



AIR TOXICS MODELING

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PREFACE

This report presents the results of CRC Project A-42-1/NREL Contract KCI-8-17085-05. This work was conducted in two Phases. Accordingly, this report consists of two distinct parts, corresponding to Phase I and Phase II.

In Phase I, we review the current status of air toxics modeling and provide insights into the strengths and potential weaknesses of existing modeling approaches. This critical review provides the basis for the development of an integrated modeling approach that is presented in Phase II. Some facets of this modeling approach are exemplified by means of case studies for two air toxics, benzene and diesel particles. Recommendations for applications of other aspects of this integrated modeling approach are provided to conclude Phase II.

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GLOSSARY OF ABBREVIATIONS

3-D:	Three-dimensional
AB 2588:	California Assembly Bill 2588
ACH:	Air changes per hour
ADEQ:	Arizona Department of Environment Quality
ADOM:	Acid Deposition and Oxidant Model
AER:	Atmospheric & Environmental Research, Inc.
AERMOD:	American Meteorological Society (AMS)/EPA Regulatory Model Improvement Committee (AERMIC) Model
AirPEX:	Air Pollution Exposure Model
ALAPCO:	Association of Local Air Pollution Control Officials
ARB:	California Air Resources Board
ASHRAE:	American Society of Heating, Refrigerating and Air Conditioning Engineers
ASPEM:	Assessment System for Population Exposure Nationwide
BC:	Boundary conditions
BEADS:	Benzene Exposure and Absorbed Dose Simulation
BEAM:	Benzene Exposure Assessment Model
CAAA:	Clean Air Act Amendments
CACM:	Caltech Atmospheric Chemistry Mechanism
CAL3QHCR:	California Line Source dispersion Model version 3 with queue length and highway capacity, refined version
CALINE:	California Line source dispersion model
CALINE3:	California line source dispersion model, version 3

CALINE4:	California line source dispersion model, version 4
CALMET:	California Air Resources Board Meteorological model
CALPUFF:	California Air Resources Board Puff model
CAPCOA:	California Air Pollution Control Officers Association
CATMoN:	Texas Community Air Toxic Monitoring Network
CBM-IV:	Carbon-bond mechanism version IV
CCOS:	Central California Ozone Study
CDROM:	Compact Disk with Read Only Memory
CFR:	Code of Federal Regulations
CHAD:	Comprehensive Human Activity Database
CIT:	Caltech/Carnegie-Mellon Institute of Technology model
CMAQ:	Community Multiscale Air Quality Modeling System
CMB:	Chemical Mass Balance
CMC:	Canadian Meteorological Centre
CPIEM:	California Population Indoor Exposure Model
CRC:	Coordinating Research Council
CRPAQS:	California Regional PM Air Quality Study
CTM:	Chemical Transport Model
DTSC:	Department of Toxic Substances Control
EC:	“Elemental” Carbon
EMFAC 2000:	ARB’s mobile source Emission Factor model version 2000
EMFAC7:	ARB’s mobile source Emission Factor model version 7
EPA:	United States Environmental Protection Agency

EPRI:	(Formerly) Electric Power Research Institute
ETS:	Environmental Tobacco Smoke
FDDA:	Four-Dimensional Data Assimilation
GATOR:	Gas Aerosol Transport Radiation Model
GEIA:	Global Emissions Inventory Activity
GMT:	Greenwich Mean Time
GUI:	Graphical User Interface
HAP:	Hazardous Air Pollutant(s)
HAPEM:	Hazardous Air Pollution Exposure Model
HAPEM4:	Hazardous Air Pollution Exposure Model version 4
HAPEM-MS:	Hazardous Air Pollution Exposure Model for Mobile Sources
HEM-II:	Human Exposure Model version II
HVAC:	Heating, ventilation and air conditioning
HYROAD:	Hybrid Roadway Intersection Model
HYSPLIT:	Hybrid Single-Particle Lagrangian Integrated Trajectory model
IAQM:	Indoor Air Quality Model
IC:	Initial Conditions
IJC:	International Joint Commission
ISC:	Industrial Source Complex model
ISC-LT:	Industrial Source Complex model – Long Term version
ISC-ST:	Industrial Source Complex model – Short Term version
ISCST3:	Industrial Source Complex model – Short Term version 3
KTT:	Kunz Technologie Transfer

LADCO:	Lake Michigan Air Directors Consortium
LWC	Liquid water content
MACT:	Maximum Achievable Control Technology
MATES-II:	Multiple Air Toxics Exposure Study
MAVRIQ:	Model for Analysis of Volatile and Residential Indoor-air Quality
MC2:	Mesoscale Compressible Community Model
MCCEM:	Multichamber Consumer Exposure Model
MEI:	Maximally Exposed Individual
MIAQ:	Multicompartment Indoor Air Quality Model
MISCAM:	Micro Scale Air Pollution Model
MM4:	Mesoscale Meteorological model 4 th generation
MM5:	Mesoscale Meteorological model 5 th generation
MOBILE5:	EPA's Mobile source model version 5
MOBILE6:	EPA's Mobile source model version 6
NAAQS:	National Ambient Air Quality Standards (U.S.A.)
NARSTO:	(Formerly) North American Research Strategy for Tropospheric Ozone
NCHRP:	National Cooperative Highway Research Program
NEI:	National Emission Inventory
NEM:	NAAQS Exposure Model
NESCAUM:	Northeast States for Coordinated Air Use Management
netCDF:	Network Common Data Format
NETSIM:	Traffic Network Simulation Model

NFRAQS:	Northern Front Range Air Quality Study
NGM:	Nested Grid Model
NOAA:	National Oceanic and Atmospheric Administration
NREL	National Renewable Energy Laboratory
NTI:	National Toxics Inventory
OAQPS:	Office of Air Quality Planning and Standards (EPA)
OC:	“Organic” Carbon
OME:	Ontario Ministry of the Environment
OPPT:	Office of Pollution Prevention and Toxics
ORD:	Office of Research and Development (EPA)
PAH:	Polycyclic Aromatic Hydrocarbons
PAMS:	Photochemical Assessment Monitoring Stations
PCB:	Polychlorinated biphenyls
PCDD/F:	Polychlorinated dibenzo-p-dioxins/polychlorinated dibenzo furans
PM:	Particulate matter
PM _{2.5} :	PM with aerodynamic diameter less than 2.5 µm
pNEM:	Probabilistic NAAQS Exposure Model
POC:	Particulate Organic Compounds
POM:	Polycyclic Organic Matter
PRIME:	Plume Rise Model Enhancements
PSCF:	Potential Source Contribution Function
RACM:	Regional Atmospheric Chemistry Mechanism
RADM2:	Regional Acid Deposition Model chemical kinetic mechanism

version 2

RAMS:	Regional Atmospheric Modeling System
REHEX:	Regional Human Exposure model
REI:	Reasonably Exposed Individual
RELMAP:	Regional Lagrangian Model of Air Pollution
REMSAD:	Regulatory Modeling System for Aerosols and Deposition
RIVM:	National Institute of Public Health and the Environment of the Netherlands
RSEI:	Risk-Screening Environmental Indicators model
RTA:	Residence Time Analysis
RUC:	Rapid Update Cycle model
SAMHSA:	Substance Abuse and Mental Health Services Administration, Department of Health and Human Services
SAPRC:	Statewide Air Pollution Research Center chemical kinetic mechanism
SCAQMD:	South Coast Air Quality Management District (Los Angeles basin, California, USA)
SCC:	Source category codes
SCICHEM:	SCIPUFF with Chemistry
SCIPUFF:	Second-order Closure Integrated Puff model
SHAPE:	Simulation of Human Air Pollution Exposure
SMOKE:	Sparse Matrix Operator Kernel Emissions System
SoCAB:	California South Coast Air Basin
STAPPA:	State and Territorial Air Pollution Program Administrations
STREET	Roadway dispersion model that uses precalculated flow fields

SVOC:	Semi-volatile organic compounds
TEAM:	Trace Element Analysis Model
TexAQ5 2000:	Texas Air Quality Study of 2000
TKE:	Turbulent kinetic energy
TRI:	Toxics Release Inventory
TRIM:	Total Risk Integrated Model
UAM:	Urban Airshed Model
UAM-AERO:	Urban Airshed Model with aerosols
UAM-IV:	Urban Airshed Model version IV
UAM-TOX	Urban Airshed Model – Toxics
UBA:	Umweltbundesamt (German Ministry of the Environment)
UTM:	Universal Transverse Mercator
VMT:	Vehicle-miles traveled
VOC:	Volatile organic compounds



**CRITICAL REVIEW OF AIR TOXICS MODELING
CURRENT STATUS AND KEY ISSUES**

**CRC Project Number A-42-1
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EXECUTIVE SUMMARY

The estimation of population exposure to air toxics comprises several components, including the calculation or measurement of outdoor and indoor air toxics concentrations, and the calculation of the population exposure to those air toxics in a variety of microenvironments. We discuss these various components below.

E.1 Air Toxics Outdoor Concentrations

The estimation of air toxics outdoor concentrations is a difficult problem because (1) available ambient data are generally sparse and (2) source-based model simulations have uncertainties that result from their formulation and inputs (emissions, meteorology, upwind background concentrations). Consequently, an optimal approach must combine the use of source-based models to obtain the necessary spatial and temporal resolutions with the use of all available reliable data to minimize the model uncertainties. We outline the implementation of such an approach below.

The three-dimensional (3-D) time-dependent (e.g., hourly) concentrations of air toxics at regional and urban scales can be calculated using a 3-D gridded model. 3-D gridded models are preferable to plume models for several reasons. First, the large variety of emission sources (point, area and mobile sources) is more conducive to the use of a 3-D gridded model than a plume model. Second, many of the plume models currently in use (e.g., ISC-ST and ISC-LT) are not applicable beyond about 50 km, and air toxics may persist beyond such travel distances.

The four 3-D gridded models (ADOM, Models-3/CMAQ, REMSAD and UAM-IV) that have been applied to air toxics to date are suitable for such applications. However, all models have certain limitations and one should be aware of such limitations prior to selecting a model for a specific application. For example, UAM-IV is an urban scale model that should not be applied at regional scales because it does not provide sufficient treatment of transport processes (e.g., cloud venting) in the free troposphere.

At the local scale, plume models should be used to address the near-source impacts of stationary sources and roadway dispersion models should be used to address

the impacts of traffic emissions. For modeling, it is important to have a proper treatment of plume dispersion and downwash. Therefore, models that include higher-order closure algorithms for dispersion and a plume downwash algorithm such as PRIME are preferable.

When combining the results of regional/urban scale modeling with those of local scale modeling, care must be taken not to double-count the impacts of the local emissions.

The model simulation results should be compared with available data. If model performance is satisfactory, the model results can then be scaled to match the data, thereby providing a 3-D concentration field that (1) is consistent with the data but (2) provides spatial and temporal resolution not available in the data.

E.2 Air Toxics Indoor Concentrations

It is imperative to characterize air toxics concentrations in indoor environments with as much accuracy as feasible because most people spend the majority of their time indoors. The use of infiltration factors (i.e., ratio of indoor to outdoor air toxics concentrations) represents the simplest approach when data on indoor concentrations are not available. Such an approach should be considered a screening approach because it fails to account for the transient aspects of air toxics penetration (e.g., lag time between the peak outdoor and indoor concentrations) and, in most cases, for indoor sources. More accurate assessments should use indoor models that explicitly treat the flow of air toxics between the outdoor and indoor microenvironments as well as the indoor sources and sinks.

E.3 Population Exposure

The estimation of population exposure is a very difficult task because it requires information on the activity patterns of the population as well as information on the air toxics concentrations to which that population is exposed. Although several databases have been developed to characterize activity patterns, inter-individual variability and

variability among different geographical regions introduce additional uncertainty. We propose the following approach.

First, both outdoor and indoor air toxics concentrations should be characterized as accurately as possible. Second, it is essential to provide a realistic description of the population movements in a given area. This implies that the population must be broken down into subgroups (or cohorts) with specific activity patterns. Population movement should account for time spent in various microenvironments as well as time spent in various geographical subregions of the study area.

Finally, the uncertainties and variability associated with many of the inputs and parameters of the exposure models strongly suggest that a probabilistic approach should be used. A deterministic approach should only be considered suitable for screening purposes and should typically be designed to provide upper bounds of population exposure.

E.4 Air Toxics Studies

Air toxics studies that have been completed to date can be grouped into three major categories:

- Studies that address air toxics emissions from stationary sources
- Studies that address air toxics emissions from mobile sources
- Studies that address air toxics emissions from all major outdoor sources

E.4.1 Air toxics emissions from stationary sources

The studies that address stationary sources include the U.S. Environmental Protection Agency (EPA) Toxics Release Inventory (TRI) screening assessment, the EPA electric utility study and the California AB 2588 studies. All those studies used either ISCST3 or ISC-LT to calculate the ambient outdoor air toxics concentrations. The TRI and AB 2588 studies made no correction for indoor exposure; the electric utility study used HEM-II and, therefore, accounted for indoor exposure using penetration

efficiencies. As discussed above, there are limitations associated with ISC and the resulting uncertainties in the air toxics concentrations will directly affect the population exposure estimates.

E.4.2 Air toxics emissions from mobile sources

The EPA mobile source study, the EPA diesel particle study and the STAPPA/ALAPCO diesel particle study focused solely on mobile source emissions. The two EPA studies assumed that air toxics emitted from mobile sources were correlated with CO emissions and used CO exposure as the basis for estimating (via scaling) air toxics exposure. Indoor exposure was explicitly taken into account by means of infiltration factors. The STAPPA/ALAPCO study is highly simplistic in its methodology since it uses a single assumed concentration of diesel particles for each urban area and does not correct for indoor exposure.

E.4.3 Air toxics emissions from all major sources

The EPA integrated urban air toxics strategy, the SCAQMD MATES-II study of the California South Coast Air Quality Management District (SCAQMD) and the Arizona Department of Environmental Quality (ADEQ) study attempted to include all major sources of urban air toxics. The EPA study so far has used ISCST3 whereas the other two studies have used 3-D air quality models, UAM-IV and ADOM. As discussed above, we do not recommend using ISCST3 for integrated assessments that include all major source types and recommend instead the use of 3-D models.

MATES-II focused on the ambient air toxics concentrations and implicitly included all air toxics emissions (i.e., stationary and mobile sources). Regional modeling in MATES-II was conducted using UAM-IV and, for reactive organic compounds, a modified version called UAM-TOX. The local impacts from stationary sources were simulated using ISCST3.

In the ADEQ study, the modeling results were scaled to match the available air toxics ambient data, thereby combining the reliability of ambient measurements with the

spatial and temporal resolution provided by a 3-D gridded model. As we mentioned above, we recommend this methodology to the extent that the data are available and reliable.

The ARB neighborhood assessment program will combine regional/urban-scale modeling using a 3-D air quality models with local-scale modeling using a combination of point, area and line source dispersion models. Such an approach is promising although care must be taken not to double-count emissions in the two modeling components.

All these studies, however, present the same flaw: no correction is made to correct for indoor exposure. We recommend that urban air toxics exposure studies be conducted with a combination of 3-D gridded models and local-scale dispersion models, and that these outdoor air quality models be coupled with a comprehensive exposure model such as REHEX or pNEM, so that the time spent by people indoors is properly accounted for.

E.4.4 General remarks

All air toxics studies described above failed to take into account the contributions from indoor sources to air toxics levels. Although it can be argued that the objective of those studies was to assess the incremental impact of outdoor emission sources on population exposure, it is important to understand the relative contributions of outdoor and indoor air toxics sources to population exposure.

The air toxics exposure studies discussed above rely either on emissions inventories and/or ambient measurement of air toxics or a surrogate (e.g., CO). There are uncertainties associated with those data.

Finally, the models used for these studies have limitations. Clearly, there is a need for comprehensive evaluations of air toxics exposure models before one can have confidence in the results of such exposure studies.

E.5 Key Issues

Our review of the status of air toxics modeling suggests that there are many issues that need to be addressed before we can gain confidence in air toxics modeling studies.

E.5.1 Emissions

There are significant uncertainties associated with emissions of air toxics from both mobile and stationary sources. Air quality simulations conducted for the Los Angeles basin suggest underestimations as large as 2-3 times less than ambient observations for individual VOC such as benzene, 1,3-butadiene, formaldehyde and acetaldehyde. PM emissions from diesel and gasoline vehicles are underestimated by emission models. Diesel PM emissions from stationary sources may also be underestimated.

E.5.2 Meteorology

To the extent possible, prognostic meteorological modeling should include four-dimensional data assimilation, particularly under conditions which are the most difficult to simulate (e.g., calm conditions, complex terrain, land/sea breeze). Precipitation events are difficult to predict accurately and short-term concentrations of toxics subject to wet deposition may be predicted incorrectly. For local impact assessments, the use of local meteorological data is essential.

E.5.3 Ambient concentrations

Ambient concentrations are needed as inputs to air quality models as well as to evaluate their performance. The Photochemical Assessment Monitoring Station (PAMS) networks provide concentrations of several VOC including benzene, formaldehyde and acetaldehyde (1,3-butadiene data are not considered reliable). However, PAMS networks are limited to areas which are in non-attainment of the O₃ standard. Some states have their own VOC networks, however, that can be used to supplement PAMS data (e.g., the Texas Community Air Toxic Monitoring Network, CATMoN). The Particulate Matter (PM) speciation network provides PM speciation, including metals, “organic” carbon

(OC) and “elemental” carbon (EC). However, the detection limits of many metals are too high to be used for air toxic impact assessments.

Some special studies have been conducted to study O₃, PM and/or air toxics. Studies focusing on O₃ typically provide VOC data whereas studies focusing on PM provide PM speciated data and some VOC data. Two major special air toxic studies include the Arizona hazardous air pollutants research program conducted in 1994-95 in four communities and the Multiple Air Toxics Exposure Study-II (MATES-II) conducted in 1998-99 in the Los Angeles basin. Special air toxics studies tend to provide data bases that are well suited for air toxics impact assessments. However, issues such as spatial coverage, temporal resolutions and detection limits remain.

E.5.4 Transformations

The chemical transformations of most VOC need to be taken into account since (1) they can be oxidized rapidly in the atmosphere and (2) some VOC such as aldehydes can also be formed. The origin (anthropogenic or biogenic) of the precursors of secondary aldehydes is an issue that has not been addressed to date in air toxic studies. Chemical transformations of SVOC are of interest only at regional scales. The gas/particle partitioning of some SVOC may, however, be important for their removal as well as chemistry. Chemical transformations of trace metals are believed to be important only for chromium and mercury. The chemical reactions of some highly reactive inorganic gases such as Cl₂ must also be considered.

E.5.5 Removal

There are few data on the dry deposition of VOC and most air quality models use default values (e.g., no dry deposition of aromatics in Models-3/CMAQ). Therefore, experimental data are needed for the most important toxic VOC.

Dry and wet deposition rates of particulate-bound toxics depend on the particle size distribution. Data are needed to characterize those size distributions.

E.5.6 Indoor sources

For some chemicals, indoor sources may dominate the indoor environment. For example, the ratio of indoor to outdoor concentrations of formaldehyde has been reported to be in the range of 6 to 7. Therefore, it is essential to include such indoor sources when conducting population exposure assessments in order to properly account for the relative contributions of outdoor and indoor sources to total exposure.

E.5.7 Population activity patterns

Population activity patterns that are fairly reliable exist for a few cities. However, activity patterns may vary significantly by region, and uncertainties in this critical exposure model input may be significant outside the areas for which they have been developed.

E.5.8 Air toxics modeling

There is a need to combine regional/urban-scale modeling with local-scale modeling to properly predict air toxic concentrations at the neighborhood level. Moreover, the estimation of population exposure must take into account population dynamics through various microenvironments and within the study area. To date, no such air toxics modeling study has been conducted. We will develop the design for such a comprehensive modeling approach in Phase II of this project.

1. INTRODUCTION

Hazardous air pollutants, hereafter referred to as air toxics, are the subject of several regulations issued by the U.S. Environmental Protection Agency (EPA) and several states. Under Section 112 of the Clean Air Act, emissions from stationary sources must be addressed for over 100 air toxics. In a first step, maximum achievable control technology (MACT) was implemented on most industrial facilities. Following MACT implementation, EPA must address the public health risks associated with the residual air toxics emissions (i.e., residual risk). Mobile sources are addressed under Section 202 of the Clean Air Act and are not subject to the same requirements as stationary sources. Recently, EPA has developed the National Air Toxics Program (Federal Register, Vol. 64, No. 137, 38706-38740, July 19, 1999) to integrate stationary and mobile sources in an overall strategy aimed at reducing ambient air toxics concentrations with particular focus on urban areas.

Air toxics regulations have also been issued by states. In some cases, the approach taken by states differed from the federal approach (e.g., Ohshita and Seigneur, 1993). For example, California Assembly Bill 2588 (AB 2588) set a systematic approach to evaluate the health risks associated with air toxics emissions from industrial facilities and to control those emissions only if deemed necessary. Thus, the California approach was primarily driven by the assessment of the public health risk associated with industrial emissions. Emission controls were only implemented if warranted by the results of the health risk assessment.

This large array of federal and state air toxics control programs has led to a mosaic of modeling approaches to assess the ambient air toxics concentrations, the associated population exposure and public health risks. While some of those modeling approaches reflect the current state of the science, others are too simplistic. Moreover, many modeling approaches have yet to be subjected to proper performance evaluations, as is required for models used to evaluate the ambient concentrations of criteria pollutants (e.g., ozone, O₃; nitrogen dioxide, NO₂; carbon monoxide, CO; particulate matter, PM). There is, therefore, a need to review existing approaches, develop a coherent, scientifically-credible approach for air toxics modeling, identify the data needed for

performing air toxics modeling and articulate the key issues associated with air toxics modeling.

We present here a critical review of air toxics modeling. First, we review the current status of air toxics modeling. Air toxics modeling may be considered to consist of (1) simulating the fate and transport of air toxics in the atmosphere using chemical transport models (CTMs) and (2) estimating the exposure of the population to those air toxics. We review CTMs that have been used for air toxics modeling in Section 2. The modeling of human exposure is reviewed in Section 3. The simulation of indoor air toxics concentrations is also included in Section 3. Then, some recent air toxics model applications by EPA, states and interstate associations are described in Section 4. Finally, data needed for air toxics modeling and key issues are discussed in Section 5. A glossary of abbreviations used in this report is provided in Appendix A.

2. CHEMICAL TRANSPORT MODELING

We review in this section the models that have been used to simulate the outdoor concentrations of air toxics (the simulation of indoor concentrations is reviewed in Section 3). We distinguish among three major categories of models:

- Three-dimensional (3-D) grid-based models
- Plume models
- Roadway dispersion models
- Diagnostic models

The first three categories are source-based models that use air toxics emissions as input to calculate the atmospheric ambient air toxics concentrations using meteorological, terrain, source and chemical-specific information. Diagnostic models use available ambient data on air toxics concentrations to construct air toxics concentration fields using spatial interpolation. In most cases, models that were developed for criteria pollutants (e.g., SO₂, O₃, PM, CO) or acid deposition were modified for air toxics. Therefore, we refer to previous detailed reviews of those models when appropriate and focus here on their air toxics formulation.

2.1 Three-dimensional Grid-based Models

We identified four 3-D grid-based models that have been used to simulate air toxics in the United States:

- The Acid Deposition & Oxidant Model (ADOM) and its derivative versions
- The Models-3 Community Multiscale Air Quality Model (CMAQ)
- The Regional Modeling System for Aerosols and Deposition (REMSAD)
- The Urban Airshed Model version IV (UAM-IV)

We review the formulation and previous applications of these four models below.

2.1.1 ADOM

ADOM is a comprehensive 3-D Eulerian model that was originally developed for acid deposition and oxidant simulations. The first version was developed in the 1980s under the sponsorship of the Ontario Ministry of the Environment (OME), Environment Canada and EPRI. A European version of the model was supported by the German Umweltbundesamt (UBA). Subsequently, ADOM has been modified and applied to simulate air toxics concentrations. In the United States, the Arizona Department of Environmental Quality (ADEQ) sponsored an air toxics modeling study where concentrations of several air toxics were simulated with ADOM over an entire year (see Section 4.3 for a description of that study). ADOM has also been modified to simulate the atmospheric fate and transport of mercury. In the United States, EPRI sponsored the development and application of the Trace Element Analysis Model (TEAM) that is based on ADOM and incorporates an explicit representation of mercury physico-chemical processes (Pai et al., 1997). In Europe, Petersen et al. (1998) also modified ADOM for atmospheric mercury simulations.

A detailed review of the formulation of ADOM is available in Karamchandani et al. (2001). ADOM was also included in the review by Russell and Dennis (2000). We summarize here the most salient features of the model. ADOM uses a polar stereographic projection for the horizontal coordinates. The vertical layers are logarithmically-spaced, with higher resolution in the lowest layers to resolve the higher concentration gradients in the boundary layer. Note that the layer heights are fixed for all grid cells, since the model does not employ a terrain-following coordinate system.

Meteorological inputs have been derived from a variety of models in past applications including a diagnostic model from the Canadian Meteorological Centre (CMC), the Mesoscale Compressible Community Model (MC2), the Nested Grid Model (NGM) and the Europa model from the German weather service.

ADOM uses hourly emissions with separate files for area sources and major point sources. Plume rise calculations are conducted within the model.

For air toxics applications, a semi-Lagrangian scheme has been used for advective transport. Vertical turbulent transport is treated using a K-diffusion algorithm. Convective transport is treated at the subgrid scale in the presence of cumulus clouds. Two cloud modules are used to represent cumulus and stratus clouds.

As mentioned above, gas-phase and aqueous-phase chemical mechanisms were incorporated into ADOM for mercury simulations. For the ADEQ study, the air toxics simulated were assumed to be inert (see Section 4.3). For the simulation of volatile and semi-volatile toxic organic compounds at urban and regional scales, an appropriate chemical kinetic mechanism would need to be added.

Dry deposition is simulated according to the resistance approach for both gases and particles. Wet deposition is calculated with different algorithms for cumulus and stratus clouds. It is calculated according to solubility for gases and a scavenging rate for particles. In some formulations, washout (i.e., scavenging of gases and particles by precipitation below cloud base) is also simulated (Seigneur et al., 2001).

The application of ADOM for air toxics in Arizona is the most relevant here and is described in detail in Section 4.3.

2.1.2 Models-3/CMAQ

Models-3/CMAQ was developed under the leadership of EPA's Office of Research & Development. Models-3 provides the overall framework including a graphical user interface (GUI) and CMAQ is the air quality modeling system. It is not necessary to use Models-3 for CMAQ simulations as CMAQ is a stand-alone model. To date, most CMAQ applications have been for ozone, PM and acid deposition simulations. However, there are plans to also use CMAQ for air toxics modeling, and a version of CMAQ that treats mercury has been developed by EPA.

A detailed description of the CMAQ formulation is available (Byun and Ching, 1999). It was included in the reviews by Karamchandani et al. (2001) and Russell and Dennis (2000). A brief description is provided here.

CMAQ uses a generalized coordinate system for the horizontal and vertical coordinates. For the horizontal coordinate, the user can select a Lambert conformal conic

projection, a universal transverse Mercator projection, or a polar stereographic projection. The Lambert conformal conic projection is recommended for mid latitudes and is also consistent with the grid structure of the models typically used to develop meteorological inputs for CMAQ. For the vertical coordinate, a terrain-following sigma-pressure system is used. This coordinate is time dependent for hydrostatic simulations and time independent for non-hydrostatic simulations. Previous applications of CMAQ have used a Lambert conformal conic projection with a terrain-following time independent sigma-pressure coordinate.

The input/output applications programming interface (I/O API) provides efficiency for data access. All input and output files are in network common data form (netCDF) which makes them machine independent.

Meteorological inputs must be prepared from a prognostic meteorological simulation. Currently, CMAQ is compatible with two meteorological models, MM5 and RAMS. There has been, however, one application conducted with inputs from the diagnostic meteorological model CALMET.

CMAQ uses hourly gridded emissions. The Sparse Matrix Operator Kernel Emissions (SMOKE) modeling system has been designed to be compatible with CMAQ. The plume rise calculations for major point sources are performed in the emissions processor (e.g., SMOKE) and CMAQ takes a single 3-D emissions file as input.

CMAQ offers the flexibility of several options for simulating certain processes. Advective transport can be simulated using either the Bott algorithm or the piecewise parabolic method. Vertical turbulent transport is simulated with a K-diffusion algorithm. Convective transport is simulated at the subgrid scale when cumulus clouds are present. Clouds resolved by the grid system are obtained from the meteorological model and include stratus, cumulus and cirrus clouds. Precipitation rates are also obtained from the meteorological model.

For the application of CMAQ to mercury, the existing gas-phase and aqueous-phase chemical mechanisms were augmented by reactions pertinent to the reduction-oxidation cycle of mercury. Although the gas-phase chemical kinetic mechanisms available in CMAQ treat the chemical transformations of several air toxics such as formaldehyde, other chemical species are either lumped in organic classes (e.g.,

acetaldehyde with higher aldehydes, 1,3-butadiene with olefins) or not treated because they do not contribute to ozone formation (e.g., benzene). Under the California Air Resources Board (ARB) neighborhood assessment program, however, such a detailed mechanism for air toxics may be incorporated into CMAQ (see Section 4.2.3).

Dry deposition is simulated using a resistance approach for gases and particles; two different parameterizations are available. For particles, the deposition velocity is a function of particle size. For organic gases, dry deposition is calculated for some organic classes (e.g., aldehydes, acids, organic nitrates) but is neglected for others (e.g., aromatics). Wet deposition is calculated from the precipitation rate and chemical concentrations of the cloud droplets and raindrops. Both rainout and washout are simulated. However, for washout of gases, the chemical's Henry's law coefficient is used instead of the effective Henry's law coefficient, which could lead to underestimates of washout for gases such as HNO₃ that ionize significantly.

CMAQ applications to air toxics have been limited to mercury to date and simulation results are not yet available. ARB plans to apply CMAQ with the chemical kinetic mechanism SAPRC 99 modified for air toxics to southern California for the year 1998 (see Section 4.2.3). As discussed in Section 4.1, the Total Risk Integrated Model (TRIM) being developed by EPA is supposed to be compatible with CMAQ.

2.1.3 REMSAD

REMSAD was developed under the sponsorship of the EPA Office of Air Quality Planning & Standards (OAQPS). It is a 3-D grid-based model designed to simulate PM concentrations and air toxics deposition at large regional scales over long time periods (e.g., 1 year). A comprehensive peer-review of REMSAD Version 4 was prepared by Seigneur et al. (1999). A summary of the model formulation is provided here.

The REMSAD horizontal grid structure is based on a latitude/longitude system and the vertical grid structure is based on a terrain-following sigma-pressure coordinate system.

In its past applications, REMSAD has been applied with meteorological fields obtained from MM4 and MM5 simulations as well as from the Rapid Update Cycle (RUC) prognostic meteorological model.

REMSAD uses an externally generated emission inventory that includes separate files for point and area sources. Plume rise of major point sources is calculated in REMSAD. The emissions model SMOKE has been modified to produce emission files that are compatible with REMSAD.

Advective transport is solved using the Smolarkiewicz algorithm. Horizontal turbulent diffusion is calculated although it is likely negligible compared to horizontal advection and numerical diffusion. Vertical turbulent diffusion is simulated using K-theory. Convective transport is treated as a subgrid parameterization when cumulus clouds are present. Cloud fields are obtained from the meteorological simulation. Clouds are either resolved by the REMSAD grid structure or treated at the subgrid scale.

REMSAD has been applied to date to five air toxics: mercury, dioxins, cadmium, polycyclic organic matter (POM) and atrazine. A chemical mechanism was incorporated for mercury. Reactions of dioxins, POM and atrazine with OH radicals are also treated. REMSAD does not treat volatile organic air toxics explicitly, except formaldehyde. Dry deposition is simulated for gases and particles using a resistance approach. Wet deposition is parameterized for both gases and particles and is a function of the rainfall rate and cloud characteristics.

REMSAD has been applied to simulate PM concentrations over the entire United States. It has also been applied to simulate air toxics deposition under the Great Waters Study. The most recent version of REMSAD that is currently operational is Version 6 (available from EPA's Office of Water or EPA's Office of Air Quality Planning and Standards). Version 7 is currently under development; it will include additional improvements made in response to the review of Seigneur et al. (1999).

2.1.4 UAM-IV

UAM-IV is an urban-scale 3-D grid-based model that was originally developed for ozone simulations under the sponsorship of EPA. It has been subsequently

augmented with an aerosol module and an aqueous-phase chemistry module under projects funded by the South Coast Air Quality Management District (SCAQMD) and the Coordinating Research Council (CRC). It has been applied to air toxics by SCAQMD (see Section 4.2.2). ADEQ also used it for air toxics simulations in Arizona (see Section 4.3).

The technical formulation of UAM-IV has been described by Scheffe and Morris (1993). UAM-IV was reviewed by Seigneur (1994a) and Russell and Dennis (2000).

UAM-IV uses a Universal Transverse Mercator (UTM) horizontal coordinate system. The vertical resolution typically consists of four to six layers that vary in depth with the mixing height. Because the formulation of UAM-IV focuses primarily on the planetary boundary layer and not on the free troposphere, it is an urban-scale model and it is generally not suitable for regional applications.

Meteorological inputs can be obtained either from a diagnostic meteorological model or a prognostic meteorological model.

Advective transport is solved using the Smolarkiewicz algorithm. A constant coefficient is used for horizontal turbulent diffusion. Vertical turbulent diffusion is simulated using K-theory. There is no treatment of clouds and convective subgrid-scale transport.

In its applications to air toxics to date, no chemistry was simulated. Its future application under the ARB neighborhood assessment program will, however, include detailed chemistry for several air toxics (see Section 4.2.3). Although a version of UAM exists with an explicit treatment of droplet chemistry (CRC version), the standard UAM-IV version does not treat wet processes.

Dry deposition is simulated using the resistance approach. Wet deposition is not simulated.

UAM-IV and its derivative for PM, UAM-AERO, have been applied to the simulation of ozone and PM episodes. The application of UAM-IV to air toxics (modified version referred to as UAM-TOX) by SCAQMD is described in Section 4.2.2.

2.1.5 Other 3-D air quality models

Air quality models that have been developed and applied for photochemical air quality, PM and acid deposition can be modified to simulate air toxics. The models described above are examples of 3-D air quality models that have already been applied to air toxics. Clearly, other 3-D air quality models could also be modified to treat air toxics. The reader is referred to the reviews by Russell and Dennis (2000), Seigneur et al. (1998) and Karamchandani et al. (2001) for recent reviews of other available 3-D air quality models.

2.2 Plume Models

We identified three plume models that have been applied to simulate air toxics concentrations:

- The Industrial Source Complex – Short Term model (ISC-ST)
- The Industrial Source Complex – Long Term model (ISC-LT)
- The Hybrid Single-Particle Lagrangian Integrated Trajectory model (HYSPLIT)

2.2.1 ISC-ST

ISC is a plume model that was developed under EPA sponsorship (Bowers et al., 1989). The treatment of plume dispersion and transport involves several assumptions. Plume transport occurs along a straight line, and changes in wind direction along a plume trajectory cannot be taken into account. Plume dispersion involves the fundamental assumption that the crosswind concentration profiles are Gaussian. In the vertical direction, the Gaussian profiles are modified to take into account reflection at the ground and at the top of the mixing layer (i.e., temperature inversion height). The algorithm that governs the rate of plume dispersion is based on empirical data most suitable for elevated releases over flat terrain. Although dry and wet deposition processes can be simulated

with ISC, regulatory applications typically ignore deposition processes. It is recommended that ISC not be applied beyond 50 km from the source. ISC can treat point, area and volume sources. For point sources, ISC includes a treatment of plume rise. ISC exists in two versions: the short-term version, ISC-ST, predicts hourly concentrations (as well as longer time averaged periods such as daily, monthly and annual) whereas the long-term version, ISC-LT (see Section 2.2.2) only predicts monthly, seasonally, quarterly or annual concentrations. ISC has been reviewed by Venkatram and Seigneur (1993).

ISC-ST uses hourly meteorological data (wind speed and direction, temperature, mixing height and atmospheric stability) that are available from routine weather-monitoring stations or can be deduced from available data (e.g., atmospheric stability can be estimated from wind speed and sky cover or deduced from wind direction fluctuations).

As indicated by Venkatram and Seigneur (1993), there are several limitations in the ISC formulation. The assumptions of straight-line transport may not hold in areas with complex terrain or strong spatial gradients in wind direction. The use of the empirical Pasquill-Gifford-Turner (PGT) coefficients to characterize plume dispersion leads to several types of uncertainties. First, recent comparisons of algorithms for plume dispersion against atmospheric data have shown that the PGT algorithm performs poorly compared to first-order and second-order closure algorithms (Gabruk et al., 1999; Seigneur et al., 2000). Second, the PGT algorithm implies that the entire boundary layer is characterized by a single stability category. In reality, the atmospheric stability can be quite different at the surface and aloft. The treatment of plume downwash (i.e., aerodynamic effect of a building or structure on elevated plumes) is outdated and can lead to overestimation of concentrations during stable conditions near the point of release. A better plume downwash algorithm, PRIME, is now available. Although PRIME has been implemented within ISC-ST (Schulman et al., 2000), ISC-PRIME is not yet the EPA-recommended version.

ISC-ST has been applied in the context of air toxics by EPA for its urban air toxics strategy (see Section 4.1.1), the State of California under its statewide air toxics

“hot spots” program (see Section 4.2.2) and the California South Coast Air Quality Management District under MATES-II (see Section 4.2.2).

2.2.2 ISC-LT

ISC-LT is the long-term version of ISC. Instead of hourly meteorological inputs, it uses average joint frequencies of wind speed, wind direction, and atmospheric stability. These frequencies can be defined on a monthly, quarterly, seasonal, or annual basis and averaged over several years. Mixing height is entered according to wind speed and stability categories; temperature is entered according to stability categories. ISC-LT uses sector-averaged concentrations in the horizontal crosswind direction instead of the Gaussian profiles calculated by ISC-ST. ISC-LT is computationally more efficient than ISC-ST since it relies on a smaller input data set. It outputs period-average values. In direct comparisons, ISC-LT and ISC-ST agree within about 30% (see Venkatram and Seigneur, 1993).

The limitations mentioned above for ISC-ST apply also to ISC-LT. For cases, where one is interested in the long-term impacts of air toxics, it is appropriate to use ISC-LT rather than ISC-ST.

ISC-LT has been improved for air toxics applications with new treatments of dry deposition and wet deposition (Constantinou and Seigneur, 1993), and gas-particle partitioning of dioxins (Lohman and Seigneur, 2001).

ISC-LT has been applied by EPA in a variety of air toxics studies (see Section 4.1) and by others in screening studies for air toxics (see, for example, Lorber et al., 2000; Lohman and Seigneur, 2001).

2.2.3 HYSPLIT

HYSPLIT is a plume model that was developed by the National Oceanic and Atmospheric Administration (NOAA) (Draxler and Hess, 1998). In HYSPLIT, the transport and dispersion calculations are conducted along trajectories that are obtained (after some processing) from the output of a meteorological model. Therefore, HYSPLIT

trajectories are not necessarily straight-lines, an obvious advantage over the ISC formulation for long-range transport. However, HYSPLIT does not include any treatment of plume rise and buoyancy. Puffs are released at regular intervals from hypothetical sources and tracked through an Eulerian grid. The impact from a specific source can be estimated by spatial interpolation among the closest hypothetical sources. Puff dispersion is treated in two major steps. Until the puffs have a size less than that of the Eulerian grid, a parameterization based on micrometeorological data is used. Once the puff size exceeds that of the Eulerian grid, the dispersion characteristics of the Eulerian grid domain are used. This two-tier approach allows HYSPLIT to be computationally efficient when applied to the long-range transport of air contaminants.

Dry deposition is treated for gases and particles using a deposition velocity and the concentration of the chemical species over the depth of the pollutant layer. The dry deposition velocity can be calculated using the resistance approach. Wet deposition includes two components: in-cloud scavenging of pollutants by cloud droplets (rainout) and below-cloud scavenging by rain drops (washout). A scavenging ratio is used for rainout, whereas a scavenging coefficient is used for washout (see Seinfeld and Pandis, 1998, pp. 1000-1002, for the definitions of scavenging ratio and scavenging coefficient).

HYSPLIT has been applied to a variety of scenarios including radionuclide dispersion from the 1986 Chernobyl nuclear power plant accident, the 1994 Rabaul volcanic eruption (Draxler and Hess, 1998), the Kuwait oil fires, the long-range transport of sulfate in the United States (Rolph et al., 1992, 1993) and the long-range transport of dioxins over North America and the Arctic (IJC, 1999; Commoner et al., 2000). It has also been coupled to an Eulerian photochemistry model to simulate O₃ formation (Stein et al., 2000).

2.2.4 Other plume models

Plume models in general can be applied to simulate air toxics concentrations and deposition. No modifications are needed for air toxics that are chemically inert and pseudo-first-order kinetics can easily be implemented for the degradation of some air toxics (e.g., dioxins). There is a myriad of plume models currently available. We briefly

summarize here the major features of selected plume models. Other plume models that are accepted by EPA are listed under Appendix A or B of the EPA Guideline for Air Quality Modeling (40 CFR, Ch. 1, Part 51, Appendix W).

ISC-PRIME is a version of ISC that includes an improved treatment for building downwash. Since many sources of air toxics in urban areas are at low heights or near buildings, a proper treatment of downwash to correctly simulate dispersion from such sources is desirable. However, ISC-PRIME has not yet been listed as either a preferred or alternative model under the EPA Guideline for Air Quality Modeling.

CALPUFF: CALPUFF is conceptually similar to HYSPLIT since it tracks Lagrangian puffs within a fixed Eulerian grid. Unlike HYSPLIT, CALPUFF simulates plume rise for point emission sources. It treats puff dispersion using an empirical algorithm. Deposition of particles and gases is simulated using a resistance transfer approach. Typically, CALPUFF uses the meteorological fields predicted by the diagnostic wind model CALMET. Alternatively, a single meteorological sounding can be used if a single source (or a few collocated sources) is being simulated. EPA recommends that CALPUFF not be applied beyond 100 km from a source. CALPUFF is listed in Appendix A of the EPA Guideline.

AERMOD: The American Meteorological Society (AMS)/EPA Regulatory Model Improvement Committee (AERMIC) developed the AERMIC model (AERMOD) to provide a state-of-the-science representation of atmospheric transport and dispersion and, eventually, replace ISC. AERMOD includes new or improved algorithms for the treatment of dispersion in both the convective and stable boundary layers, plume rise and buoyancy, plume penetration into elevated inversions, vertical profiles of wind, turbulence and temperature, and the urban boundary layer (Cimorelli et al., 1998). The state-of-the-science downwash algorithm PRIME is currently being incorporated into AERMOD.

SCIPUFF: SCIPUFF (Sykes et al., 1993; Sykes and Henn, 1995) uses the same concept as HYSPLIT and CALPUFF by tracking Lagrangian puffs on an Eulerian grid. SCIPUFF differs from those other models, however, in several ways. First, it uses a second-order closure algorithm for puff dispersion that has been shown to perform better than empirical or first-order closure algorithms (Gabruck et al., 1999; Seigneur et al.,

2000). It uses a puff splitting algorithm that allows an effective treatment of puff dispersion under wind shear. A puff merging algorithm also allows the treatment of calm conditions when several puffs may overlap. A chemically reactive version of SCIPUFF, SCICHEM, has been developed that allows the treatment of chemically reactive puffs, including the treatment of non-linear reactions in overlapping puffs (Karamchandani et al., 2000). SCIPUFF includes a pre-processor to prepare the wind fields (either from meteorological soundings or from the output of a meteorological model). Its advanced treatment of puff dispersion allows its application to short as well as to long distances. The plume rise module PRIME is currently being incorporated into SCICHEM.

ARB is planning to apply ISCST3, AERMOD and CALPUFF in their neighborhood assessment program for air toxics (see Section 4.2.3).

2.3 Roadway Dispersion Models

Several models have been developed to simulate the concentrations of air pollutants near roadways. These models have been applied primarily to calculate CO concentrations and in some cases NO₂ and PM concentrations. To date, there have been no published applications to air toxics although ARB is planning to apply a roadway dispersion model to assess local air toxics impacts (see Section 4.2.3). The two models that are the most widely used are CALINE and STREET. CALINE is the preferred roadway dispersion model in the United States and STREET is widely used in several countries in Europe. In addition, a new model, the Hybrid Roadway Intersection Model (HYROAD) was recently developed. We focus our review on these three major models.

2.3.1 CALINE

CALINE was developed by the California Department of Transportation (Caltrans). CALINE Version 3 (CALINE3) is currently recommended by EPA under the name CAL3QHCR and CALINE Version 4 (CALINE4) is used by ARB. We first describe CALINE3. Then, we describe the differences between CALINE4 and CALINE3.

The fundamental dispersion algorithm used in the CALINE family of models is the Gaussian dispersion equation. CALINE3 divides individual roadway links into a set of segments. The Gaussian dispersion equation is then applied to each of those segments to calculate the downwind concentrations attributed to each segment. Since CALINE3 applies to inert pollutants, the concentrations contributed by different segments can be summed at selected receptors to provide the total concentration due to the roadway.

CALINE3 allows the user to select up to 20 roadway links and 20 receptors. A link is defined as a straight element of roadway with constant characteristics (i.e., width, height, traffic volume, vehicle emission factors). CALINE3 treats elevated roadways, (i.e., above grade level referred to as embankments), bridges and depressed roadways (below grade level). For embankments, the air flow is assumed to follow the terrain, whereas for bridges, the roadway is treated as an elevated source. CALINE3 can also be applied to simulate the impacts of parking lots with some small adjustments in the mixing zone characteristics.

Dry deposition of particulate pollutants is treated by taking into account both dry deposition due to atmospheric turbulence and Brownian diffusion to the surface, and gravitational settling of the larger particles.

CALINE4 includes some refinements over CALINE3. An option for modeling intersections was added. Also, the formulation of lateral plume spread and vehicle-induced thermal turbulence was improved. The Gaussian dispersion formulation has limitations in settings with non-homogeneous terrain. Algorithms were added to handle bluff and canyon settings by means of reflection of the plume on terrain features. The roadway and wind direction are then assumed to be parallel to the boundaries of the bluff or canyon.

A performance evaluation of CALINE3 and CALINE4 was conducted by Benson (1992) using data from five different experimental field studies. CALINE4 showed slightly better performance than CALINE3. Both models reproduced spatial concentration patterns fairly well (e.g., decreasing concentrations away from the roadway) but showed lower performance for the temporal concentration trends. Comparisons of simulated and measured tracer concentrations for two field studies showed correlation coefficients (r) of 0.87 (General Motors study) and 0.51 (Caltrans

Highway 99 study) with 85% of the simulated values within a factor of two of the measured values. The model tends to overpredict median (50th percentile) concentrations during conditions when the wind direction is parallel to the roadway. Model performance also decreased as the wind speed decreased; this result is typical since it is difficult to correctly predict ambient concentrations under calm conditions (e.g., wind speed less than 1 m/s).

CALINE3 and CALINE4 simulate hourly concentrations; longer time-averages (e.g., 8-hour average for CO) can then be derived from these hourly concentrations. Although these models were not designed originally to calculate long-term averages such as annual-average values, the latest EPA version of CALINE3, CAL3HQCR, can be applied to calculate annual average values. ARB is planning to apply CAL3HQCR for an entire year (see Section 4.2.3).

2.3.2 HYROAD

HYROAD has been developed by ICF Consulting under funding from the National Cooperative Highway Research Program (NCHRP) (Carr and Ireson, 2000). This model combines three modules to simulate traffic, emissions and atmospheric dispersion in an integrated system. The traffic module is based on the Traffic Network Simulation model (NETSIM). The emissions module uses emission factors from EPA's MOBILE5 model and the output of the traffic module to calculate the vehicular emissions. The atmospheric dispersion module consists of two distinct models. For calm conditions (i.e., wind speeds below 1 m/s), a Lagrangian puff module is used that accounts for the dominance of the traffic flow influence on atmospheric dispersion. For conditions with moderate and high wind speeds, the atmospheric dispersion module of CALINE4 is used. The Lagrangian puff module can be used for all conditions if desired; however, it is computationally more expensive than the CALINE4 module. A comparison of the CALINE3, CALINE4 and HYROAD Lagrangian puff dispersion module against measured ambient concentrations of CO at a road intersection showed better performance of the Lagrangian puff module (Carr and Ireson, 2000).

2.3.3 STREET

STREET is a roadway impact model that was developed originally by the Environment Ministry of the Land Baden-Württemberg, Germany. The French version was developed by Kunz Technologie Transfer (KTT) and Targeting. The current version is STREET Version 4.0.

For the dispersion of the pollutants, STREET relies on pre-calculated 3-D concentration fields. These 3-D concentration fields were obtained with the computational fluid dynamics model MISCAM for 98 different roadway configurations and 30 meteorological conditions. Because MISCAM provides a detailed description of the wind flow from the primitive equations, it allows a better treatment of the complex wind flows (e.g., recirculation in the wake of buildings) under strict canyon conditions than Gaussian models such as CALINE. These concentration fields were pre-calculated with unit emission rates. Then, STREET combines those pre-calculated 3-D fields with the pollutant emission rates corresponding to the actual roadways being simulated.

STREET is written in ACCESS since its main calculations consist in combining the databases of pre-calculated 3-D concentration fields with databases of emission factors and traffic flows.

In its current version, STREET can treat primary VOC (including benzene), particulate matter, NO₂, CO and SO₂. The NO₂ concentrations are calculated from the NO_x concentrations using empirical formulas developed from field measurement campaigns conducted in Germany.

STREET calculates annual average concentrations, with, in addition, some percentiles (50th and 98th) for NO₂. STREET is not designed to calculate short-term averages such as one-hour or daily average values.

2.4 Diagnostic Models

Several air toxics studies have used ambient monitoring data to estimate population exposure. Since monitoring data are typically available at only a few sites, it is necessary to interpolate (and, in some cases, extrapolate) among those sites to obtain a

spatially continuous field of air toxics concentrations. To that end, several interpolation models (referred to here as diagnostic models) have been used.

It is important to note that diagnostic models require existing data and, therefore, cannot be used to predict future conditions except in the extreme case where all concentrations in a given area would decrease by the same proportionate amount across-the-board. In contrast, the 3-D, plume and roadway dispersion models described in Sections 2.1, 2.2 and 2.3 can be used to predict the effect of future emission scenarios on ambient air toxics concentrations.

The simplest diagnostic model consists in assuming a single average concentration based on available data for an area. This approach has been used for example by the State and Territorial Air Pollution Program Administrators (STAPPA) and the Association of Local Air Pollution Control Officials (ALAPCO) (see Section 4.4).

A more refined approach consists in assigning population to the nearest monitoring site.

Finally, an interpolation technique such as $1/r^2$ weighting (where r is the distance from a monitoring site) can be used to construct spatially continuous concentration fields. More refined interpolation techniques that take measurement error into account can also be used (e.g., Langstaff et al., 1987).

2.5 Recommendations

The estimation of air toxics outdoor concentrations is a difficult problem because (1) available ambient data are generally sparse and (2) source-based model simulations have uncertainties that result from their formulation and inputs (emissions, meteorology, upwind background concentrations). Consequently, an optimal approach must combine the use of source-based models to obtain the necessary spatial and temporal resolutions with the use of all available reliable data to minimize the model uncertainties. Such an approach was used, for example, by the Arizona Department of Environmental Quality (ADEQ) (see Section 4.3). We outline the implementation of such an approach below.

The 3-D time-dependent (e.g., hourly) concentrations of air toxics at the regional and urban scales can be calculated using a 3-D gridded model. 3-D gridded models are preferable to plume models at urban scales for several reasons. First, the large variety of emission sources (point, area and mobile sources) is more compatible with the use of a 3-D gridded model than a plume model. Second, many of the plume models currently in use (e.g., ISC-ST and ISC-LT) are not applicable beyond about 50 km, and air toxics may persist beyond such travel distances.

The four 3-D gridded models that have been applied to air toxics to date are suitable for such applications. However, all models have certain limitations and one should be aware of such limitations prior to selecting a model for a specific application. For example, UAM-IV is an urban scale model that should not be applied at regional scales because it does not provide sufficient treatment of transport processes (e.g., cloud venting) in the free troposphere.

At the local scale, plume models should be used to address the near-source impacts of stationary sources and roadway dispersion models should be used to address the impacts of traffic emissions. It is important to have a proper treatment of plume dispersion and downwash. Therefore, models that include higher-order closure algorithms for dispersion and a plume downwash algorithm such as PRIME are preferable.

When combining the results of regional/urban scale modeling with those of local scale modeling, care must be taken not to double-count the impacts of the local emissions.

The model simulation results should be compared with available data. If model performance is judged satisfactory, the model results can then be scaled to match the data, thereby providing a 3-D concentration field that (1) is consistent with the data but (2) provides spatial and temporal resolution not available in the data.

3. EXPOSURE MODELING

We review in this section the models that have been used to simulate the exposure of human individuals, population subgroups (also referred to as cohorts) or a total population to air toxics. In the previous section, we reviewed models that simulate the outdoor concentrations of air toxics. Since people spend on average most of their time indoors (typically, over 80%), the calculation of human exposure requires in addition to the air toxics outdoor concentrations, the indoor concentrations of those same air toxics. Therefore, we first review the models used to calculate indoor air toxics concentrations. Next, we review the models that calculate human exposure. Such models combine air toxics concentrations with estimates of the time spent being exposed to these air toxics concentrations. Human exposure models can be grouped into two major categories: those that track individuals or groups of individuals through various microenvironments (including outdoor) and those that assume some average frequency of exposure of those individuals or groups of individuals in representative microenvironments. We refer to the first category as deterministic and to the second category as statistical. We can further differentiate between exposure models that calculate the exposure of individuals and those that calculate the exposure of a population of individuals (including in some cases subgroups/cohorts of that population).

3.1 Indoor Air Toxics Models

3.1.1 Fundamental equations

The estimation of air toxics concentrations in indoor microenvironments is essential for human exposure modeling because (1) indoor concentrations may differ significantly from outdoor concentrations and from one indoor microenvironment to the next, and (2) most people spend the majority of their time indoors.

An indoor air toxics model typically simulates the concentrations of air toxics in the microenvironment as a function of the exchange rates with the other

microenvironments, removal rate within the microenvironment and source rate within the microenvironment.

A microenvironment is generally assumed to be well-mixed; i.e., the air toxics concentration is assumed to be uniform within the microenvironment. The general equation for the concentration of an air toxics within a microenvironment is as follows.

$$V \frac{dC_i}{dt} = Q_{inf} \mathbf{a}_{inf} C_o + Q_o \mathbf{a}_o C_o + Q_R \mathbf{a}_R C_i - (Q_{inf} + Q_o + Q_R) C_i - v_d A C_i + S \quad (3-1)$$

where V is the volume of the indoor microenvironment; Q_{inf} , Q_o , and Q_R are the flow rates for infiltration, outdoor air intake and indoor air recirculation, respectively; \mathbf{a}_{inf} is a coefficient that represents the fraction of the air toxics entering the indoor environment during infiltration (equal to 1 if infiltration does not affect the air toxics concentration in the infiltrating air); \mathbf{a}_o and \mathbf{a}_R are the filtration factors for outdoor and recirculation air flows (equal to 1 for no filtration and to 0 for 100% filtration efficiency); C_o and C_i are the outdoor and indoor chemical concentrations, respectively; v_d is the chemical dry deposition to surfaces, A is the indoor surface area and S is the indoor chemical emission rate. (Infiltration refers to the diffusion of outdoor air into a building through cracks and other openings; outdoor air intake refers to the inflow of outdoor air by forced intake with a mechanical ventilation device.) This equation can be extended to treat multicompartments that are connected (e.g., Nazaroff and Cass, 1986). Comparisons of such models with measured indoor concentrations have shown satisfactory performance when the indoor environment characteristics are known. For example, Weschler et al. (1996) simulated particle concentrations in an office in southern California over a week. Simulated concentrations were within 50% of the observations except for a brief period on the second day.

One should note that the assumption of a well-mixed microenvironment may not always hold. For example, for air toxics that are emitted by individuals (e.g., hair spray aerosol), concentrations in the personal cloud (i.e., the volume within arm length of an individual) are likely to be greater than in the remaining volume of the microenvironment (Furtano et al., 1996).

An example of an indoor model is the Indoor Air Quality Model (IAQM) (Hayes, 1991). IAQM was originally designed to estimate indoor ozone levels by microenvironment and configuration. The microenvironments are home, office, and vehicle. The possible configurations are opened windows, closed windows, older construction, weatherized, and air conditioned. IAQM is based on the recursive solution of a one-compartment mass-balance model. It has been used to estimate distributions of ozone exposures (Hayes and Lundberg, 1985) and to evaluate mitigation strategies for indoor exposures to selected pollutants for various scenarios, such as exposure to CO from a gas boiler in a school (Eisinger and Austin, 1987). IAQM is the indoor exposure portion of NEM (see Section 3.2.2.3).

Other examples that use the same conceptual approach include the INDOOR model developed by the Indoor Air Branch of EPA (Sparks, 1988; Sparks et al., 1993), the Multichamber Consumer Exposure Model (MCCEM) (Koontz and Nagda, 1992) and the Caltech model (MIAQ) of Nazaroff and Cass (1989).

A common simplification consists in assuming equilibrium between an indoor and outdoor environment. In that case, Equation (3-1) can be rewritten for steady state as follows.

$$C_i = \frac{C_o (a_{inf} Q_{inf} + a_o Q_o) + S}{Q_{inf} + Q_o + (1 - a_R) Q_R + v_d A} \quad (3-2)$$

If we assume that there are no indoor sources, the contribution of outdoor air to the indoor air concentration is simply proportional to the outdoor air concentration.

$$C_i = C_o \frac{a_{inf} Q_{inf} + a_o Q_o}{Q_{inf} + Q_o + (1 - a_R) Q_R + v_d A} \quad (3-3)$$

In the absence of indoor sources, the ratio of the indoor and outdoor concentrations is generally referred to as the infiltration factor, F.

In the absence of indoor air recirculation and deposition, the indoor and outdoor concentrations are related as follows.

$$C_i = C_o \frac{a_{inf} Q_{inf} + a_o Q_o}{Q_{inf} + Q_o} \quad (3-4)$$

The proportionality constant is then called the penetration efficiency (P).

$$P = \frac{C_i \text{ (from outdoor contribution)}}{C_o} \quad (3-5)$$

The penetration efficiency is routinely used in indoor exposure studies and Equation (3-3) is sometimes written as follows (e.g., Wilson and Suh, 1997).

$$C_i = C_o \frac{P(Q_{inf} + Q_o)}{(Q_{inf} + Q_o) + (1 - a_R)Q_R + v_d A} \quad (3-6)$$

If there is no filtration of recirculated air, it is further simplified as follows (e.g., Lang et al., 2001).

$$C_i = C_o \frac{P(Q_{inf} + Q_o)}{(Q_{inf} + Q_o) + v_d A/V} \quad (3-7)$$

If indoor deposition is negligible, the simplest form of the relationship between indoor and outdoor concentrations is obtained.

$$C_i = P C_o \quad (3-8)$$

The infiltration factor, F, is equal to the penetration efficiency if there is no filtration of recirculated air and no indoor deposition.

If there are indoor sources of the air toxics of interest, the indoor concentration is sometimes expressed as follows according to the superposition principle (i.e., contribution from outdoor and indoor sources are additive).

$$C_i = FC_o + C_i (\text{from indoor sources}) \quad (3-9)$$

where C_i (from indoor sources) can be calculated from the indoor source emission rate, S , as follows.

$$C_i (\text{from indoor sources}) = S / (Q_{inf} + Q_o + (1 - a_R) Q_R) + v_d A \quad (3-10)$$

It should be noted that Equations (3-2) through (3-10) are approximations since there is generally a time lag between outdoor and indoor concentrations which cannot be accounted for by these equations.

3.1.2 Indoor sources of air toxics

There are a variety of indoor sources of air toxics including cooking, smoking, use of household products and volatilization of chemicals from tap water and degassing from house furnishing and building materials.

Such emissions require information on the specific microenvironment considered. Several databases exist for typical household activities (e.g., Stallings et al., 2000; Wiley, 1991a, 1991b; Schwab et al., 1992; McCurdy, 1999). Volatilization of chemicals from tap water requires information on the chemical concentration in the water and the water usage. Several models have been developed to represent volatilization of chemicals from the kitchen tap, shower and bath. These models account for the mass transfer of chemicals from the water to the air and vary in complexity depending on the simplifying assumptions that have been made. The basic equations are presented by Moya et al. (1999). Most of the work related to the volatilization of chemicals from tap water has focused on showers. There is now good agreement among the various experimental studies. Volatilization depends primarily on the water temperature and the Henry's law constant of the chemical; other variables such as flow rate, room ventilation rate and water spray type (i.e., droplet size distribution) are less influential. Chemical species that have low Henry's law constant such as toluene ($H = 0.27 \text{ m}^3 \text{ water/m}^3 \text{ air at } 25^\circ \text{ C}$) will

have a large fraction volatilized (e.g., more than 50% for a typical shower). For particulate compounds, exposure takes place primarily by inhalation of droplets that are in the respirable range.

3.1.3 Indoor sinks of air toxics

Some indoor air toxics can be removed efficiently via dry deposition. Walls and carpets can absorb or adsorb some gaseous air toxics and particles may deposit on indoor surfaces.

Dry deposition of particles (soiling) has been modeled as well as measured, for example, in museum environments (Nazaroff et al., 1990).

Dry deposition of gases has also been modeled and some experimental data are becoming available. Van Loy et al. (2001) reported recently on the absorption of organic compounds by indoor surfaces such as carpet and wallboard.

3.2 Deterministic Exposure Models

3.2.1 Individual exposure

The fundamental exposure equation is as follows.

$$E = \int_0^T C(x,t) dt \quad (3-11)$$

where E is the individual cumulative exposure, $C(x,t)$ is the air toxics concentration in the relevant microenvironments as a function of space (x) and time (t) and T is the period of exposure. We can also define the time-weighted average exposure, TWE, as E/T .

Many air toxics regulations use simplifying assumptions that lead to the calculation of special forms of their equation. For example, the exposure of a maximally exposed individual (MEI) is calculated assuming that the MEI is located at the location of maximum concentration for his/her entire lifetime, T_{li} (generally, assumed to be 70 years).

$$E_{MEI} = \int_0^{T_t} C(x,t)dt \quad (3-12)$$

The calculation of the exposure of a reasonably exposed individual (REI) is similar but involves the relaxation of some of the assumptions. For the inhalation of air toxics, assumptions commonly made are (1) to use the outdoor air toxics concentrations at the location of residence and (2) to use the average residence time, T_{rt} (generally 7 years), for the exposure period:

$$E_{REI} = \int_0^{T_{rt}} C(x_{residence}, t)dt \quad (3-13)$$

These integral equations are solved by using summations over the output time steps of the air toxics model. The REI exposure equation can be further modified by taking into account the time spent indoors and by calculating indoor concentrations from outdoor concentrations. The indoor concentrations can be calculated by means of species-specific infiltration factors or using the result of microenvironmental model calculations.

The Model for Analysis of Volatiles and Residential Indoor-air Quality (MAVRIQ) is an example of an individual exposure model with treatment of microenvironments. It was developed under funding from EPA (Wilkes et al., 1992). It simulates the time-dependent exposure of individuals within a building. It is based on Equation (3-1) for the calculation of the indoor concentrations of air toxics. MAVRIQ includes a source term for the volatilization of VOC from tap water that requires calibration for different types of showers.

3.2.2 Population exposure

The calculation of population exposure consists in adding all the individual exposures over an entire population. The worst-case analysis simply applies the MEI exposure to the entire population. More refined estimates take into account the spatial

distribution of the population, air toxics concentrations in microenvironments and the movement of the population throughout these microenvironments. Deterministic population exposure models are based on the following equation.

$$E_i = \sum_k C_{jk} t_{ijk} \quad (3-14)$$

where the indices refer to the individual or population subgroup (also called cohort) i , the microenvironment j and the time step k , C_{jk} is the air toxics concentration in microenvironment j during time step k and t_{ijk} is the time spent by individual/subgroup i in microenvironment k . This equation is equivalent to the MEI exposure equation if one assumes that the outdoor location of maximum impact is the only environment considered and the sum of the time intervals corresponds to the lifetime.

Microenvironments that are typically considered in population exposure models include outdoors and indoor locations such as vehicle, home residence and office.

Two major categories can be considered for the treatment of the population: (1) static population and (2) dynamic population. Models that use a static population generally distribute the population according to census tract data. Then, two approaches are commonly used to calculate exposure: (1) the outdoor air toxics concentration at the centroids of the respective census tracts are used for the calculations or (2) the population located within a given area (grid cell, circular area) is assigned to the concentration at the center of that area. Models that use a dynamic population require more input information since they must take into account the population movement among the various microenvironments and areas of the airshed being modeled.

Static population data are available from the U.S. Census Bureau on many different geographical scales. The smallest geographical unit available from the Census Bureau is the block. Blocks are usually bounded by streets, legal boundaries, or geographical features. There are 8.5 million blocks in the United States. The next largest geographical unit is the block group. As the name suggests, this is an aggregate of blocks. Census tracts are the next largest population unit. These areas consist of several block groups and contain an average of 4,000 persons. The Census Bureau also aggregates data to other larger areas such as: counties, metropolitan areas, minor civil

divisions, places, urban areas, voting districts, zip code tabulation areas, and states (and equivalent areas).

Some of the 2000 Census data has already been released, particularly data necessary for political redistricting. Other data and data products will be released on a rolling basis through 2003.

The use of either a static or dynamic population requires information on the movements of the population through the various microenvironments. To that end, the population is divided into subgroups and activity patterns are assigned to each subgroup. These activity patterns will generally differ between weekday and weekend and may also depend on season. Models that use a dynamic population must also track the movement of the population subgroups through the various areas of the airshed. Activity patterns are obtained from data bases that have been developed for various parts of the country (e.g., CHAD). Population dynamics is estimated using transportation data.

We summarize below some existing population exposure models. These population exposure models are categorized as follows (Seigneur, 1994b).

- Models that use a static population
- Models that use a population that is dynamic through various micro-environments but static within the study region
- Models that use a population that is dynamic through various microenvironments and also within the study region

3.2.2.1 Models with static population

These models represent the simplest form of population exposure modeling. The population spatial distribution is typically obtained from census tract data. There is no treatment of population movement among census tracts nor among different micro-environments. Examples of such models that have been applied to air toxics include the Assessment System for Population Exposure Nationwide (ASPEN) and the Risk-Screening Environmental Indicators Model (RSEI). Both models have been developed by EPA.

In ASPEN, the air toxics concentrations are calculated with ISC-LT (see Section 2.2.2) at the centroid of the population census tracts. The population exposure is then calculated by multiplying the calculated outdoor air toxics concentration by the corresponding population.

RSEI was developed by the EPA's Office of Pollution Prevention and Toxics (OPPT) to calculate risk-related values from the emission information reported in the Toxics Release Inventory (TRI). RSEI uses ISC-LT (see Section 2.2.2) to calculate the expected concentrations in the area surrounding a source. These concentrations are then weighted by toxicity and population density within that area to produce a chronic human health indicator of the potential human health impacts of a facility's emissions. The indicator provides a relative risk estimate, not an absolute risk estimate. It can only be used to compare the potential risk of different chemicals and/or facilities. Currently, RSEI only calculates a chronic human health indicator. OPPT plans to include an acute human health indicator in the future but there is currently not enough data available in the TRI database for an acute calculation. RSEI operates in the Windows[®] environment.

3.2.2.2 Models with population movement among microenvironments

These models use population census tract data (i.e., the population is static within the study region) but the assumption of constant exposure to outdoor air toxics concentrations has been removed. The population is exposed to outdoor concentrations only for a fraction of time and is exposed to indoor concentrations in a variety of micro-environments for the rest of the time. One such model is the Human Exposure Model version II (HEM-II) developed by EPA.

In HEM-II, the air toxics concentrations are calculated with ISC-LT (see Section 2.2.2). Indoor concentrations in up to ten micro-environments are calculated using infiltration factors (i.e., Equation 3-3). Only one population group is considered, i.e., population subgroups (cohorts) with different activity patterns are not treated. The activity patterns of the whole population that determine the time spent in each microenvironment are specified by the user. HEM-II includes the possibility of taking into account population growth using either user-specified or default growth factors.

Another example is the California Population Indoor Exposure Model (CPIEM). It was developed by the California Air Resources Board (ARB) to estimate indoor exposure to air toxics for the general population as well as population subgroups. CPIEM estimates indoor exposure by combining indoor air concentration distributions with California location/activity patterns. The model is designed to use samples of indoor concentration values from different indoor environments around the state to determine indoor air concentrations. However, since for many compounds, there is very little information or no measured data, the model also has the capability of estimating indoor air concentration distributions. The modeled indoor air concentration distributions are developed with a mass balance model (Equation 3-1) using input information on emission rates, building volume, and air exchange rates. A Monte Carlo sampling routine combines the activity profile samples and the indoor air concentrations. CPIEM calculates three types of output distributions: (1) total air exposure and dose, (2) total indoor air exposure and dose, and (3) exposure and dose in a specific type of environment. There are three exposure durations available: 24-hour, 12-hour daytime and 12-hour nighttime.

3.2.2.3 Models with population movement within the study area and among microenvironments

These models currently represent the state-of-the-science for human exposure modeling. They account for the movement of the population (or population subgroups) among various microenvironments and also treat the movement of the population among various parts of the study area. Models that use this comprehensive approach include the NAAQS Exposure Model (NEM), the Hazardous Air Pollution Exposure Model (HAPEM), the Regional Human Exposure Model (REHEX) and the Benzene Exposure Assessment Model (BEAM). Each of these models can be operated in both deterministic and statistical modes.

NEM was developed by EPA in the 1970s to estimate population exposure to criteria pollutants and has been modified and improved many times since then. It has been applied to O₃, NO₂, CO and PM. Initially, NEM was a deterministic model. NEM

simulates the movement of specific cohorts through zones of varying air quality. The zones are defined by age of the cohort population, geographic location, and microenvironment. The indoor air concentrations are calculated by mass balance using IAQM, rather than the simplified indoor-outdoor ratios in many of the other models. NEM calculates exposure estimates for one-hour intervals. There are three different pollutant-specific versions of NEM: ozone (NEMO₃), carbon monoxide (NEMCO), and particulate matter (NEMPM).

A new version of the model has recently been developed that allows for probabilistic inputs and results. This new version is referred to as pNEM (Johnson and McCurdy, 1992, McCurdy, 1997). The activity data in pNEM are taken from the Comprehensive Human Activity Database (CHAD) (Stallings et al., 2000). The commuting pattern information is from a commuting database developed by the U.S. Census Bureau. Previous versions of NEM could only be run on a mainframe computer; however, pNEM may be run on a personal computer.

HAPEM is another indoor exposure model developed by EPA that has gone through many updates and improvements since it was originally created in the 1980s. HAPEM was designed to determine long-term risk estimates, such as cancer risk, due to pollutants released by mobile sources. Because long-term estimates are needed, the results are calculated as seasonally (3 month) averaged diurnal profiles with one-hour increments.

HAPEM uses indoor-outdoor infiltration factors to calculate indoor concentrations. Previous versions of the model required outdoor concentrations to be input from fixed CO monitors. Exposure to a particular pollutant was then assumed to be proportional to the annual average CO exposure. The latest version of the model, HAPEM4 (Rosenbaum, 2000), allows the user to provide outdoor concentrations from both modeled and measured sources. This allows pollutants to be modeled individually rather than being scaled from CO exposure. Like pNEM, HAPEM4 was updated to include probabilistic inputs and outputs and to use activity data from CHAD as well as specific commuting pattern data. The model can now be applied, in conjunction with an air dispersion model, anywhere in the country, since it is no longer tied to CO monitors which tend to be clustered in urban areas.

REHEX was developed under the sponsorship of the California South Coast Air Quality Management District (SCAQMD) (Lurmann and Korc, 1994). It was originally designed to address population exposure to O₃ and NO₂ in the Los Angeles basin. It was recently applied to benzene in the Los Angeles basin (Fruin et al., 2001). It is currently being applied to Houston, Texas. The structure of REHEX allows for spatial and temporal variations in concentrations, variations in human activity, and the mobility of the population between subregions. The model can be applied to a maximum of thirty-five different microenvironments.

In REHEX, the chemical concentrations are calculated according to one of four possible methods:

- 1) scaling of ambient concentrations using indoor-outdoor infiltration factors
- 2) sampling from user supplied concentration distributions for the microenvironment
- 3) a combination of 1 and 2
- 4) applying an indoor air quality mass balance model

REHEX provides exposure estimates for the exposure of individuals or cohorts of the general population for intervals between one and twenty-four hours.

The Benzene Exposure Assessment Model (BEAM) was developed by EPA's Office of Research and Development (ORD) to generate benzene exposure profiles for different population subgroups. BEAM is based on the SHAPE (Simulation of Human Air Pollution Exposure) model that was developed by Ott et al. (1983, 1989). BEAM can be run in both deterministic and statistical modes. In the statistical mode, the model selects a concentration for a given hour from a probability distribution of concentrations for the appropriate microenvironment. The concentration in a given microenvironment is calculated by adding the concentration due to indoor sources to the concentration due to outdoor sources according to the superposition hypothesis (see Equation 3-9). The benzene concentration data can be from either measured or modeled sources.

3.2.3 Statistical population exposure models

The calculation of population exposure involves a large amount of uncertainties since (1) one does not have exact information on the activity patterns of all individuals within a population and (2) air toxics concentrations, particularly indoors, are uncertain. Therefore, using a deterministic approach where population subgroups are tracked in a serial manner throughout the days may be too detailed considering the input uncertainties. Another approach consists in using more general information on the frequencies spent by population subgroups in their various microenvironments (i.e., an approach similar to that used by ISC-LT to treat meteorology as opposed to the serial hourly data used by ISC-LT). As discussed in Section 3.2.2, CPIEM, pNEM, HAPEM4, REHEX and BEAM may each be run in a probabilistic mode. Other models which were especially designed to use a statistical approach are AirPEX and BEADS.

AirPEX is an indoor air quality model developed by the National Institute of Public Health and the Environment (RIVM) in the Netherlands. AirPEX is based on NEM and is designed to evaluate the time and space dependency of inhalation exposure. AirPEX can be used to evaluate the exposure of both individuals and populations. Population exposure is determined by calculating the exposure to each individual from a random sample of the population. The individual exposures are used to form a population density function, which can then be applied to the larger population. The design of the model allows the user to analyze the socio-economic characteristics of the individuals with the highest exposure and identify the groups most likely to be heavily impacted.

AirPEX utilizes a database of Netherlands activity data with 15-minute resolution. The model also has default values already entered for benzene, benzo(a)pyrene, ozone, and PM that may be used as provided or updated by the user. The user can also model other toxics by inputting chemical-specific information for each additional toxic modeled. The exposure estimates are produced using 15-minute time steps for each microenvironment in order to correlate with the activity data. AirPEX runs in a Windows[®] environment.

The Benzene Exposure and Absorbed Dose Simulation (BEADS) model was also designed as a probabilistic exposure model (MacIntosh et al., 1995). It treats all routes of exposure (i.e., inhalation, ingestion and dermal absorption) among various microenvironments. It is computationally more efficient than other models such as SHAPE, REHEX, HAPEM, BEAM or pNEM because it does not correlate the exposure concentrations to the exposure time. The other models match the time spent in a specific microenvironment (activity patterns) to the air toxics concentration (observed or simulated) at that specific time. BEADS treats the time spent in each microenvironment independently of the air toxics concentrations in that microenvironment. The approach used in BEADS is valid as long as there is no correlation between the temporal profiles of the activity patterns and those of the air toxics concentrations. According to MacIntosh et al., this assumption is appropriate for all microenvironments except vehicles because air toxics concentrations inside vehicles are correlated with traffic density. However, they consider that this specific microenvironment has a small contribution to total benzene exposure and, therefore, the formulation of BEADS is appropriate for estimating benzene exposure.

A qualitative comparison of simulated and observed probability distributions of benzene exposure concentrations showed that BEADS could satisfactorily reproduce interindividual variability. Total exposure was calculated to be dominated by indoor exposure with indoor benzene concentrations originating primarily from outdoor sources.

3.3 Recommendations

Table 3-1 summarizes the major characteristics of the exposure models discussed in this section.

The estimation of population exposure is a very difficult task because it requires information on the activity patterns of the population as well as information on the air toxics concentrations to which that population is exposed. Although several databases have been developed to characterize activity patterns, inter-individual variability and variability among different geographical regions introduce additional uncertainty.

Table 3-1. Summary of Selected Exposure Models (see text and references for more detail).

Model	Population simulated	Outdoor concentrations	Indoor concentrations	Indoor sources and sinks	Population dynamics	Deterministic mode	Probabilistic mode
ASPEN	Total	ISC-LT	Outdoor only	No	Static	Yes	No
RSEI	Total	ISC-LT	Outdoor only	No	Static	Yes	No
HEM-II	Total	ISC-LT	Penetration efficiencies	No	Microenvironments	Yes	No
MAVRIQ	Individual	NA	Mass balance	Yes	Microenvironments	Yes	No
CPIEM	Cohorts	Data or model	Mass balance or data	Yes	Microenvironments	Yes	Yes
NEM/pNEM	Cohorts	Data or model	Mass balance	Yes	Microenvironments and subregions	Yes	Yes
HAPEM	Cohorts	Data or model	Penetration efficiencies	No	Microenvironments and subregions	Yes	Yes
REHEX	Cohorts	Data or model	Mass balance or data	Yes	Microenvironments and subregions	Yes	Yes
BEAM	Aggregate ^(a)	Data or model	Penetration efficiencies	Yes ^(b)	Microenvironments	Yes	Yes
AirPEx	Aggregate ^(a)	Data or model	Penetration efficiencies	No	Microenvironments	No	Yes
BEADS	Cohorts	Data or model	Penetration efficiencies or data	No	Microenvironments	No	Yes

(a) simulations conducted for individuals are aggregated to construct a population distribution

(b) indoor sources treated according to principle of superposition (see Equation 3-9).

Because most people spend the majority of their time indoors, it is essential to properly characterize indoor concentrations of air toxics. However, most available data are for outdoor concentrations. These issues must be taken into account when selecting a methodology to estimate population exposure to air toxics. We propose the following approach.

First, it is imperative to characterize air toxics concentrations in indoor environments with as much accuracy as feasible because most people spend the majority of their time indoors. The use of infiltration factors represents the simplest approach when data on indoor concentrations are not available. Such an approach should be considered a screening approach because it fails to account for the transient aspects of air toxics penetration (e.g., lag time between the peak outdoor and indoor concentrations) and, in most cases, for indoor sources. Variability among seasons, regions and individual microenvironments may also not be properly characterized by generic infiltration factors (Long et al., 2001). More accurate assessments should use indoor models that explicitly treat the flow of air toxics between the outdoor and indoor microenvironments as well as the indoor sources and sinks.

Second, it is essential to provide a realistic description of the population movements in a given area. This implies that the population must be broken down into subgroups (or cohorts) with specific activity patterns. Population movement should account for time spent in various microenvironments as well as time spent in various geographical subregions of the study area.

Finally, the uncertainties and variability associated with many of the inputs and parameters of the exposure models strongly suggest that a probabilistic approach should be used. A deterministic approach should only be considered suitable for screening purposes and should typically be designed to provide upper bounds of population exposure.

4. RECENT AIR TOXICS MODEL APPLICATIONS

We review in this section some recent applications of air toxics models that have been conducted by EPA and some states. A recent application by the State and Territorial Air Pollution Program Administrators (STAPPA) and the Association of Local Air Pollution Control Officials (ALAPCO) is also discussed. Finally, current plans at EPA and in some states are described.

4.1 EPA

Air toxics and exposure models have been applied by various EPA offices. Some of those applications have regulatory or policy implications whereas others are for risk communication. We discuss the major recent EPA applications below.

4.1.1 Integrated urban air toxics strategy

An overview of EPA's integrated urban air toxics strategy was presented in the Federal Register (FR, Vol. 64, No. 137, 19 July 1999, 38706-38740). This urban air toxics strategy addresses all sources of air toxics, i.e., stationary and mobile sources. Thirty-three air toxics are included; in addition, air toxics specifically relevant to mobile sources, such as diesel particulate matter, will be considered. EPA lists several models that will be used to simulate air toxics concentrations and exposures. These models include ASPEN (see Section 3.2.2), ISCST3 (see Section 2.2.1), Models-3/CMAQ (see Section 2.1.2), HAPEM4 (see Section 3.2.2) and TRIM (Palma et al., 1999). Among these models, two are fate and transport models (ISCST3 and Models-3/CMAQ) whereas the others are exposure models. To date, ISCST3 has been applied to two urban areas, Phoenix, Arizona and Houston, Texas. Models-3/CMAQ has been modified to treat one air toxic, mercury; however, its operational evaluation will not be completed until the end of 2001. Among the exposure models, ASPEN is considered a screening model. It is likely to be applied nationwide to obtain order-of-magnitude estimates of population exposure to urban air toxics. HAPEM4 is an improved version of HAPEM-MS; it will

likely be applied to selected urban areas. It provides better estimates of exposure than ASPEN because corrections are made for time spent indoors. TRIM is still under development. It is supposed to be a modular construct for exposure/risk calculations that is compatible with fate and transport models such as Models-3/CMAQ and ISCST3; it will likely be applied to address multipathway exposure (i.e., inhalation, ingestion and dermal absorption).

National inhalation exposure estimates will also be developed. ASPEN will be used to develop annual average national air quality concentrations, which will then be input into HAPEM to determine expected national exposure values. The results from the national scale study will be used to target pollutants and sources of greatest impact on a national scale.

4.1.2 TRI

In order to provide a comparison of potential health risks from facilities reporting to TRI (Toxics Release Inventory), EPA's OPPT developed the RSEI model and applied it to every facility listed in TRI. The United States were divided into a 1-km by 1-km grid system. Each facility was located at the center of the grid cell in which it is reported to be located. There are 607 chemicals and chemical categories listed in the TRI. Of those, 411 chemicals have available toxicity data and, therefore, could be included in the toxicity-weighting portion of the analysis. For each facility, the RSEI model was applied to each stack and fugitive air release. Emissions are weighted according to the toxicity of the chemicals. The model then calculates a surrogate dose based on the local population, and a chronic human health indicator.

This approach provides comparisons of risk-related impacts of different chemicals, facilities, industries, and geographical regions. Because emission and population data over a ten-year period were included, changes over time can also be compared. The results of the TRI/RSEI modeling have been released by EPA as a CDROM.

4.1.3 Electric utility study

The EPA Study of Hazardous Air Pollutants Emissions from Electric Utility Steam Generating Units (EPA, 1996) was conducted by the EPA Office of Air Quality Planning and Standards (OAQPS) to analyze the impacts of air toxics emissions from power plants in the United States. The modeling analysis consisted of regional and local analyses. The regional modeling was conducted using a Lagrangian model, RELMAP. However, this model has since then been superseded by other EPA models, namely, Models-3/CMAQ and REMSAD, that are Eulerian (see Sections 2.1.2 and 2.1.3). The local modeling analysis was conducted with HEM-II (see Section 3.2.2). HEM-II was applied to 830 U.S. power plants for 11 air toxics. This study probably represents the latest application of HEM-II on a nationwide basis.

4.1.4 Motor vehicle related air toxics strategy

EPA was directed by the Clean Air Act Amendments to complete a study of the need for, and feasibility of, controlling emissions of toxic air pollutants which are unregulated under the Act and associated with motor vehicles and motor vehicle fuels. The study was to focus specifically on those categories of emissions that pose the greatest risk to human health or about which significant uncertainties remain. The pollutants studied included benzene, formaldehyde, 1,3-butadiene, diesel particles, gasoline particles, and gasoline vapors.

Because the focus of the mobile sources study was on cancer risk, HAPEM-MS (an earlier version of HAPEM4) was used to estimate annual average exposure. In HAPEM-MS, CO was used as a surrogate for motor vehicle emissions. CO exposure was calculated for urban and rural scenarios for the year 1988. The data to calculate CO exposure came from fixed site monitors, personal monitoring studies, and personal activity studies. The CO exposure results were then scaled by emission factors to give toxic exposure results for the toxics being studied.

In this study, 6 population cohorts were moved through 5 microenvironments. To determine representative sites, eleven urban locations and two rural areas were modeled

with HAPEM-MS. In total, 323 urban areas in the United States were scaled to those eleven urban sites by scaling estimated CO emissions. All rural areas were grouped with one of the two rural sites and scaled according to their estimated CO emissions. These results were then used to develop annual average urban and rural CO exposures, which were in turn used to calculate expected annual average toxics exposures.

4.1.5 Heavy-duty engine and vehicle standards and highway diesel fuel sulfur control study

EPA conducted an analysis of the potential risks of diesel emissions on the U.S. population. In that analysis, HAPEM-MS3 was used to simulate the fate and transport of diesel particles and the resulting population exposure. A ratio of diesel particles to CO measurements was used. The exposure modeling was conducted for 1990 using CO concentration data from the urban areas. The correlation between gaseous and PM emissions from mobile sources was found to be poor (e.g., the correlation between CO and PM emissions had an r^2 value of 0.11, Norbeck et al., 1998). Therefore, any CO/diesel particle ratio can be expected to be highly variable. The constant CO/diesel particle ratio is a major assumption in this study that can lead to significant uncertainties in the population exposure results.

4.2 California

There have been two major air toxics programs implemented in California. We describe these two programs below. In addition, ARB is planning an air toxics assessment program that is also summarized below.

4.2.1 AB 2588

The Air Toxics "Hot Spots" Information and Assessment Act of 1987 (known as Assembly Bill 2588 or AB 2588) was passed to assess and, if warranted, reduce air toxics emissions from stationary sources. The first step for facilities is to prepare an air toxics

emission inventory that is submitted to the local air quality agency (i.e., air quality management district or air pollution control district). Emissions of about 100 air toxics must be quantified. Then, the local agency requires that the facilities with the highest air toxics emissions conduct health risk assessments following the guidelines established by the California Air Pollution Control Officers Association (CAPCOA), the Department of Toxic Substances Control (DTSC) and the local air quality agencies. Depending on the outcome of the risk assessment, a facility may be required to notify the public of its exposure to air toxics and to reduce its air toxics emissions.

The methodology used to assess the public health risk under AB 2588 relies on ISCST3 for atmospheric dispersion (see Section 2.2.1).

It is important to note that AB2588 pertains to the incremental risk of individual facilities (i.e., the background risk from other air toxics emission sources is not taken into account), although the local air quality agency can address this problem by combining various individual risk assessments. Air toxics emissions from mobile sources are not addressed under AB2588.

4.2.2 MATES-II

The Multiple Air Toxics Exposure Study (MATES-II) is an air toxics program that was conducted by the South Coast Air Quality Management District (SCAQMD) for the Los Angeles Basin. This program includes a monitoring component as well as a modeling component.

In the monitoring program, over thirty air toxics were measured at 10 fixed sites once every six days for an entire year (April 1998 to March 1999). In addition, microscale monitoring was conducted in residential neighborhoods that were potentially impacted by nearby air toxics emission sources. The microscale monitoring used three platforms, located for one-month periods in a total of fourteen neighborhoods during the one-year program. MATES-II, therefore, focused on the ambient air toxics concentrations and implicitly included all air toxics emissions (i.e., stationary and mobile sources).

On average, the public health risk due to ambient air toxics was attributed primarily to diesel particulate emissions (70%) and other air toxics associated with mobile sources such as benzene, 1,3-butadiene and formaldehyde (20%). Air toxics emissions from stationary sources were estimated to contribute only 10% of the public health risk on average. These conclusions from MATES-II are, however, a function of the cancer unit risk factors used for the health risk calculations and there are considerable uncertainties in unit risk factors of many air toxics including diesel particles.

A modeling study was also conducted under MATES-II to complement the monitoring program. This modeling study included two components: (1) regional modeling and (2) local modeling.

The regional modeling was conducted using UAM-IV (see Section 2.1.4). UAM-IV was modified for this study to account for the chemistry of individual organic compounds that are not explicitly included in the original CBM-IV formulation (e.g., 1,3-butadiene, styrene, toluene, aldehydes); the modified version is referred to as UAM-TOX. Thus, two models were applied for a full year, UAM-IV for inert species and UAM-TOX for reactive organic air toxics. Thirty-four air toxics were modeled. Model performance was evaluated for 28 chemical species. For annual concentrations averaged over all ten fixed monitoring sites, reasonable agreement (within 15%) was obtained for some chemical species such as benzene, formaldehyde, toluene, chloromethane, arsenic, elemental carbon and organic carbon. However, 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). No comparison was reported for specific sites or time periods.

The local modeling was conducted using ISCST3 (see Section 2.2.1) for the 14 microscale monitoring sites. The options for urban dispersion and a minimum wind speed of 1 m/s were selected. The model simulations were conducted for the local stationary source emissions. The modeling results suggested that stationary source emissions do not contribute significantly to air toxics levels at the microscale monitoring sites and that, consequently, air toxics levels are dominated by mobile source emissions.

4.2.3 ARB neighborhood assessment program

The California Air Resources Board (ARB) is planning a neighborhood assessment program for air toxics. The overall goals of this program are to assess the impacts of criteria air pollutants and air toxics in communities affected by multiple emission sources and to develop guidelines for evaluating strategies aimed at reducing air pollution at the neighborhood scale. To attain these goals, the program will (1) develop and evaluate a methodology to calculate annual-average ambient concentrations of air pollutants at the neighborhood scale and (2) recommend a method to local air quality management districts to perform neighborhood assessments.

Modeling of the atmospheric fate and transport of air pollutants will be conducted at a regional scale with a spatial resolution of 4 km and at a neighborhood scale with a spatial resolution of a few hundred meters. The regional domain will cover most of southern California including the Los Angeles basin and the San Diego metropolitan area. Regional modeling will be conducted for thirty air toxics (19 VOC including benzene, 1,3-butadiene, formaldehyde and acetaldehyde; 10 trace metals and diesel PM) for the entire year 1998 with UAM-TOX and for some episodes with CMAQ. The CMAQ version to be used will include the gas-phase chemical kinetic mechanism SAPRC 99 augmented with species and reactions specific to the air toxics VOC assessed under the program.

The neighborhood-scale modeling will probably use several atmospheric dispersion models for point and area sources (ISC-ST3, AERMOD and CALPUFF) and CAL3QHCR for mobile sources. In addition, a Lagrangian particle dispersion model that is currently under development may be applied for near-field impacts.

An issue that arises when combining the results of local-scale dispersion modeling with those of regional-scale modeling is the possible double counting of local air toxic emissions. To address this problem, ARB plans to take out the local air toxics emissions from the regional-scale inventory in the case of inert species. Since taking out the local emissions of reactive species may adversely impact the accuracy of the chemistry in the regional-scale model, ARB plans at the moment to keep them in the regional-scale inventory, thereby leading to double-counting of the reactive air toxics

emissions. A better approach would be to include those emissions in the regional-scale modeling but use a methodology to correct for the double-counting of these reactive species. An alternative modeling approach would consist in developing a plume-in-grid treatment for roadway emissions; thus, fine spatial resolution would be obtained near roadways without leading to double counting of emissions since the roadway emissions would be part of the emissions inventory of the 3-D grid model. We will elaborate on such technical approaches in Phase II (Integrated Approach to Air Toxics Modeling).

Meteorological inputs for the regional modeling will be obtained from both prognostic simulations (with MM5) and diagnostic modeling (with CALMET), using data from a 10 station network of upper air data. A combination of regional upper air data and local surface data will be used for the neighborhood-scale modeling.

Emissions inventories will be developed for both regional- and local-scale modeling. Emissions of the neighborhood being studied via local-scale modeling will be removed from the regional inventory to avoid double-counting those emissions. Issues that may arise from the development of such emissions inventories are currently being considered by ARB. Such issues are discussed in Section 5.

4.3 Arizona

The Arizona Department of Environmental Quality (ADEQ) sponsored a study to estimate the public health risks associated with air toxics in four areas: two urban areas (Phoenix and Tucson), a low-desert community with a variety of sources including agriculture (Casa Grande) and a high-elevation community with a variety of sources including residential wood burning (Payson) (Heisler et al., 1995).

A 3-D atmospheric model, ADOM (see Section 2.1.1) was used to simulate the fate and transport of air toxics in three of these geographic regions (Phoenix, Tucson and Casa Grande). Because of the small spatial scale of the Payson area, available data were used directly. The horizontal resolution ranged from 2 km in Casa Grande to 4 km in Phoenix and Tucson. The simulations were conducted for an entire year using meteorological data from 1994. The simulated air toxics included several gaseous organic compounds (including benzene, 1,3-butadiene and formaldehyde). Most

simulated air toxics concentrations were within a factor of two of the observations. The model simulation results were scaled to match available measurements. The scaling was performed using spatially- and temporally-averaged values. Such calibration of model simulation results with available data is also recommended by EPA, for example, for PM modeling (EPA, 2001). Although this calibration allows one to make the most of model simulations and data, it should not be seen as a substitute for model performance evaluation and should not be carried out if model performance is judged to be unsatisfactory.

Subsequently, UAM-IV (see Section 2.1.4) was applied to the U.S./Mexico border town of Nogales. The Phoenix analysis was also extended to address diesel particulate matter using the same emissions factor and cancer unit risk factor as used in MATES-II (see Section 4.2.2); elemental carbon measurements were used as a surrogate for diesel particulate matter to scale the model results and diesel particulate emissions were patterned after those of benzene emissions.

4.4 STAPPA/ALAPCO

The State and Territorial Air Pollution Program Administrators (STAPPA) and the Association of Local Air Pollution Control Officials (ALAPCO) recently developed estimates of cancer risk due to diesel particulate matter. They estimated that for the existing U.S. population about 125,000 cancer cases would result from exposure to diesel particulate matter. However, the methodology used by STAPPA/ALAPCO is quite simplistic. They used the results of the MATES-II study conducted by SCAQMD (see Section 4.2.2) as the basis for their calculations. They assumed that diesel particulate matter levels in metropolitan areas besides Los Angeles were half those observed in Los Angeles and that those in non-metropolitan areas were 10% of those observed in Los Angeles. Next, it was assumed that 80% of the U.S. population live in metropolitan areas and that 20% live in non-metropolitan areas. The same cancer unit risk factor as used by SCAQMD was used by STAPPA/ALAPCO.

STAPPA/ALAPCO did not rely on any modeling but used instead the simplest diagnostic analysis available, i.e., a single (assumed) concentration for each metropolitan area.

Clearly, this methodology is flawed at many levels. First, such an approach should rely at least on available measurements of diesel particulate matter in several metropolitan and non-metropolitan areas. Second, corrections should be made for the time that people spent indoors. Infiltration factors for fine particulate matter are typically less than 1. For example, Vette et al. (2001) recently reported infiltration factors in the range of 0.5 to 0.9 for detached residences in Fresno, California, Abt et al. (2000) reported infiltration factors in the range of 0.38 to 0.94 for fine particles (less than 0.5 μm in diameter) for four homes in Boston, and Lang et al. (2001) reported an average infiltration factor of 0.74 for nine homes in the Boston area.

4.5 NESCAUM/LADCO

An air toxics data analysis project is currently being sponsored by the Lake Michigan Air Directors Consortium (LADCO), the Northeast States for Coordinated Air Use Management (NESCAUM) and the California Air Resources Board (ARB). A comparison of the results of the ASPEN modeling conducted by EPA with observations will be conducted. As a supplement to this program, NESCAUM intends to conduct some air toxics modeling to support the design of the monitoring network. However, no details on this modeling project are available yet.

4.6 Summary

Air toxics studies that have been completed to date can be grouped into three major categories:

- Studies that address air toxics emissions from stationary sources
- Studies that address air toxics emissions from mobile sources
- Studies that address air toxics emissions from all major outdoor sources

4.6.1 Air toxics emissions from stationary sources

The studies that address stationary sources include the EPA TRI screening assessment, the EPA electric utility study and the California AB 2588 studies. All those studies used either ISCST3 or ISC-LT to calculate the ambient outdoor air toxics concentrations. The TRI and AB 2588 studies made no correction for indoor exposure; the electric utility study used HEM-II and, therefore, accounted for indoor exposure using infiltration factors. As discussed in Section 2, there are limitations associated with ISC and the resulting uncertainties in the air toxics concentrations will directly affect the population exposure estimates.

4.6.2 Air toxics emissions from mobile sources

The EPA mobile source study, the EPA diesel particle study and the STAPPA/ALAPCO diesel particle study focused solely on mobile source emissions. The two EPA studies assumed that air toxics emitted from mobile sources were correlated with CO emissions and used CO exposure as the basis for estimating (via scaling) air toxics exposure. Indoor exposure was explicitly taken into account by means of infiltration factors. The STAPPA/ALAPCO study is highly simplistic in its methodology since it uses a single assumed concentration of diesel particles for each urban area and does not correct for indoor exposure.

4.6.3 Air toxics emissions from all major sources

The EPA integrated urban air toxics strategy, the SCAQMD MATES-II study and the ADEQ study attempted to include all major sources of urban air toxics. The EPA study so far has used ISCST3 whereas the other two studies have used 3-D air quality models, UAM-IV and ADOM (MATES II also used ISCST3 but only for local impacts from stationary sources). As discussed in Section 2.4, we do not recommend using

ISCST3 for integrated assessments that include all major source types and recommend instead the use of 3-D models.

In the ADEQ study, the modeling results were scaled to match the available air toxics ambient data, thereby combining the reliability of ambient measurements with the spatial and temporal resolution provided by a 3-D gridded model. As we mentioned in Section 2.4, we recommend this methodology to the extent that the data are available and reliable.

All these studies, however, present the same flaw: no correction was made to correct for indoor exposure. We recommend that urban air toxics exposure studies conducted with 3-D gridded models be coupled with a comprehensive exposure model such as REHEX or pNEM, so that the time spent by people indoors is properly accounted for.

4.6.4 General remarks

All air toxics studies described in this section failed to take into account the contributions from indoor sources to air toxics levels. Although it can be argued that the objective of those studies was to assess the incremental impact of outdoor emission sources on population exposure, it should be of interest to understand the relative importance of outdoor and indoor air toxics sources for population exposure.

The air toxics exposure studies discussed above rely either on emissions inventories and/or ambient measurement of air toxics or a surrogate (e.g., CO). There are uncertainties associated with those data. Those uncertainties are discussed next.

Finally, the models used for these studies have limitations. Those limitations were discussed in Sections 2 and 3. Clearly, there is a need for comprehensive evaluations of air toxics exposure models before one can have confidence in the results of such exposure studies.

5. KEY ISSUES IN AIR TOXICS MODELING

The previous sections focused on the formulation of the models used to calculate the ambient air concentrations of toxic compounds and the associated human exposure. We focus in this section on the inputs needed to conduct air toxics modeling. Such inputs include emissions, meteorology, ambient outdoor concentrations, transformations, removal, indoor sources, and population activity patterns. We address the major issues associated with each of those items below. We conclude with a summary assessment of the current status of air toxics modeling.

5.1 Emissions

Emissions are a primordial input to air toxics models, and it is essential to assess the current status of emissions inventories for air toxics. We address emissions of volatile toxics and semi-volatile/particulate toxics separately since those are typically estimated with different emission factor models.

5.1.1 Volatile Toxics

Volatile toxics include both inorganic and organic species. Inorganic volatile toxics include for example metals such as mercury (Hg) and acids such as sulfuric acid (H₂SO₄). Those inorganic volatile toxics are primarily emitted from stationary sources and their emissions are obtained typically from the National Toxics Inventory (NTI) for 1993 and 1996, and National Emission Inventory (NEI) for 1999. Volatile organic compounds (VOC) on the other hand are emitted from both mobile and stationary sources. Their emissions inventories have typically been developed for total VOC to address O₃ non-attainment issues. Chemical speciation is subsequently performed using either standard or specialized chemical profiles that are source specific. Since VOC are the most relevant to the problem at hand, we focus our discussion on VOC emissions inventories for stationary and mobile sources.

Fraser et al. (2000) simulated the atmospheric fate and transport of 125 individual VOC with a 3-D air quality model for a 2-day episode in the Los Angeles basin. In that study, emissions from stationary sources were obtained from the California South Coast Air Quality Management District (SCAQMD). On the other hand, the SCAQMD inventory for VOC emissions from mobile sources was multiplied by a factor of 3 to reflect ambient VOC measurements obtained in the Van Nuys Traffic Tunnel (Fraser et al., 1998). Such an adjustment has been used in many air quality studies, thereby suggesting that VOC emissions estimated with EMFAC7 are severely underestimated. A comparison of model simulated concentrations with measurements obtained at four locations within the Los Angeles basin was conducted for 104 VOC. The normalized gross error ranged from 0.27 for n-butane and cyclopentane to 15.5 for dehydroabietic acid. The normalized gross error was 0.5 or less for 30 VOC. The normalized gross errors for 1,3-butadiene, benzene, formaldehyde and acetaldehyde were 0.58, 0.40, 2.52 and 2.32, respectively. Thus, the concentrations of 1,3-butadiene and benzene were underestimated by about a factor of 2 whereas the concentrations of formaldehyde and acetaldehyde were overestimated by a factor of 2 to 3.

The uncertainties in the simulated ambient concentrations result from uncertainties in the emissions inventory as well as the model formulation. A species such as 1,3-butadiene will react fairly rapidly in the Los Angeles basin whereas species such as formaldehyde and acetaldehyde are both consumed and produced in the atmosphere. Benzene is not very reactive. Therefore, uncertainties associated with both the atmospheric chemical mechanism (for 1,3-butadiene and the aldehydes) and the transport processes (for benzene as well as the other species) can contribute to the uncertainties in the model results.

The local emissions inventory that was developed for the ARB Barrio Logan neighborhood assessment program provides valuable information on the uncertainties associated with stationary sources. ARB developed an emissions inventories for 30 air toxics through a comprehensive inspection of the 200 facilities located in that neighborhood. Thirty of those facilities were subject to air toxics emission reporting under the California AB 2588 rule (see Section 4.2.1). Among the facilities that were exempt from the AB 2588 rule, thirty had air quality permits. The remaining facilities

did not have any permit requirements. An inspection of a subset of permitted and non-permitted facilities was conducted to estimate their air toxic emissions. Although the “AB 2588” facilities contributed the majority of the air toxics emissions, significant amounts of air toxics emissions were attributed to permitted facilities exempt from the “AB 2588” rule (40% of toluene, 30% of perchloroethylene and 14% of methyl ethyl ketone emissions) and to facilities not subject to air emission permits (10 to 15% of methanol, toluene and naphthalene emissions).

These results suggest the following conclusions:

- Emissions of VOC from mobile sources as estimated by EMFAC7 are likely to be too low by about a factor of 3. The uncertainty associated with estimates from EMFAC2000 and MOBILE6 should be assessed.
- After correction of the VOC mobile source inventory, the simulated concentrations of toxic VOC such as 1,3-butadiene, benzene, formaldehyde and acetaldehyde were typically within a factor of 2 to 3 of the measured values.
- Emissions of VOC from stationary sources are also likely to be uncertain for some compounds.

5.1.2 Semi-volatile and particulate toxics

Semi-volatile and particulate toxics include both inorganic species such as trace metals and organic species. Anthropogenic emissions of trace metals originate primarily from stationary sources. Semi-volatile organic compounds (SVOC) and particulate organic compounds (POC) originate from both stationary and mobile sources.

Fraser et al. (2000) simulated the fate and transport of 31 POC for the two-day episode in the Los Angeles basin mentioned above. Emission sources for those POC included meat cooking operations, wood combustion, natural gas combustion, tire-wear particles, paved-road dust, gasoline-powered vehicles and diesel engines.

A comparison of model simulation results with measurements was presented for steranes and three organic acids. Although the diurnal variation of the observed

concentrations of the organic acids was not reproduced by the model, the simulated values were commensurate with the measurements. For fine carbon particle concentrations, the model showed an average bias of -44% of the mean observed value for organic carbon and -16% for black carbon. These results suggest that the black carbon emissions inventory and the simulation of the transport processes are satisfactory.

The emissions inventory developed by ARB for the Barrio Logan neighborhood assessment suggests that diesel PM emissions from stationary sources may actually be underestimated. However, the magnitude of this underestimate was not quantified.

Several studies (Norbeck et al., 1998; Whitney, 1998) have shown that emission inventory models, such as PART 5 and EMFAC 7G, consistently underestimate PM emissions from gasoline and diesel light duty vehicles. Gasoline vehicles are a relatively small source of PM compared to diesel vehicles (Gillies et al., 2001; Cadle et al., 1999) and PM from gasoline vehicles is currently not considered to be a hazardous air pollutant. Uncertainties in diesel PM mobile emissions need to be reduced for reliable source model applications.

5.2 Meteorology

Meteorological data govern the transport, dispersion and removal of air toxics and, for some toxic compounds, their partitioning between the gas and particulate phases.

For 3-D modeling of air toxics at urban and regional scales, meteorological fields are now typically prepared using prognostic meteorological models with four-dimensional data assimilation (FDDA). Reviews of meteorological modeling for air quality applications are available (Seaman, 2000; Pielke and Uliasz, 1998) and, consequently, we focus here primarily on the major issues associated with uncertainties in the meteorological outputs.

Stagnant conditions are typically conducive to air pollution because the low wind speeds lead to the accumulation of the pollutants over limited areas. Meteorological models perform best under conditions of organized flow, i.e., with moderate or high wind speeds. Under the calm conditions typical of stagnation episodes (i.e., wind speeds of the order of 1 m/s or less), the performance of meteorological models tends to degrade.

Areas with complex wind flow patterns (e.g., complex terrain, land/sea or land/lake breeze phenomena) will also inhibit the performance of meteorological models, unless a significant number of measurements are available for meteorological data at the surface and aloft.

The prediction of precipitation events is generally difficult, although meteorological models may on average predict the correct precipitation spatial patterns and amounts. Consequently, short-term concentrations of toxics that are highly soluble or easily scavenged by precipitation may be predicted incorrectly. Long-term concentrations of air toxics will also be predicted incorrectly if long-term precipitation amounts are over- or underpredicted. The use of actual precipitation data may help alleviate this potential problem, however, care must be taken when using actual data because large uncertainties are associated with such data as shown in comparisons of collocated precipitation samples.

For modeling of air toxics at regional scales, treatment of convective transport at the subgrid scale is essential since such cloud venting can greatly enhance the long-range transport and dispersion of air toxics.

For modeling of air toxics at local scales, i.e., local impacts of stationary sources or exposure to mobile source emissions near roadways, local meteorological data are preferable.

For local impacts, atmospheric dynamic processes such as plume downwash for stack plumes that are affected by the wake induced by nearby buildings and eddies generated within street canyons must be treated. We discussed the PRIME algorithm for plume downwash in Section 2.2 and the simulation of street canyon effects in Section 2.3.

5.3 Ambient Concentrations

Ambient concentrations of air toxics are needed to provide boundary conditions to urban/regional scale models and background concentrations to local scale models, and to evaluate the performance of air toxics models. Such data may be available from routine

monitoring networks as well as from special studies. We review below the main features of the major monitoring networks and special studies.

5.3.1 Routine measurement networks

5.3.1.1 PAMS network

The Photochemical Assessment Monitoring Station (PAMS) network monitors in and around cities that are not in compliance with the NAAQS for O₃. PAMS monitors measure many air toxics, including benzene, formaldehyde, and acetaldehyde. The sites monitor these toxics at different frequencies and sampling periods depending on instrumentation and choice of toxics modeled. These can range from 24 1-hour measurements every day to four 3-hour measurements every sixth day.

For an urban area designated as non-attainment for O₃, there are typically 4 to 10 stations. There are about 24 urban areas that currently have PAMS networks. Clearly, areas that are in attainment of the O₃ NAAQS are not equipped with PAMS and, consequently, it is unlikely that routine data on toxic VOC will be available unless a local network has been set up.

5.3.1.2 PM Speciation Network

The Particulate Matter (PM) speciation network was mandated to provide monitoring data to assess the attainment status of urban areas for the PM_{2.5} and PM₁₀ NAAQS. It includes also some stations that are located in non-urban areas in order to provide data on the regional aspects of PM transport.

PM stations measure both PM_{2.5} and PM₁₀ using the Federal Reference Method (FRM) (see McMurry, 2000 for a discussion of the FRM). These particulate measurements are then speciated. The metallic speciation covers all metals. However, the toxicity of some metals, such as chromium (Cr) and nickel (Ni), depends on their valence state (Cr(VI) is carcinogenic whereas Cr(III) is not) or speciation (different toxicities are assigned by EPA to Ni carbonyl, Ni refinery dust, Ni₃S₂ and Ni soluble

salts). The detection limit for the metals is typically in the range of 2 to a few ng m⁻³. Such a detection limit is too high for the most toxic metals. For example, a detection limit of 2.4 ng/m³ for arsenic leads to a corresponding incremental cancer risk in excess of ten per million. Risks are typically considered to become significant within the range of 1 per million to 100 per million. For example, under State of California law, risks in excess of 10 per million trigger the requirement to warn the public. It would be best to develop measurement protocols with detection limits that are consistent with the guidelines for public health risk assessment (Seigneur et al., 1995).

Measurement frequency and sampling period vary depending on location. At urban locations, samples are typically taken with shorter averaging times than at rural sites. Most measurements take place over 24-hours every sixth day.

5.3.1.3 Texas CATMoN

The Texas Community Air Toxic Monitoring Network (CATMoN) consists of 45 monitoring sites located mainly in urban areas. It has operated since 1993. Measurements are 24-hour samples of non-polar VOC collected every 6th day. In addition, aldehydes are measured at 5 PAMS locations in Houston, El Paso and Dallas.

5.3.2 Special studies

Several special studies have been conducted for O₃ and PM assessments that may provide some data on volatile and particulate air toxics. We provide below summaries of some of the major special studies.

5.3.2.1 Arizona HAP research program

The Arizona Department of Environmental Quality (ADEQ) and the Arizona Department of Health Services conducted a research program to evaluate the existing risk to public health in Arizona related to hazardous air pollutants (HAP) (see summary in Section 4.3). Four sampling sites were established in Phoenix, Tucson, Payson, and Casa

Grande to represent typical communities in Arizona. In addition, a background site was chosen at Hillside. Sampling at the community sites was carried out for one year starting in Spring 1994 on a 6-day sampling schedule. All samples were collected over 24 hours and analyzed for 73 VOC compounds (including 1,3-butadiene and benzene), 13 aldehydes (including formaldehyde and acetaldehyde), and semi-volatile and particulate compounds. A source chemical speciation profile was developed for diesel exhaust.

5.3.2.2 SCOS

The Southern California Ozone Study (SCOS) was conducted in the California South Coast Air Basin (SoCAB) in 1997. It focused primarily on O₃ but also included some PM measurements. Measurements of VOC and speciated PM_{2.5} and PM₁₀ are available at eight locations in the SoCAB. During six intensive operational periods, four 3-hour measurements of hydrocarbons (including benzene and 1,3-butadiene) and carbonyls (including formaldehyde and acetaldehyde) were taken at 18 sites. Additional 12-hour samples were taken at three background/offshore sites. Speciated PM_{2.5} measurements (including elemental carbon (EC), organic carbon (OC), sulfate, nitrate, ammonium, and trace elements) were obtained at 6 sites during several PM episodes for special studies. Only one monitor routinely supplemented 24-hour data on trace elemental composition of PM_{2.5} every sixth day.

5.3.2.3 NFRAQS

The Northern Front Range Air Quality Study (NFRAQS) (<http://www.nfraqs.colostate.edu>) consisted of three field campaigns conducted in the Denver area during winter 1996, summer 1996 and winter 1997. NFRAQS included semi-volatile OC measurements as well as PM measurements. There were three core sites, where 6-hour or 12-hour filter pack samples were taken for PM_{2.5} mass and chemistry (up to three samples per day). Six satellite sites measure 24-hour average concentrations of PM_{2.5} and composition. For NFRAQS, the detection limits, calculated

as 3 times the standard deviation of the field blanks, range from 1 ng m⁻³ for Ni to 7 ng m⁻³ for Cd.

5.3.2.4 MATES-II

The Multiple Air Toxics Exposure Study-II (MATES-II) that was summarized in Section 4.2.2) included measurements of air toxics at ten monitoring sites within the Los Angeles basin from April 1998 to March 1999 (some sites started monitoring as late as July 1998). The species monitored included nineteen VOC (including benzene, 1,3-butadiene, formaldehyde and acetaldehyde), thirteen trace metals, polycyclic aromatic hydrocarbons (PAH), black carbon and particulate organic carbon. 1,3-Butadiene was calculated to contribute between 24 and 37% of the cancer risk (excluding diesel PM); benzene between 22 and 27%, and aldehydes between 7 and 12%, depending on the site. The detection limits were in the range of 0.07 to 3.5 µg/m³ for VOC, and 0.001 to 0.003 µg/m³ for trace metals (0.00006 µg/m³ for hexavalent Cr). It should be noted that the detection limits for some trace metals are too high. For example, a detection limit of 0.003 µg/m³ for arsenic leads to a corresponding cancer risk in excess of ten per million (1.3×10^{-5}) and a detection limit of 0.001 µg/m³ for cadmium leads to a corresponding cancer risk of 1.8×10^{-6} ; 95 to 100% of arsenic samples and 99% of cadmium samples were below detection limits. The risks to public health cannot be dismissed or verified without more sensitive measurements.

5.3.2.5 CCOS

The Central California Ozone Study (CCOS) was conducted in the Central Valley of California during September 2000. Measurements of VOC (including benzene, 1,3-butadiene, formaldehyde and acetaldehyde) were conducted at 11 Type 1 Supplemental sites (Type S1), five Type 2 Supplemental sites (Type S2) and three research (Type R) sites. Four 3-hour average VOC samples were taken per day. Data are available for 15 days during the study period.

5.3.2.6 CRPAQS

The California Regional PM Air Quality Study (CRPAQS) was conducted in the Central Valley of California from December 1999 through January 2001. Measurements included primarily PM_{2.5} speciation although some speciated PM₁₀ measurements were also taken. VOC measurements included light (e.g., benzene, 1,3-butadiene) and heavy hydrocarbons, and aldehydes (e.g., formaldehyde and acetaldehyde) at 4 locations during 15 winter episode days. The time resolution for the VOC were 5 to 8 hours, 4 samples per day. In addition, some 24-hour samples of hydrocarbons were available at these sites during the winter study period.

5.3.2.7 TexAQS 2000

The Texas Air Quality Study (TexAQS) was conducted in eastern Texas, Oklahoma, Arkansas and Louisiana during August and September 2000. VOC and speciated PM measurements were conducted at 4 “level three” sites, including one on top of a skyscraper.

5.4 Transformations of Air Toxics

It may be appropriate to assume that some air toxics are chemically inert; however, it is necessary for the modeling of many air toxics to take into account their atmospheric chemical transformations to ensure that their atmospheric impacts are properly characterized. Moreover, some air toxics may be present in both the gas phase and the particulate phase. Since gases will typically have deposition velocities that differ from those of particles, it is also important to characterize the gas/particle partitioning of those air toxics. We discuss the atmospheric transformations of major air toxic categories below.

5.4.1 VOC

Many VOC are involved in the formation of O₃ and consequently their atmospheric chemistry has been studied and chemical kinetic mechanisms have been developed to describe their atmospheric oxidation. However, chemical mechanisms that have been included in most air quality models do not treat individual molecules (with a few exceptions such as formaldehyde) but instead use simplifying representations based either on functional groups (e.g., Carbon Bond Mechanism) or surrogate molecules (e.g., SAPRC mechanisms, RADM2, RACM, CACM). It is, however, necessary when addressing the atmospheric fate of air toxics to incorporate the atmospheric chemistry of individual air toxics into the air quality model.

Fraser et al. (2000) incorporated a detailed chemical kinetic mechanism for about 120 individual VOC into the 3-D CIT model. ARB is planning to use SAPRC 99 with detailed mechanisms for the 19 air toxics to be investigated under their neighborhood assessment program. Such approaches will need to be used when assessing air toxics impacts.

One issue that must be addressed in the atmospheric chemistry of air toxics is the source of secondary chemical species such as formaldehyde and acetaldehyde. Such species may be emitted directly into the atmosphere or produced via oxidation of other VOC from anthropogenic or biogenic origins. It is desirable to identify the origin (i.e., anthropogenic vs. biogenic) of such species in air quality modeling, for example, by tagging the secondary species of biogenic origin within the chemical kinetic mechanism.

5.4.2 SVOC

In the case of SVOC, both chemical transformations and gas/particle conversion must be taken into account (e.g., Franklin et al., 2000). For SVOC such as PCDD/F, PCB and PAH, the reactions of interest are oxidation by OH radicals. Partitioning between the gas and particulate phases can be treated either as an adsorption or absorption process (Cousins and Mackay, 2001). Some measurements suggest that adsorption on soot particles may prevail in urban areas but absorption into aged aerosols

may become the dominant process in rural areas (Dachs and Eisenreich, 2000). The light SVOC tend to have a significant fraction in the gas phase whereas the heavier SVOC can be assumed to be totally in the particulate phase.

5.4.3 Trace metals

Most trace metals can be treated as chemically inert since their toxicity is not listed as a function of their chemical speciation. Exceptions include nickel (Ni) which has different cancer slope factors for different species and chromium (Cr) which is considered to be carcinogenic if hexavalent but non-carcinogenic if trivalent. Also, the chemical speciation of mercury significantly affects its atmospheric lifetime and, therefore, the zone of influence of its emission sources. Chemical kinetic mechanisms have been developed for Cr (Seigneur and Constantinou, 1995) and Hg (Lin and Pehkonen, 1999; Ryaboshapko et al., 2001). Such mechanisms should be considered for incorporation into air quality models when addressing the potential impacts of those species.

5.4.4 Non-metallic inorganic species

Species such as HCl, HF and Cl₂ are considered to be air toxics. Cl₂ is highly reactive in the atmosphere. It dissociates rapidly in the presence of sunlight and can contribute to significant O₃ formation. Experimental results from TexAQS 2000 suggest, for example, that in the Houston area Cl₂ may play a major role in O₃ formation. Clearly, Cl₂ should be included in the chemical kinetic mechanisms of air quality models if Cl₂ emissions are found to be important for the area of interest. HCl and HF may also be involved in atmospheric chemical reactions, however, it is generally appropriate to assume that they retain their integrity.

5.5 Removal of Air Toxics

Air toxics can be removed from the atmosphere via dry and wet deposition processes. Indoor, dry deposition on surfaces can be significant for some air toxics.

Most deposition studies have focused on criteria pollutants (e.g., O₃, SO₂) or acid deposition (e.g., sulfate and nitrate species). There are few experimental data available for the deposition of air toxics such as VOC, SVOC and particulate-bound chemicals. As a result, modeling of air toxics must rely on default values that may have large associated uncertainties.

For example, the treatment of dry deposition of VOC in Models-3/CMAQ uses distinct deposition velocities for (1) aldehydes, (2) acids and (3) peroxyacetylnitrate, but assumes no dry deposition for aromatics, paraffins and olefins. Dry deposition of particles is a strong function of particle size and the particle size distributions of particulate bound toxics are uncertain since few data are available.

The treatment of wet deposition for volatile chemicals is typically based on the calculation of the gas/liquid partitioning of the chemicals (e.g., using the effective Henry's law constant). Removal of particles by wet deposition is more problematic because it depends on the activation of particles into cloud or fog droplets, the collision of particles with existing cloud or fog droplets and, below clouds, the scavenging of particles by precipitation.

For example, in Models-3/CMAQ, it is assumed that nearly all particles activate into cloud droplets. Such an assumption may overestimate the actual number of particles that actually activate.

Deposition processes are unlikely to be important at local scales and, in the absence of precipitation, even at urban scales for most organic toxics. However, at regional scales, deposition processes need to be properly treated. This is particularly important for those air toxics that have long chemical lifetimes since removal processes will then govern their atmospheric lifetime. For example, benzene may be removed from the atmosphere to a large extent by dry deposition since its chemical half-life is a few days and it is only slightly soluble in water. Also, diesel PM will be removed via dry and wet processes since it is considered to be chemically inert. Therefore, experimental data

are needed for the dry deposition of those VOC that have long chemical half-lives (e.g., greater than one week) and for the size distribution of those particulate-bound air toxics.

5.6 Indoor Sources

Many air toxics studies address population exposure in a multicompartamental environment (i.e., taking into account time spent indoor), however; the indoor sources of air toxics are often ignored. For some chemicals, indoor concentrations are dominated by outdoor sources. Such chemicals may include, for example, 1,3-butadiene, diesel PM and, in the homes of non-smokers, benzene (e.g., Cocheo et al., 2000). In the homes of smokers, however, benzene can account for a substantial fraction of the indoor concentrations (up to 40% according to Heavner et al., 1992). For some other chemicals, indoor sources dominate the indoor environment. This is the case, for example, for aldehydes that can be both emitted from indoor materials and produced by the oxidation of VOC indoor. The ratio of indoor to outdoor concentrations of formaldehyde has been reported to be in the range of 6 to 7 (Reiss et al., 1995; Zhang et al., 1994).

Consequently, it is essential to include indoor sources of those chemicals for which indoor concentrations are significantly affected by such sources.

5.7 Population Activity Patterns

The calculation of population exposure requires knowledge of population activity patterns. As discussed in Section 3.2, the most desirable approach should take into account the movement of population cohorts among various microenvironments and also within various spatial areas of the study domain. Such information has been developed in the United States for several cities such as Los Angeles and Houston. However, such information on movement of the population within the study domain is not available for most cities.

Activity patterns of population cohorts have also significant uncertainties. In areas that have been thoroughly studied such as Los Angeles (Wiley et al., 1991a), such activity patterns are probably reasonably reliable. However, activity patterns may vary

significantly by region and uncertainties in this critical exposure model input may be significant outside the areas for which they have been developed.

5.8 Status of Air Toxics Modeling

To date, most air toxics modeling studies have fallen into two categories: (1) modeling studies for outdoor air toxics concentrations and (2) modeling studies of population exposure to air toxics. Among the modeling studies of outdoor air toxic concentrations, some studies used advanced 3-D air quality models which are best suited for regional- and urban-scale impacts whereas others used Gaussian dispersion models which are best suited for local impacts. Among the population exposure modeling studies, some used ambient data whereas others used the results of a model simulation for the air toxics concentrations. Also, some population exposure studies used simplifying assumptions such as outdoor exposure and a static population whereas others used advanced representations of a dynamic population moving through microenvironments and within the study area.

This review of the studies performed to date suggests that there has been no study yet that combines a comprehensive treatment of outdoor air toxics modeling at all scales of interest (i.e., regional, urban and local) with a comprehensive treatment of population exposure that takes into count population dynamics and air toxics concentrations in indoor microenvironments. The design of such an approach will be developed under Phase II of this project.

Once a suitable modeling approach has been satisfactorily evaluated with ambient data, the model(s) can be used to attribute air toxics concentrations to various individual sources or source categories. Several approaches have been used to perform source attribution. For example, in the regional modeling of mercury, one model, REMSAD, has been applied with several tracer mercury species assigned to distinct source categories whereas another model, TEAM, has been applied using several simulations with distinct source categories turned off. Both approaches are viable although the use of tracer species may become cumbersome when simulating chemicals species with nonlinear chemistry. Sensitivity analysis is another approach that can be used for source

attribution; however, it has not been applied to air toxics modeling to date. Recommendations for source attribution techniques will be provided under Phase II of this project.

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**INTEGRATED APPROACH TO
AIR TOXICS MODELING**

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EXECUTIVE SUMMARY

Under Phase I of this project, we presented a review of the current status of air toxics modeling, discussed the major weaknesses identified in air toxics modeling studies, and provided some initial recommendations (Seigneur et al., 2001a). Here, we elaborate on those recommendations and present our proposed integrated approach to air toxics modeling. We also use case studies to address two major issues in air toxics modeling: (1) the ability of air quality models to simulate air toxics concentrations at regional scales and (2) the importance to taking into account indoor concentrations when estimating population exposure. Benzene and diesel particles were selected for these case studies. These air toxics are emitted from mobile sources as well as from other source categories. On-road mobile sources account for about 80% and 40% of benzene and diesel particle emissions, respectively, in the eastern United States.

E.1 Integrated Approach to Air Toxics Modeling

Because there are some large uncertainties associated with air toxics modeling, we recommend an overall approach that combines source modeling and receptor modeling. Large uncertainties in emission rates may significantly limit the use of source modeling for some primary species (i.e., those species that are directly emitted into the atmosphere). Receptor modeling techniques do not rely on emission rates (although some techniques require emission speciation profiles) and can, therefore, be used to provide quantitative information for primary species. Receptor modeling techniques can also be used, to some extent, for source attribution of secondary species (i.e., those species that are formed in the atmosphere) but source models are typically better suited to address secondary species. Because source models can in theory address all species over a variety of spatial and temporal scales, we recommend that source modeling be used as the backbone of our integrated approach. We recommend receptor modeling as a complementary approach that can be used to either corroborate source modeling results or palliate deficiencies in source modeling.

This integrated approach is based on the concept of multi-scale modeling with modeling domains possibly ranging from the globe to the local scale. Global modeling is required for air toxics with atmospheric lifetimes on the order of one month or more. Local modeling is needed to characterize the near-source impacts of emissions from major point sources, some major stationary area sources and mobile vehicles. In addition, it is essential to characterize the indoor concentrations of air toxics because (1) most people spend the majority of their time indoor and (2) indoor concentrations can differ significantly from outdoor concentrations. Because air toxics include a large number of compounds that have widely different atmospheric lifetimes, the specific modeling needs are likely to differ from one air toxics to the next.

E.2 Case Studies – Regional Modeling of Outdoor Concentrations

As discussed in the Phase I report, most air toxics modeling studies conducted to date have not addressed the regional component of air toxics concentrations properly except for some specific air toxics known to have global impacts (e.g., mercury).

The Community Multiscale Air Quality model (CMAQ) was used here for regional modeling. CMAQ was modified to simulate the atmospheric fate and transport of benzene and diesel particles. We simulated the 11-15 July 1995 episode over a domain covering the eastern United States with a 12 km horizontal resolution and a finer (4 km) resolution over a part of the northeastern United States that includes Washington, D.C. and New York City. The meteorological fields were obtained from an MM5 simulation conducted earlier. Gridded inventories of benzene and diesel particle emissions were developed using SMOKE.

The results of the model simulations showed that benzene concentrations were commensurate with available measurements. Over the 4 km resolution domain, a comparison between simulated and measured concentrations showed a fractional error of 0.44, a fractional bias of 0.15 and a coefficient of determination (r^2) of 0.25. A comparison between benzene concentrations in New York City and in Brigantine National Wildlife Refuge, NJ, showed that the urban concentrations were greater than the remote area concentrations by a factor of two to five.

The results of the diesel particle simulations showed spatial and temporal patterns that were similar to those obtained for benzene. However, because of the lesser contribution of on-road mobile sources to diesel particle emissions compared to benzene emissions, diesel particle concentrations showed stronger gradients between urban areas and remote areas. A comparison between diesel particle concentrations in New York City and in Brigantine National Wildlife Refuge, NJ, showed that the urban concentrations were greater than the remote area concentrations by a factor of two to ten. Assuming that diesel particles consist of 50% “elemental” carbon (EC), the simulated EC concentrations were in close agreement (within 10%) with the measured concentration in the urban area (Washington, D.C.), but were significantly lower than the measured EC concentrations in the remote areas. This result suggests that other sources beside diesel fuel engines contribute to atmospheric EC concentrations and that EC may not be a good surrogate for diesel particles.

E.3 Case Studies – Indoor Concentrations

Simulations of indoor concentrations were conducted for New York City. The results of the regional simulations with 4 km horizontal resolution were used to represent the outdoor concentrations. Three major types of indoor environments were simulated: a home, an office and a car. For benzene, environments with and without environmental tobacco smoke (ETS) were simulated since smoking is a significant source of benzene. A probabilistic approach was used to account for the variability and uncertainties associated with many of the input parameters (outdoor concentration, indoor volume, surface/volume ratio, air change rate, indoor removal rate and indoor emission rate).

The results of the simulations showed that indoor concentrations can differ significantly from the outdoor concentrations. On average, the indoor/outdoor concentration ratio is less than one for benzene in the absence of ETS (mean values of 0.87, 0.88 and 0.99 for homes, offices and cars, respectively) and for diesel particles (mean values of 0.75, 0.22 and 0.90 for homes, offices and cars, respectively). The lower values for the indoor/outdoor concentration ratios of diesel particles result from the fact that the particles can be removed more efficiently by filters and deposit more on indoor

surfaces than benzene. Note that the indoor/outdoor concentration ratio can be greater than one for a given hour because of the variability in outdoor concentrations and the lag time between the indoor and outdoor concentrations. It is greater than one for benzene in the presence of ETS (mean values of 1.06, 2.63 and 1.88 for homes, offices and cars, respectively).

These results strongly suggest that it is imperative to include the simulation of indoor micro-environments when estimating population exposure to air toxics.

E.4 Recommendations

The case studies presented here provide an initial application of our modeling approach. Further applications should focus on the following areas:

- Other air toxics, such as formaldehyde and 1,3-butadiene, should be modeled and model results should be compared to observations.
- Local modeling should be conducted to evaluate the relative contributions of urban/regional sources and local sources (e.g., roadways) in urban environments.
- A comparison of source attributions conducted with source modeling (as presented in the two case studies) and receptor modeling is recommended.

1. INTRODUCTION

Under Phase I of this project, we presented a review of the current status of air toxics modeling, discussed the major weaknesses identified in air toxics modeling studies, and provided some initial recommendations (Seigneur et al., 2001a). Here, we elaborate on those recommendations and present our proposed integrated approach to air toxics modeling. Furthermore, we present case studies for air toxics modeling that address two major issues: (1) the ability of air quality models to simulate air toxics concentrations at regional scales and (2) the importance to taking into account indoor concentrations when estimating population exposure.

Because there are some large uncertainties associated with air toxics modeling, we propose an overall approach that combines source modeling and receptor modeling. As discussed by Seigneur et al. (1999), large uncertainties in emission rates may significantly limit the use of source modeling for some primary species (i.e., those species that are directly emitted into the atmosphere). Receptor modeling techniques do not rely on emission rates (although some techniques require emission speciation profiles) and can, therefore, be used to provide quantitative information for primary species. Receptor modeling techniques can also be used, to some extent, for source attribution of secondary species (i.e., those species that are formed in the atmosphere) but source models are typically better suited to address secondary species. Because source models can in theory address all species over a variety of spatial and temporal scales, we use source modeling as the backbone of our integrated approach. We recommend receptor modeling as a complementary approach that can be used to either corroborate source modeling results or palliate deficiencies in source modeling.

The description of our approach to air toxics modeling addresses the treatment of various spatial and temporal scales, and the formulation of the relevant processes (i.e., transport processes, atmospheric transformations, and deposition processes). Next, we discuss the need for comprehensive model performance evaluations and how to conduct source attribution. Receptor modeling is discussed as a means of conducting source attribution.

The case studies focus on two air toxics that are emitted from mobile sources among other sources: benzene and diesel particles. As discussed in the Phase I report, most air toxics modeling studies conducted to date have not properly addressed the regional component of air toxics concentrations for some specific air toxics known to have global impacts (e.g., mercury). Moreover, a common weakness of most air toxics modeling studies is the lack of treatment of indoor concentrations. Consequently, our case studies address these two specific elements of the integrated approach.

2. CHEMICAL TRANSPORT MODELING FOR AIR TOXICS

The modeling of the atmospheric fate and transport of air toxics with chemical transport models (CTM) requires the consideration of several issues including spatial and temporal scales, and the formulation of the CTMs to simulate the relevant processes. We describe our recommendations regarding those issues below.

2.1 Spatial Scales

Air toxics comprise a myriad of chemical species that can be either primary (e.g., benzene, diesel particles, 1,3-butadiene) or both primary and secondary (e.g., formaldehyde). Some of those chemical species have a short atmospheric lifetime (e.g., 1,3-butadiene has a half-life on the order of a few hours in a polluted urban atmosphere), whereas others have a long atmospheric lifetime (e.g., benzene has a half-life on the order of several days). Consequently, some chemical species will have impacts at urban scales and other species will have impacts that can range from urban to regional and even global scales. Moreover, concentrations of air toxics near their source of emissions will greatly exceed their typical urban or regional concentrations, thereby requiring the ability to simulate such local impacts. It is, therefore, necessary to consider a modeling approach that spans a wide range of geographical scales from local to urban, regional, continental and global scales. In addition, a proper treatment of population exposure requires simulating air toxics concentrations in distinct microenvironments. Figure 2-1 depicts the overall hierarchy of models that may be required to provide a comprehensive description of the atmospheric fate and transport of air toxics. Clearly, the simulation of specific air toxics may not require the full range of geographical scales and this generic conceptual approach needs to be tailored for specific applications.

In the approach presented in Figure 2-1, the global model is used to provide the boundary conditions to the continental model. Similarly, the continental model will provide the boundary conditions to the regional model, which then provides the boundary conditions to the urban model. This nested grid approach has been used routinely for O₃ modeling and, more recently, for PM and mercury modeling. For example, Jacobson

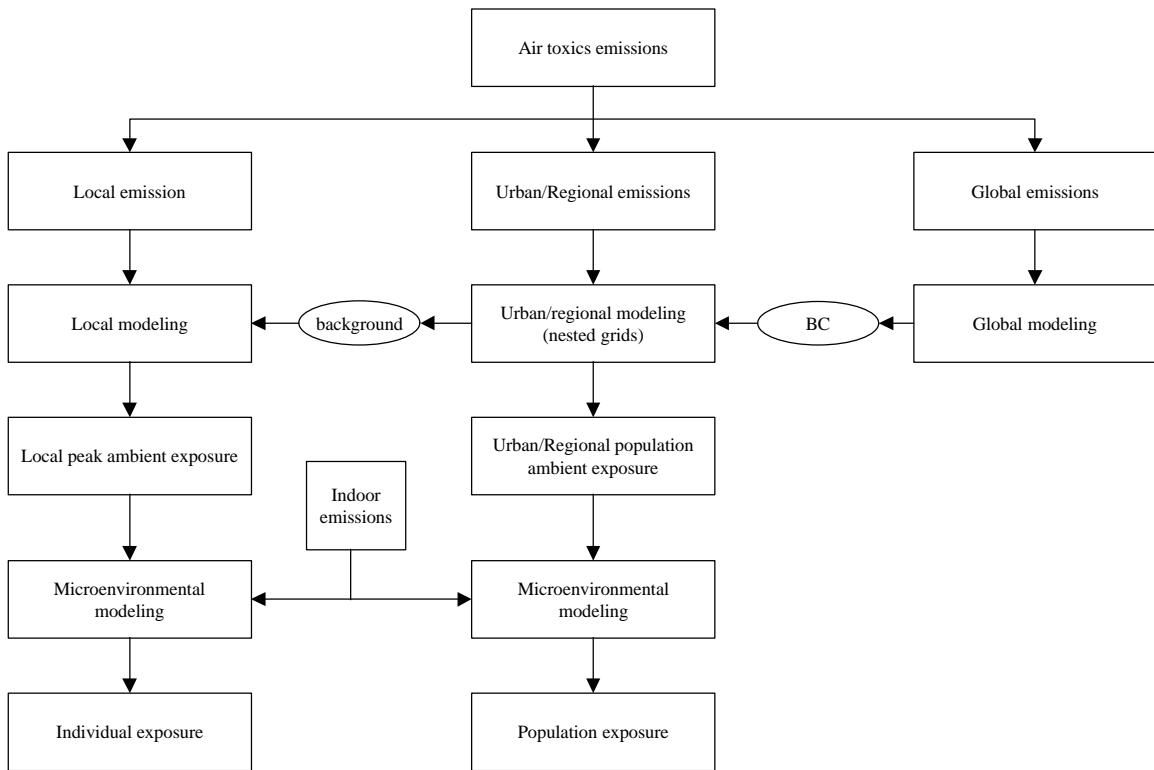


Figure 2-1. Integrated approach to air toxics modeling.

(2001) used the same model, GATOR, for O₃ simulations ranging from the global scale to a regional scale (California) and an urban scale (San Francisco Bay Area). For mercury, Seigneur et al. (2001b, 2002a) used one model for the global scale and another model for the continental scale (North America) and regional scale (midwestern and northeastern U.S.).

Nested domains have not been used down to local scales, because models suitable for local impacts are typically based on plume or puff algorithms rather than grid representations. In theory, two approaches are possible. In one approach, the local chemical transport model (CTM) is applied to simulate the impact of local emission sources using the regional/urban grid model to provide the background concentrations. In another approach, the local CTM is imbedded within the formulation of the 3-D regional/urban grid model. We discuss each of these approaches below.

In the first approach, the local CTM simulation results are obtained separately from those of the regional/urban model and it is, therefore, necessary to combine the results of the two simulations to obtain the contributions of the local and regional/urban sources to concentrations in the local-scale domain. Care must, therefore, be taken not to double-count emissions from the local-scale domain. For inert air toxics, it suffices to remove from the urban/regional simulation those emissions that are included in the local simulation. Thus, when combining the results of the two simulations, there will be no double-counting of those emissions. For reactive air toxics, this approach is not suitable because removing the local reactive emissions from the urban/regional simulation will affect the chemical concentrations of species simulated at the urban/regional scale. It is, therefore, necessary to have an approach that will maintain the integrity of the chemical reactivity of the local emissions in the urban/regional simulation but will avoid double-counting those emissions in the local and urban/regional simulations. The following approach will meet these requirements. First, it is necessary to keep those reactive local emissions in the urban/regional simulation so that they can participate in the relevant chemical transformations. Adding surrogate inert species for the local emissions to the urban/regional simulations will provide the required information on the concentrations of those species in the urban/regional simulation, if they did not react. When combining urban/regional and local impacts, the surrogate inert concentrations can be subtracted

from the concentrations predicted in the urban/regional simulation to obtain the representative “background” concentrations of these species. The representative “background” concentration is then added to the results of the local simulation to generate the total concentration. Thus, there is no double-counting since the contribution of the inert surrogate species in the urban/regional simulation corresponds to their contribution in the local simulation. This approach maintains the integrity of the chemical transformations in the urban/regional simulation while avoiding double-counting the contribution of those emissions when combining the local and urban/regional simulations. We assumed in the above approach that these emissions were treated as inert in the local simulation which in most cases is an appropriate assumption because the small local scales limit the time available for chemical reaction. If the emissions are treated as reactive in the local simulation (e.g., with a first-order decay rate), then the surrogate species simply need to be treated with the same reactivity in the urban/regional simulation.

In the second approach, the local CTM is imbedded within the 3-D urban/regional model to treat the local emissions at the subgrid scale. Such an approach is currently used, for example, in (1) the simulation of the plumes from large point sources (Karamchandani et al., 2001) and (2) the simulation of the local effects of roadway emissions in street canyons on O₃, NO and NO₂ concentrations (Stern and Yamartino, 2001). However, there has been to date no application of subgrid-scale treatments to air toxics modeling. This approach is technically more sound than the previous one because the local emissions are then treated within the 3-D gridded host model using local-scale transport and dispersion algorithms; thus, there is no double-counting of the local emissions and their local impacts are appropriately represented by the subgrid-scale algorithm.

Microenvironmental modeling is the finest spatial scale to be used in air toxics modeling. A microenvironmental model will take air toxic concentrations predicted by an urban/regional CTM or a local dispersion model as input of outdoor concentrations. Since indoor emissions are not included in emission inventories for ambient modeling of air toxics, these indoor emissions will not be double-counted and no adjustment is needed when conducting the microenvironmental modeling.

2.2 Temporal Scales

Air toxics may lead to health effects through chronic (long-term) or acute (short-term) exposure. Chronic exposure generally refers to a period of exposure that can be of several weeks (generally referred to as subchronic) up to several years or decades (e.g., lifetime exposure). Acute exposure refers to exposure that is generally less than a day and typically of one to a few hours. For carcinogenic effects, acute exposure is generally not considered because typical ambient concentrations of carcinogenic chemical species do not lead to significant cancer risk unless exposure times are on the order of several months or years. For non-carcinogenic health effects, the threshold is significantly greater for acute exposure than for chronic exposure. Consequently, for air toxics modeling, both chronic and acute exposure scenarios must be considered.

For air toxics modeling conducted at global, continental, regional and urban scales, air toxics concentrations are sufficiently low that acute exposure is unlikely to be an issue and only chronic exposure needs to be considered. For local impacts, acute exposure may in some cases be an issue and exposure to maximum concentrations for short time periods (e.g., one hour) may need to be considered. Therefore, the temporal scales to be considered for air toxics modeling are as follows:

- For all spatial scales (see Section 2.1), long-term modeling must be conducted to calculate chronic exposure. The simulation period must be at least one full year in order to encompass all seasonal variations. Ideally, it should extend over several years to take into account the interannual variability of meteorology.
- For local impacts, some short-term modeling may need to be conducted to calculate acute exposure. The short-term time averaging should typically be of one hour when considering ambient air pollution (shorter time periods may be relevant for accidental releases of toxic chemicals; however, accidental releases are outside the scope of the present project).

Long-term modeling can be a challenging task because of the computational resources that can be associated with the simulations of long periods. Long-term modeling has been conducted using a single year that is assumed to be representative of a typical meteorology, or multiple years that can account for the variability of meteorology among several years.

Modeling with 3-D grid models at scales ranging from urban to global is conducted generally for a single year. There are, however, two possible approaches: (1) using a specific year or (2) constructing a synthetic year by aggregating meteorological episodes. The first approach offers the advantage of using actual meteorology for an entire year; however, it may not be representative of the meteorology over several years. The second approach presents the possible shortcoming of not using an actual meteorology for an entire year; however, the aggregation of meteorological episodes with weighting factors that correspond to their frequency allows the representation of multi-year meteorology. Such an aggregation technique can be a powerful approach as long as the number of episodes considered is statistically sufficient to capture the relevant features of the meteorology. For example, Cohn et al. (2001) calculated that 20 meteorological episodes were sufficient to represent the meteorological characteristics relevant to atmospheric visibility degradation. Thus, although modeling of a large number of episodes with aggregation can be nearly as computationally demanding as modeling an entire year, it offers the advantage of simulating conditions that are more representative of a multi-year meteorology.

Modeling of local impacts is conducted with plume or puff models that are significantly less demanding computationally than 3-D models. Therefore, it is feasible to simulate several years to ensure that the meteorology is representative of long-term conditions. For example, modeling with ISC-ST under the California air toxics program AB 2588 (see Seigneur et al., 2001a) requires three to five years of meteorological data. However, long-term modeling can also be conducted with plume models using long-term frequencies of meteorological conditions. For example, Venkatram and Seigneur (1993) recommended using ISC-LT for modeling the long-term impacts of air toxic emissions; ISC-LT uses meteorological frequencies of wind speed and wind direction, and stability category as well as average mixing heights by stability category and wind speed category,

and ambient temperature by stability category, which is conceptually similar to constructing a synthetic year via episode aggregation as discussed above. It must be noted, however, that a model such as ISC-LT is not compatible with population activity patterns that include diurnal and seasonal profiles.

2.3 Transport and Dispersion Processes

Transport and dispersion processes are treated differently depending on the geographical scales of interest.

2.3.1 Global-scale modeling

For air toxics that have atmospheric lifetimes that exceed several days, global scale modeling may be required. Transport processes treated in global-scale models represent mainly the synoptic aspects of meteorological transport. Issues of particular interest are interhemispheric transport and vertical transport within the troposphere and between the troposphere and the stratosphere. Interhemispheric transport must be represented properly to reflect the limited mixing that occurs between the northern and southern hemispheres. Vertical transport is also essential as it is a primary means of transport for pollutants from the planetary boundary layer to the free troposphere and eventually to the stratosphere. Transport across latitudes may occur more efficiently in the upper troposphere (e.g., Hadley cells) than in the boundary layer. Consequently, vertical motions must be properly represented within a global distribution of air toxics with long lifetimes.

Transport processes in global-scale models have been evaluated against data. For example, Jacob et al. (1987) tested interhemispheric transport in global CTM using krypton as a tracer and Jacob and Prather (1990) evaluated convective transport using radon. Recent simulations of the global cycle of an air toxic with a 1-year atmospheric lifetime, mercury, showed that the major spatial patterns of global concentrations were well reproduced (Seigneur et al., 2001b).

2.3.2 Continental/regional-scale modeling

For continental/regional-scale modeling, transport processes such as advection, vertical turbulent diffusion and subgrid-scale convective mixing dominate. Horizontal turbulent diffusion is sometimes treated in continental/regional models, however, it can generally be neglected because it tends to be small in comparison to other processes, including numerical diffusion associated with the solution of the advective transport equations.

Several techniques have been used to solve the advective transport equations that represent the transport of pollutants with the mean wind flow. Such techniques include finite difference techniques, semi-Lagrangian techniques and finite element techniques. In an Eulerian system, the solution of the advection equation involves some numerical diffusion. Numerical diffusion results in the spreading of peak values across neighboring grid cells. For example, emissions from a large point source will typically spread more rapidly in a gridded model than in reality because of such numerical diffusion. This artificial phenomenon can be minimized by using a smaller grid size (but at the expense of increased computations) and by using numerical techniques designed to reduce the numerical diffusion. Oscillations may also appear in the solution of the advection equation and numerical techniques must also minimize such oscillations.

Vertical turbulent diffusion needs to be parameterized. Currently, the three major approaches used in 3-D CTMs include first-order K-diffusion algorithms, turbulent kinetic energy (TKE) algorithms, and asymmetric convective mixing algorithms. Figure 2-2 depicts the conceptual approaches of these algorithms.

Subgrid-scale convective mixing is particularly important in continental/regional scale modeling because the vertical air motions induced by convective cumulus clouds are typically not resolved at the spatial resolution of those models. Such cloud venting can transport pollutants from the boundary layer to the free troposphere where higher wind speeds and possibly different wind directions can transport those pollutants over long distances before they are brought back toward the surface.

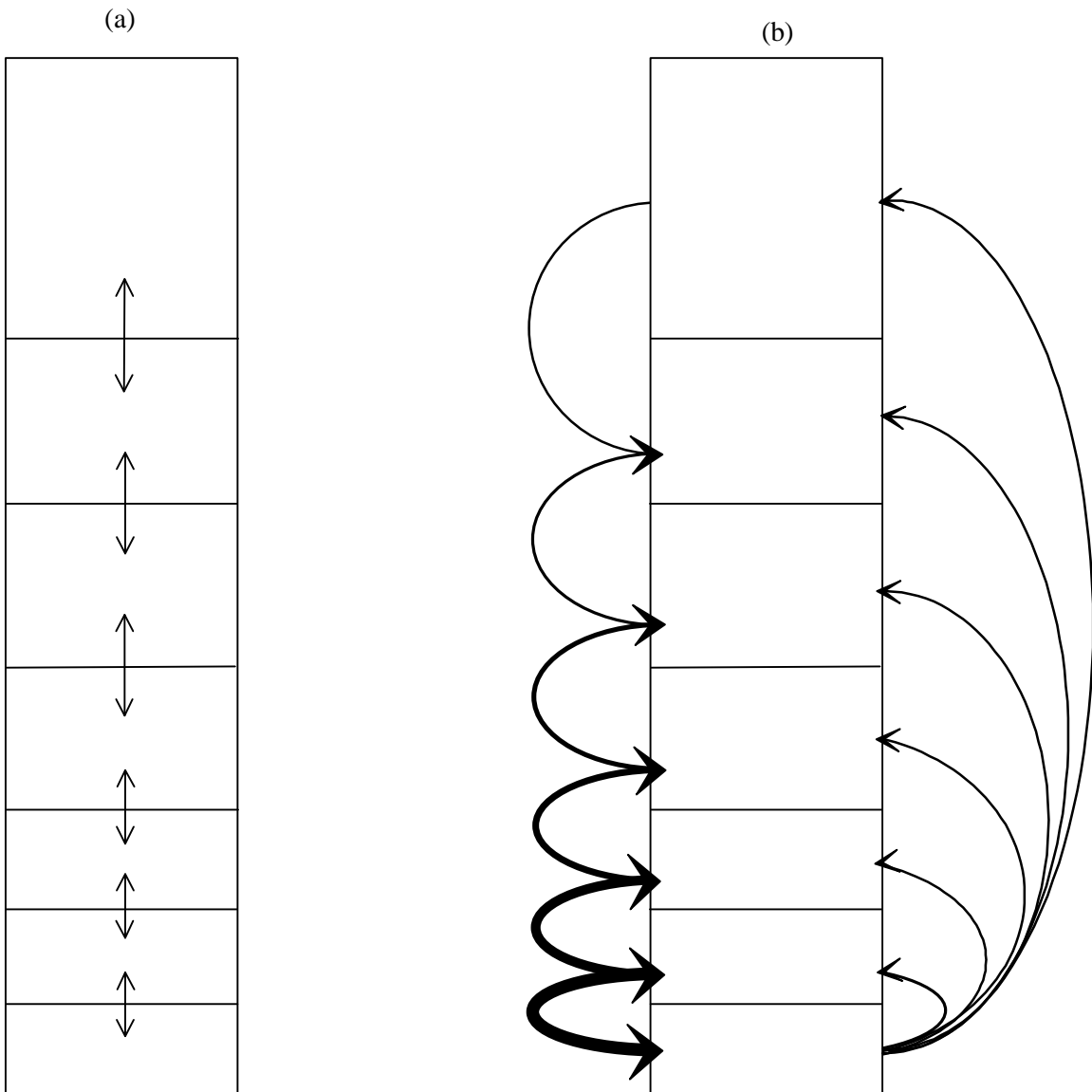


Figure 2-2. Schematic description of the (a) K-diffusion and Turbulent Kinetic Energy approaches and (b) the Asymmetric Convective Mixing approach.

2.3.3 Urban-scale modeling

The processes treated in urban scale models are generally similar to those treated in continental/regional scale models. Some differences may however exist because some urban scale models are designed for finer spatial resolution (typically 4 to 5 km) than continental/regional scale models (typically, 10 to 100 km).

Some urban-scale models have been designed for photochemical smog simulations that are generally associated with clear sky conditions; thus, cloud processes are not treated and subgrid-scale convective mixing is not simulated. Horizontal turbulent diffusion is more often simulated in urban-scale models than in continental/regional-scale models because of the finer spatial resolution of the former.

For air toxics, a nested configuration of regional/urban-scale models is likely to be necessary. Therefore, we recommend that the same model be used for all scales, to the extent possible. Thus, processes such as advective transport, vertical turbulent diffusion and subgrid-scale convective mixing will be treated with the same algorithms from the urban to the continental scale.

2.3.4 Local-scale modeling

For the local impacts of air toxics, the simulation of transport processes must focus on the near-source dispersion processes of plumes or puffs released from stationary sources and mobile sources.

For stationary sources, most air toxics applications to date have used the Gaussian plume dispersion model ISC. However, the formulation of dispersion processes in ISC is now outdated and more recent models such as AERMOD or SCIPUFF/SCICHEM should be used (see Seigneur et al., 2001a). These models use more advanced algorithms to simulate atmospheric dispersion and, consequently, lead to better performance when compared to ambient data (Sykes et al., 1993).

For mobile sources, three models were reviewed under Phase I (Seigneur et al., 2001a), including CALINE, STREET and HYROAD. Among those models, STREET is based on a more advanced treatment of atmospheric dispersion in a complex environment

since it uses concentration fields precalculated by a computational fluid dynamics model. However, no comparison exists of performance among STREET and the other two Gaussian-based models, CALINE and HYROAD. We recommend that such a comparative evaluation be conducted.

2.3.5 Microenvironmental exposure

We reviewed in Phase 1 (Seigneur et al., 2001a) the various models available to estimate population exposure to air toxics. A major conclusion was that indoor exposure must be taken into account because most people spend the majority of their time indoors. The simplest approaches to account for this indoor exposure consist in using empirical indoor/outdoor concentration ratios or penetration efficiencies to scale outdoor concentrations to indoor concentrations. Although such an approach is a definite improvement over the use of outdoor concentrations, it does not reflect the dynamics of indoor concentrations. Therefore, we recommend the use of a dynamic model that accounts for the temporal evolution of indoor concentrations with microenvironments. Such a dynamic approach also allows one to take into account indoor sources of air toxics which can be significant for some air toxics such as aldehydes.

2.4 Atmospheric Transformations

Chemical transformations and gas/particle conversion may affect air toxics concentrations significantly. Consequently, they must be treated explicitly in the models for those air toxics that are chemically reactive, formed in the atmosphere and /or semi-volatile.

2.4.1 Chemical transformations

Under Phase I, the chemical transformations that are relevant to air toxics were reviewed (Seigneur et al., 2001a). These transformations include the oxidation reactions of VOC that have atmospheric half-lives of a few minutes (e.g., formaldehyde), hours

(e.g., 1,3-butadiene) or days (e.g., benzene, dioxins, and PAHs); the production of VOC that are listed as air toxics (e.g., formaldehyde, acetaldehyde, pentachlorophenol); the reduction and oxidation reactions of some trace metals such as chromium and mercury; and the reactions of some gaseous inorganic gases (e.g., Cl₂).

The half-lives of the reactions can be used to identify at which geographical scales the chemical transformations must be considered. For example, it is appropriate to neglect chemical transformations in local-scale modeling (i.e., within a few kilometers from the source) since the relevant transport times will be on the order of one hour or less. Although some air toxics may undergo significant reaction even in such short time periods (e.g., formaldehyde), the local-scale modeling will provide an upper bound to local concentrations.

Chemical kinetic mechanisms have been developed to simulate chemical transformations of most air toxics. However, they have been incorporated to date only in a few CTMs. Under the ARB neighborhood assessment program, a detailed mechanism for 19 VOC that are listed as air toxics is being incorporated into two CTMs, UAM and Models-3/CMAQ.

2.4.2 Gas/particle conversion

Several air toxics are semi-volatile, that is, they can be converted from a gaseous compound to a particulate compound and vice-versa. Such conversions are important because they may affect the chemical reactivity of the compound and its rate of removal from the atmosphere since dry and wet deposition rates typically differ for gases and particles.

Semi-volatile air toxics include, for example, dioxins and furans, PCBs and PAHs. Several algorithms have been developed to characterize their gas/particle partitioning. The major algorithms are based either on adsorption or absorption theories (Cousins and Mackay, 2001). Table 2-1 presents the major adsorption and absorption algorithms. Although adsorption may be important in urban areas where concentrations of fresh particles are high, absorption is currently the preferred algorithm used in CTMs. For absorption, the gas/particle partitioning can be calculated using either the subcooled

Table 2-1. Major models of gas/particle partitioning of organic species (ϕ is fraction of organic species in particulate phase). (Source: Seigneur, 2001).

Process	Mathematical Relationship	Parameters
Vapor saturation	$\phi = \text{Max} \left(\frac{P_o - P_s}{P_o} \right); 0$	P_o : partial pressure of chemical before partitioning P_s : saturation vapor pressure
Adsorption	$\phi = \left(\frac{K_{ad} S}{1 + K_{ad} S} \right)$	K_{ad} : adsorption equilibrium parameter (cm^3/cm^2); S : surface area concentration of PM (cm^2/cm^3)
Absorption	$\phi = \left(\frac{K_{ab} C_{om}}{1 + K_{ab} C_{om}} \right)$	K_{ab} : absorption equilibrium parameter ($\text{m}^3/\mu\text{g}$); C_{om} : organic PM concentration ($\mu\text{g}/\text{m}^3$)
Dissolution	$\phi = \left(\frac{H_e \text{LWC}}{1 + H_e \text{LWC}} \right)$	H_e : effective Henry's law parameter of chemical (m^3/L); LWC : liquid water content of PM (L/m^3)

liquid vapor pressure or the octanol/air partition coefficient. This area of research is evolving relatively rapidly and new advances (e.g., the possible importance of adsorption in urban areas) should be reflected in the formulation of CTMs as they become available.

Both adsorption and absorption algorithms require knowledge of aerosol characteristics; the particle surface areas for adsorption and the particulate organic matter concentration for absorption. Such characteristics can be specified as fixed inputs in the gas/particle partition algorithm. A better approach, however, consists in using a CTM that simulates these aerosol characteristics as a function of space and time so that the gas/particle partitioning of the semi-volatile air toxics can take into account this variability.

2.5 Deposition Processes

Removal of air toxics from the atmosphere can occur via chemical reaction (see above), dry deposition to surfaces and wet deposition.

2.5.1 Dry deposition

Dry deposition in 3-D CTMs is represented according to the resistance transfer theory. The lower part of the atmosphere is assumed to consist of three layers that act as resistances to the dry deposition process. First, pollutants are brought near the surface via turbulent mixing. Such a process is a function of the dynamics of the atmosphere and does not depend on the properties of the trace pollutant. Near the surface, pollutants are transported into contact with the surface via a mass transfer process in a quasi-laminar flow. This Brownian diffusion process depends on the properties of the gases (molecular weight) or particles (size) and the local characteristics of the air near the surface (temperature, density). Finally, pollutants are removed at the surface according to their physico-chemical characteristics (such as solubility and reactivity) and the properties of the surface (e.g., wet surface). In addition, gravitational settling (also referred to as sedimentation) needs to be simulated for particles, although this process is more important for coarse particles than fine particles. The dry deposition velocity of gases is

calculated as the inverse of the three resistances in series (i.e., aerodynamic, quasi-laminar boundary layer and surface resistances). For particles, the sedimentation term is added to the deposition velocity (Venkatram and Pleim, 1999). Particle size affects both the sedimentation term and the diffusion process in the laminar sublayer.

Currently, there are large uncertainties regarding the deposition of air toxics. For example, most experimental data available on dry deposition velocities are for inorganic gases, such as O₃, SO₂, HNO₃ and NO₂. There are few data available for organic compounds and default deposition parameters must be used in CTMs. As discussed in the Phase 1 report, the dry deposition velocity of some air toxics (e.g., toluene, xylene, benzene, 1,3-butadiene) is assumed to be zero in some CTMs. Although such an assumption may be justified for compounds that are highly reactive (i.e., they will be removed significantly faster via chemical degradation than via deposition), it may not be appropriate for compounds that have low reactivity and can be transported at regional scales (e.g., benzene).

For particles, the size distribution influences the rate of dry deposition. However, there is very little information on the size distribution of particulate air toxics. For example, Lohman and Seigneur (2001) reviewed the literature for the size distribution of emissions and ambient concentrations of dioxin/furan particles. They identified some very limited data sets and had to make assumptions for the particle size distribution of dioxin/furan emissions for most source categories. Experimental data are needed for the particle size distributions associated with air toxics such as dioxins, PAHs, PCBs and trace metals. In the absence of such data, a default particle size distribution must be assumed. Lohman and Seigneur (2001) showed that such default assumptions can lead to significant uncertainties in the predictions of air toxics concentrations and deposition fluxes. Dry deposition of gases and particles indoors may be a significant sink for air toxics and it should be taken into account in the microenvironmental model.

2.5.2 Wet deposition

Wet deposition includes in-cloud scavenging of gases and particles by droplets (rainout) and below-cloud scavenging of gases and particles by raindrops (washout).

Many 3-D grid-based CTMs include cloud and precipitation processes. Wet deposition of gases is treated according to their solubility. Wet deposition of particles depends on their size distribution, which is sometimes taken into account in the CTM algorithms.

Wet deposition for most organic air toxics, however, is not treated explicitly in CTMs, except for the model development done under the ARB neighborhood assessment program. Therefore, it will be necessary to modify the formulation of CTMs to account for the wet deposition of individual air toxics. To that end, it is necessary to know the gas/droplet partitioning of gaseous air toxics (i.e., Henry's law coefficient) and the particle size distribution associated with particulate air toxics.

2.6 Initial and Boundary Conditions

Initial and boundary conditions (IC/BC) must be defined based on available data and/or professional judgment. These IC/BC can, in some cases, have great influence on model simulation results and we discuss their treatment for air toxics modeling accordingly.

2.6.1 Initial conditions

For long-term modeling of air toxics, the influence of initial conditions can easily be minimized by using a spin-up period that allows enough time to flush this initial material out of the modeling domain. The spin-up period depends on the size of the domain and the meteorological conditions. For 3-D grid-based modeling at the urban scale, two spin-up days are typically used. For continental-scale domains, up to a week may be necessary, whereas for regional-scale domains, two to five days may be required depending on the wind flow. Global-scale modeling typically balances sources and sinks and simulations are conducted until a global steady state is achieved; thus, initial conditions have no effect. For local-scale modeling, the initial conditions are typically set to zero.

For short-term modeling, we are interested in the incremental impacts of local sources and initial conditions can be set to zero or, if warranted, to background conditions.

2.6.2 Boundary conditions

The influence of boundary conditions can be significant on concentrations of some air toxics within the domain. For continental to urban-scale modeling, the concentrations of air toxics at the inflow boundaries may dominate the concentrations within the domain if the air toxic has an atmospheric lifetime commensurate with or greater than its residence time within the domain and emissions and/or formation within the domain are commensurate or less than the incoming mass. For example, regional simulations over the Nashville/western Tennessee domain (400 km x 260 km) and a northeastern United States domain (540 km x 396 km) have shown that O₃ and PM_{2.5} concentrations were dominated by the boundary conditions (Pun et al., 2001).

The selection of the boundary conditions is challenging because data at the surface are generally sparse for air toxics and are non-existent aloft. Professional judgment can palliate to some extent the paucity of data but one must recognize that large uncertainties are likely to be associated with the boundary conditions. A sensitivity simulation should be conducted to assess quantitatively the influence of the boundary conditions. If the boundary conditions are deemed to be influential on air toxics concentrations within the domain, one of two approaches should be implemented: (1) upper and lower bounds should be used for those boundary conditions in two simulations that will consequently bracket the problem or (2) the boundary conditions should be obtained from a simulation conducted over a larger domain nesting the domain of interest.

For local-scale modeling, the boundary conditions are replaced by the background concentrations. Those background concentrations are provided by the urban-scale model according to the integrated modeling approach described in Section 2.1.

For microenvironmental modeling, the boundary conditions consist of the outdoor concentrations calculated by either the urban/regional-scale model or the local-scale model.

2.7 Emissions

Emission inventories suitable for atmospheric modeling are typically not available. Nationwide inventories are developed by EPA. The National Toxics Inventories (NTI) have now been replaced by the National Emission Inventories (NEI), which now include both air toxics and criteria pollutants. Point sources are grouped into two categories: major point sources (i.e., those that emit more than 10 tons/yr of a single air toxic or more than 25 tons/yr of several air toxics) and emission point sources (i.e., those that emit less than the above thresholds). Minor point sources are treated within the area source category. For major point sources, data are obtained from a variety of sources including information on sources subject to Maximum Achievable Control Technology (MACT) and Section 129 of the Clean Air Act, information from the Toxic Release Inventory (TRI) and other information provided by industry. For area sources, EPA has generated information for 30 source categories. For mobile sources, EPA now uses the Mobile 6 emission model to estimate air toxics emissions. The spatial resolution for area and mobile sources is on a county level whereas major point sources are characterized with their exact location.

Some state or local air quality agencies have developed air toxics emission inventories for their own air toxics management programs. Such examples include the State of Arizona and the California South Coast Air Quality Management District. However, such air toxics programs are rare and there is a need for an integrated approach that will provide air toxics emission inventories for the entire United States using a coherent approach. Such inventories should provide measures of uncertainties associated with them.

In order to characterize the current status of air toxics emission inventories in the United States, we provide below several case studies that cover a wide range of air toxics

including inorganic gaseous and particulate compounds, and organic gaseous, semi-volatile and particulate compounds.

2.7.1 Inorganic gaseous air toxics: Mercury

Mercury (Hg) is present in the atmosphere primarily in gaseous form, either as elemental or divalent Hg. It was identified as an air toxic requiring a special study under Section 112 of the Clean Air Act Amendments of 1990. Consequently, EPA developed an inventory for anthropogenic emissions of Hg within the United States (EPA, 1997). The electric utility industry, which is a major source category for Hg emissions, developed its own emission inventory in parallel under the sponsorship of EPRI (Pai et al., 2000; Seigneur et al., 2001b). Although there are some differences between the EPA and EPRI emission inventories, these two inventories are in general agreement regarding the total anthropogenic emissions, the major source categories, and to some extent, the chemical speciation of the Hg emissions. Similar inventories have been developed for Canada under the sponsorship of Environment Canada (Deslauriers, 2001) and EPRI (Pai et al., 2000; Seigneur et al., 2001b). Global emission inventories have also been developed (GEIA, 2000; Seigneur et al., 2001b) but large uncertainties are associated with emissions from countries outside the United States, Canada and Europe.

2.7.2 Inorganic particulate air toxics: Chromium

Chromium is present in the atmosphere in particulate form, either in hexavalent, Cr(VI), or trivalent, Cr(III), state. Only Cr(VI) is believed to be carcinogenic. Therefore, an emission inventory for chromium must include speciation according to Cr(VI) and Cr(III).

Chromium emissions fall into two categories: direct and indirect. Direct emissions refer to those from intentional uses of chromium such as in refining or chromium plating. Indirect emissions are those where chromium is released because it is contained in the feedstock or fuel of the facility's primary function such as municipal waste incineration or coal burning.

The NEI provides a national inventory for chromium compounds. However, these values are not speciated into Cr(III) and Cr(VI). Additionally, a few states and regional groups include chromium in their toxics inventories (e.g., California Toxics Inventory and the Great Lakes Regional Toxics Emission Inventory).

2.7.3 Volatile organic compound: Benzene

Benzene is considered to be a human carcinogen. It is listed as a hazardous air pollutant in Section 112 of the 1990 Clean Air Act Amendments (CAAA). Benzene is ubiquitously emitted from mobile sources, area sources, and point sources, because of its presence in transportation fuels and its key use as a solvent.

EPA developed the 1996 National Toxics Inventory (NTI) during the implementation of Section 112 of the CAAA. Data for NTI were obtained from state and local inventories, existing data bases relating to the Maximum Achievable Control Technology programs, the Toxic Release Inventory, and EPA estimates of mobile and area source emissions. Benzene is one of the top emitted pollutants in each of the mobile, area, and point source inventories.

2.7.4 Semi-volatile organic compound: Dioxins

Polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans (hereafter referred to as dioxins for brevity) are considered to be carcinogenic if chlorine atoms are located in positions 2, 3, 7 and 8 on the carbon rings. Dioxins are associated with emissions of combustion products where chlorinated compounds were in the input stream. Major source categories include municipal waste combustors, medical waste incinerators, secondary copper smelters, cement kilns, and sinter plants. Power plants and diesel vehicles are minor source categories of dioxins.

Two distinct emission inventories currently exist at EPA. One inventory has been compiled by the Office of Air Quality Planning and Standards (OAQPS) based on information made available by the states. The other inventory was developed by the Office of Research and Development (ORD) using technical information available on the

various source categories. There are significant differences between these two inventories and, at the moment, EPA does not recommend either of those inventories. Rather, EPA is working on the development of a new single inventory for the year 1999 that will bring consensus among the various entities involved in the inventory development. However, such an inventory is still under development.

2.7.5 Particulate carbonaceous compounds: Diesel particles

Diesel particles consist of a mixture of elemental carbon (black carbon), organic compounds and some inorganic compounds such as sulfate. Carbonaceous compounds constitute the majority of diesel particle mass (e.g., Shi et al., 2000). They are emitted for diesel fuel powered vehicles as well as from a variety of stationary combustion sources operated with diesel fuel.

Diesel-fueled engines are used in every category of on-road vehicles except motorcycles, including light to heavy-duty trucks, buses, and passenger vehicles. Off-road equipment fueled by diesel includes categories of construction, agriculture, airport ground support, transportation refrigeration, lawn and garden, marine vessels, locomotives, etc. Stationary sources include diesel power generators, pumps, and other engines used in compressors, cranes, and similar equipment.

While diesel PM is recognized by EPA as a hazardous air pollutant, it is not included in the current version of NTI. No official diesel PM inventory was identified, although a California inventory was compiled by the California Air Resources Board in support of its diesel PM risk reduction plan (ARB, 2000). However, since the current methodology for emission source categorization relies on the type of fuel as a descriptor, a reasonable diesel PM inventory can be generated by compiling PM_{2.5} emissions from combustion sources that burn diesel fuel.

2.8 Model Performance Evaluation

2.8.1 Data needs

Before a CTM for air toxics can be applied to estimate population exposure or to conduct source attribution, it is necessary to evaluate the performance of the model by comparing the model simulation results to available data. To that end, it is essential to have comprehensive data bases of the major air toxics of interest with sufficient temporal and spatial resolutions.

We reviewed in Phase I the major available data bases of ambient air toxics concentrations in the United States (Seigneur et al., 2001a). Most of those data bases do not focus on air toxics but on other pollutants (e.g., VOC are measured as precursors of O₃ in non-attainment areas; trace metals are measured as components of PM). Therefore, the spatial and temporal coverage, speciation, and detection limits of those measurements are generally not consistent with the needs of air toxics modeling.

The ambient monitoring of air toxics should take their toxicity into account since the ultimate objective is the quantitative assessment of public health risks. That is, priority must be given to those air toxics that contribute most to public health risks, either because of carcinogenic or noncarcinogenic health effects. Such compounds include, at current ambient concentrations in urban areas, benzene, 1,3-butadiene, formaldehyde, diesel particles, some chlorinated organic compounds such as dioxins/furans, carbon tetrachloride and perchloroethylene, some PAHs, and some heavy metals such as hexavalent chromium, arsenic, and cadmium. Other compounds should be included if large emission sources of other air toxics are identified in specific areas. The detection limits of measurements must be consistent with the toxicity of the individual compounds measured; that is, the detection limit should be sufficiently low that a non-detected concentration will lead to a carcinogenic risk less than one per million and a non-carcinogenic hazard quotient less than unity (Seigneur et al., 1995).

Currently, VOC are measured in urban areas that are in non-attainment of the O₃ National Ambient Air Quality Standard and in a few other areas that have special networks (e.g., Texas). Measurements of those VOC that may dominate public health

risks (see above) should be conducted in a larger number of urban areas and with better spatial and temporal resolution than currently provided by most Photochemical Assessment Monitoring Stations (PAMS) networks. Temporal resolution must be sufficient to allow the reconstruction of annual average concentrations with acceptable statistical significance. Spatial resolution must provide enough information on “hot spots” (e.g., near heavy traffic areas, near industrial areas) and in “urban background” locations. Then, the CTMs can be evaluated for their ability to calculate ambient air toxics concentrations over a wide range of conditions.

Most trace metals are measured as part of PM measurements. Such measurements provide some temporal resolution although daily resolution is certainly desirable. However, the spatial resolution may not focus on air toxics “hot spots” since those may not be relevant to PM concentrations (e.g., high concentrations of arsenic or hexavalent chromium near an industrial area may not necessarily correspond to high PM concentrations). Detection limits for most toxic trace metals are typically not low enough for public health risk assessment and, therefore, need to be revised accordingly (see Seigneur et al., 2001a).

Some air toxics are transported over long distances and non-urban measurements are needed to evaluate the performance of regional, continental and global models.

Measurements are typically scarce for SVOC such as dioxins/furans, PCB, and PAH. Such compounds are transported over long distances and measurements are required in both urban areas near their emission sources where their concentrations may be high and in remote areas where they may be transported to sensitive receptors. Measurements for dioxins, PCB and PAH must include gas and particle concentrations of the lighter compounds because those compounds can partition between the gas and particulate phases. For dioxins and PCB, measurements of all relevant congeners are required.

Although diesel particles are now considered toxic by EPA, they cannot be measured directly in the ambient atmosphere because the composition of diesel particles varies with sources. Furthermore, coagulation with other particles and condensation of secondary compounds (sulfate, nitrate, organic compounds) on their surface change the characteristics of diesel PM away from its source. Elemental carbon has been used as an

indicator for diesel particles. It may be an appropriate indicator for urban areas where diesel emissions dominate but it may be a misleading indicator in areas that are significantly affected by other sources of elemental carbon (e.g., biomass burning).

2.8.2 Performance evaluation

The performance evaluation of CTMs should follow the same general protocol as used for O₃ CTMs (EPA, 1991) or recommended for PM_{2.5} CTMs (EPA, 2001; Seigneur et al., 2000). For the models used for local impacts, the performance evaluation should follow those recommended for plume models (e.g., EPA) or for roadway models (e.g., Benson, 1992).

Statistical measures recommended include the normalized bias of the peak concentration (paired in space but not necessarily in time), normalized bias and error for all concentrations above a certain threshold, fractional bias and error for all concentrations above a certain threshold, and correlation statistics (e.g., coefficient of determination, r^2).

Graphical displays of time series and spatial patterns should also be used to depict the model performance in terms of temporal and spatial characteristics, respectively.

2.9 Source Attribution

Following a satisfactory performance evaluation of the air toxics model(s), the model(s) can be applied to quantitatively estimate which sources contribute most to air toxics concentrations (and, subsequently, exposure and potential health effects). Several approaches are available to perform source attribution.

2.9.1 Model calibration

Once the performance of a model has been judged satisfactory, it is appropriate to calibrate the model simulation results with the available data. If more than one air toxics is modeled, it is likely that the outcome of the source attribution procedure will involve

weighting the air toxics concentrations by their toxicities (i.e., cancer slope factor, unit risk factor, reference dose or reference concentration). Therefore, it is desirable to reduce the uncertainties associated with the model predictions since different air toxics are likely to have different uncertainties (e.g., overestimate vs. underestimate). However, one must emphasize that scaling model predictions to observations should not be a substitute for model performance evaluation and should only be performed if model performance results are judged to be acceptable.

Such model calibration has been recommended by EPA (2001) for PM_{2.5} and regional haze modeling. It is, therefore, a well-accepted technique in the regulatory context.

2.9.2 Tracers

One approach to conducting source attribution is to use tracers that are specific to individual sources or source categories. For inert species, this technique is straightforward as the tracer is conserved between its emission sources and the receptor (some fraction is of course removed by dry and wet deposition processes). For reactive species, the tracer species must be subject to the same chemical reactions as the air toxics of interest and the computational burden may be significant particularly for non-linear chemistry.

The use of tracers has been applied, for example, to mercury modeling over the contiguous United States. Four source categories were represented with individual tracers. At a given receptor site, those tracers can then be used to quantify the contribution of each of the corresponding source categories to the air toxics concentration or deposition at that receptor.

One must emphasize that the use of tracers requires careful validation of the model computer code to ensure that the tracers mimic exactly the behavior of the air toxics species.

2.9.3 Individual sensitivity simulations

Another approach that is commonly used consists in conducting model simulations without a given source or source category. For inert air toxics and air toxics with linear chemistry, such an approach provides the contribution of that source category to a given receptor by subtracting the results of the sensitivity simulation from those of the base case simulation. For example Seigneur et al. (2002b) used this approach for mercury, an air toxics species with linear chemistry. For air toxics that are involved in nonlinear chemistry, one must note that there is no unique solution. For example, different contributions will be obtained if the sensitivity simulation is conducted without the source category of interest or with only that source category (whereas the same contribution will be obtained for an inert air toxics or an air toxics with linear chemistry). In the case of air toxics with nonlinear chemistry, it is then recommended to bound the problem by conducting the two simulations just mentioned. For example, Pun et al. (2001) used this bounding approach to estimate the contribution of biogenic compounds to O₃ and PM_{2.5} concentrations.

2.9.4 Sensitivity analysis

An alternative approach consists in applying sensitivity analysis techniques to the CTM. Such sensitivity analysis techniques include, for example, variational methods, the direct method, the Green's function method and stochastic methods. Among those, the direct method has been the most commonly applied to 3-D CTMs. The decoupled direct method (Dunker, 1981), a version of the direct method, has been applied to several O₃ simulations and could similarly be applied to air toxics simulations. The same restrictions as mentioned above will apply to air toxics that are affected by nonlinear chemistry, i.e., the contribution of a source category will depend on the extent of the perturbation. Since the typical application of the direct method is for first-order, it applies to small perturbations and will deviate from the exact solution for significant perturbations (in the case of previous applications to O₃, about 30 to 40% changes from nominal values).

2.9.5 Receptor modeling

Receptor modeling techniques use quantitative information on ambient concentrations and, for some techniques, emission sources profiles to attribute concentrations at a receptor to specific source categories. We differentiate among two major categories (Seigneur et al., 1999):

- Techniques such as chemical mass balance (CMB) that rely on source emission profiles
- Factor analysis techniques that do not require source emission profiles; however, they require a large number of ambient data

In addition, those techniques can be combined with back-trajectories to provide information on the geographical areas where the contributing sources are located. Techniques that combine back-trajectories with CMB or factor analysis techniques are referred to as hybrid techniques and include, for example, potential source contribution function (PSCF) and residence time analysis (RTA).

Receptor modeling has been applied to particulate inorganic compounds (see Seigneur et al., 1998 for a recent review), particulate organic compounds (e.g., Schauer and Cass, 2000) and VOC (e.g., Henry et al., 1997; Fujita et al., 1994, 1995).

Receptor modeling is particularly useful to corroborate results of CTMs source attributions. CTM results are directly affected by uncertainties in emission inventories whereas receptor modeling techniques do not depend on absolute estimates of emissions (CMB requires source profiles but not emission levels). Thus, receptor modeling can complement or even supplement CTMs in many applications.

3. CASE STUDY – OUTDOOR CONCENTRATIONS OF BENZENE AND DIESEL PARTICLES

We present in this section a case study for two air toxics that are emitted by motor vehicles among other sources. These two air toxics are benzene and diesel particles. Benzene is a VOC which has low reactivity. It is oxidized in the atmosphere slowly by hydroxyl (OH) radicals; its atmospheric lifetime is on the order of one week. Diesel particles are emitted from diesel engines with a particle size distribution that is centered around 0.1 to 0.4 μm in diameter (Shi and Harrison, 1999; Kleeman et al., 2000). These fine particles coagulate and are subjected to condensation of secondary aerosols (sulfate, nitrate, ammonium, organic compounds) and grow into the accumulation mode (i.e., in the range of 0.1 to 1 μm in diameter) as they age. The composition of diesel particles is variable. It consists primarily of carbonaceous compounds with “elemental” carbon (EC) typically accounting for 25 to 60% (Norbeck et al., 1998; Whitney, 1998; Schauer et al., 1999; Cadle et al., 1999; Shi et al., 2000), with estimates ranging from 5 to 90% (Moosmüller et al., 2001) and “organic” carbon (OC) typically accounting for 20 to 50% (Schauer et al., 1999; Shi et al., 2000) of total mass. Sulfate and nitrate may account for up to 12% and 4%, respectively, of total mass (Shi et al., 2000).

We simulate a five-day episode, 11-15 July 1995, over the northeastern United States using a three-dimensional (3-D) air quality model, the EPA Community Multiscale Air Quality model (CMAQ). First, we describe the episode and the modeling domain. Then, we discuss the development of the gridded emission inventories. Next, we present the modifications made to CMAQ to simulate benzene and diesel particles. Finally, we describe the model simulations and compare the simulation results with available data.

3.1 Description of the Episode

During the July 11 to 15 episode, there was a synoptic scale midtropospheric flow with a westerly component across the Appalachian Mountains. In the leeward side of the mountains, air sank and warmed, creating the mesoscale Appalachian lee trough. Winds ahead of the trough turned cyclonically and flowed in a south-southwesterly direction up

the urban corridor. Having a marine origin, this air remained slightly cooler than the air to the west of the Appalachian Mountains. The result was a shallow boundary layer capped by hot midwestern air mass at middle levels. Nocturnal jets may have also played a role in long-range transport of pollution up the coast.

The modeling domain consists of two nested grids as shown in Figure 3-1. The outer domain has a horizontal resolution of 12 km and the inner domain has a horizontal resolution of 4 km. The vertical resolution consists of 13 layers with finer resolution near the ground.

The full five-day episode (ending July 15 00 GMT) was simulated in the 12-km domain, while the 4-km simulation commence on July 12, using results from the 12-km simulation as boundary and initial conditions. Results from the last three simulation days were analyzed.

3.2 Emission Inventories

3.2.1 Benzene

The 1996 EPA National Toxics Inventory (NTI) was used as the basis for the development of the gridded emission inventory. The year 1996 was the year closest to 1995 for which an emission inventory was available. NTI is an annual inventory with a county-based spatial resolution. To develop gridded emission inventories with 12 km and 4 km spatial resolution and a 1-hour temporal resolution, we used the Sparse Matrix Operative Kernel Emission model (SMOKE).

The emissions from 30 states and the District of Columbia were used for the modeling domain considered here (some states were only partially contained within the domain). The breakdown of this emission inventory by major source categories is summarized in Table 3-1. On-road motor vehicles represent a large percentage (~80%) of the inventory. Point sources represent a small fraction (about 4%) of the total benzene emissions. Benzene emissions are lower on weekends (314 tons/day) than weekdays (341 tons/day), i.e., a 7.9% decrease from a typical weekday to a weekend day.

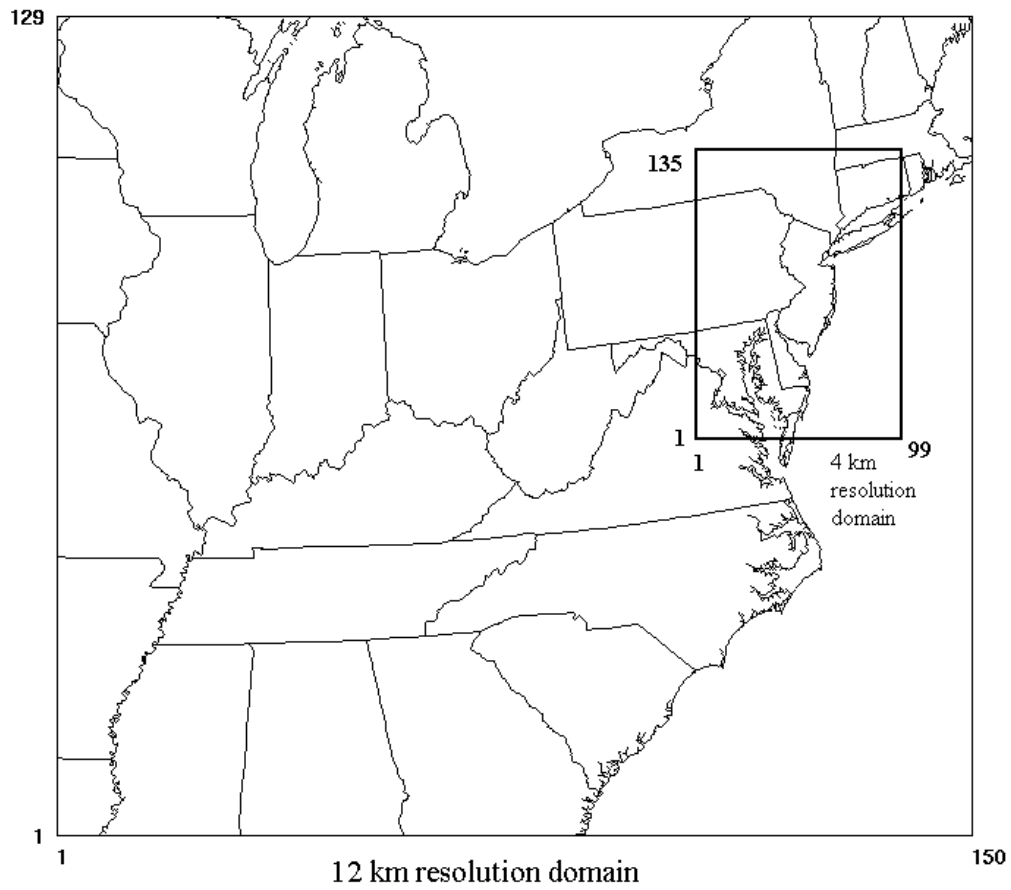


Figure 3-1. Modeling domains for the NARSTO-Northeast simulation.

Table 3-1. Breakdown of the 1996 benzene NTI by major source categories.

Source category	Emissions (tons/day) ⁽¹⁾	% of total
Point sources	12.60	3.7
On-road mobile sources	273.16	80.1
Off-road mobile sources	3.67	1.1
Storage and transport	8.62	2.5
Fuel combustion	4.28	1.3
Industrial processes	2.56	0.8
Waste disposal	2.17	0.6
Miscellaneous area sources	33.87	9.9
Total	340.91	100

(1) Emissions within the 12 km resolution domain on July 12, a typical weekday.

In order to develop a gridded inventory from the county-based NTI, it is necessary to use surrogates that allow the spatial distribution of the available emissions. Major point sources are distributed according to their exact location specified by latitude and longitude. Plume rise is calculated within SMOKE to distribute the point source emissions in the appropriate layer.

On-road mobile sources were distributed as follows. Benzene emissions and vehicle-miles traveled (VMT) were available by county (source: <http://www.ladco.org/emis/guide/ems95.html>). VMT were also available by road type (e.g., rural interstate, rural major and minor arterial, rural major and minor collector, rural local, urban interstate, urban freeways, urban major and minor arterial, urban collector, and urban local). For each road type, we assumed that emissions were proportional to VMT and used separate spatial surrogates for non-urban highways and all other road types. For non-urban highways, we used the exact locations of these highways to distribute the emissions among the grid system. For all other road types, we assumed that VMT were proportional to population and used population distribution as the spatial surrogate. Benzene emissions are further distributed among vehicle types, including light duty gasoline vehicles, two categories of light duty gasoline trucks, heavy duty gasoline vehicles, light duty diesel vehicles, light duty diesel trucks, heavy duty diesel vehicles, and motor cycles. We assumed that the distribution of vehicle types was uniform across all roadways. This is a reasonable assumption if we consider that this assumption is applied at the county scale.

Spatial surrogates for area and non-road sources are available for the unified grid (<http://www.ladco.org/emis/unified/unified.html>), which can be applied to the NARSTO/Northeast domain with no change in the coordinate system. These surrogates include agriculture, airports, housing, major highways, ports, population, railroads, water, rural area, urban area, forest, and total area. Each area or non-road mobile source is matched to one of these surrogates within SMOKE for spatial allocation. For example, non-road mobile sources are allocated according to population.

SMOKE provides temporal emission profiles according to source category codes (SCC). The temporal resolution includes a distribution of the annual emissions by season, a distribution among weekdays and week-end days and a diurnal profile. For the

five-day episode simulated here, there were four week days (July 11 to 14, Tuesday to Friday) and one weekend day (July 15, a Saturday).

Figure 3-2 presents the benzene emission inventory for the 12 km domain at 3 p.m. on 15 July 1995. Areas with the highest emissions densities include primarily urban areas since these correspond to the highest traffic densities. Benzene emissions from marine vessels can be seen in Figure 3-2 at ports along the Great Lakes and the Mississippi River. Major point sources include refineries in Tennessee and New Jersey and industrial sources in Ohio.

3.2.2 Diesel particles

The 1996 EPA National Emission Inventory (NEI) for PM_{2.5} was used to generate diesel particle emissions. The year 1996 is the closest base year to 1995 for which an inventory was available. All PM_{2.5} emitted from sources that burn diesel fuel were defined to constitute diesel PM emissions.

Table 3-2 presents a summary of the major source categories for diesel particle emissions. Major point sources constitute about 5% of the total diesel particle emissions. On-road motor vehicles constitute 40%, and non-road sources account for more than 50% of total diesel particle emissions. No area source was listed in the 1996 NEI that emit diesel particles. Diesel particle emissions are decreased by 8.5% on weekends (705 tons/day) relative to weekdays (771 tons/day), based on temporal profiles applied in SMOKE to diesel sources.

For the spatial and temporal distribution of the emission inventory, we used the same methodology as for benzene with one exception. The 1996 NEI provides county-specific road type and vehicle class information for mobile source diesel PM emissions; therefore, no VMT-based allocation to roads was needed. SMOKE was used to generate point, mobile, and non-road diesel PM emissions with the same spatial surrogates as described above.

Figure 3-3 presents the diesel particle emission inventory for the 12 km domain at 3 p.m. on Saturday, 15 July. As for benzene, urban areas present the highest emission fluxes. Emissions occurring on rural highways are clearly visible. Other significant

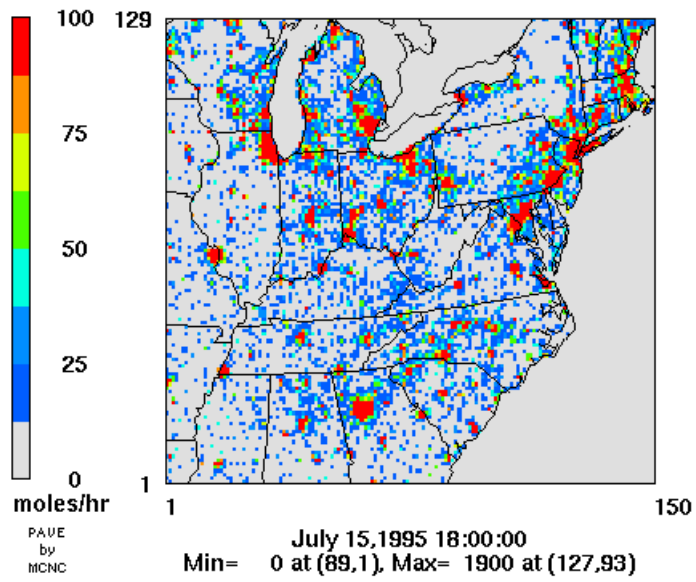


Figure 3-2. Benzene emissions inventory at 3 p.m. on Saturday, 15 July 1995.

Table 3-2. Breakdown of the 1996 diesel particles NEI by major source categories.

Source category	Emissions (tons/day) ⁽¹⁾	% of total
Point sources	34.83	4.5
On-road mobile sources	304.20	39.5
Construction equipment	183.14	23.8
Agricultural equipment	61.18	7.9
Commercial marine vessels	54.09	7.0
Railroad engines	35.81	4.6
Industrial equipment	50.54	6.6
Logging equipment	10.39	1.3
Miscellaneous off-road mobile sources	36.74	4.8
Total	770.92	100

(1) Emissions within the 12 km resolution domain on July 12, a typical weekday.

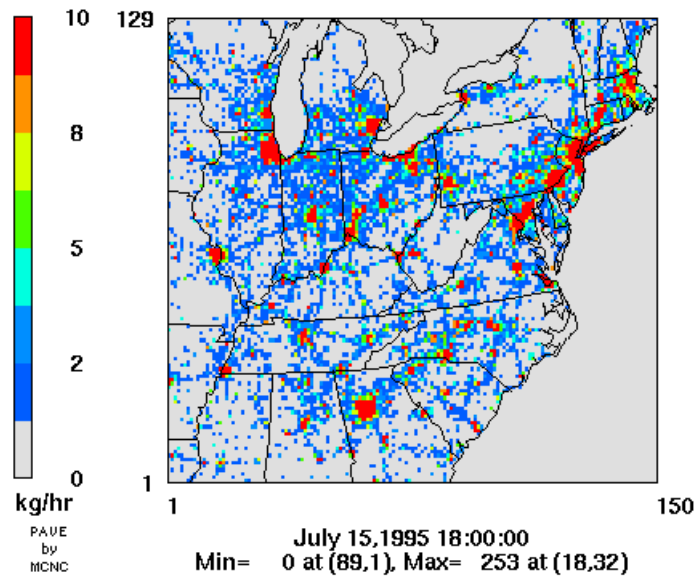


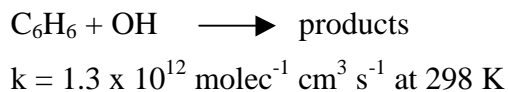
Figure 3-3. Diesel PM emissions inventory at 3 p.m. on Saturday, 15 July 1995.

emission fluxes include some point sources (e.g., diesel-powered electricity generating units in Ohio and Tennessee) and commercial ports along the Mississippi and on the shores of the Great Lakes.

3.3 Modifications to CMAQ

The toxics simulation of benzene and diesel PM builds upon an O₃ base case simulation that was conducted for the NARSTO/Northeast domain under CRC project A-24. Modifications were made to CMAQ since benzene and diesel particles are not included explicitly in the original model formulation.

Benzene (C₆H₆) is not included in VOC emission inventories developed for O₃ formation. Consequently, its chemistry is not treated in the CBM-IV and RADM2 gas-phase chemical mechanisms available in CMAQ. Benzene reacts with OH radicals and has an atmospheric lifetime of about one week for a typical OH concentration of 10⁶ radicals cm⁻³.



This reaction was added to the CBM-IV chemical kinetic mechanism used in the simulation conducted here.

Dry deposition was assumed to be negligible for benzene, akin to other aromatic species simulated in CMAQ.

Particles are treated in CMAQ, however, the speciation of primary particles is limited to elemental carbon (EC), organic compounds (OC) and sulfate. Therefore, it was necessary to modify CMAQ to treat diesel particles explicitly. Diesel particles consist of EC, OC and some sulfate. Including diesel particles in the CMAQ primary particle categories would have been cumbersome because it would have been necessary to avoid double-counting of some EC, OC and sulfate. We selected to add a new “species” representing diesel particles.

Diesel particles are emitted primarily as fine particles (Kleeman et al., 2000). In the ambient environment, they grow through coagulation and condensation of secondary aerosol species into an accumulation mode with diameter primarily in the range of 0.1 to 1 μm . A bimodal distribution of diesel particles was assumed for ambient diesel particles, with modes centering around 0.055 and 0.5 μm . Dry deposition characteristics were calculated based on this bimodal distribution using the approach of Venkatram and Pleim (1999).

3.4 Model Simulation for Benzene

Initial and boundary concentrations of benzene were set to zero for the 12-km simulation. A two-day spin-up period was used to minimize the potential influence of the initial conditions and we present results for the last three days. The use of zero boundary concentrations as well as no Canadian emissions implies that we are analyzing solely the effect of U.S. benzene emissions within the modeling domain. As shown below, the rapid decrease of benzene concentrations away from emission source areas justifies this approach.

The diurnal profiles of benzene concentrations obtained from the 4 km simulation are presented in Figure 3-4 for an urban location, New York City, and a rural location, Brigantine National Wildlife Refuge. As expected, the concentrations of benzene is about a factor of 4 higher in the urban location relative to the rural location. The temporal variability of benzene is very pronounced in the urban area, with peak concentrations in the mornings and evenings. The peak concentrations during commute hours are consistent with a predominance of on-road mobile sources in the benzene inventory. High concentrations of benzene from the evening traffic sometimes persist past midnight. With lower concentrations, the rural Brigantine National Wildlife Refuge site displays a less pronounced diurnal profile of benzene. Nonetheless, similar features in the diurnal peaks can be observed in the rural profile as in the urban profile. The 24-hour average measured benzene concentration available at the New York City location on 14 July shows that the simulated concentrations are consistent with the available data.

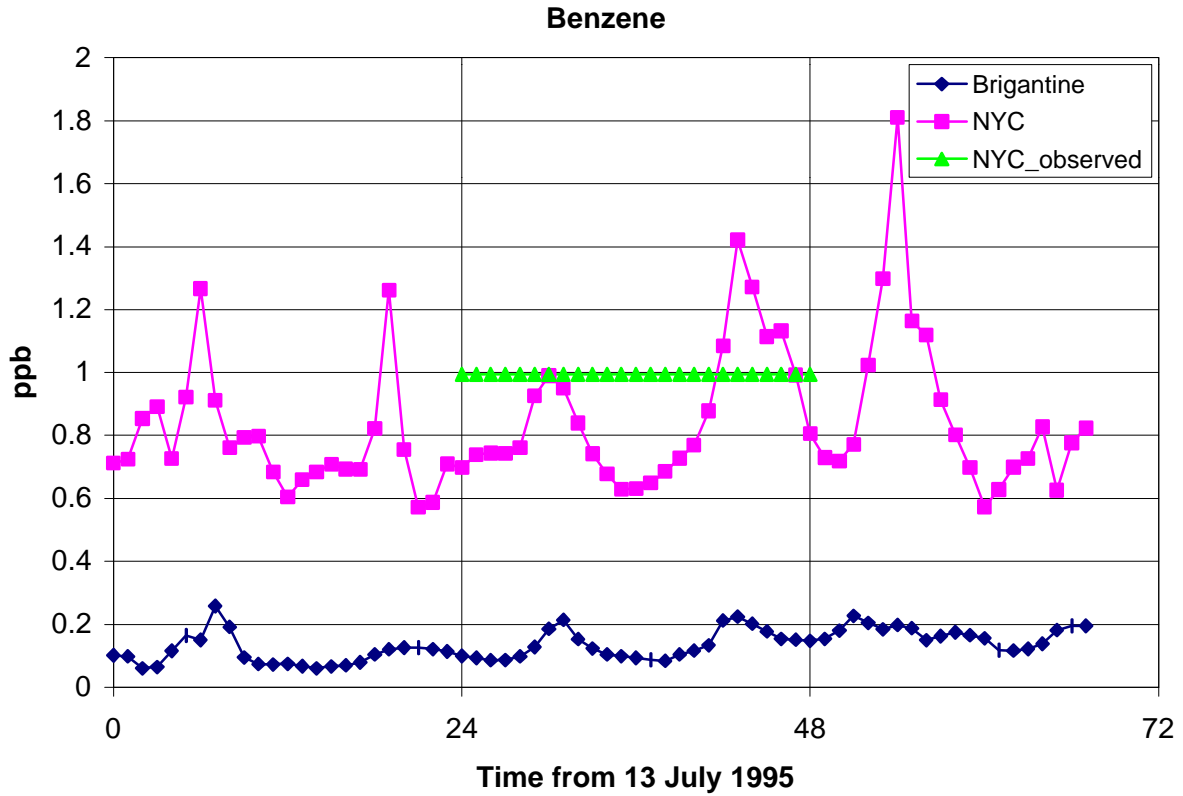


Figure 3-4. Temporal profiles of benzene concentrations in New York City, NW and Brigantine National Wildlife Refuge, NJ.

The simulated benzene concentrations are presented for the entire modeling domain in Figure 3-5 for July 13, 14 and 15 (Thursday through Saturday). The concentrations are presented for 6 a.m. which corresponds to a period when benzene concentrations tend to be high because the low mixing height minimizes dilution of the primary emissions. Results are presented for both the outer and inner domains. High concentrations are typically simulated around cities and major source areas. In the spatial plots of the 12 km domain, plumes of benzene are visible along the northeast corridor connecting major urban areas and from urban areas in the Midwest and southern United States. The plume of benzene along the northeast coast is the dominant feature of the spatial plots for the 4 km domain. Outside of source areas, the concentrations of benzene drop quite rapidly to rural background concentrations that may be lower than the urban concentrations by as much as a factor of 10.

Table 3-3 presents a general comparison of the simulated benzene concentrations with values available from the literature. It appears that the ranges of simulated and observed values are comparable except for the highest benzene concentrations observed in urban areas. This is explained by the fact that the horizontal resolution of 4 km used in the model simulation will dilute the primary emissions of benzene whereas measurements conducted near a roadway, for example, will characterize benzene concentrations near mobile vehicle exhausts.

Benzene is a target species monitored at the Photochemical Assessment Monitoring Stations (PAMS), which are set up in metropolitan areas in non-attainment of ozone, including upwind and downwind locations to monitor the evolution of pollution. During the period between 13 to 15 July 1995, more than 50 PAMS were operational within the larger domain with sampling schedules varying from every day to one in three or six days. Twenty-six PAMS were operational within the smaller domain. Twenty PAMS provided 24-hour average measurements of benzene concentration; seven PAMS provided hourly measurements (one PAMS provided both 24-hour average and hourly measurements). Table 3-4 summarized measured benzene concentration within the 4 km resolution domain. The model performance statistics for 24-hour average benzene concentrations in the 12 km and 4 km resolution domains are presented in Table 3-5. The coefficient of determination (r^2) between the simulated and observed 24-hour average

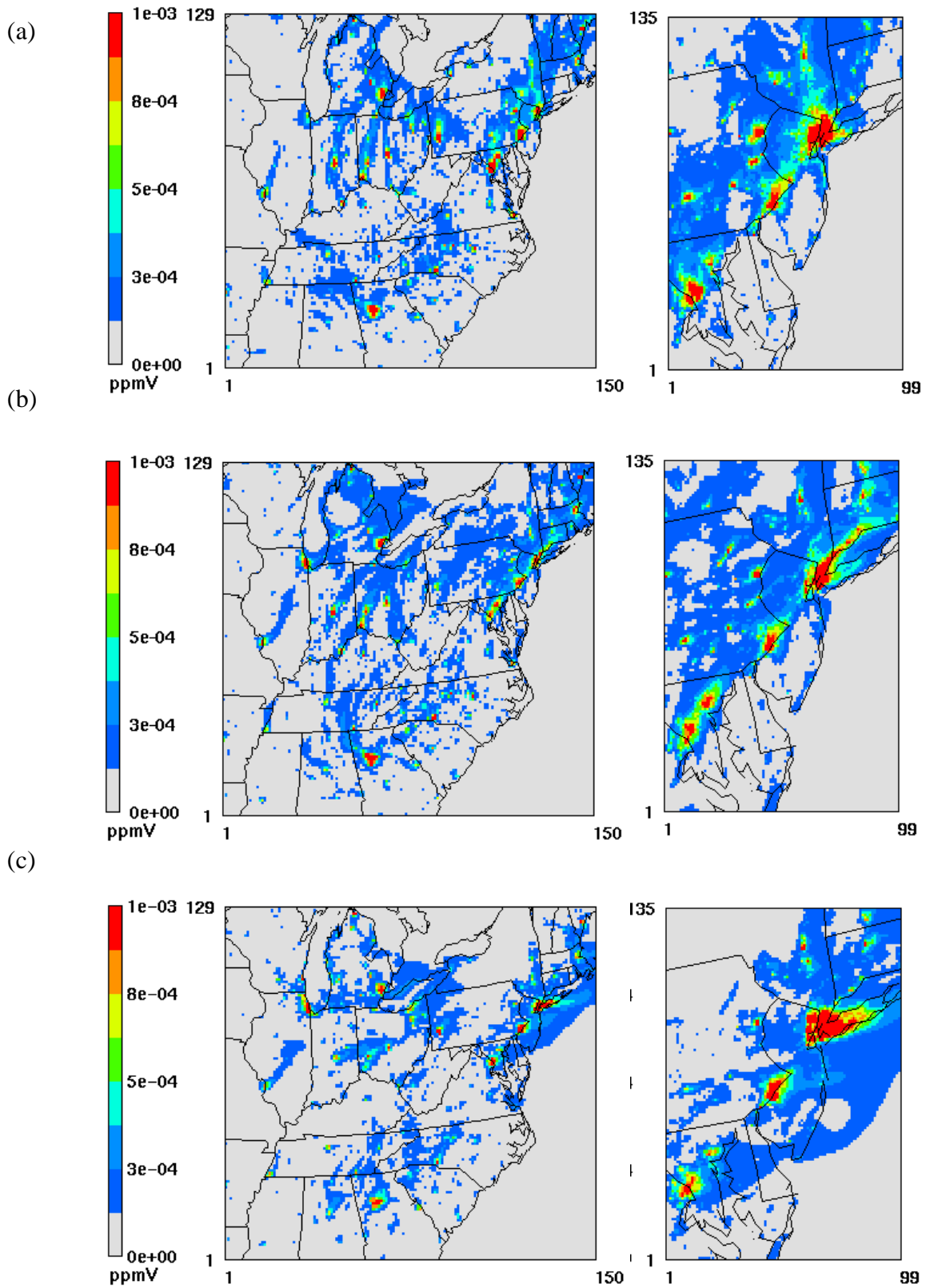


Figure 3-5. Benzene concentrations at 6 a.m. on (a) 13, (b) 14, and (c) 15 July 1995 (Thursday through Saturday).

Table 3-3. General comparison of the simulated benzene hourly concentrations with measurements reported in the literature (ppb).

Location	Simulation	Measurements ^(a)
Urban	1 – 5	0.9 – 26
Suburban – Rural	0.1 – 0.5	0.1 – 0.6
Remote	< 0.1	< 0.008 – 0.2

(a) Finlayson-Pitts and Pitts (1999)

Table 3-4. Benzene concentrations measured within the 4 km horizontal resolution domain.

AIRS Site No.	Street Address	24-hour average benzene concentrations ^(a,b)		
		July 13	July 14	July 15
2400310034	Anne Arundel Co. Public Works Bldg., Baltimore, MD	–	1.320	–
2451000064	NE Police Sta., 1900 Argonne Dr, Baltimore, MD	–	0.820	–
2451000404	Old Town Fire Dept St. 34, Baltimore, MD	–	0.580	–
2451000434	Fort McHenry Visitors Center, Baltimore, MD	–	0.620	–
2451000504	Clifton Park, Rose Street, Baltimore, MD	–	0.510	–
3401300114	St. Charles between Kossuth & Kameron, Newark, NJ	1.350	–	–
3604700994	850 Grand Avenue, Brooklyn, NYC, NY	–	0.994	–
3608500554	Post Office, 364 Port Richmond Ave., NYC, NY	–	0.384	–
3608500664	PS 26, 4108 Victory Blvd., Travis, NYC, NY	–	0.408	–
3608501014	2500 Richmond Ave., NYC, NY	–	0.280	–
3608501024	IS 75 Hughenot & Woodrow Aves., NYC, NY	–	0.179	–
3608501034	Section 1/9 Freshkills, NYC, NY	–	0.252	–
3608501044	Compositing Facility Freshkills, NYC, NY	–	0.177	–
3608501054	Freshkills Landfill Met. Tower, NYC, NY	–	0.164	–
3608501064	Unloading Zone Freshkills, NYC, NY	–	0.315	–
3608501074	Arthurkill Road, NYC, NY	–	0.230	–
3608501084	Richmond Av., NYC, NY	–	0.106	–
3608501094	PS 69 144 Keating Place, NYC, NY	–	0.279	–
4210100044	1501 E Lycoming Av Ams Lab., Philadelphia, PA	–	0.640	–
5103300014	U.S. Geodetic Survey, Off Route 2, Corbin, VA	–	0.178	–
0900310034	McAuliffee Park, Hartford, CT	–	0.603	–
0901310014	Rte 190, Shenipsit State Forest, Stafford, CT	0.258	0.244	0.134
1100100434	SE End McMillian Reservoir, Washington, DC	–	0.578	0.665
1000310074	Lums Pond State Park, DE	–	0.256	0.356
2451000504	Clifton Park, Rose Street, Baltimore, MD	0.514	0.446	0.380
2501300084	Anderson Road Air Force Base, Chicopee, MA	0.339	0.326	–
3402100054	Rider College; Lawrence Township, NJ	0.421	0.317	0.240

(a) –: no data collected

(b) The first twenty rows correspond to 24-hour average measurements; the last seven rows correspond to hourly measurements averaged over 24-hours for this table.

Table 3-5. Model performance statistics^(a) for 24-hour average benzene concentrations.

	12 km resolution domain	4 km resolution domain
No. of sites	53	27
Normalized error	52%	61%
Normalized bias	9.6%	39.2%
Fractional error	0.52	0.44
Fractional bias	-0.12	0.15

(a) see Seigneur et al. (2000) for definitions of performance statistics.

benzene concentrations within the 4 km resolution domain is 0.25. Note that the spatial variability of benzene concentrations can be quite significant. At 8 sites located within metropolitan New York, the 24-hour average concentrations of benzene varied from 0.16 ppb to 0.99 ppb on 14 July 1999 (i.e., a factor of 6). For model grid cells that include more than one PAMS measurement, the variability among those measurements spans a factor of 1.6 to 2.5 (where the variability factor is defined as the ratio of the maximum and minimum measured concentrations within a given grid cell).

Figure 3-6 shows an evaluation of the hourly temporal profiles of simulated benzene concentrations at the seven sites for which hourly benzene measurements were available within the smaller domain (see Table 3-4). The temporal evolution of benzene concentrations is fairly well reproduced. For example, the morning and evening peaks appear clearly in both the measurements and the simulation results at Hartford, CT; Washington, DC; and Baltimore, MD. The model results are consistent with the measured concentrations except for some overpredictions of the peak values. The lower concentrations are well simulated at these four sites. The four other sites (Stafford, CT; Lums Pond State Park, DE; Chicopee, MA and Lawrence Township, NH) show lower benzene concentrations for both modeled values and measurements. Measured values are between 0.1 and 0.4 ppb with some higher values for the Chicopee and Lawrence Township sites. The model reproduces well these ranges of values except for some overpredictions of peak values and a general underprediction at the Lums Pond State Park site.

Figure 3-7 shows a quantile-quantile (Q-Q) plot of these hourly benzene concentrations. This plot highlights some of the results shown in Figure 3-6, in particular, the low observed benzene concentrations tend to be underpredicted and the peak observed benzene concentrations tend to be overpredicted. The coarse resolution of the 3-D grid model may explain the underpredictions at the low end of the concentration distribution but another source of uncertainty must be the cause of the overpredictions at the high end of the distribution. It would be useful to conduct local modeling of benzene concentrations near a few of these sites with hourly data to further investigate the possible causes of these discrepancies between observed and simulated values.

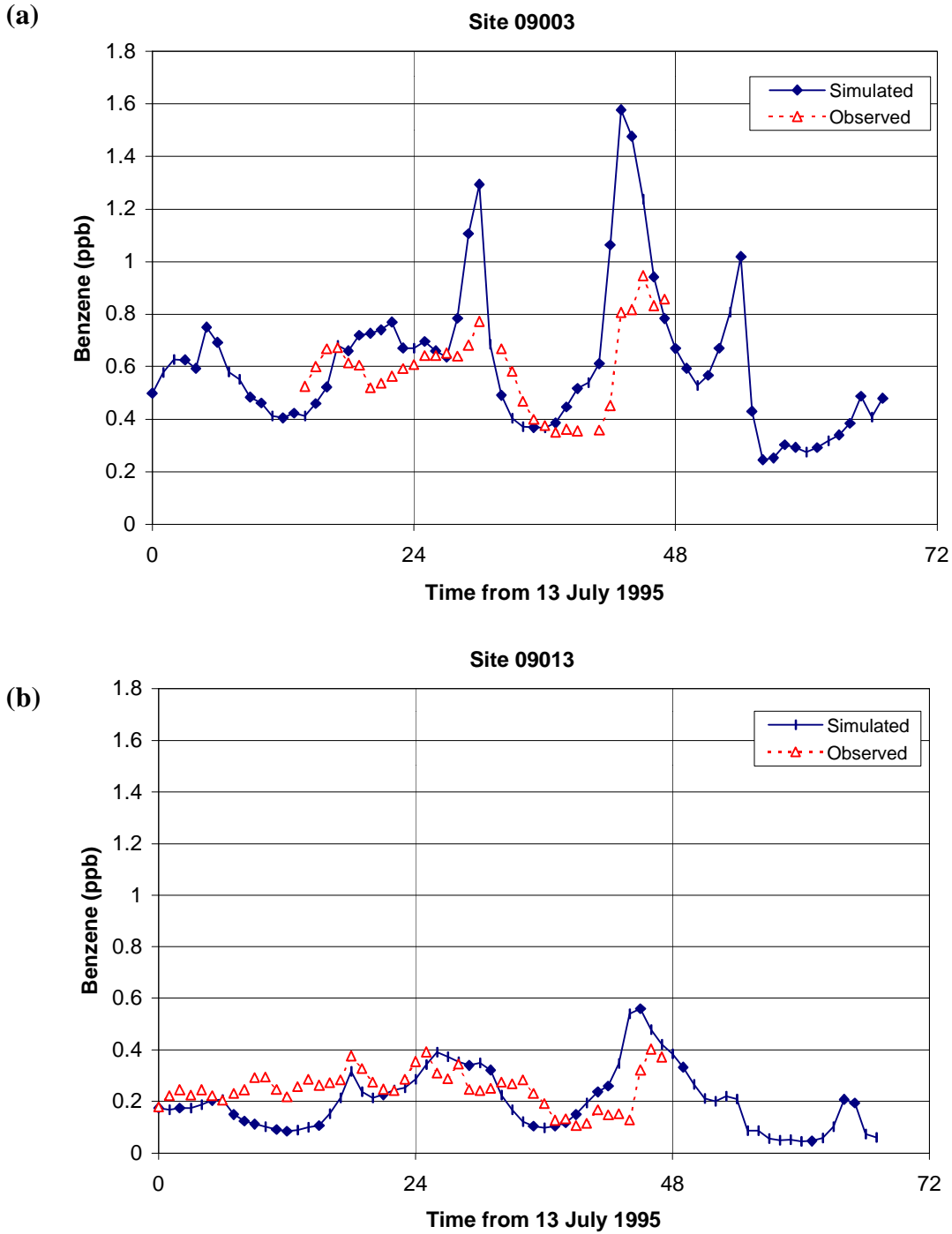


Figure 3-6. Comparison of simulated and observed hourly benzene concentrations: (a) Hartford, CT; (b) Stafford, CT; (c) Washington, DC; (d) Lums Pond State Park, DE; (e) Baltimore, MD; (f) Chicopee, MA; (g) Lawrence Township, NJ.

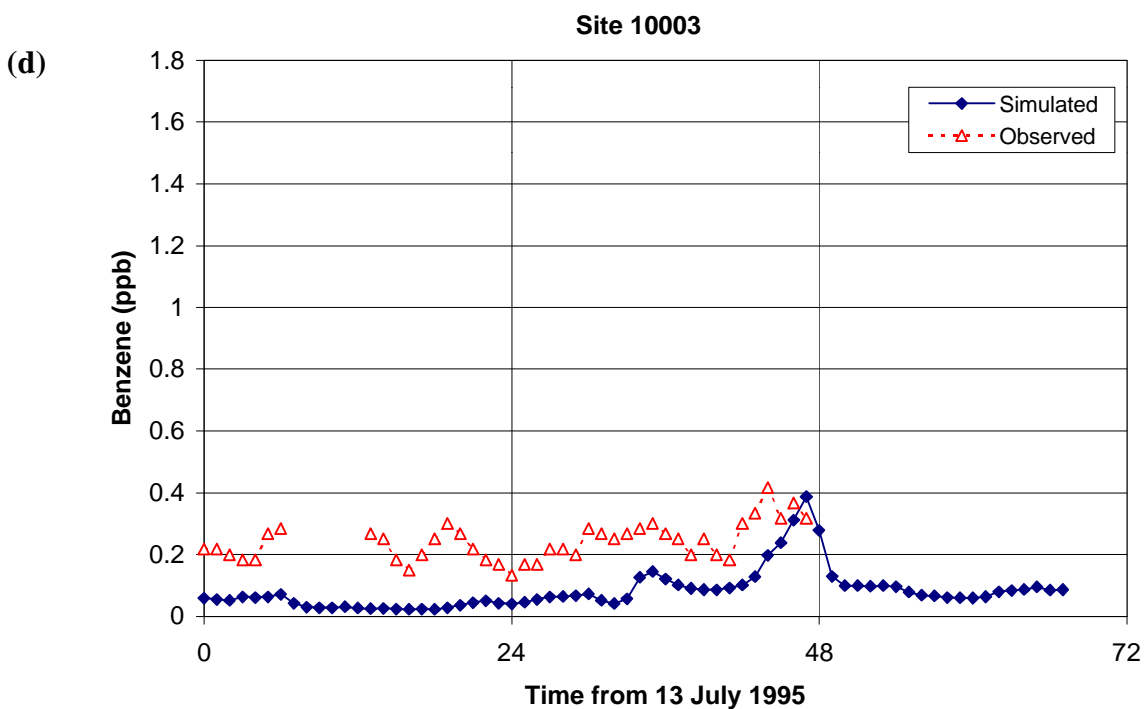
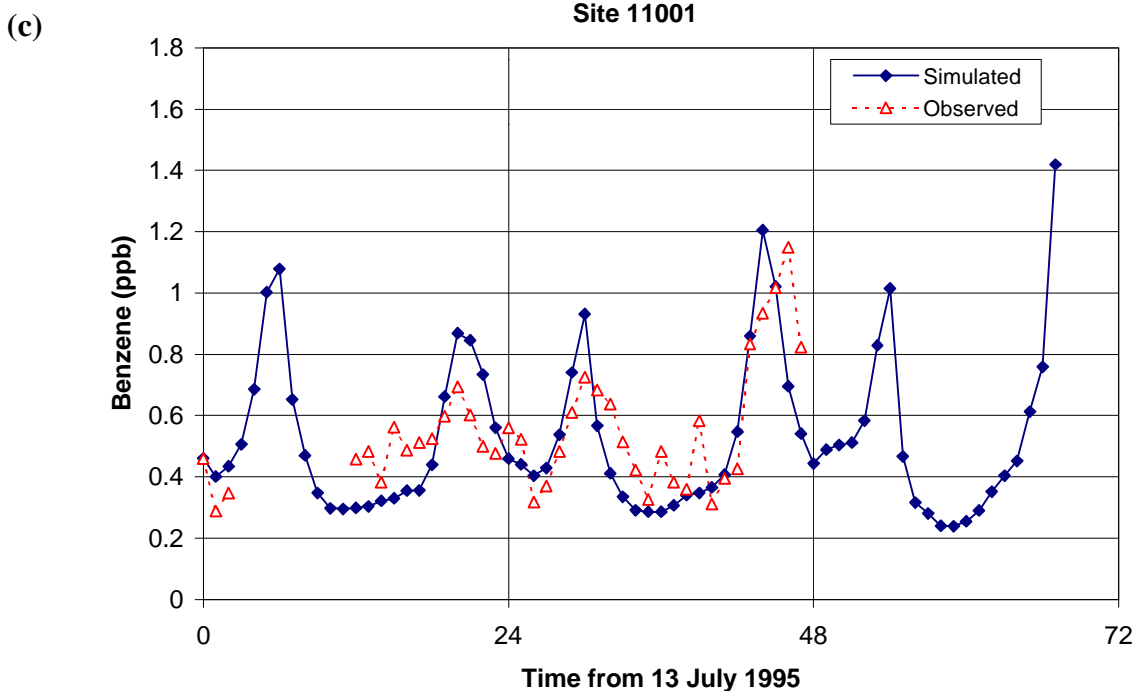


Figure 3-6. Comparison of simulated and observed hourly benzene concentrations: (a) Hartford, CT; (b) Stafford, CT; (c) Washington, DC; (d) Lums Pond State Park, DE; (e) Baltimore, MD; (f) Chicopee, MA; (g) Lawrence Township, NJ (continued).

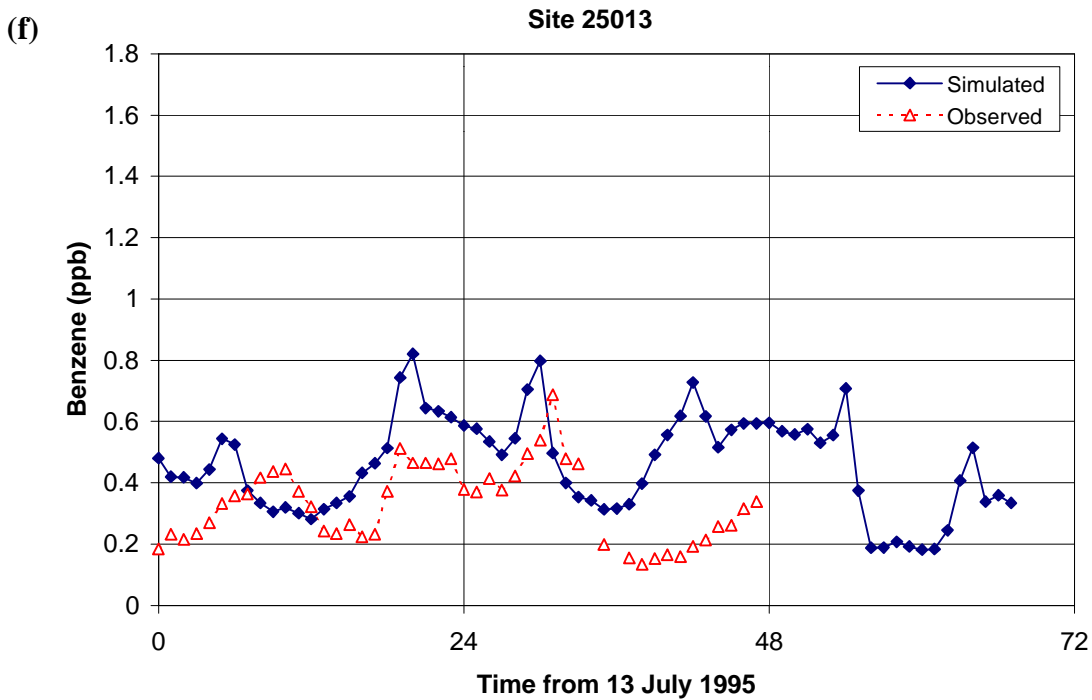
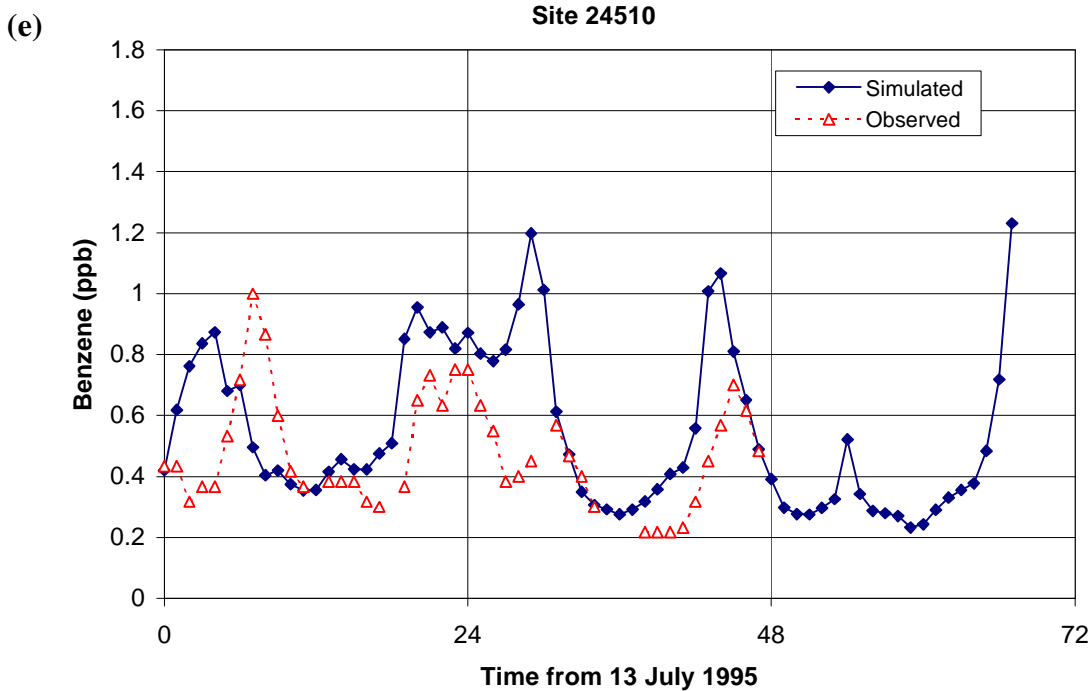


Figure 3-6. Comparison of simulated and observed hourly benzene concentrations: (a) Hartford, CT; (b) Stafford, CT; (c) Washington, DC; (d) Lums Pond State Park, DE; (e) Baltimore, MD; (f) Chicopee, MA; (g) Lawrence Township, NJ (continued).

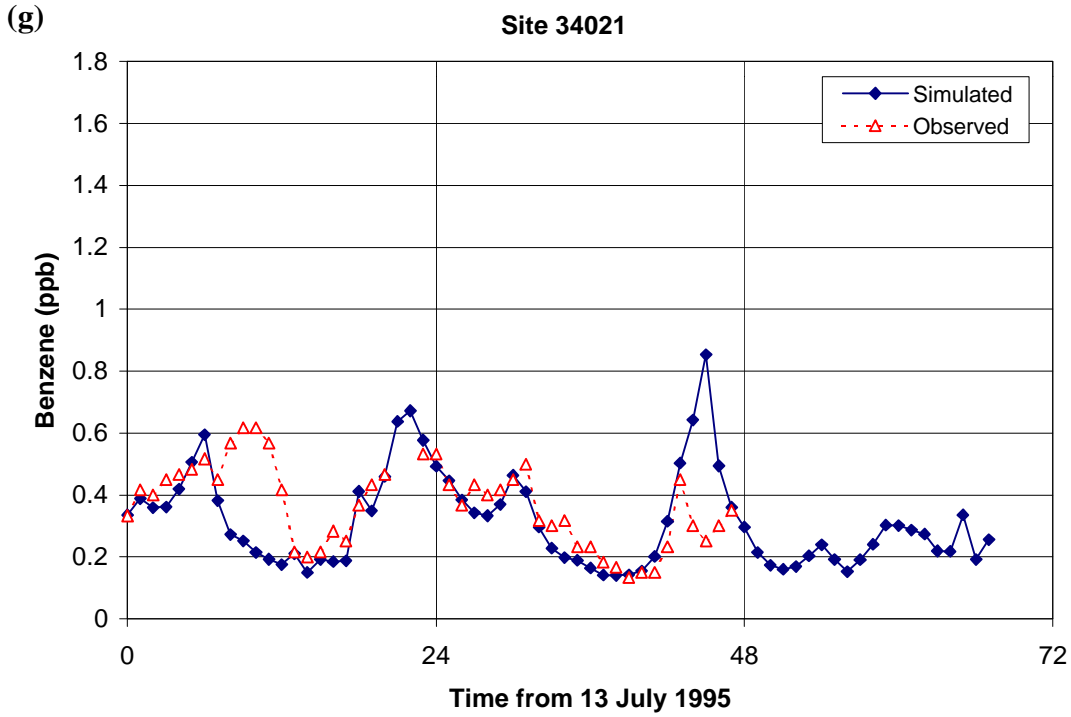


Figure 3-6. Comparison of simulated and observed hourly benzene concentrations: (a) Hartford, CT; (b) Stafford, CT; (c) Washington, DC; (d) Lums Pond State Park, DE; (e) Baltimore, MD; (f) Chicopee, MA; (g) Lawrence Township, NJ (continued).

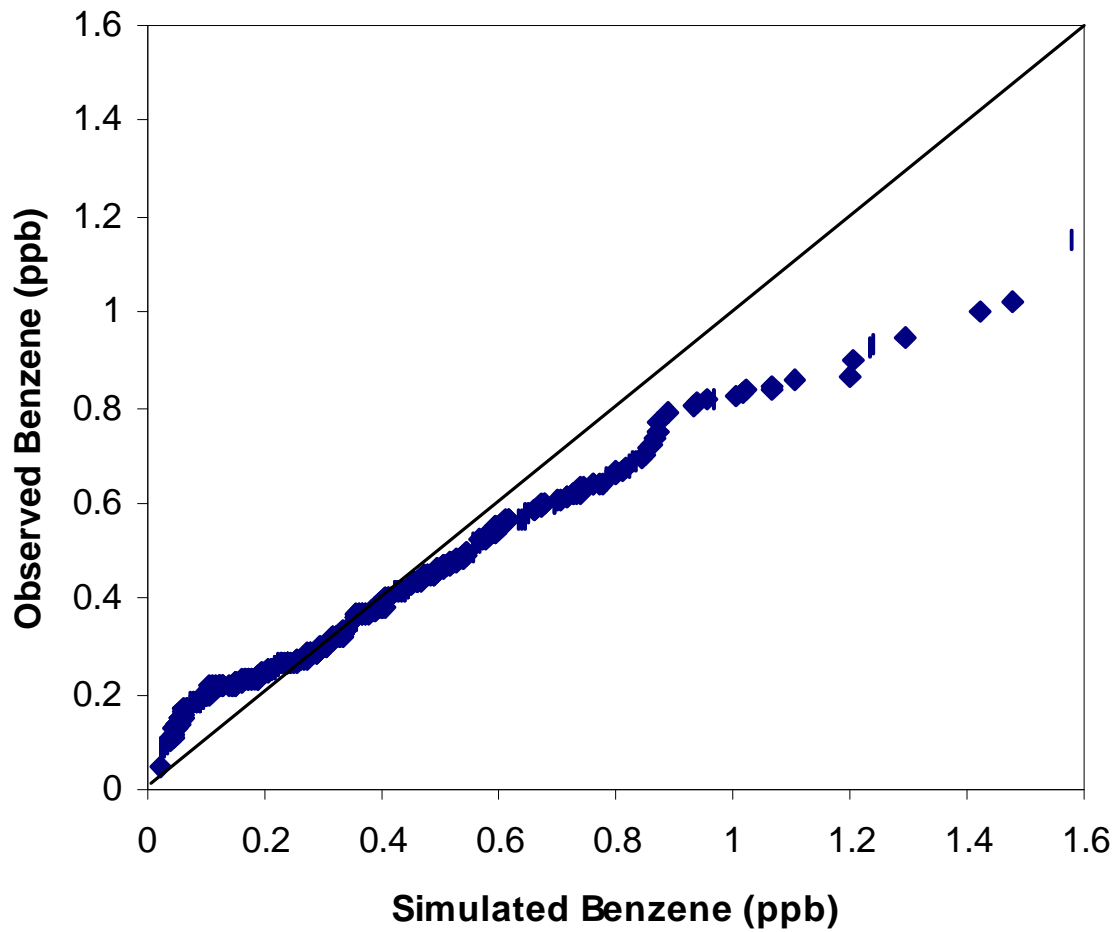


Figure 3-7. Quantile-quantile plot of observed and simulated benzene concentrations within the 4 km horizontal resolution domain.

3.5 Model Simulation for Diesel Particles

A similar modeling approach was used for diesel particles as was used for benzene. Initial and boundary concentrations were set to zero for the 12 km simulation and we present results for the last three days of the simulation.

Figure 3-8 shows the diurnal concentrations of diesel particles in New York City and Brigantine National Wildlife Refuge, a rural location. Concentrations of diesel particles are typically a factor of five higher at the urban site than at the rural site. More significant temporal fluctuations can also be seen at the urban site. At Brigantine National Wildlife Refuge, diesel particle concentrations tend to be high at night and lower during the day. The effect of direct emissions on the simulated concentrations of diesel particles at this non-urban site seems less significant than in the case of benzene. The reason is that on-road mobile sources contribute about 80% of benzene emissions whereas they contribute only about 40% of diesel particle emissions; other major source categories for diesel particle emissions tend to be located in populated areas (e.g., construction equipment, industrial equipment), i.e., away from remote Class I areas.

The simulated concentrations of diesel particles are presented in Figure 3-9 for July 13, 14, and 15. As for benzene, results are presented at 6 a.m. for both the outer and inner modeling domains. As is the case for benzene, diesel concentrations are highest around source areas such as Chicago, Atlanta, and New York. The concentrations decrease rapidly outside source areas to relatively low background concentrations. In the 4 km domain, a discernable plume of diesel particles is simulated along the Mid-Atlantic coast. Superimposed on the regional plume are individual urban plumes corresponding to emissions from individual cities, such as Washington, D.C., Philadelphia, and New York. Outside the regional diesel particle plume, simulated concentrations are below $0.5 \mu\text{g m}^{-3}$ in rural areas.

Diesel particles lose their identity rapidly as they coagulate with other particles and act as condensation sites for secondary aerosol species. Consequently, diesel particles are not measured in the ambient atmosphere and a formal model performance evaluation is not feasible. As mentioned above, diesel particles contain on average about 50% “elemental” carbon (EC). Therefore, an approximate evaluation of the model

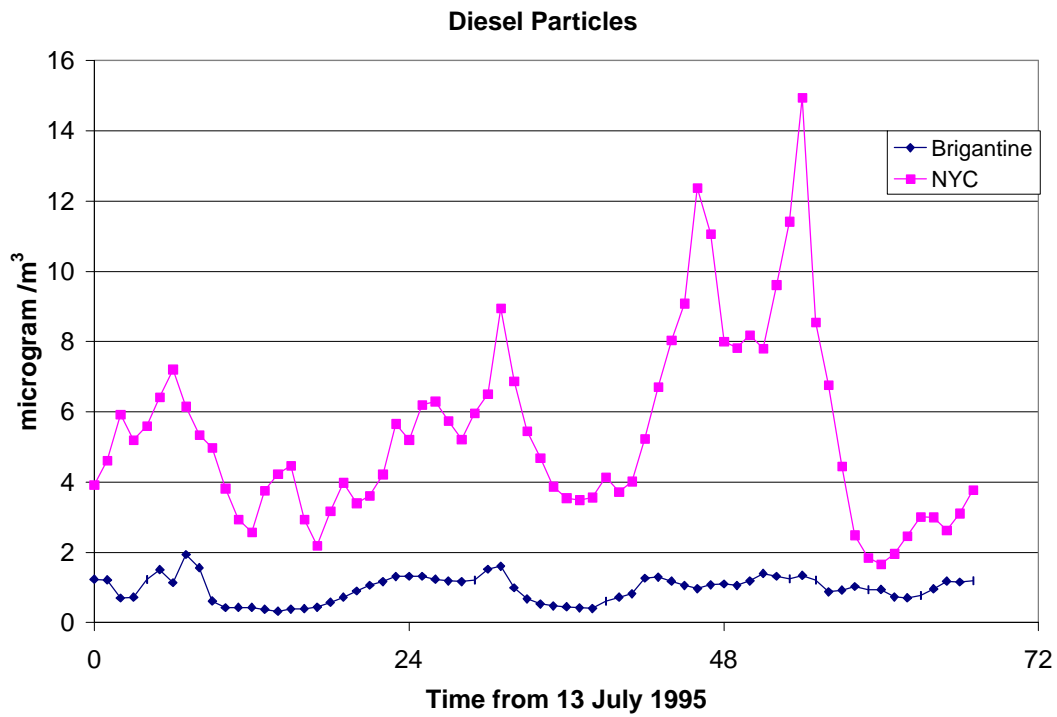


Figure 3-8. Temporal profiles of diesel particle concentrations in New York City, NW and Brigantine National Wildlife Refuge, NJ.

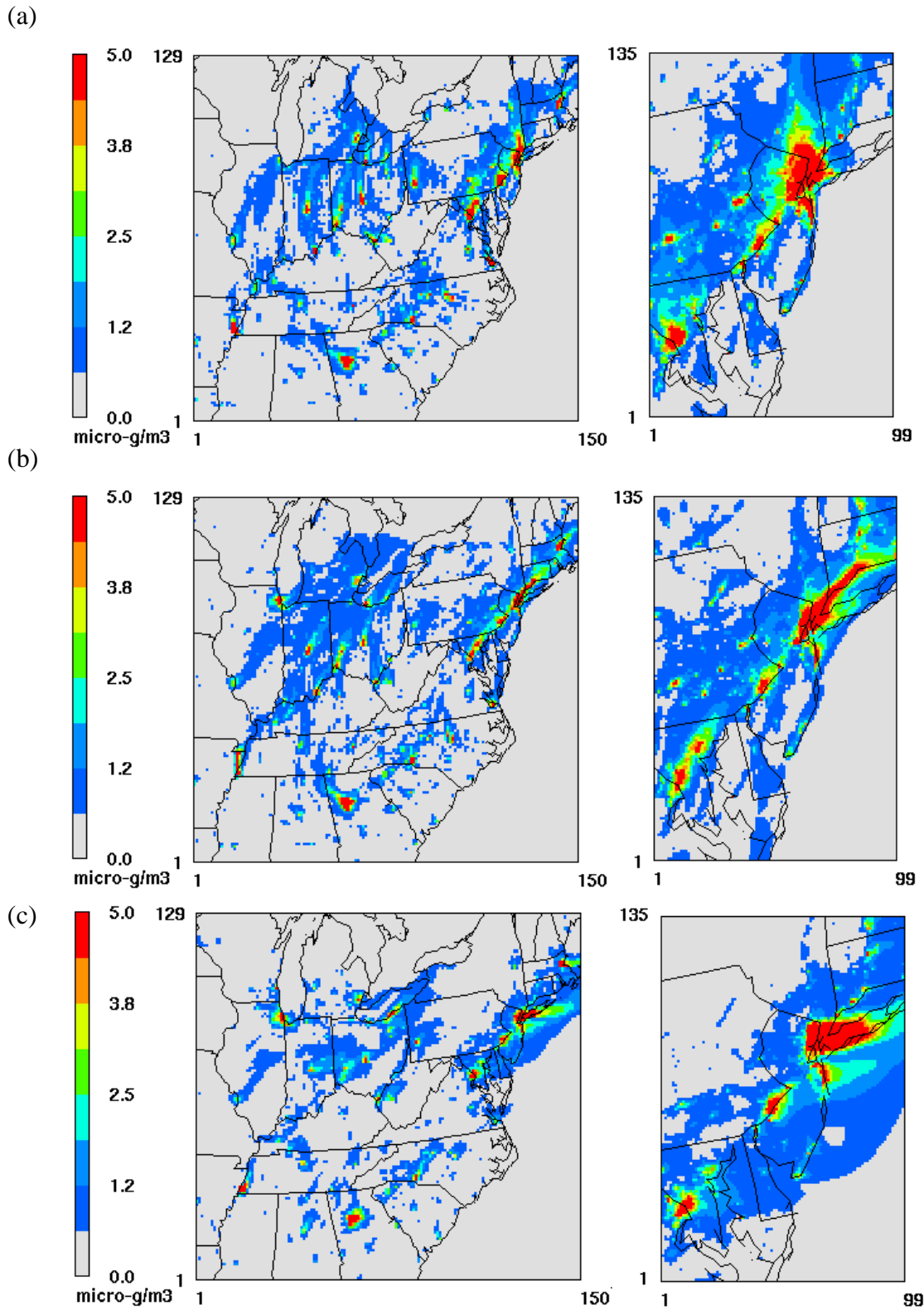


Figure 3-9. Diesel PM concentrations at 6 a.m. on (a) 13, (b) 14, and (c) 15 July 1995 (Thursday through Saturday).

simulation results can be conducted using EC as a surrogate for diesel particles. This is an approximate evaluation because there are other sources of EC, such as biomass burning and exhaust from gasoline-powered vehicles (as much as 50% of total carbon measured in the cold-start PM from gasoline-powered vehicles in the Northern Front Range Air Quality Study was EC (www.nfraqs.colostate.edu)).

Table 3-6 presents a general comparison of EC concentrations simulated with CMAQ (assuming diesel particles consist of 50% EC) with measurements reported in the literature for different environments. Overall, the general magnitudes of EC concentrations in urban, suburban/rural, and remote environments are well reproduced by the model simulation.

Table 3-7 shows a comparison of EC simulated values (19-hour average values) with measurements (24-hour average values) for 15 July 1995 at two Class I areas, Brigantine National Wildlife Refuge in New Jersey and Washington D.C. (the discrepancy between the averaging periods results from the fact that the simulation ends at midnight GMT). The comparison of simulated and observed concentrations in the 12 km resolution domain shows that the model simulation is lower than the measured value at the remote Class I areas than the observed concentrations by factors of 2 to 50 but commensurate with the observed concentration at the urban Washington D.C. site. Similar results are obtained in the 4 km resolution domain with the simulated value being lower than the observed value by 70% at Brigantine National Wildlife Refuge, but by only 10% in Washington D.C. These results are consistent with the fact that diesel particles are expected to contribute more to EC concentrations in an urban area such as Washington D.C. than in remote areas, such as Brigantine National Wildlife Refuge and other Class I areas.

Table 3-6. General comparison of EC concentrations ($\mu\text{g}/\text{m}^3$).

	Simulated diesel particle concentration	Simulated EC ⁽¹⁾ concentration	Measurement
Urban	2 - 41	1 - 21	2.5 - 20
Suburban - Rural	1 - 4	0.5 - 2	1 - 4
Remote	0.1 - 0.4	0.05 - 0.2	0.06 - 0.5

(1) assuming 50% of diesel particles compose of EC

(2) Seinfeld and Pandis (1998)

Table 3-7. Comparison of diesel PM concentration ($\mu\text{g}/\text{m}^3$) with EC concentrations ($\mu\text{g}/\text{m}^3$) on Saturday, July 15, 1995.

Sites ⁽¹⁾	Diesel PM ⁽²⁾	EC from Diesel ⁽³⁾	Measured EC concentration
	12 km resolution simulation		
Brigantine NWR	0.90	0.45	1.16
Dolly Sods W	0.27	0.13	0.66
Great Gulf W	0.20	0.10	0.52
Great Smoky Mountains NP	0.19	0.09	0.65
Jefferson W	0.41	0.21	0.84
Mammoth Cave NP	0.48	0.24	0.52
Cape Romain NWR	0.01	0.006	0.30
Shenandoah NP	0.32	0.16	0.86
Shining Rock W	0.27	0.13	0.50
Sipsey W	0.19	0.09	0.88
Washington, D.C.	3.20	1.57	1.89
	4 km resolution simulation		
Brigantine NWR	1.06	0.53	1.16
Washington, D.C.	3.02	1.51	1.89

(1) NWR = National Wildlife Refuge; NP = National Park; W = Wilderness Area

(2) 19-hour average

(3) assumed 50% of diesel PM is EC

4. CASE STUDIES – INDOOR CONCENTRATIONS OF BENZENE AND DIESEL PARTICLES

Most Americans spend the majority of their time (~ 90%, EPA, 2002) indoors. However, most exposure models simply calculate the potential health impacts on the population from outdoor concentrations (Seigneur et al., 2001a), which may lead to misleading results. In order to obtain more realistic population exposure estimates, it is, therefore, essential to take indoor concentrations into account. In the case studies described below, we use a model that relates indoor and outdoor concentrations and apply it to benzene and diesel particles. The outdoor concentrations for benzene and diesel particles calculated with CMAQ for New York City are used to represent the outdoor concentrations.

4.1 Description of the Indoor Air Quality Model

The basic equations for indoor air quality modeling are as follows:

$$V_i \frac{dC_i}{dt} = \sum_{j=0}^n [Q_{ji}C_j - Q_{ij}C_i] + [Q_{xi}C_x - Q_{ix}C_i] - \alpha_i Q_i C_i + S_i - k_s A_i C_i \quad (1)$$

$$C_x = \frac{\sum_{j=0}^n (1 - \alpha_{jx}) Q_{jx} C_j}{\sum_{j=0}^n Q_{xj}} \quad (2)$$

where C_i is the concentration in compartment i , C_o is the outdoor concentration, C_x is the concentration in the ventilation system, Q_{ij} is the flow rate from compartment i to j , V_i is the volume of compartment i , α_i is the filter efficiency for air flow from compartment i , A_i is the surface area of compartment i , k_s is the deposition velocity on indoor surfaces, S_i is the indoor emission rate of the chemical, and t is the time. Chemical reactions can also

be included for both production and destruction of the chemical (e.g., Nazaroff and Cass, 1989). In the AER indoor air quality model, this general multicompartment mass balance equation is simplified for a single compartment. A term for outdoor air infiltration is also included.

$$V \frac{dC}{dt} = Q_i C_o + Q_o (1 - F) C_o + Q_R (1 - F) C - (Q_i + Q_o + Q_R) C - k_v A C + S \quad (3)$$

where Q_i , Q_o , Q_R are the flow rates for infiltration, outdoor air intake and recirculated indoor air, respectively, and F represents the fraction of pollutant removed by the ventilation system filter ($1 - \alpha$). Hayes (1989) included a mixing factor with each flow rate term. We assumed here that the air in each microenvironment is well mixed and no mixing factor term is needed.

4.2 Indoor Air Quality Scenarios

Although people spend the majority of their time indoors, they do not remain in the same location throughout the day. People move amongst home, office, retail facilities, assembly halls, schools, and different forms of transportation, to name a few. To address this variability among microenvironments, the indoor model was run for various scenarios. These scenarios included the two air toxics studied here (benzene and diesel particles) and three microenvironments (home, office, and car). Not all indoor air quality problems are caused by outdoor air entering the microenvironment. Indoor sources of pollution may cause indoor concentrations just as high or higher than those caused by outdoor air. Smoking indoors, for example, dramatically increases the indoor concentration of benzene. Therefore, the benzene simulations included scenarios with and without indoor sources, i.e., environmental tobacco smoke (ETS). No simulations were included with indoor sources of diesel particles. The scenarios considered here are summarized in Table 4-1.

Table 4-1. Indoor Air Quality Scenarios.

	Contaminant	Micro-environment	Indoor Sources
Scenario 1	Benzene	Home	No
Scenario 2	Benzene	Home	Yes
Scenario 3	Benzene	Office	No
Scenario 4	Benzene	Office	Yes
Scenario 5	Benzene	Car	No
Scenario 6	Benzene	Car	Yes
Scenario 7	Diesel Particles	Home	No
Scenario 8	Diesel Particles	Office	No
Scenario 9	Diesel Particles	Car	No

The characteristics of the microenvironments studied here may vary significantly and it is important to include such variability in an analysis of indoor air concentrations. Consequently, a probabilistic approach was selected where the inputs to the indoor air quality model were defined as probability distributions representative of the plausible range of values of those inputs.

The distributions for the indoor model's input parameters were determined according to literature searches whenever possible. Occasionally, no data could be found and assumptions needed to be made for those parameters. The probability distributions for the input parameters used in the simulations are provided in Table 4-2.

Many of the input parameters are dependent on each other and could not be entered as independent parameter distributions, because unrealistic scenarios could then be created. For example, although a room of a certain volume may have many different possible surface areas, depending on room configuration, the volume and area are nonetheless related. A room with a very large volume and a very small surface area would be unrealistic. Similarly, room flow rates are entered as air change rates (flow rate/volume) rather than absolute flow rates to account for the dependence on room size. We discuss below the values of the input parameters used in the scenario simulations here.

Volume (V)

The volume of the average American home has been estimated in a few studies and summarized in EPA (1997). The distribution used here for the home was derived from those estimates. No data were found on the volumes of offices, so a distribution based on estimates of office sizes was developed. The distribution ranges from the size of a small single person office to a large "cubicle farm" sized space. Similarly, no distributions were found to describe the interior volume of passenger cars. Instead, a distribution was developed based on information provided in manufacturers' descriptive information for their passenger car lines.

Table 4-2. Input Parameters for the Indoor Air Quality Scenarios.

Parameter	Micro-environment	Air Toxic	Distribution Probability	Scenarios ^(b)	References
V(m ³)	Home	Both ^(a)	Lognormal $\mu=369$ $\sigma=209$	1, 2, 7	(EPA, 1997)
V(m ³)	Office	Both	Lognormal $\mu=65$ $\sigma=75$	3, 4, 8	Estimated
V(m ³)	Car	Both	Lognormal $\mu=3$ $\sigma=0.75$	5, 6, 9	Estimated based on manufacturers' data
A/V(m ⁻¹)	Home	Both	Lognormal $\mu=1.81$ $\sigma=0.19$	1, 2, 7	Hayes, 1989
A/V(m ⁻¹)	Office	Both	Lognormal $\mu=0.9$ $\sigma=0.19$	3, 4, 8	Hayes, 1989
A/V(m ⁻¹)	Car	Both	Lognormal $\mu=3.0$ $\sigma=0.15$	5, 6, 9	Estimated
Q _i /V(h ⁻¹)	Home	Both	Lognormal $\mu=0.73$ $\sigma=0.58$	1, 2, 7	Sherman & Dickerhoff, 1994
Q _i /V(h ⁻¹)	Office	Both	Lognormal $\mu=0.3$ $\sigma=0.15$	3, 4, 8	ASHRAE, 2001
Q _i /V(h ⁻¹)	Car	Both	Lognormal $\mu=18$ $\sigma=9$	5, 6, 9	Helnsohn et al., 1993
Q _v /V(h ⁻¹)	Home	Both	Lognormal $\mu=5$ $\sigma=1.5$	1, 2, 7	Hayes, 1991
Q _v /V(h ⁻¹)	Office	Both	Normal $\mu=6.0$ $\sigma=1.25$	3, 4, 8	ASHRAE, 1999; Porges, 1995; Bearg, 1993
Q _v /V(h ⁻¹)	Car	Both	Lognormal $\mu=66$ $\sigma=25$	5, 6, 9	Helnsohn et al., 1993
Q _o /Q _v	Home	Both	Lognormal $\mu=0.2$ $\sigma=0.05$	1, 2, 7	Hayes, 1991
Q _o /Q _v	Office	Both	Lognormal $\mu=0.16$ $\sigma=0.05$	3, 4, 8	Bearg, 1993
F	Home	Diesel particles	Lognormal $\mu=0.1$ $\sigma=0.1$	7	Hayes, 1991
F	Office	Diesel particles	Lognormal $\mu=0.45$ $\sigma=0.05$	8	ASHRAE, 1999
F	Car	Diesel particles	Lognormal $\mu=0.1$ $\sigma=0.1$	9	Used values from Home Microenvironment
k _s (m/h)	Home, Office, Car	Benzene	Exponential Rate = 5	1, 2, 3, 4, 5, 6	Estimated
k _s (m/h)	Home, Office, Car	Diesel particles	Lognormal $\mu=0.25$ $\sigma=0.04$	7, 8, 9	Fogh, et al., 1997; Kleman et al., 1999
S(μg/h)	Home, Office, Car	Benzene	Normal $\mu=195.8$ $\sigma=100.0$	2, 4, 6	Singer et al., 2002

^(a) Benzene and diesel particles

^(b) See Table 4-1.

Surface Area/Volume (A/V)

Average surface area/volume ratios for home and office microenvironments were found in Hayes (1989). However, no distributions were given. Instead, distributions were developed based on room dimension examples provided in EPA (1997). No surface area/volume ratios were found for cars and thus a distribution was developed which assumed a larger surface area/volume ratio in cars than in homes or offices.

Infiltration (Q_i/V)

Infiltration is the seeping of air into a microenvironment through cracks, doorways, and other unintentional inlets. Many studies have been conducted for infiltration of outdoor air into homes. This is generally a large source of outdoor air flow into homes. Values for the infiltration mean and standard deviation from Sherman and Dickerson (1994) were available for New York State. Infiltration into office spaces, on the other hand, is relatively low when compared to both infiltration in homes and mechanical ventilation of office buildings. ASHRAE (2001) estimates a range of 0.1 to 0.6 air changes per hour (ACH) for office buildings. The impact of infiltration on individual office space is assumed to be lower than for the entire building because most of the infiltration would occur around exterior doors. For cars, the infiltration rate depends largely on the speed at which the vehicle is travelling. Helnshon et al. found an average infiltration rate of 36 ACH for a highway speed of 50 miles/hour. A mean speed of 25 mph was used here and a distribution was developed assuming that infiltration is proportional to speed. The actual speed of traffic in New York City was not available and a generic distribution was assumed with a range of traffic speeds from 5 to 85 mph.

Ventilation (Q_v/V , Q_o/V)

Ventilation refers to the intentional movement of air into a microenvironment, either through a mechanical ventilation system or through open windows. Intentional ventilation of a microenvironment is made up of outdoor air and/or recirculated air. The amounts of outdoor air intake and recirculated air are often related and are, therefore,

grouped together as the ventilation rate (Q_v). Since the episode considered here takes place in July, the impact of furnaces and other heating equipment was not studied. Instead, it was assumed that any ventilation was due to either open windows or air conditioning.

In homes, ventilation may occur through either air conditioning or open windows. It was assumed that residents either opened their windows or ran their air conditioning but did not do both. Approximately 62% of the population of New York State have air conditioners (DOE, 1997). This statewide percentage was applied to New York City. For purposes of this study, it was assumed that all residents who had air conditioners used them and that those who did not have air conditioners opened their windows. Air conditioners use a mix of recirculated air and outdoor air. Hayes (1991) estimated the fraction of outdoor air used in air conditioners to be 0.2, with a range of 0.1 to 0.3.

In office buildings, ventilation is usually centrally controlled and windows are generally closed. In this study, we assumed that all ventilation occurred through the central HVAC system. Many different sources provide information on the ventilation rates used in office buildings (ASHRAE, 1999; Porges, 1995; and Bearg, 1993). A normal distribution was created around these data. In office buildings, a balance is struck between drawing in new outdoor air and recirculating office air. This balance is estimated to be around 0.14 to 0.2 outdoor air to total air (Bearg, 1993).

In cars, the occupants choose both the ventilation rate and the air source, fresh outdoor air or recirculated air. Because the car's occupants choose the ventilation rate, it is difficult to determine the average rate of ventilation. Helnsohn et al. chose two speeds in their study, a low fan setting and a high fan setting. The low fan setting of approximately 60 ACH was used as the mean. The distribution of fan speeds is uncertain, therefore, a large standard deviation was chosen. The maximum value was truncated to prevent an unreasonably large flow rate from being simulated. Because no data were found on the use of fresh versus recirculated air, it was assumed that outdoor air was chosen half of the time and recirculated the other half of the time. Therefore, for half of the simulation, ventilation air is made up only of recirculated air and for the other half it is made up only of outdoor air. No simulations were conducted for occupants with

their car windows rolled down because such a scenario would be very similar to exposure to outdoor air.

Filter Removal (F)

Filters are generally included in any kind of ventilation system. Benzene was not expected to be significantly removed by filters in the ventilation systems of any of the three microenvironments. In homes and in cars, these ventilation filters are generally intended for keeping large debris such as leaves out of the ventilation system rather than for filtering small particles out of the air, although some homes do have special air filters included in their ventilation systems. Nevertheless, it was assumed that a fraction of the diesel particles could be removed by the home and car ventilation system air filters. A distribution was developed based on the information that filters for home air conditioners may remove anywhere from 0 to 30% of the particles in the air (Hayes, 1991).

Office buildings frequently have filters designed to reduce the particulate content of the air in the building. Office building ventilation system filters are generally rated 35 to 60% effective for particle removal (ASHRAE, 1999). However, these filters are not necessarily designed to remove particles as small as diesel particles. Since no other data were available, the listed filter removal rates were applied to diesel particles.

The effective filtration of particles inside the air conditioner condenser is not included in the removal rates for physical filters. Cooling the air in the condenser may cause wet deposition of particles inside the air conditioner. This process is not explicitly treated in these simulations.

Deposition velocities (k_s)

Once indoors, air toxics may be removed from the air through deposition. It is not expected that benzene will readily deposit (Freijen and Bloemer, 2000); however, it may adsorb to the walls or upholstery in a microenvironment and, therefore, a distribution of small deposition velocities was allotted to benzene. An exponential distribution was used so that most of the deposition velocities would be zero or very close

to zero and no deposition velocity would exceed 1 cm/s. Diesel particles, on the other hand, would be expected to deposit to surfaces. The deposition velocity of diesel particles was calculated in two stages. First, a typical particle size distribution was selected (Kleeman et al.,1999). Then, an empirical equation that represents the indoor deposition of particles according to their size (Fogh et al., 1997) was used to determine the average indoor deposition velocity for diesel particles as well as the overall distribution.

Sources (S)

Not all contaminants in an indoor environment come from outdoor sources. There are many indoor sources that may, in fact, contribute much more to the indoor concentration than the outdoor sources. Environmental tobacco smoke (ETS), in particular, can cause large quantities of indoor pollution. One of the contaminants released in ETS is benzene. The indoor simulations for each of the microenvironments were repeated for benzene assuming an indoor source of benzene. The emission rates for the indoor source were developed from ETS emission factors (Singer et al., 2002) and smoking rates for residents of New York State (SAMHSA, 2000). The same emission rate was used in all three microenvironments. Although smoking is generally not allowed inside office buildings in many parts of the country, ETS is the most studied indoor source of benzene and the only one for which emission factors were identified. No indoor sources of diesel particles were simulated.

4.3 Indoor Model Simulation for Benzene

Each scenario was simulated by first selecting the grid cells from the fine grid CMAQ simulation corresponding to New York City (see Section 3). Forty-eight grid cells were included and the benzene concentrations were extracted for each time step. Next, the distributions for the microenvironment and toxics parameters were generated using the Crystal Ball software (Decisioneering, 1996). For each scenario, 10,000 Monte Carlo iterations were performed. The initial twenty-four hours of data from each scenario

were not used in determining the results in order to allow the indoor concentration levels to “spin up”.

The results of the indoor simulations for benzene are summarized in Table 4-3. For the benzene scenarios without indoor sources the indoor/outdoor ratio is close to one (see Figure 4-1). This is due to the fact that benzene is not affected by most filters and does not deposit quickly. Therefore, the indoor concentration tends to be similar to the outdoor concentration. The ratios above one are due to the time lag caused by air seeping into the microenvironments when the outdoor concentration decreases with time. The ratios below one are due to deposition as well as the time lag. The car microenvironment in particular is very close to one because there is almost no time lag due to the large infiltration and ventilation rates.

A time series profile of the indoor and outdoor benzene concentrations from one of the office microenvironments is shown in Figure 4-2. This figure demonstrates the relationship between indoor and outdoor concentrations as well as the small time lag that occurs.

For the benzene scenarios with indoor sources, the indoor/outdoor ratio is greater than one (see Figure 4-3). In some cases, the indoor/outdoor ratio is much greater than one, because smoking indoors causes indoor concentrations to increase quickly. This is particularly true for cars because of their small volumes; even with a quick turnover of outside air, the indoor concentration is greater than one. Moreover, when recirculated air is used rather than fresh air for ventilation, the indoor concentrations can become much larger than the outdoor concentrations.

Figures 4-4, 4-5, and 4-6 compare the same indoor/outdoor ratios of benzene with and without indoor sources for the home, office, and car microenvironments, respectively. In each of these cases, the scenarios including indoor sources have a much wider distribution than those without indoor sources. This difference is most important in the car microenvironment because the indoor/outdoor ratio is nearly always one without indoor sources, but the ratio significantly exceeds one when an indoor source is included.

Table 4-3. Statistics of indoor/outdoor concentration ratios of the indoor modeling scenarios for benzene.

Scenario	Mean	Median	Standard Deviation	10%	90%
Home, No Indoor Sources	0.87	0.91	0.13	0.69	0.99
Home, Indoor Sources	1.06	1.00	0.46	0.80	1.29
Office, No Indoor Sources	0.88	0.90	0.13	0.72	1.02
Office, Indoor Sources	2.63	1.75	4.16	1.04	4.64
Car, No Indoor Sources	0.98	0.99	0.03	0.94	1.00
Car, Indoor Sources	2.79	1.70	4.93	1.12	5.04

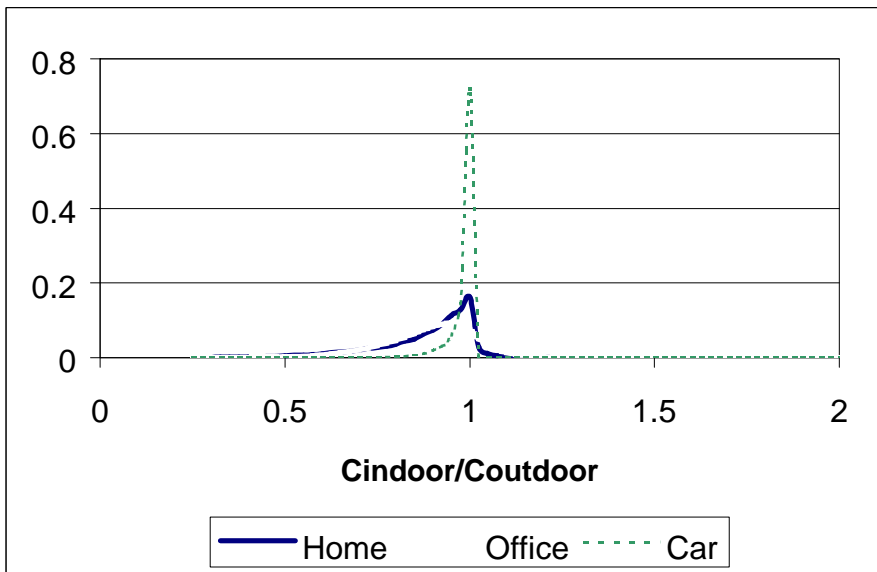


Figure 4-1. Distributions of indoor/outdoor ratios of benzene concentrations in microenvironments without indoor sources.

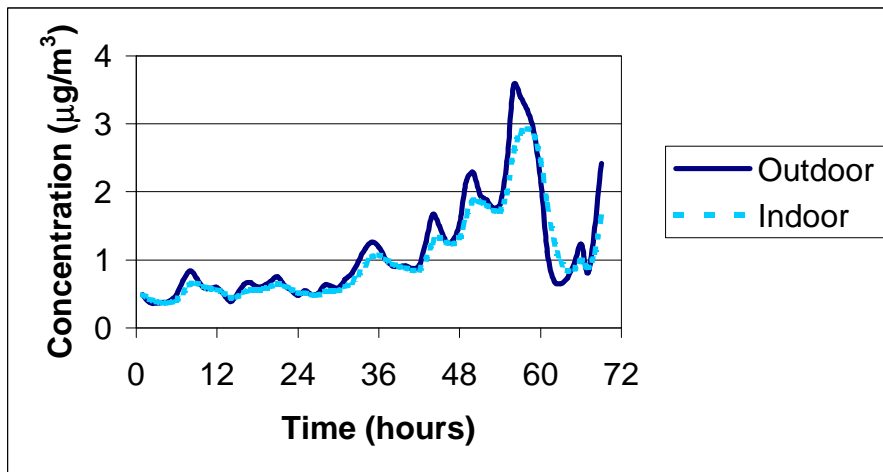


Figure 4-2. Time series profile of indoor and outdoor concentrations of benzene for the office microenvironment.

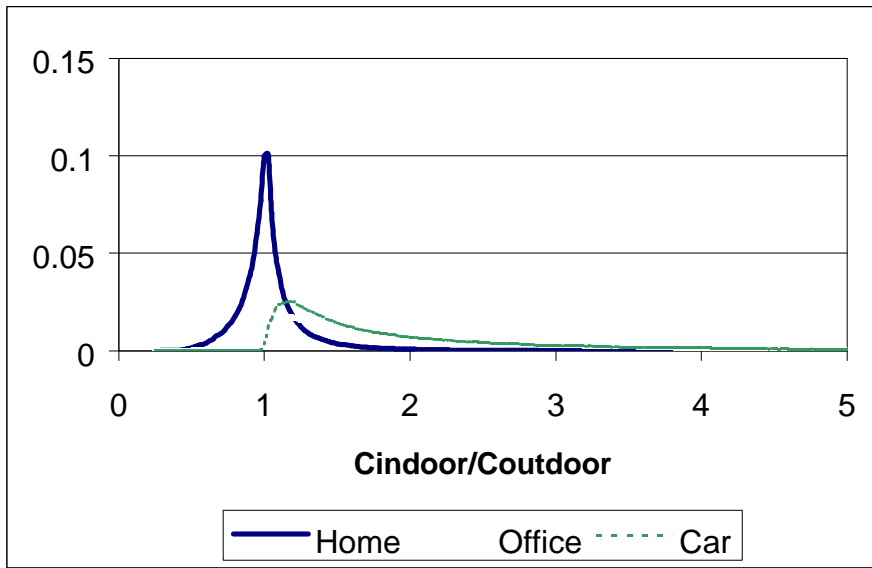


Figure 4-3. Distributions of indoor/outdoor ratios of benzene concentrations in microenvironments with indoor sources.

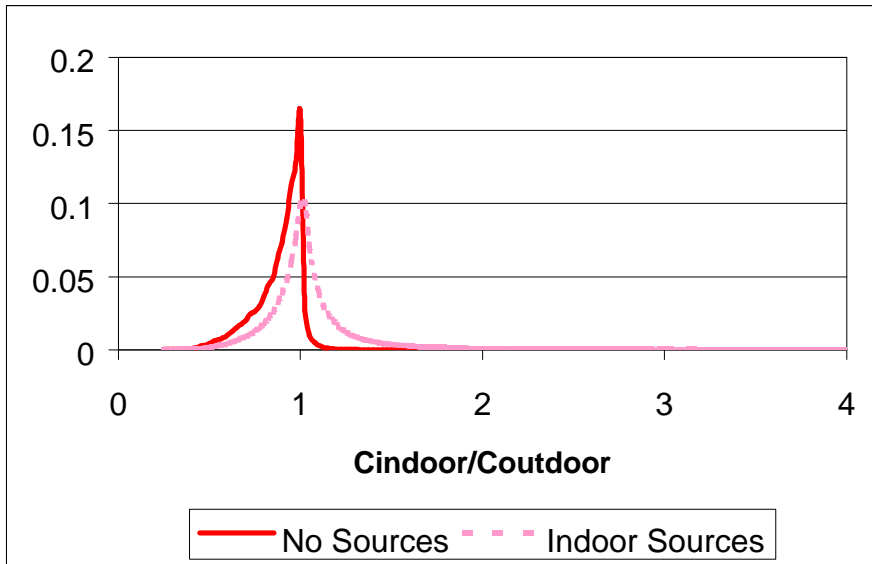


Figure 4-4. Distributions of indoor/outdoor ratios of benzene concentrations in the home microenvironment.

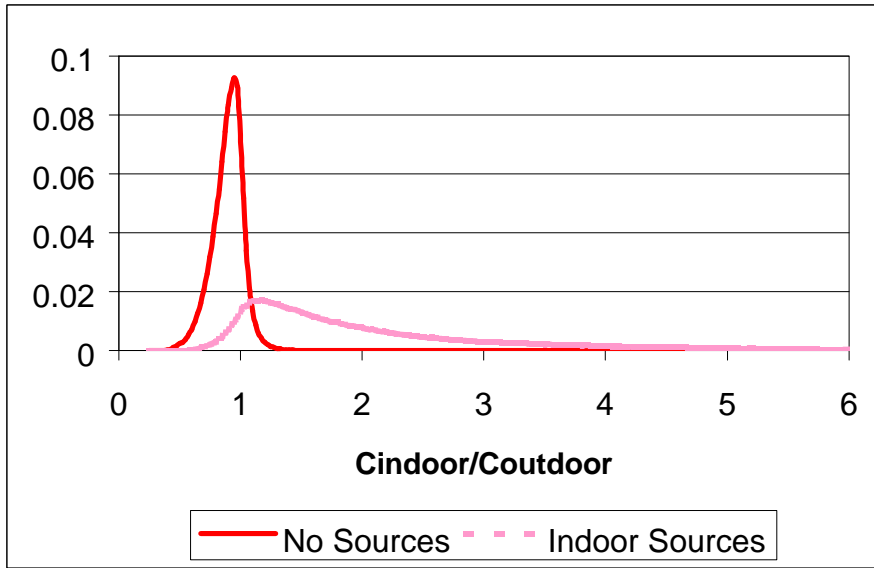


Figure 4-5. Distributions of indoor/outdoor ratios of benzene concentrations in the office microenvironment.

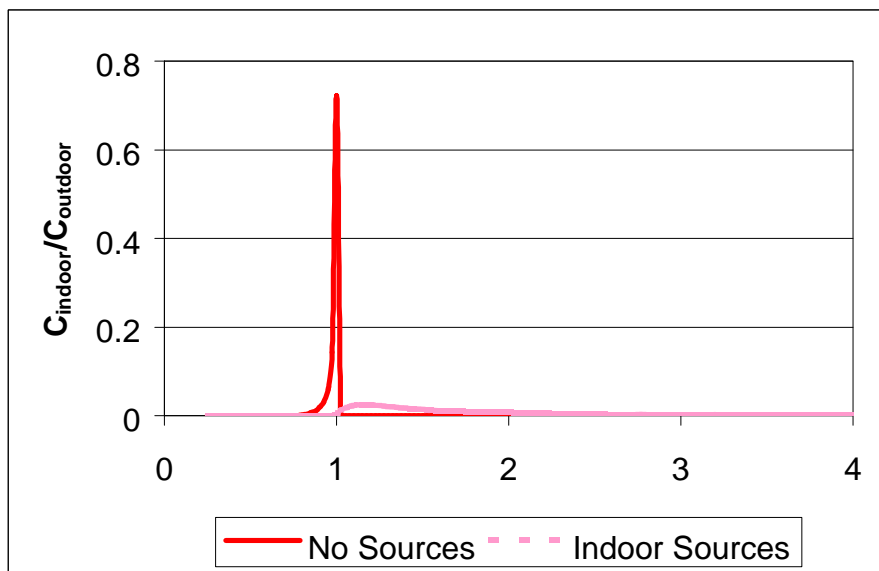


Figure 4-6. Distributions of indoor/outdoor ratios of benzene concentrations in the car microenvironment.

4.4 Indoor Model Simulation for Diesel Particles

The results for the three diesel scenarios are summarized in Table 4-4. As seen in Figure 4-7, the results of the three diesel scenarios are very different from each other. The office scenario has very low indoor/outdoor concentration ratios. These ratios are much lower than those seen in the other diesel scenarios or any of the benzene scenarios. This is because the office ventilation system was assumed to be centrally controlled, with very little infiltration and no open windows. Therefore, nearly all of the air entering the office has first passed through filters. Also much of the air circulated through the ventilation system is recirculated and, therefore, is filtered more than once and more time is available to remove particles through deposition. A time series profile of the indoor and outdoor diesel particle concentrations for one of the office microenvironments are shown in Figure 4-8.

As in the benzene simulation, the car microenvironment leads to indoor/outdoor ratios close to one. However, because of filtration and higher deposition rates, the diesel scenario results have a wider distribution than the benzene simulation results.

The indoor/outdoor ratio distribution for the home microenvironment presents an unusual shape with two modes (see Figure 4-7). The ventilation for the home microenvironment was split 62/38 in terms of air conditioning versus open windows and this split appears clearly in the results in the form of a bimodal distribution. The mode of lower ratios is due to homes with air conditioning, while the mode of values very close to one is due to homes with ventilation from open windows. The home ventilation system has lower particle filtration rates and higher infiltration rates than the office scenario, which leads to more unfiltered particles in the air. Therefore, the ratios in the lower mode of the home microenvironment distribution are higher than the ratios in the office simulation. Some measurements of particle penetration into microenvironments are available. These particle measurements are not specifically for diesel particles but are for size specific particles, making it possible to compare them to the results of this study. For example, Abt et al., (2000) measured indoor and outdoor concentrations in several homes and then used a model to determine how much of the particles in the homes could

Table 4-4. Statistics of the indoor/outdoor concentration ratios for the indoor modeling scenarios for diesel particles.

Scenario	Mean	Median	Standard Deviation	10%	90%
Home	0.75	0.75	0.16	0.53	0.94
Office	0.22	0.22	0.05	0.16	0.30
Car	0.90	0.91	0.12	0.75	1.01

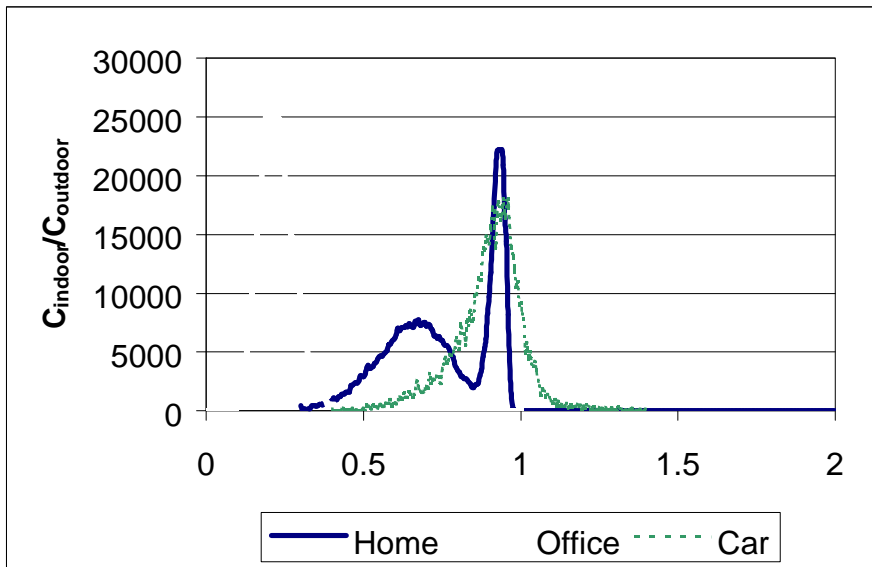


Figure 4-7. Distributions of indoor/outdoor ratios of diesel particle concentrations.

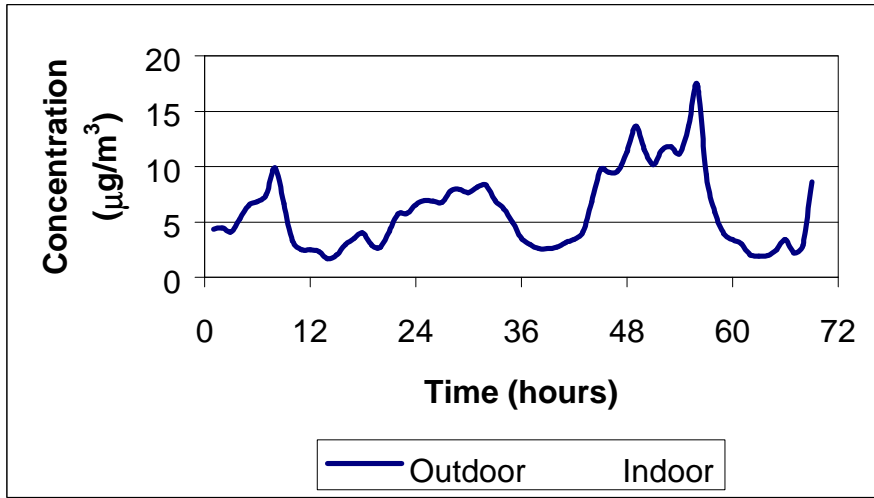


Figure 4-8. Time series profile of indoor and outdoor concentrations of diesel particles for an office microenvironment.

be expected to be due to outdoor sources. Their study found an indoor/outdoor ratio of 0.38 to 0.94 for particles ranging in size from 0.02 to 0.5 μm . This is similar to the range for diesel particles in the home microenvironment in this study.

Weschler et al. (1996) compared indoor and outdoor concentrations of particles for a commercial office building. This study found a large difference between the concentration of indoor and outdoor particles. For example, in their study, the outdoor concentration of 0.5 to 1.0 μm particles ranged from 10,000 to 3,500,000 counts/ ft^3 . At the same time the indoor concentration of 0.5 to 1.0 μm particles ranged from 1,000 to 1,000,000 counts/ ft^3 . While indoor/outdoor concentration ratios were not provided for the observed data, the very low indoor/outdoor concentration ratios calculated in this study were consistent with the results from the Weschler et al. (1996) study.

5. CONCLUSION

5.1 Summary

We have presented an integrated approach to air toxics modeling. Because air toxics include a large number of compounds that have widely different atmospheric lifetimes, the specific modeling needs are likely to differ from one toxic air pollutant to the next.

This integrated approach is based on the concept of multi-scale modeling with modeling domains possibly ranging from the globe to the local scale. Global modeling is required for air toxics with atmospheric lifetimes on the order of one month or more. Local modeling is needed to characterize the near-source impacts of emissions from major point sources, some major stationary area sources and mobile vehicles. In addition, it is essential to characterize the indoor concentrations of air toxics because (1) most people spend the majority of their time indoor and (2) indoor concentrations can differ significantly from outdoor concentrations.

In Phase I (Seigneur et al., 2001a), we reviewed the current status of air toxics modeling and concluded that, currently, major weaknesses include the atmospheric modeling of air toxics at regional scales and the absence of indoor modeling for many exposure studies. Consequently, we focused our case studies on these two topics.

The two air toxics selected for the case studies are benzene and diesel particles. On-road mobile sources account for about 80% and 40% of benzene and diesel particle emissions, respectively, in the eastern United States.

The Community Multiscale Air Quality model (CMAQ) was used for regional modeling. We simulated the 11-15 July 1995 episode over a domain covering the eastern United States with a 12 km horizontal resolution and a finer (4 km) resolution over a part of the northeastern United States that includes Washington, D.C. and New York City.

The results of the model simulations showed that benzene concentrations were commensurate with available measurements. Over the 4 km resolution domain, a comparison between simulated and measured concentrations showed a fractional error of 0.44, a fractional bias of 0.15 and a coefficient of determination (r^2) of 0.25. A

comparison between benzene concentrations in New York City and in Brigantine National Wildlife Refuge, NJ, showed that the urban concentrations were greater than the remote area concentrations by a factor of two to five.

The results of the diesel particle simulations showed spatial and temporal patterns that were similar to those obtained for benzene. However, because of the lesser contribution of on-road mobile sources to diesel particle emissions compared to benzene emissions, diesel particle concentrations showed stronger gradients between urban areas and remote areas. A comparison between diesel particle concentrations in New York City and in Brigantine National Wildlife Refuge, NJ, showed that the urban concentrations were greater than the remote area concentrations by a factor of two to ten. Assuming that diesel particles consist of 50% EC, the simulated EC concentrations were in close agreement (within 10%) with the measured concentration in the urban area (Washington, D.C.), but were significantly lower than the measured EC concentrations in the remote areas. This result suggests that other sources besides diesel-fueled engines (e.g., gasoline-powered engines) contribute to atmospheric EC concentrations and that EC may not be a good tracer for diesel particles.

Simulations of indoor concentrations were conducted for New York City. The results of the regional simulations with 4 km horizontal resolution were used to represent the outdoor concentrations. Three major types of indoor environments were simulated: a home, an office and a car. For benzene, environments with and without environmental tobacco smoke (ETS) were simulated since smoking is a significant source of benzene indoors. A probabilistic approach was used to account for the variability and uncertainties associated with many of the input parameters (outdoor concentration, indoor volume, surface/volume ratio, air change rate, indoor removal rate and indoor emission rate).

The results of the simulations showed that indoor concentrations may differ significantly from the outdoor concentrations. On average, the indoor/outdoor concentration ratio is less than one for benzene in the absence of ETS (mean values of 0.87, 0.88 and 0.98 for homes, offices and cars, respectively) and for diesel particles (mean values of 0.75, 0.22 and 0.90 for homes, offices and cars, respectively). The lower values for the indoor/outdoor concentration ratios of diesel particles result from the fact

that the particles can be removed more efficiently by filters and deposit more readily on indoor surfaces than benzene. Note that the indoor/outdoor concentration ratio can be greater than one for a given hour because of the variability in outdoor concentrations and the lag time between the indoor and outdoor concentrations. It is greater than one for benzene in the presence of ETS (mean values of 1.06, 2.63 and 2.79 for homes, offices and cars, respectively). These results strongly suggest that it is imperative to include the simulation of indoor micro-environments when estimating population exposure to air toxics.

It should be noted that the errors that may result from not simulating the indoor microenvironments are commensurate with the errors obtained in the air quality simulation (e.g., due to grid volume averaging). It is, therefore, important that the errors associated with the outdoor concentrations be minimized by means of better emissions inventories and, if feasible, modeling of the meteorology and air quality with better spatial resolution.

5.2 Recommendations

The case studies presented here provide an initial application of the modeling approach described in Section 2. Further applications should focus on the following areas.

- Other air toxics (e.g., formaldehyde, 1,3-butadiene) should be modeled and model simulation results should be compared to observations to the extent possible. Formaldehyde is of particular interest because (1) it is emitted from mobile vehicles, (2) it is also a secondary pollutant that is formed in the atmosphere from the oxidation of other VOC and (3) there are significant indoor sources of formaldehyde. As discussed in the Phase I report, we expect indoor sources to dominate formaldehyde concentrations indoors and, consequently, the indoor/outdoor concentration ratio should be significantly greater than one for most indoor microenvironments.

- Local modeling should be conducted to evaluate the relative contributions of urban/regional sources and local sources (e.g., roadways) in urban environments. To address this issue, a comparison of various modeling techniques described in the Phase I report appears warranted. A possible study is the application of three models, CALINE4, HYROAD and STREET to a few typical urban settings and their evaluation against available ambient data for air toxics (e.g., benzene, 1,3-butadiene). Such modeling appears warranted to address the problem of grid volume averaging associated with 3-D gridded models.
- A comparison of source attributions conducted using source modeling (as used in the two case studies presented here) and receptor modeling (as recommended in Section 2) is recommended. Source modeling involves uncertainties associated with the emission inventories, meteorological simulation and air quality simulation. Receptor modeling involves uncertainties associated with the available ambient data and, in the case of techniques such as the Chemical Mass Balance, emission source profiles. Applying such different approaches to a same problem, i.e., source attribution for major air toxics, will allow us to identify areas of agreements and discrepancies and, consequently, help us focus where uncertainties need to be reduced most. Receptor modeling has been applied to VOC (see Phase I report) and could be applied, for example, to conduct a source attribution for benzene. For example, receptor modeling studies conducted in Houston (Henry et al., 1997) and Atlanta (Henry et al., 1994) have included benzene. PAMS data can be used to that end. However, Schauer and Cass (2000) cautioned that there may be some unidentified sources of benzene that may adversely affect source apportionment when using chemical mass balance. Sensitivity simulations using CMAQ can be conducted in parallel to estimate the contributions of major source categories to ambient benzene concentrations. The results of these two approaches can then be compared and, if warranted, reconciled.

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