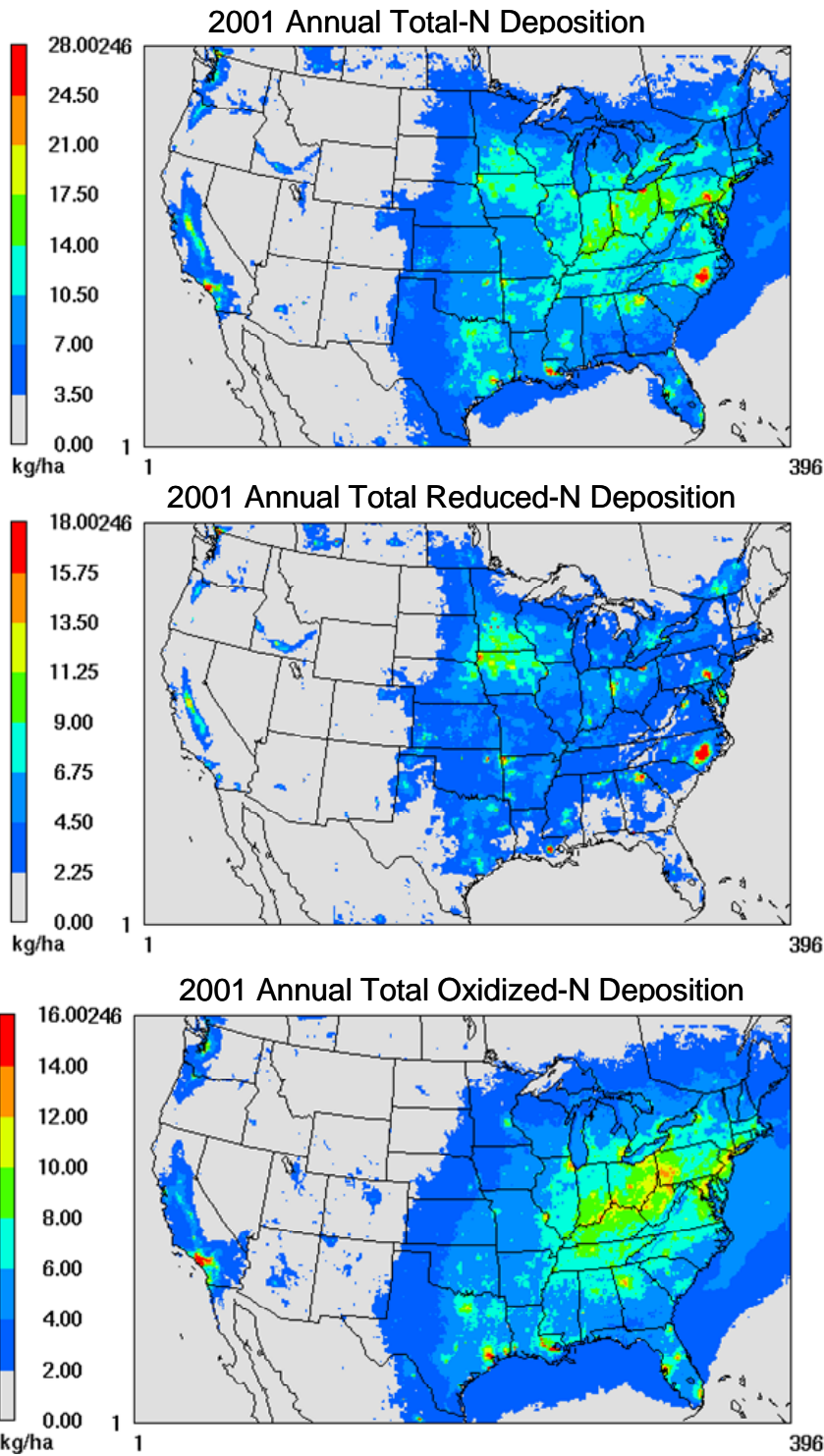
2001 Annual Total Oxidized-N Deposition

Figure 8.8. Total wet + dry nitrogen deposition simulated for 2001 emissions over the continental United States with the U.S. EPA Community Multiscale Air Quality model (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.