

Advanced chemical transport modeling of fine particulate matter to support exposure assessment

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Abstract

Fine particulate matter with aerodynamic diameter less than 2.5 μm ($\text{PM}_{2.5}$) has been associated with public health concerns due to short and long-term exposure. Chemical transport models (CMTs) are frequently used for developing air quality and emissions control policies that protect public health. To evaluate these policies, Chemical transport models (CTMs) must simulate $\text{PM}_{2.5}$ concentrations and their response to changes in emissions accurately. At high resolutions, the geographical distribution of $\text{PM}_{2.5}$ concentrations can have sharp gradients. During the last decades, regulations by the U.S. Environmental Protection Agency have led to significant reductions of the emissions of atmospheric pollutants including $\text{PM}_{2.5}$.

The CTM PMCAMx is used here to assess the impact of increasing model resolution on the model's ability to predict the variability, sources and population exposure of $\text{PM}_{2.5}$ concentrations at 36 x 36, 12 x 12, 4 x 4 and 1 x 1 km resolutions over the city of Pittsburgh; to evaluate the PMCAMx predictions at various grid resolutions against measurements of $\text{PM}_{2.5}$ concentration and composition; and to estimate the concentration, composition and sources of $\text{PM}_{2.5}$ over 20 years in the U.S.

At the finest resolution, the model successfully resolved intra-urban variations and individual roadways. Pollutants with significant local emissions such as elemental and organic carbon have gradients that can only be resolved at the finest resolution. PMCAMx predicts sulfate, elemental carbon and organic aerosol concentrations well with fractional biases below 10%. Agreement with total $\text{PM}_{2.5}$ measurements is also encouraging with a fractional bias of 3%. Prediction performance improves with increasing resolution reducing the average fractional error from 16% at 36 x 36 km to 12% at 1 x 1 km.

EC concentrations reduced by 23% due to a 37% reduction on emissions from 1990 to 2010. SO₂ emissions were reduced by 63% causing a large reduction of sulfate concentrations in the northeast of the U.S. A comparison between the predicted and observed reductions of EC, sulfate, and PM_{2.5} showed excellent correlations.

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Chapter 1. Introduction

Fine particulate matter with aerodynamic diameter less than $2.5\ \mu\text{m}$ ($\text{PM}_{2.5}$) contributes to poor air quality throughout large parts of the United States, which has been associated with public health concerns due to short and long-term exposure. Some of the health effects of $\text{PM}_{2.5}$ include premature death due to cardiovascular disease, increased chance of heart attacks and strokes, reduced lung development and function in children and people with lung diseases such as asthma and increases in hospital admissions due to heart and lung disease (Dockery and Pope, 1994; US EPA, 2012). Chemical transport models (CTMs) are frequently used for developing air quality and emissions control policies that protect public health. To evaluate these policies, CTMs must simulate $\text{PM}_{2.5}$ concentrations and their response to changes in emissions accurately.

At high resolutions, local sources such as commercial cooking, on-road traffic, residential wood combustion, and industrial activities can have sharp gradients that influence the geographical distribution of $\text{PM}_{2.5}$ concentrations. High-resolution measurements of PM_1 have found gradients of up to $\sim 2\ \mu\text{g m}^{-3}$ between urban background sites and those with high local emissions (Gu et al., 2018; Robinson et al., 2018).

During the last decades, regulations by the U.S. Environmental Protection Agency (EPA) have led to significant reductions of the emissions of SO_2 , NO_x , CO, volatile organic compounds (VOCs), and primary $\text{PM}_{2.5}$ from electrical utilities and other industrial sources, transportation, and other sources. Xing et al., (2013) estimated emissions reductions from 1990 to 2010 primary $\text{PM}_{2.5}$ by 34%. At the same time, there have been significant reductions of the $\text{PM}_{2.5}$ levels in practically all areas of the US (Meng et al., 2019).

The demographic characteristics of the population can have large variations at the neighborhood scale and it is important to assess the exposure of different sub-populations to air pollutants and the resulting health effects, a concept known as Environmental Justice (Anand, 2002). These demographic characteristics have also changed in time, as the social and economic characteristics of the country have evolved. CTMs can be useful tools to address environmental justice issues associated with particulate matter since they simulate all the major processes that impact $PM_{2.5}$ concentrations and transport. CTMs can also assess the contribution of different sources and how those vary in space and time. In this work, the Particulate Matter Comprehensive Air quality Model with Extensions (PMCAMx) (Karydis et al., 2010; Murphy and Pandis, 2010; Tsimpidi et al., 2009) is used to predict $PM_{2.5}$ concentrations at high resolutions in the city of Pittsburgh and from 1990 to 2010 in the U.S.

Chapter 2 addresses the impact of increasing model resolution on the model's ability to predict the variability, sources and population exposure of $PM_{2.5}$ concentrations at 36 x 36, 12 x 12, 4 x 4 and 1 x 1 km resolutions over the city of Pittsburgh. Emissions were calculated using the EPA's Emission Modeling Platform (v6.3) for the National Emissions Inventory for 2011 (NEI11) (Eyth and Vukovich, 2016) using the default 2017 projected values. New spatial surrogates for commercial cooking and on-road traffic were also created for the finest grid.

The impact of increasing model resolution on the model's ability to predict $PM_{2.5}$ variations on the urban scale in Pittsburgh is examined in Chapter 3. We evaluate the PMCAMx predictions at various grid resolutions against regulatory measurements of $PM_{2.5}$ concentration and composition, research measurements by an Aerosol Mass Spectrometer (Gu et al., 2018), and measurements from a network of low-cost sensors (Zimmerman et al., 2018).

In Chapter 4 we use the source resolved, historic emission inventories of Xing et al. (2013) with biogenic emissions calculated using MEGAN3 (Jiang et al., 2018) to estimate the concentration, composition, and sources of PM_{2.5} over 20 years in the U.S. The model predictions are compared with the available measurements. The sources responsible for the PM_{2.5} reductions in various areas of the country are identified and their contribution to the reductions is quantified.

The results and conclusions of this work are summarized in Chapter 5 along with recommendations for future work.

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Chapter 2. Source-Resolved Variability of Fine Particulate Matter in an Urban Area

2.1 Introduction

Particulate matter with aerodynamic diameter less than $2.5\ \mu\text{m}$ ($\text{PM}_{2.5}$) contributes to poor air quality throughout large parts of the United States. These particles directly affect visibility (Seinfeld and Pandis, 2006) and have been associated with long and short-term health effects such as premature death due to cardiovascular disease, increased chance of heart attacks and strokes, reduced lung development and function in children and people with lung diseases such as asthma and increases in hospital admissions due to heart and lung disease (Dockery and Pope, 1994; US EPA, 2012).

At high resolutions, local sources such as commercial cooking, on-road traffic, residential wood combustion, and industrial activities can have sharp gradients that influence the geographical distribution of $\text{PM}_{2.5}$ concentrations. High-resolution measurements of PM_1 have found gradients of up to $\sim 2\ \mu\text{g m}^{-3}$ between urban background sites and those with high local emissions (Gu et al., 2018; Robinson et al., 2018).

A key limiting factor on the modeling of particulate matter at high resolutions is the geographical distribution of emissions. Previous studies have found that coarse grid emissions interpolated to higher resolutions have small to modest improvements in model predictive ability for ozone (Arunachalam et al., 2006; Kumar and Russell, 1996), secondary organic aerosol (Fountoukis et al., 2013; Stroud et al., 2011) and nitrate (Zakoura and Pandis, 2019, 2018). Pan et al., (2017) used the default approach from the U.S. Environmental Protection Agency (EPA) National Emissions Inventory (NEI) to allocate county-based emissions to model grid cells at $4\ \text{x}$

4 and 1 x 1 km and found only small changes to model performance for NO_x and O₃, while the 1 x 1 km case showed more detailed features of emissions and concentrations in heavily polluted areas.

Improvements in the resolution of emission inventories have been focused on traffic as this source exhibits significant variability at high resolutions. Recent approaches to building high-resolution traffic inventories include origin-destination by vehicle class (Ma et al., 2019), synthetic population mobility (Elessa Etuman and Coll, 2018) and fuel sales combined with traffic counts (McDonald and McBride, 2014). Other sectors such as biomass burning for residential heating and commercial cooking have been identified as very uncertain in current inventories (Day et al., 2019). Recent versions of the NEI have made progress addressing the total emissions and temporal distributions of biomass burning and commercial cooking (Eyth and Vukovich, 2016) but there is still significant uncertainty on their geographical location at a sub-county scale. Robinson et al., (2018) found greatly elevated organic aerosol concentrations (10s of $\mu\text{g m}^{-3}$) in the vicinity of numerous individual restaurants and commercial districts containing multiple restaurants indicating that commercial cooking is a source of large gradients on the urban scale.

Population density and the socio-economic indicators of that population, such as income or access to healthcare, show large gradients in the urban scale. It is important to assess the exposure of different sub-populations to air pollutants and the resulting health effects, a concept known as Environmental Justice (Anand, 2002).

We use the Particulate Matter Comprehensive Air quality Model with Extensions (PMCAMx) to study the impact of increasing model resolution on the model's ability to predict the variability, sources and population exposure of PM_{2.5} concentrations on the urban scale in Pittsburgh. We compare predicted variability at 36 x 36, 12 x 12, 4 x 4 and 1 x 1 km resolutions

over the city of Pittsburgh during one typical summer and one typical winter month of 2017. Additional sensitivity simulations were performed to determine contributions from selected sources to concentrations. The results of the winter simulations are used to estimate exposure to PM_{2.5} at all resolutions and from the selected sources.

2.2 PMCAMx Description

The Particulate Matter Comprehensive Air quality Model with Extensions (PMCAMx) (Karydis et al., 2010; Murphy and Pandis, 2010; Tsimpidi et al., 2009), uses the framework of the CAMx model (Environ, 2006) to describe horizontal and vertical advection and diffusion, emissions, wet and dry deposition, gas, aqueous and aerosol-phase chemistry. A 10-size section aerosol sectional approach is used to dynamically track the evolution of the aerosol mass distribution. The aerosol species modeled include sulfate, nitrate, ammonium, sodium, chloride, elemental carbon, water, primary and secondary organics, and other non-volatile aerosol components. The SAPRC99 (Statewide Air Pollution Research Center) photochemical mechanism (Carter, 1999) is used for the simulation of gas-phase chemistry. The version of SAPRC used here includes 237 reactions and 91 individual and surrogate species. For inorganic growth, a bulk equilibrium approach was used, assuming equilibrium between the bulk inorganic aerosol and gas phases (Pandis et al., 1993). The partition of the various semivolatile inorganic aerosol components and aerosol water is determined using the ISORROPIA aerosol thermodynamics model (Nenes et al., 1998). The primary and secondary organic aerosol components are described using the volatility basis set approach (Donahue et al., 2006). For primary organic aerosol (POA) ten volatility bins, with effective saturation concentrations ranging from 10^{-3} to $10^6 \mu\text{g m}^{-3}$ at 298 K are used. Anthropogenic (aSOA) and biogenic (aSOA) are modeled with 4 volatility bins (1, 10, 10^2 , $10^3 \mu\text{g m}^{-3}$) (Murphy and Pandis, 2009) using NO_x dependent yields (Lane et al., 2008). More

detailed descriptions of PMCAMx can be found in Fountoukis et al., (2011) and Zakoura and Pandis, (2018).

2.3 Model Application

PMCAMx was used to simulate air quality over the metropolitan area of Pittsburgh during February and July 2017. For the base-case simulation we used a one-way nested structure with a 36 x 36 km master grid covering the continental United States, with nested grids of 12 x 12 km, 4 x 4 km in South Western Pennsylvania and a 1 x 1 km grid covering the city of Pittsburgh, most of Allegheny County and the upper Ohio River valley (Figure 2-1A). The 1 x 1 km grid covers a 72 x 72 km area (Figure 2-2B).

The surface concentrations at the boundaries of the 36 x 36 km grid are shown in Table 2-1. These values were applied to all upper air layers assuming a constant mixing ratio. Horizontal wind components, vertical diffusivity, temperature, pressure, water vapor, clouds, and rainfall were generated using the Weather Research and Forecasting (WRF v3.6.1) model over the whole modeling domain with horizontal resolution of 12 km. The data was interpolated to higher resolutions when needed. Initial and boundary meteorological conditions for the WRF simulations were generated from the ERA-Interim global climate re-analysis database, together with the terrestrial data sets for terrain height, land-use, soil categories, etc. from the United States Geological Survey (USGS) database. The WRF modeling system is prepared and configured in a similar way as described by Gilliam and Pleim, (2010). This configuration is recommended for air quality simulations (Hogrefe et al., 2015; Rogers et al., 2013).

Emissions were calculated using the EPA's Emission Modeling Platform (v6.3) for the National Emissions Inventory for 2011 (NEI11) (Eyth and Vukovich, 2016) using the default 2017 projected values. Base emissions were calculated first at a 12 km resolution for the full modeling

domain using the Sparse Matrix Operator Kernel Emissions (SMOKE) model and our WRF meteorological data. For the higher resolution grids, the spatial surrogates provided with Platform v6.3 (Adelman, 2015) were used for all sectors except commercial cooking and on-road traffic for which custom surrogates were developed. The emissions by all sources together with the chemical composition are summarized in Table 2-2.

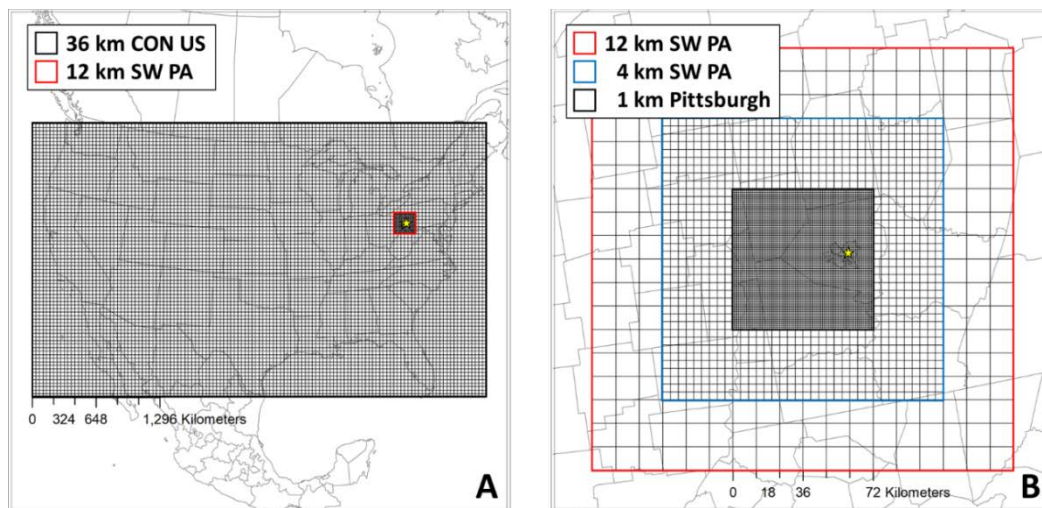


Figure 2-1. Modeling domain used for the PMCAMx simulations. (A) 36 x 36 km continental U.S. grid. (B) 12 x 12 and 4 x 4 km South Western Pennsylvania grids, and 1 x 1 km Pittsburgh nested grids.

Table 2-1. Outer (CONUS) boundary condition concentrations of major aerosol species.

Component	Concentration ($\mu\text{g m}^{-3}$)			
	West	East	South	North
Nitrate	0.01	0.01	0.03	0.03
Ammonium	0.14	0.25	0.24	0.16
Sulfate	0.64	1.12	0.81	0.68
Elemental Carbon	0.04	0.05	0.09	0.03
Organic Aerosol	0.20	0.16	0.58	0.13

In this work, we used normalized restaurant count to distribute the commercial cooking emissions in space in the 1x1 km inner domain. Geographical information was collected for all locations labeled as “restaurant” from the freely accessible Google Places Application

Programming Interface (API) for the western Pennsylvania area, eastern Ohio and northern West Virginia. Using this new spatial surrogate, PM_{2.5} emissions from commercial cooking are enhanced primarily in the Pittsburgh urban core with a maximum increase of 1200 kg g⁻¹ km⁻² (Figure 2-2A).

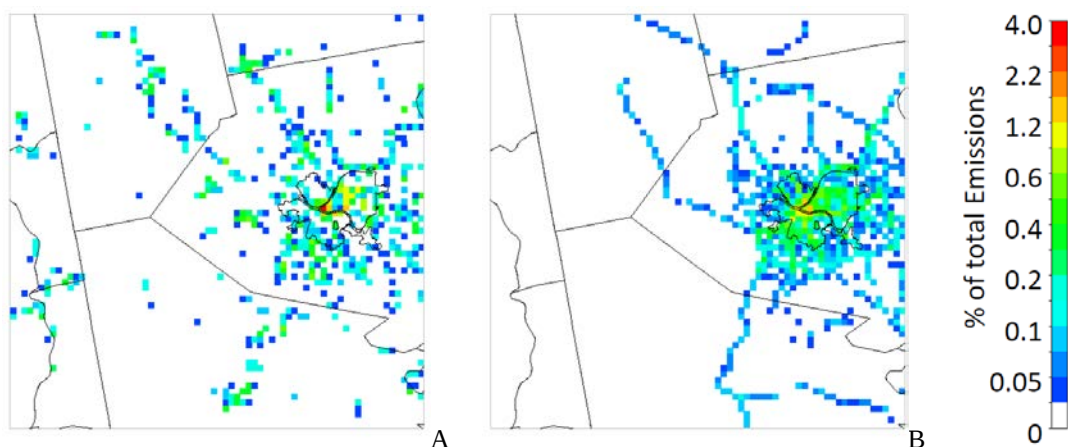


Figure 2-2. Percentage of PM_{2.5} emissions in each 1x1 km computational cell for: (A) commercial cooking and (B) on road traffic.

Table 2-2. PM_{2.5} emissions by source for the 1 x 1 km Pittsburgh domain (February 2017).

Source Type	Emissions (kg d ⁻¹ km ⁻²)								
	PM _{2.5}	OA	EC	Chl.	Na	Amm.	Nitrate	Sulfate	Other
Agricultural dust	68.7	9.7	0.4	0.2	0.1	0.1	0.1	0.7	57.2
River barges	19.0	4.2	14.7	0.0	0.0	0.0	0.0	0.1	0.1
Cooking	242	223	8.3	2.2	0.8	0.0	1.1	0.6	6.0
Misc. area sources	683	445	56.7	30.5	3.0	5.6	1.7	42	97.8
Off-road	147	56.2	73.1	0.3	0.1	0.0	0.3	1.1	16.1
Oil-gas (Area)	35.3	1.7	0.0	0.0	0.0	0.0	0.1	8.3	23.2
On-road traffic	188	84.6	75.2	0.3	0.1	1.8	0.6	8.3	16.4
Rail	40.7	8.9	31.4	0.0	0.0	0.0	0.0	0.1	0.2
Biomass burning	1,869	1,696	105	5.6	1.8	2.8	3.6	7.7	46.3
Power generation	3,517	201	194	2.8	0.0	15.7	2.6	460	2,641
Industrial	1,106	192	134	79.4	65.3	10.1	21.1	173	428
Oil-gas (point)	2.8	1.0	1.1	0.0	0.0	0.0	0.1	0.2	0.5

To accurately capture spatial patterns of on-road traffic, we use the output of a link-level, origin-destination by vehicle class traffic model of Pittsburgh (Ma et al., 2019). This traffic model simulates traffic counts and speed by hour-of-day using observations from Pennsylvania Department of Transportation sites throughout Pittsburgh. As expected, emissions in areas with major highways are quite high (Figure 2-2B). Changes in on-road emissions are smaller with an enhancement of $210 \text{ kg d}^{-1} \text{ km}^{-2}$ at a major highway intersection near downtown.

2.4 PM_{2.5} concentrations and sources during winter

2.4.1 Effect of grid resolution

The results of the simulations with the four resolutions are shown in Figures Figure 2-3 and Figure 2-4. For the area of interest, the simulations at $36 \times 36 \text{ km}$ resolves concentration fields at the county scale. The urban-rural gradient is resolved in the $12 \times 12 \text{ km}$ simulations. Increasing the resolution to $4 \times 4 \text{ km}$, large stationary sources such as power plants and large industrial installations are resolved. Finally, the resolution increase to $1 \times 1 \text{ km}$ resolves the intra-urban variations in Pittsburgh and medium-sized industrial installations.

The predicted maximum PM_{2.5} concentration in the inner domain increases from $10.5 \mu\text{g m}^{-3}$ at $36 \times 36 \text{ km}$, to $11.7 \mu\text{g m}^{-3}$ at 12×12 , to $12.8 \mu\text{g m}^{-3}$ at 4×4 , and finally to $14.2 \mu\text{g m}^{-3}$ at $1 \times 1 \text{ km}$ (Figure 2-3), a 35% increase. On the other end, the predicted minimum PM_{2.5} concentration changes from $8.2 \mu\text{g m}^{-3}$ at $36 \times 36 \text{ km}$ to $6.9 \mu\text{g m}^{-3}$ at 12×12 and remains practically the same at even higher resolutions. This corresponds to the “background” concentration level for the area during the simulation period, so further resolution enhancements do not change this value. The standard deviation of the predicted concentration can be used as a measure of the concentration variability in the area. This standard deviation changes from $0.84 \mu\text{g m}^{-3}$ at 36×36 , to $1.26 \mu\text{g m}^{-3}$ at 12×12 , to $1.48 \mu\text{g m}^{-3}$ at 4×4 and to $1.32 \mu\text{g m}^{-3}$ at $1 \times 1 \text{ km}$. These results indicate an increase of

the PM_{2.5} variability by 58% when one moves from the coarse to the finest resolution. However, most of this change in variability (51% out of the 58%) appears when one moves from 36x36 to 12x12 km.

Elemental carbon is a primary aerosol component with sources that are quite variable in space. The predicted maximum PM_{2.5} EC increased by a factor of 2.9, from 0.6 $\mu\text{g m}^{-3}$ at the 36 x 36 km resolution to 1.6 $\mu\text{g m}^{-3}$ at 1 x 1 km (Figure 2-3). The predicted maximum EC is, as expected in the Pittsburgh downtown area. On the other hand, the predicted minimum of EC is reduced by only 0.1 $\mu\text{g m}^{-3}$, from 0.34 $\mu\text{g m}^{-3}$ at 36x36 km to 0.24 at resolutions lower or equal than 4x4 km. The standard deviation of the predicted EC doubles from 0.09 $\mu\text{g m}^{-3}$ at 36 x 36 km to 0.18 $\mu\text{g m}^{-3}$ at 1 x 1 km. Approximately 66% of this increase in variability appears in the transition from the coarse to the intermediate resolution of 12 x 12 km. The fine and the finest resolutions are needed to resolve the other half of the predicted variability.

During this winter period a significant fraction (79%) of the OA in the Pittsburgh area is primary and therefore the higher resolution results in increases of the predicted maximum concentrations in space from 3 $\mu\text{g m}^{-3}$ at the coarse resolution to 4.2 $\mu\text{g m}^{-3}$ at the intermediate to 5.5 $\mu\text{g m}^{-3}$ at the finest resolution (Figure 2-3). This corresponds to an increase by a factor of 1.8, more than the total PM_{2.5}, but much less than the EC. The predicted maximum is located in downtown Pittsburgh, with additional hotspots in neighboring counties that are resolved at the fine and finest resolution. The predicted minimum changes from 2.1 $\mu\text{g m}^{-3}$ at 36x36 to 1.6 $\mu\text{g m}^{-3}$ at 12x12 with small reductions at higher resolutions. The variability (standard deviation) of the OA concentration field of the predicted concentration increases by a factor of approximately 1.6 from 0.39 $\mu\text{g m}^{-3}$ at 36 x 36, to 0.65 $\mu\text{g m}^{-3}$ at 12 x 12 km. The increase is small at even higher resolutions

with the standard deviation of OA reaching $0.68 \mu\text{g m}^{-3}$ at $1 \times 1 \text{ km}$ (an increase by a factor of 1.7).

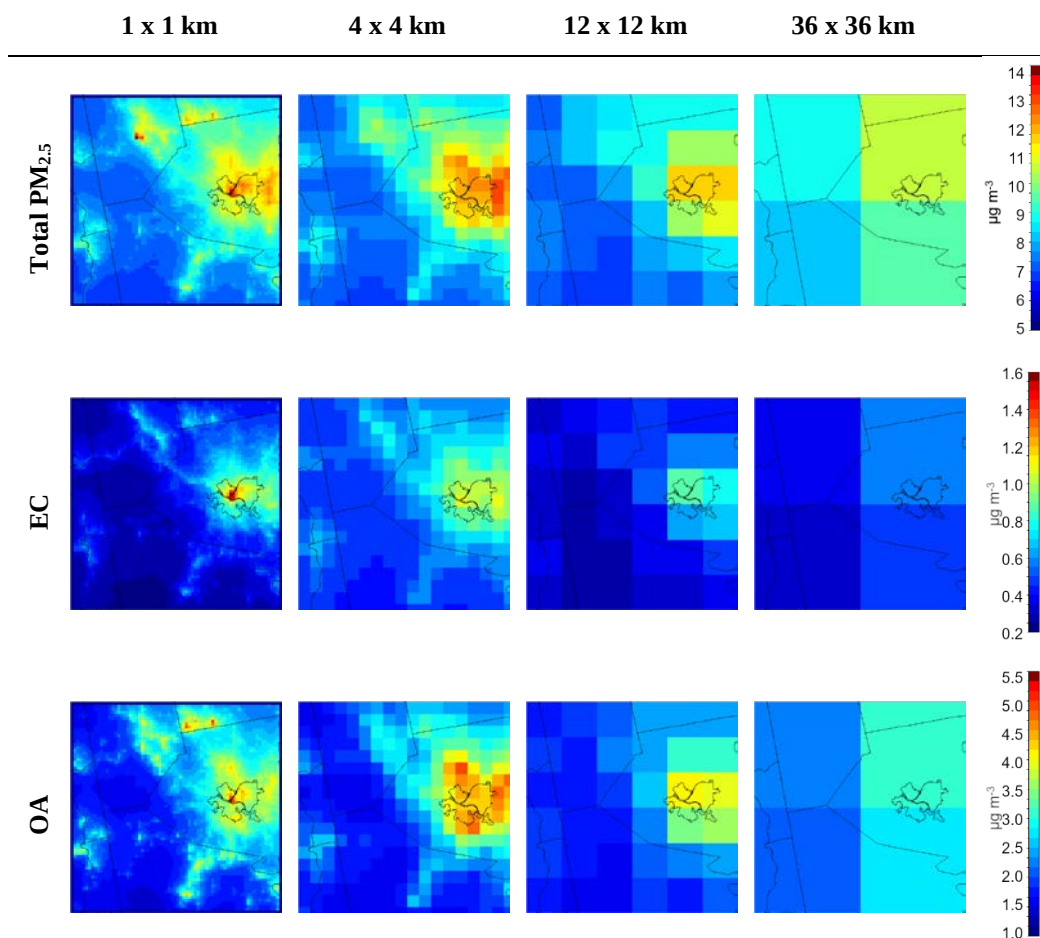


Figure 2-3 Average predicted ground-level concentration of total $\text{PM}_{2.5}$, EC, and OA at 36×36 , 12×12 , 4×4 and $1 \times 1 \text{ km}$ resolutions during February 2017.

The predicted fine nitrate levels are relatively high ranging from 2.07 to $2.63 \mu\text{g m}^{-3}$ in the coarse-resolution simulation. This is expected in this wintertime period due to the partitioning of nitric acid and ammonium in the particulate phase. This predicted concentration range increases to 1.64 - $2.40 \mu\text{g m}^{-3}$ in the finest scale simulation with higher levels in the northeast of the domain. The standard deviation of the predicted concentration does not show any significant trend changing from $0.201 \mu\text{g m}^{-3}$ at 36×36 to $0.109 \mu\text{g m}^{-3}$ at $1 \times 1 \text{ km}$.

For PM_{2.5} ammonium, changes with increasing resolution are modest with the predicted minimum being reduced from 1.3 $\mu\text{g m}^{-3}$ at 36x36 to approximately 1.1 $\mu\text{g m}^{-3}$ at all other higher resolutions. The predicted maximum also decreases from 1.5 $\mu\text{g m}^{-3}$ at 36x36 km to 1.4 $\mu\text{g m}^{-3}$ at all other higher resolutions. As with nitrate, the standard deviation does not show any significant trend changing from 0.08 $\mu\text{g m}^{-3}$ at 36 x 36, to 0.1 $\mu\text{g m}^{-3}$ at 12 x 12, to 0.07 $\mu\text{g m}^{-3}$ at 4 x 4 and to 0.09 $\mu\text{g m}^{-3}$ at 1 x 1 km.

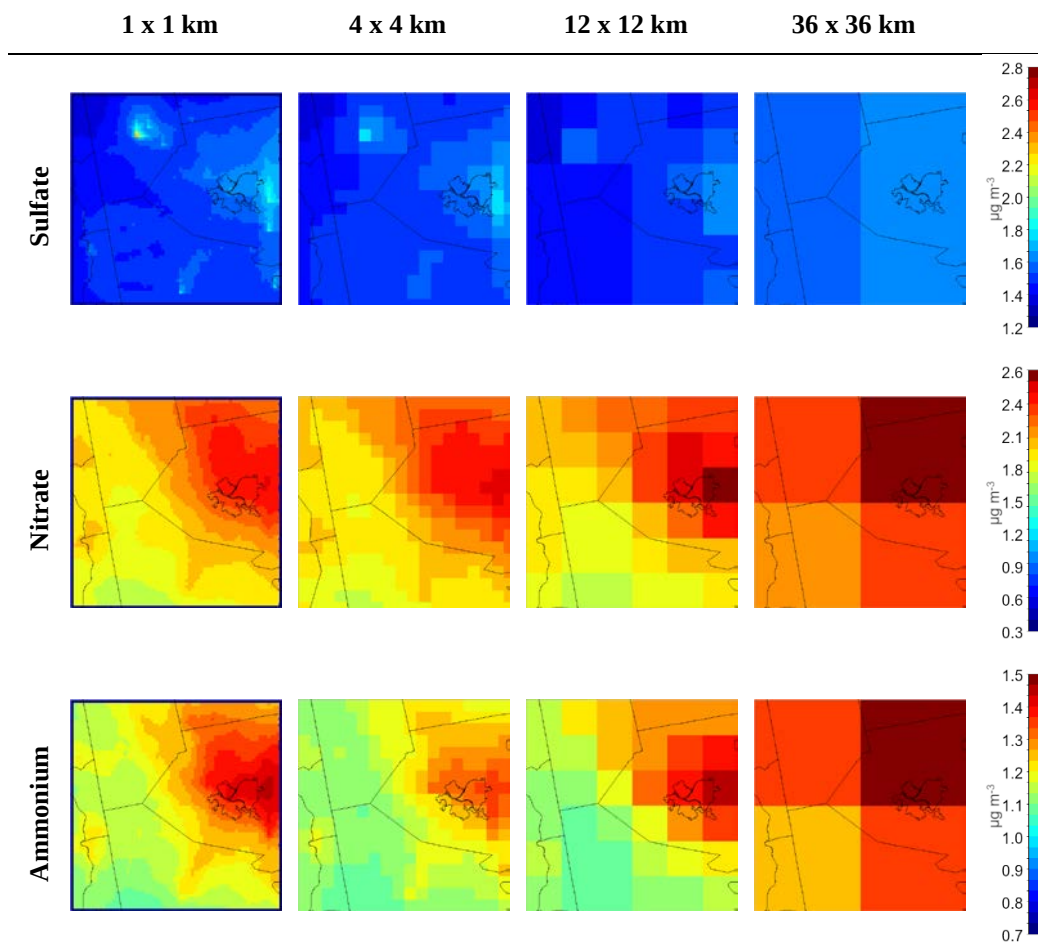


Figure 2-4. Average predicted ground-level concentration of PM_{2.5} sulfate, nitrate and ammonium at a 36 x 36, 12 x 12, 4 x 4 and 1 x 1 km resolution during February 2017.

2.4.2 Source Apportionment

We performed zero-out simulations just in the 1x1 km Pittsburgh grid to determine the contributions of eight source categories to the total $\text{PM}_{2.5}$. The local sources quantified included: commercial cooking, industrial, biomass burning, on-road traffic, power generation, and miscellaneous area sources. The miscellaneous area sources sector includes a large variety of emission sources that are not classified in any of the sources in Table 2-2. These include chemical manufacturing, solvent utilization for surface coatings, degreasing and dry cleaning, storage and transport of petroleum products, waste disposal and incineration, and cremation of human remains. The emissions from the agricultural dust, river barges, off-road equipment, oil-gas activities, and rail were grouped on the “others” source. All emissions (particulate and gas-phase) from each source were set to zero, and the results of the zero-out simulation were subtracted from those of the baseline simulation to estimate the corresponding source contribution. The contribution of long-range transport from outside the inner domain was also estimated by setting all local sources to zero.

On average, commercial cooking emissions contribute 0.9% of the $\text{PM}_{2.5}$ mass in the modeling domain with a maximum contribution of $2.43 \mu\text{g m}^{-3}$ in downtown Pittsburgh, with smaller contributions in the surrounding urban area. This contribution accounts for 18% of the $\text{PM}_{2.5}$ mass in downtown Pittsburgh. The contribution from commercial cooking is localized around downtown Pittsburgh and shows very little variability outside of the urban core with a standard deviation of $0.12 \mu\text{g m}^{-3}$. On-road traffic emissions are most important in major highway intersections and river crossings surrounding downtown Pittsburgh with a maximum contribution of $1.72 \mu\text{g m}^{-3}$ accounting for 11%. On average, on-road traffic contributes 1.4% of the $\text{PM}_{2.5}$ mass. The contribution from on-road traffic shows higher variability (standard deviation: $0.12 \mu\text{g}$

m^{-3}) since this sector contributes significantly to areas adjacent to the network of highways that radiates from the Pittsburgh downtown. Biomass burning is used during the winter for residential heating and recreation. This source contributes a maximum of $3.85 \mu\text{g m}^{-3}$ in Cranberry, a northern suburb of Pittsburgh located in the neighboring Butler county. In the downtown Pittsburgh area, the contribution from biomass burning accounts for 10% of the $\text{PM}_{2.5}$. This source shows the highest variability with a standard deviation of $0.61 \mu\text{g m}^{-3}$. The miscellaneous area source sector contributes 6% of the $\text{PM}_{2.5}$ on average. Since this sector encompasses a variety of sources and activities, its contribution shows significant variability with a standard deviation of $0.32 \mu\text{g m}^{-3}$ and an average contribution of 5.9%. The maximum contribution is located in the Pittsburgh urban core with $1.52 \mu\text{g m}^{-3}$, accounting for 10.0% of the $\text{PM}_{2.5}$.

The maximum contribution of $5.67 \mu\text{g m}^{-3}$ from industrial sources is a cluster of industrial facilities in the town of Butler, 37 km northwest of Pittsburgh. The maximum $\text{PM}_{2.5}$ concentration of the modeling domain is located here. In this location long-range transport contributes 43% of the $\text{PM}_{2.5}$ followed by industrial sources with 40% and biomass burning with 10%. On average, the contribution from industrial sources is low with 2.8%. In downtown Pittsburgh, the contribution is lower still with 2%. The power generation sector contributes a maximum of $0.43 \mu\text{g m}^{-3}$ in the plume of the Bruce Mansfield power plant northwest of Pittsburgh. This sector shows the smallest variability with $0.06 \mu\text{g m}^{-3}$.

Long-range transport from outside the inner modeling domain is the major source of $\text{PM}_{2.5}$ during this period contributing an average of 74%. This contribution varies from $7.1 \mu\text{g m}^{-3}$ in the southeast corner of the domain decreasing in the direction of the Pittsburgh urban core where the contribution is reduced to $6 \mu\text{g m}^{-3}$. In areas where there are significant local emissions such as the Pittsburgh downtown, the contribution from long-range transport decreases to 45%.

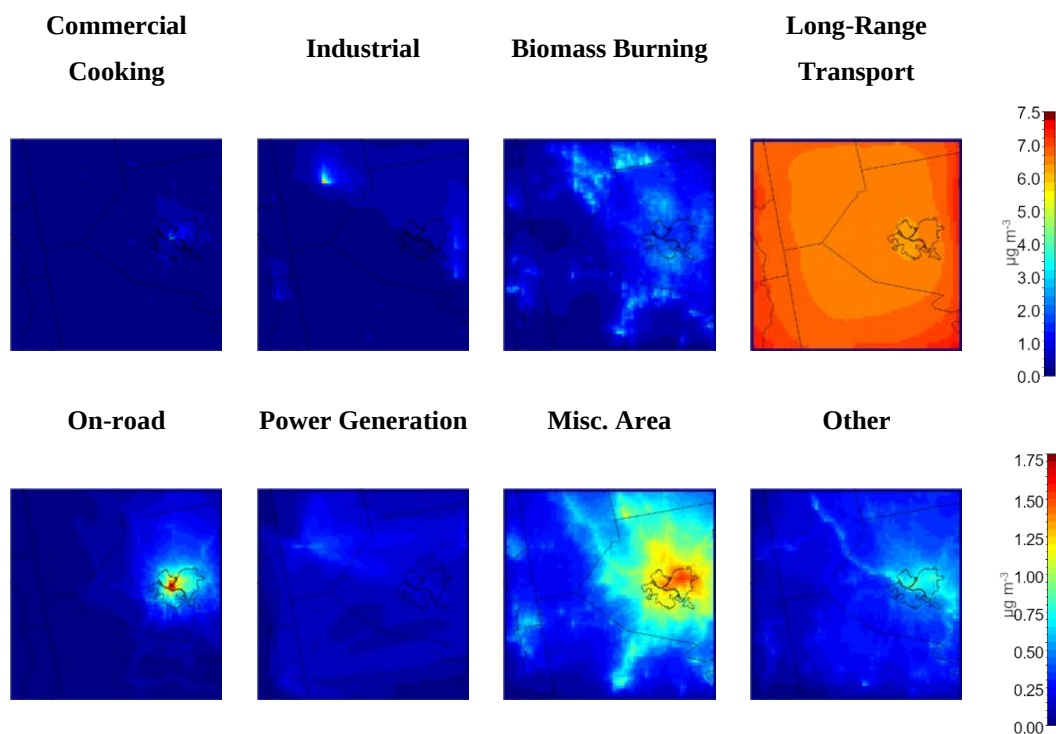


Figure 2-5. Contribution of each source to total $\text{PM}_{2.5}$ during February 2017. Two different scales are used.

Contributions for all remaining sources are largest in the Pittsburgh downtown with $0.88 \mu\text{g m}^{-3}$, accounting for 5% of the $\text{PM}_{2.5}$. This sector also significantly contributes on the Ohio and Monongahela river valleys, where there is important rail and river traffic. On average, these sources contribute 3% of the $\text{PM}_{2.5}$ and show a moderate variability with a standard deviation of $0.14 \mu\text{g m}^{-3}$.

For all local sources, the minimum contribution is close to zero (less than $0.1 \mu\text{g m}^{-3}$) and is located at the southwestern corner of the domain, near the Ohio – West Virginia border.

2.5 $\text{PM}_{2.5}$ concentrations and sources during summer

2.5.1 Effect of grid resolution

The predicted $\text{PM}_{2.5}$ concentrations in the simulated summer period are lower than during the winter period and more uniform, however, the qualitative behavior of the model at the different

scales remains the same (Figure 2-6). The spatial variability of the average PM_{2.5} concentrations is approximately 0.73 $\mu\text{g m}^{-3}$ less than during the winter. The standard deviation of the PM_{2.5} increases from 0.21 $\mu\text{g m}^{-3}$ at 36 x 36, to 0.37 $\mu\text{g m}^{-3}$ at 12 x 12, to 0.51 $\mu\text{g m}^{-3}$ at 4 x 4 and to 0.59 $\mu\text{g m}^{-3}$ at 1 x 1 km. At the finest scale, the variability in the summer is 45% of that in the winter. The behavior of the predicted extremes in the PM_{2.5} concentration field is noteworthy. While the predicted maximum increases moderately from 6.4 $\mu\text{g m}^{-3}$ at the coarse to 7.8 $\mu\text{g m}^{-3}$ at the fine resolution, the finest scale resolves better the concentration field in the cluster of industrial installations 37 km northwest of Pittsburgh where the concentration is 12.1 $\mu\text{g m}^{-3}$ at 1 x 1 km. The minimum PM_{2.5} drops from 5.8 $\mu\text{g m}^{-3}$ at 36 x 36 to 4.7 $\mu\text{g m}^{-3}$ at 12 x 12, and then only to 4.5 $\mu\text{g m}^{-3}$ at 1 x 1 km. So once more the moderate resolution appears to capture the low end of the concentrations within 5%.

The average EC is lower during the summer with 0.29 $\mu\text{g m}^{-3}$ versus 0.43 $\mu\text{g m}^{-3}$ in the winter. The standard deviation of the predicted average EC increases from 0.05 $\mu\text{g m}^{-3}$ at 36 x 36, to 0.09 $\mu\text{g m}^{-3}$ at 12 x 12, to 0.10 $\mu\text{g m}^{-3}$ at 4 x 4 km, and to 0.13 $\mu\text{g m}^{-3}$ at 1 x 1 km. The peak average EC is located in downtown Pittsburgh and increases by a factor of 3.7 (from 0.35 to 1.3 $\mu\text{g m}^{-3}$) moving from the coarse to the finest resolution.

It is noteworthy that the peak is 39% less than that of the winter when the coarse resolution is used, but only 20% when the finest resolution is used. The concentration range (difference between the maximum and the minimum) increases from 0.13 $\mu\text{g m}^{-3}$ to 1.14 $\mu\text{g m}^{-3}$ moving from the coarse to the finest resolution. This increase by a factor of 9 shows the importance of the local variations of a primary species like EC in an urban area in both summer and winter.

The OA concentration field is quite uniform at the coarse-scale varying from by only 0.2 $\mu\text{g m}^{-3}$ (from 1.5 to 1.7 $\mu\text{g m}^{-3}$) with a standard deviation of 0.08 $\mu\text{g m}^{-3}$ (Figure 2-6). There is only

a moderate increase in the variability even when one moves to the fine-scale, with the range increasing to $0.8 \mu\text{g m}^{-3}$. The significant change in OA predictions occurs at the finest scale with an increase of the predicted maximum in downtown Pittsburgh to $3.8 \mu\text{g m}^{-3}$ increasing the predicted concentration range to $2.6 \mu\text{g m}^{-3}$ and the standard deviation of the OA field to $0.2 \mu\text{g m}^{-3}$. The use of the finest scale appears to be needed for the resolution of the OA high concentration areas in the summer more than in the winter.

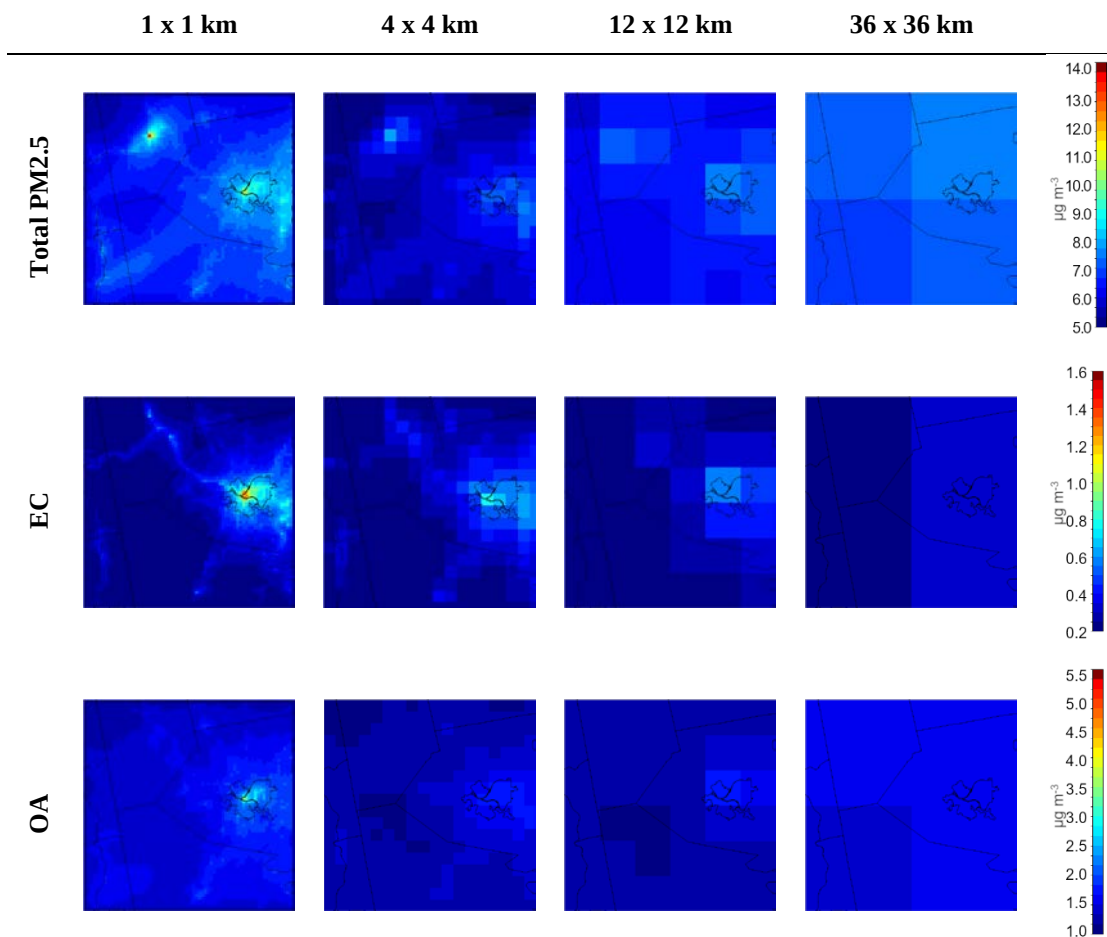


Figure 2-6 Average predicted concentration at the ground level of total PM_{2.5}, EC and OA at a 36x36, 12x12, 4x4 and 1x1 km during July 2017.

The PM_{2.5} sulfate levels during the summer period are on average 15% higher during the summertime period. At the coarse and intermediate scales, the predicted average concentration fields have relatively little structure (Figure 2-7). The corresponding concentration ranges are

relatively narrow ($0.1 \mu\text{g m}^{-3}$ at $36 \times 36 \text{ km}$ and $0.5 \mu\text{g m}^{-3}$ at $12 \times 12 \text{ km}$). However, a different picture emerges at the fine and especially the finest scales. In contrast to the winter results, the plumes from the major power plants can be clearly seen at these higher resolutions. The increase of the maximum is just $0.26 \mu\text{g m}^{-3}$ moving from the coarse to the fine-scale (from 1.9 to $2.1 \mu\text{g m}^{-3}$) and becomes important only at the finest scale (a maximum of $2.7 \mu\text{g m}^{-3}$ is predicted for downtown Pittsburgh). The predicted minimum is reduced from $1.8 \mu\text{g m}^{-3}$ at 36×36 to $1.4 \mu\text{g m}^{-3}$ at 12×12 , to $1.3 \mu\text{g m}^{-3}$ at 4×4 and $1 \times 1 \text{ km}$. The standard deviation of the predicted sulfate concentration field at the coarse resolution is low and the same as in the winter, $0.03 \mu\text{g m}^{-3}$ at the coarse resolution. However, the variability at the finest scale is twice in the summer ($0.15 \mu\text{g m}^{-3}$ at $1 \times 1 \text{ km}$) than in the winter.

The summertime nitrate concentrations are quite low in the area (average $0.53 \mu\text{g m}^{-3}$ in the coarse and $0.46 \mu\text{g m}^{-3}$ in the finest resolution). Most of the reduction of the predicted minimum happens moving from the coarsest to the intermediate resolution ($0.45 \mu\text{g m}^{-3}$ to $0.38 \mu\text{g m}^{-3}$) with a further reduction to $0.36 \mu\text{g m}^{-3}$ to the finest scale. The concentration field is quite uniform with a standard deviation of $0.06 \mu\text{g m}^{-3}$ for all grids. However, due to the reduction in the predicted minimum the concentration range increases from $0.1 \mu\text{g m}^{-3}$ at the coarse resolution to $0.3 \mu\text{g m}^{-3}$ at the fine and finest resolutions.

The $\text{PM}_{2.5}$ ammonium concentration field is quite uniform at all resolutions (Figure 2-7). The concentration range increases from 0.1 to $0.3 \mu\text{g m}^{-3}$ moving from the coarse to the finest resolution and the standard deviation increases from 0.01 to $0.04 \mu\text{g m}^{-3}$.

2.5.2 Source Apportionment

Commercial cooking emissions contribute a maximum of $1.97 \mu\text{g m}^{-3}$ to the total $\text{PM}_{2.5}$ in downtown Pittsburgh, a decrease of 19% compared with the winter. This accounts for 20% of the

PM_{2.5} mass in the city, with smaller contributions in the urban core. The contribution from commercial cooking shows little variability outside of the city center with a standard deviation of 0.09 $\mu\text{g m}^{-3}$. As in the winter period, on-road traffic emissions have the largest contribution to the PM_{2.5} in the downtown Pittsburgh area where 4 large highways intersect. In this location on-road traffic contributes 13% of the PM_{2.5} with 1.21 $\mu\text{g m}^{-3}$. On average, on-road traffic contributes less than 1% of the PM_{2.5} mass. During the summer period, the variability of the on-road traffic contribution is slightly higher with 0.14 $\mu\text{g m}^{-3}$ compared with 0.12 $\mu\text{g m}^{-3}$ during winter.

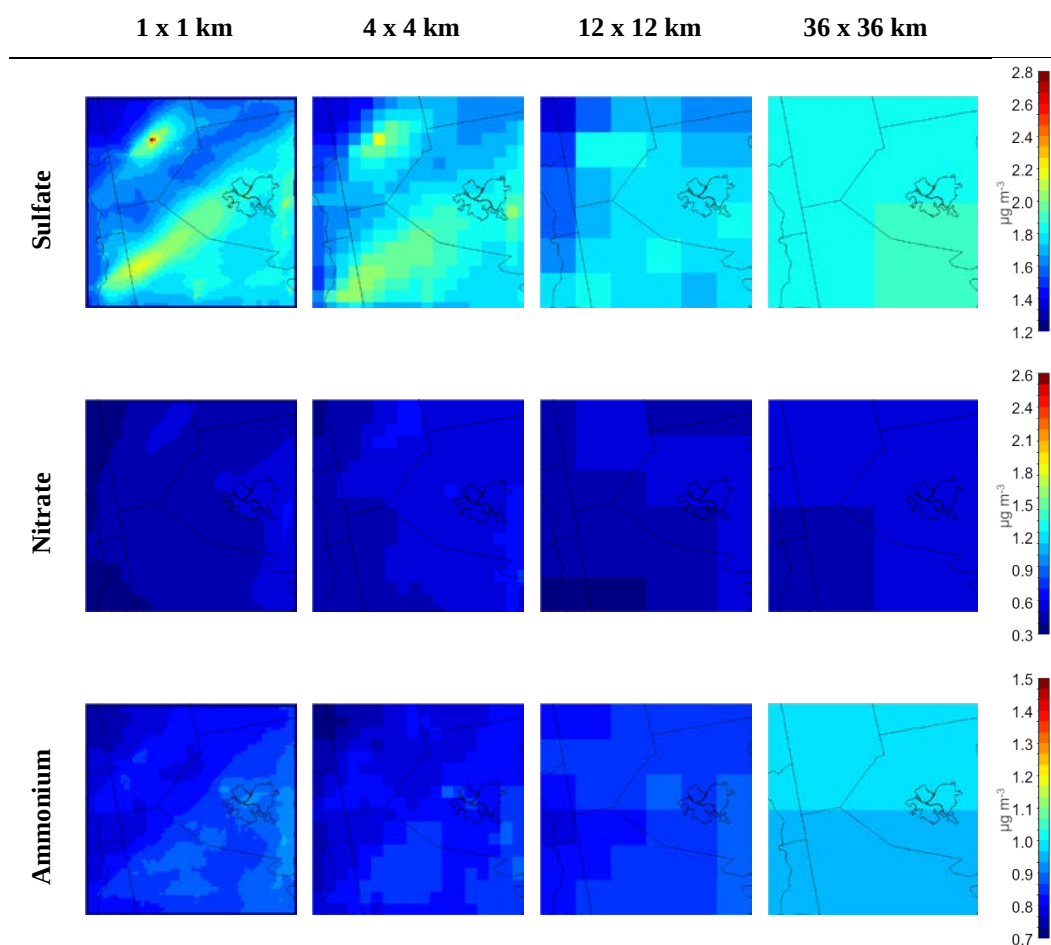


Figure 2-7 Average predicted concentration of PM_{2.5} sulfate, nitrate, and ammonium at a 36x36, 12x12, 4x4 and 1x1 km during July 2017.

During summer, residential biomass burning is minimal. This source contributes a maximum of 0.1 $\mu\text{g m}^{-3}$ and its contribution to the average PM_{2.5} is negligible. On average, the

miscellaneous area sources sector contributes $1.21 \mu\text{g m}^{-3}$ accounting for 2.6% of the $\text{PM}_{2.5}$. In downtown Pittsburgh, where the contribution is highest, this source contributes 6% of the $\text{PM}_{2.5}$.

Unlike in the winter period, in the summer, the plumes from major powerplants in the Ohio river valley can be clearly resolved. The power generation sector contributes a maximum of $1.6 \mu\text{g m}^{-3}$ in the plume of the Bruce Mansfield power plant northwest of Pittsburgh. On average, the 8.8% contribution from this sector to the $\text{PM}_{2.5}$ is much larger than in the winter where it only contributed 1.6%. The plume from the Mitchell power plant in the southwest corner of the modeling domain is clearly resolved and reaches all the way to the city. This increases the contribution from power generation to the $\text{PM}_{2.5}$ in the downtown core from $0.16 \mu\text{g m}^{-3}$ to $0.61 \mu\text{g m}^{-3}$, a 73% increase. The maximum contribution of $6.2 \mu\text{g m}^{-3}$ from industrial sources is a cluster of industrial facilities in the town of Butler, northwest of Pittsburgh. As in winter, the maximum $\text{PM}_{2.5}$ concentration on the modeling domain is located here. During summer, industrial sources account for 51% of the $\text{PM}_{2.5}$ followed by long-range transport with 36% and power generation with 8%. On-average industrial sources account for 5.1% of the $\text{PM}_{2.5}$. Additional sources such as the Edgar Thompson and Clairton Works can be resolved during summer, causing the variability to increase to $0.23 \mu\text{g m}^{-3}$ from $0.06 \mu\text{g m}^{-3}$ in the winter.

Long-range transport from sources outside the region contributes a maximum of $5 \mu\text{g m}^{-3}$ in the southeast corner of the domain decreasing in the direction of the Pittsburgh northern suburbs where the contribution is minimal with $4.1 \mu\text{g m}^{-3}$. On average, long-range transport accounts for 79% of the $\text{PM}_{2.5}$ mass. In downtown Pittsburgh, long-range transport contributes $4.19 \mu\text{g m}^{-3}$ accounting for 43% of the $\text{PM}_{2.5}$.

On average, the contribution from all remaining sources is 4.4% and shows a moderate variability of $0.11 \mu\text{g m}^{-3}$. The contribution from these sources is maximal in downtown Pittsburgh with $0.67 \mu\text{g m}^{-3}$ accounting for 7% of the $\text{PM}_{2.5}$.

For all local sources, the minimum contribution is close to zero (less than $0.1 \mu\text{g m}^{-3}$) and is located at the northwestern corner of the domain, near the Ohio – Pennsylvania border.

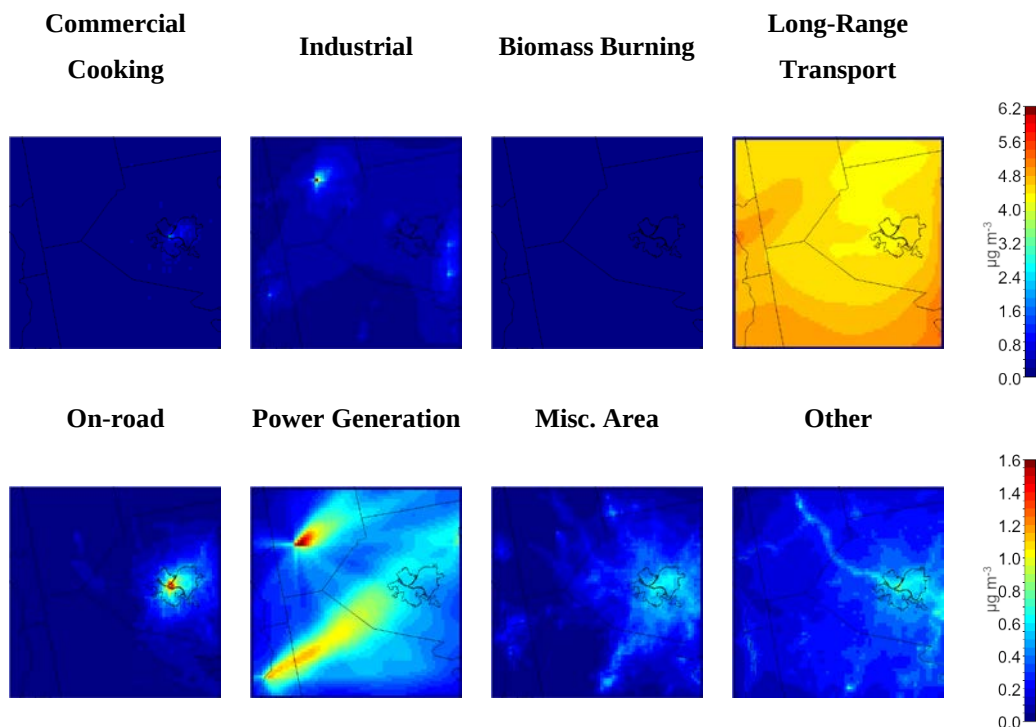


Figure 2-8 Contribution of each source to total $\text{PM}_{2.5}$ during July 2017. Two different scales are used.

2.6 Exposure to $\text{PM}_{2.5}$

The population data in the inner domain from the 2010 U.S. census was used to estimate the exposure of the population in the Pittsburgh area to model predictions of $\text{PM}_{2.5}$ during winter of 2017 at the different grid resolutions. We ranked the average $\text{PM}_{2.5}$ concentrations from all the cells in the modeling domain and created bins of $0.2 \mu\text{g m}^{-3}$. A sum of the population from all the grid cells that fall within each concentration bin was calculated and divided by the total population of the inner grid to construct population exposure histograms.

Figure 2-9 shows the population exposure histograms for each simulation grid. At the coarse resolution, there are only 4 PM_{2.5} values so very little of the exposure distribution can be observed. 46% of the population is exposed to a concentration of 10.6 $\mu\text{g m}^{-3}$ with decreasing exposure with PM_{2.5} concentration. At a 12 km resolution, the low concentration side of the distribution is better resolved but gaps can still be observed at higher levels. At this intermediate resolution, the largest fraction of the population (21%) is exposed to PM_{2.5} concentrations of 10.2 $\mu\text{g m}^{-3}$ with 15% exposed to the maximum of 11.8 $\mu\text{g m}^{-3}$.

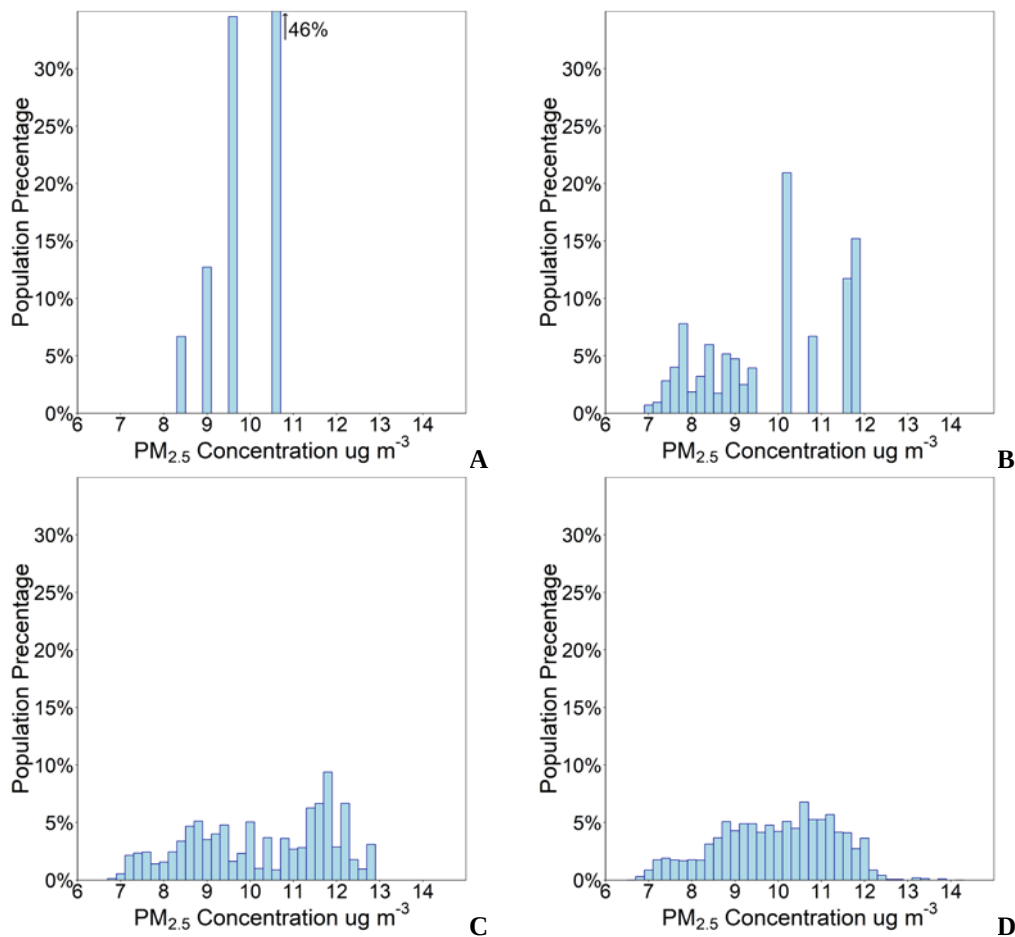


Figure 2-9 Population exposure histograms at (A) 36x36, (B) 12x 12, (C) 4x4 and (D) 1x1 km during February 2017.

When the resolution is increased to 4 km the biggest improvements on the model ability to resolve the exposure distribution happen at concentrations higher than 9.4 $\mu\text{g m}^{-3}$. At the fine

resolution, no gaps appear in the distribution. A maximum of 9% of the population is exposed to $\text{PM}_{2.5}$ concentrations of $11.8 \mu\text{g m}^{-3}$ while at the highest concentration of $12.8 \mu\text{g m}^{-3}$ 3% are exposed. At the 1 km resolution, the distribution is much smoother due to the ability of this finest grid to capture local gradients. The largest fraction of the population (7%) is exposed to $\text{PM}_{2.5}$ concentrations of $10.6 \mu\text{g m}^{-3}$. At the highest concentration of $14.2 \mu\text{g m}^{-3}$ the exposed population is less than 0.1% as this maximum point is located near industrial installations 37 km northwest of Pittsburgh where the population density is very low.

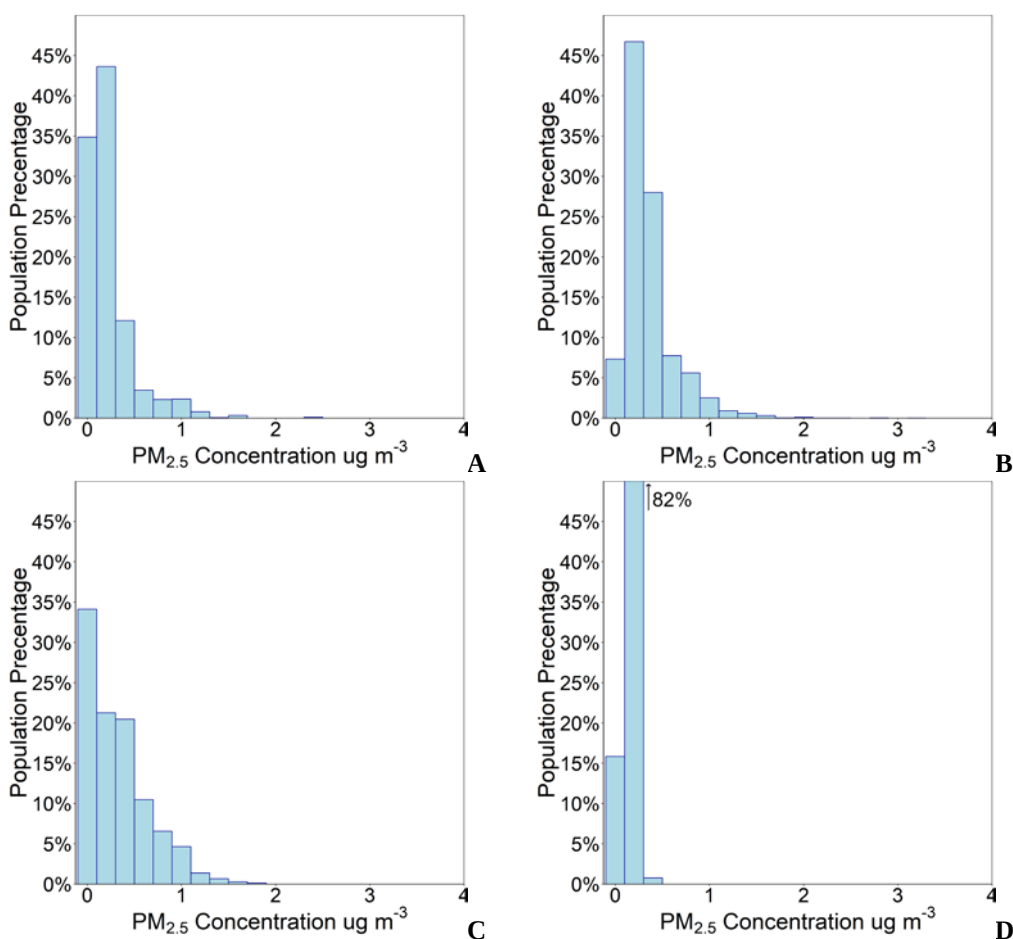


Figure 2-10 Population exposure histograms of the contribution to $\text{PM}_{2.5}$ concentrations from (A) commercial cooking, (B) industrial, (C) on-road traffic and (D) power generation sources during February 2017.

Population exposure histograms were calculated for each source using the same procedure used for the grid resolution analysis. The contribution from commercial cooking is very small

outside the Pittsburgh downtown area with 78% of the population exposed to less than $0.4 \mu\text{g m}^{-3}$ of $\text{PM}_{2.5}$ from this source. The contribution from commercial cooking to the $\text{PM}_{2.5}$ has a very localized maximum located in a single cell in downtown Pittsburgh where less than 0.1% of the population is exposed to $2.4 \mu\text{g m}^{-3}$. 34% of the population is exposed to less than $0.2 \mu\text{g m}^{-3}$ of $\text{PM}_{2.5}$ from on-road traffic, as the contributions from traffic decrease rapidly with the distance to the roads. Unlike commercial cooking, the distribution from on-road traffic doesn't have large, isolated maxima. Industrial sources contribute $0.4 \mu\text{g m}^{-3}$ to the $\text{PM}_{2.5}$ exposure for 46% of the population.

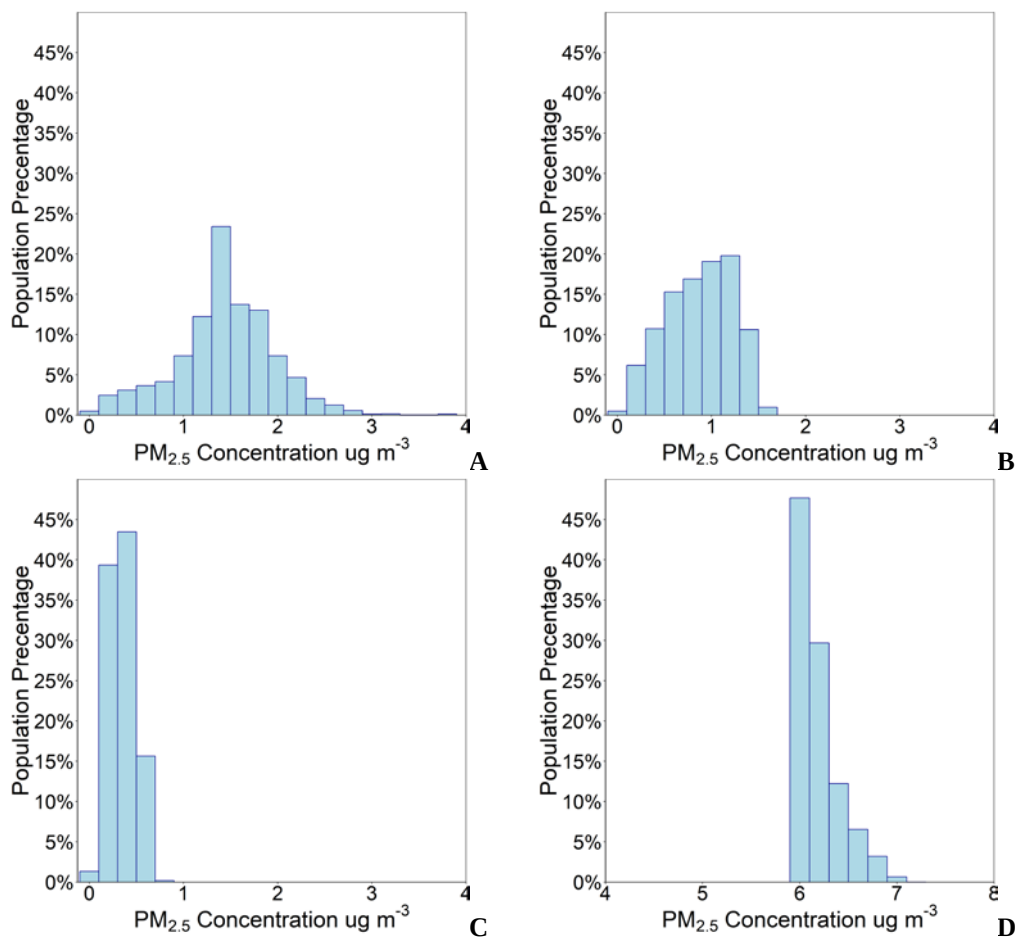


Figure 2-11 Population exposure histograms of the contribution to $\text{PM}_{2.5}$ concentrations from (A) biomass burning, (B) miscellaneous area sources and (C) all other sources during February 2017. Contributions from long-range transport (D) are shown with a different concentration scale.

Industrial sources have highly localized maxima with contributions of up to $5.6 \mu\text{g m}^{-3}$, these contributions are located in areas with very small population density exposing a very small fraction of the total population to these concentrations. The contribution from power generation sources is very uniform across the domain producing a very sharp population exposure distribution with 82% of the population exposed to $0.2 \mu\text{g m}^{-3}$.

The distribution for biomass burning shows a wide distribution with a maximum of 23% of the population exposed to $1.4 \mu\text{g m}^{-3}$ of $\text{PM}_{2.5}$. This wide distribution reflects the large geographic variability of the biomass burning contribution to the $\text{PM}_{2.5}$. The miscellaneous area sources sector also has significant geographical variability. At a concentration of $1.2 \mu\text{g m}^{-3}$ a maximum of 20% are exposed, at higher concentrations the exposure fraction decreases rapidly as this source does not have significant local maxima.

Long-range transport contributions are higher on the domain boundaries where the population density is very small and decrease towards the city of Pittsburgh where most of the population is located. 48% of the population is exposed to the lowest contribution of $6 \mu\text{g m}^{-3}$. This fraction decreases with increasing concentration so that at the maximum contribution of $7 \mu\text{g m}^{-3}$ less than 1% of the population is exposed. The contribution from all remaining sources is low for most of the modeling domain with 84% of the population exposed to less than $0.4 \mu\text{g m}^{-3}$.

2.7 Conclusions

We applied the PMCAMx chemical transport model over the city of Pittsburgh during winter using a series of telescoping grids at 36 x 36 km, 12 x 12 km, 4 x 4 km and 1 x 1 km. Emissions were calculated using 2017 projections from the 2011 NEI. Emissions were distributed geographically using the spatial surrogates provided with the NEI11 for all grids. For commercial cooking, a new 1 x 1 km spatial surrogate was developed using restaurant count data from the

Google Places API. Traffic model data was used to develop a 1 x 1 km spatial surrogate for on-road traffic emissions.

At the coarse resolution, county-level differences can be observed. Increasing the resolution to 12 x 12 km resolves the urban-rural gradient and further increasing to 4 x 4 resolves large stationary sources such as power plants. Only at the finest resolution intra-urban variations and individual roadways are resolved. Low variability, regional pollutants such as nitrate show limited improvement after increasing the resolution to 12 x 12 km while predominantly local pollutants such as elemental carbon and winter organic aerosol have gradients that can only be resolved at the finest resolution.

Biomass burning shows the largest variability during the winter period with many local maxima and significant emissions within the city and in the suburbs. During the summer contributions from this source are negligible. In contrast with the winter period, during the summer the plumes from large power plants in the Ohio river valley can be resolved. These plumes are rich in sulfates and start being resolved at 4 x 4 km with significant detail added at 1 x 1 km. During both periods the largest contributing source to the PM_{2.5} is particles from outside the modeling domain.

The model ability to resolve the exposure distribution increases at different rates according to the concentration. A significant improvement in the model ability to resolve exposure to concentrations below 9.6 g m⁻³ is achieved by increasing the resolution to 12 x 12 km. Only at the finest resolution is the exposure to concentrations above 9.6 g m⁻³ fully resolved as well as the impact of high concentration spots. Highly localized sources such as commercial cooking and industrial installations show exposure distributions clustered around very low values since large areas of the domain are not affected by these sources. During the winter, biomass burning is the

most important local contributor to PM_{2.5} exposure. Further details could be observed by restricting the area of analysis to only the urban area.

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Chapter 3. High-Resolution Modeling of Fine Particulate Matter in an Urban Area

3.1 Introduction

Fine particulate matter with aerodynamic diameter less than 2.5 μm ($\text{PM}_{2.5}$) has been associated with public health concerns due to short and long-term exposure. Some of the health effects of $\text{PM}_{2.5}$ include premature death due to cardiovascular disease, increased chance of heart attacks and strokes, reduced lung development and function in children and people with lung diseases such as asthma and increases in hospital admissions due to heart and lung disease (Dockery and Pope, 1994; US EPA, 2012). Chemical transport models are frequently used for developing air quality and emissions control policies that protect public health. To evaluate these policies, CTMs must simulate $\text{PM}_{2.5}$ concentrations and their response to changes in emissions accurately.

Grid resolution is an important factor for CTM studies since on-road traffic, commercial cooking, and industrial activities can have sharp gradients at the urban scale. High spatial resolution measurement of PM_1 in the city of Pittsburgh have observed gradients of $\sim 2 \mu\text{g m}^{-3}$ between high impact and urban background sites (Gu et al., 2018; Robinson et al., 2018). The demographic characteristics of the population can have large variations at the neighborhood scale and it is important to assess the exposure of different sub-populations to air pollutants and the resulting health effects, a concept known as Environmental Justice (Anand, 2002). The benefits of high-resolution modeling must be balanced with the increased complexity in the development of accurate, high-resolution emission inventories and increased computational cost and storage requirements.

Previous studies have found small to modest improvements on the predictive ability of regional CTMs for ozone (Arunachalam et al., 2006; Kumar and Russell, 1996), secondary organic aerosol (Fountoukis et al., 2013; Stroud et al., 2011) and nitrate (Zakoura and Pandis, 2019, 2018) with increasing resolutions. The effects were more pronounced for primary PM components and especially during the winter when the atmospheric mixing is often weaker. For example, Fountoukis et al., (2013) reported a reduction of the bias for black carbon (BC) concentrations in the northeastern US when the grid resolution was reduced from 36x36 km to 4x4 km.

One of the weaknesses of several of the above studies has been that the area emissions used at the higher resolutions were the results of interpolation. It is not clear if the remaining discrepancies between model predictions and measurements were due to errors in the spatial distribution of the high-resolution emissions, errors in the overall magnitude of the emissions over an urban area or other modeling errors in the simulation of various processes (chemistry, transport, etc.). In this work, we will explore the first hypothesis, the role of the spatial distribution of emissions in the urban area.

We use the Particulate Matter Comprehensive Air quality Model with Extensions (PMCAMx) to study the impact of increasing model resolution on the model's ability to predict $PM_{2.5}$ variations on the urban scale in Pittsburgh. We evaluate the PMCAMx predictions at various grid resolutions against regulatory measurements of $PM_{2.5}$ concentration and composition, research measurements by an Aerosol Mass Spectrometer (Gu et al., 2018), but also measurements from a network of low-cost sensors (Zimmerman et al., 2018). The evaluation focuses on a winter period is simulated, because the gradients of $PM_{2.5}$ levels in space inside the urban area are expected to be higher. The results during a summer period are briefly discussed.

3.2 PMCAMx Description

PMCAMx (Karydis et al., 2010; Murphy and Pandis, 2010; Tsimpidi et al., 2009) uses the framework of the CAMx model (Environ, 2006) to describe horizontal and vertical advection and diffusion, emissions, wet and dry deposition, gas, aqueous and aerosol-phase chemistry. A 10-size section aerosol sectional approach is used to track dynamically the evolution of the aerosol mass and composition distribution. The aerosol species modeled include sulfate, nitrate, ammonium, sodium, chloride, elemental carbon, water, primary and secondary organics, and other non-volatile aerosol components. An extended version of the SAPRC (Statewide Air Pollution Research Center) photochemical mechanism (Carter, 1999) including the volatility basis set (VBS) is used for the simulation of gas-phase chemistry (Murphy and Pandis, 2010). The version of SAPRC used here includes 237 reactions and 91 individual and surrogate species. For phase partitioning of inorganic species and water, a bulk equilibrium approach was used (Pandis et al., 1993) based on the ISORROPIA aerosol thermodynamics model (Nenes et al., 1998). Both the primary and secondary organic aerosol components are described using the volatility basis set approach (Donahue et al., 2006). For primary organic aerosol (POA) ten volatility bins, with effective saturation concentrations ranging from 10^{-3} to $10^6 \mu\text{g m}^{-3}$ at 298 K are used. Anthropogenic (aSOA) and biogenic (aSOA) are modeled with 4 volatility bins ($1, 10, 10^2, 10^3 \mu\text{g m}^{-3}$ at 298 K) (Murphy and Pandis, 2009) using NO_x -dependent yields (Lane et al., 2008). More detailed descriptions of PMCAMx can be found in Fountoukis et al., (2011) and Zakoura and Pandis, (2018).

3.3 Model Application

PMCAMx was used to simulate air quality over the metropolitan area of Pittsburgh during February and July 2017. We used a one-way nested structure with a 36 x 36 km master grid

covering the continental United States; with nested grids of 12 x 12 km and 4 x 4 km in southwestern Pennsylvania; and a 1 x 1 km grid covering the city of Pittsburgh, most of Allegheny County and the upper Ohio River valley (Figure 3-1). The 1 x 1 km grid covers a 72 x 72 km area.

Horizontal wind components, vertical diffusivity, temperature, pressure, water vapor, clouds, and rainfall were generated using the Weather Research and Forecasting (WRF v3.6.1) model over the whole modeling domain with horizontal resolution of 12 km. These data were interpolated to higher resolutions when needed. Initial and boundary meteorological conditions for the WRF simulations were generated from the ERA-Interim global climate re-analysis database, together with the terrestrial data sets for terrain height, land-use, soil categories, etc. from the United States Geological Survey (USGS) database. The WRF modeling system is prepared and configured in a similar way as described by Gilliam and Pleim (2010). This configuration is recommended for air quality simulations (Hogrefe et al., 2015; Rogers et al., 2013).

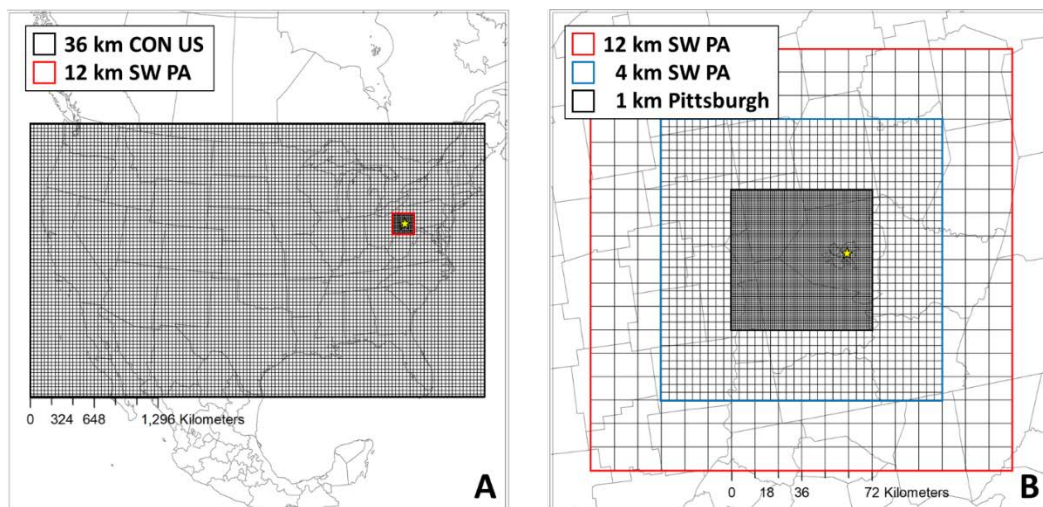


Figure 3-1. Modeling domain used for the PMCAMx simulations: (A) 36x36 km continental U.S. domain and grid. (B) 12x12 and 4x4 km South Western Pennsylvania grids, and 1x1 km Pittsburgh nested grids.

The surface concentrations at the boundaries of the 36 x 36 km grid are shown in Table 3-1. These values were applied to all upper air layers assuming a constant mixing ratio.

Table 3-1. Outer (CONUS) boundary condition concentrations of major aerosol species.

Component	Concentration ($\mu\text{g m}^{-3}$)			
	West	East	South	North
Nitrate	0.01	0.01	0.03	0.03
Ammonium	0.14	0.25	0.24	0.16
Sulfate	0.64	1.12	0.81	0.68
Elemental Carbon	0.04	0.05	0.09	0.03
Organic Aerosol	0.20	0.16	0.58	0.13

Emissions were calculated using the EPA’s Emission Modeling Platform (v6.3) for the National Emissions Inventory (NEI) projections for 2017 using the NEI for 2011 (Eyth and Vukovich, 2016). Base emissions were calculated first at a 12 km resolution for the full modeling domain using the Sparse Matrix Operator Kernel Emissions (SMOKE) model and our WRF meteorological data. For the higher resolution grids, the spatial surrogates provided with Platform v6.3 (Adelman, 2015) were used for all sectors. For commercial cooking and on-road traffic, custom surrogates were developed. These are described in the previous chapter of this thesis (CACES surrogates). Simulations with both the CACES and EPA surrogates were performed and their results are compared in a subsequent section.

3.4 Measurements for model evaluation

Model predictions of sulfate, nitrate, elemental carbon and organic aerosol were compared with measurements from 4 sites from the EPA Chemical Speciation Network (EPA-CSN) (U.S. EPA, 2006). The locations of these 4 sites are shown in Figure 3-2A. These sites include: Lawrenceville, an urban background site 4 km northeast of downtown Pittsburgh; Hillman State Park located in a state park in southwest Pennsylvania in a rural and remote location approximately 40 km upwind of Pittsburgh; Steubenville in the Ohio River Valley close to industrial installations and coal-fired power plants, and the Liberty-Clairton monitor, which is located close to the

Clairton Coke Works in the Monongahela River Valley 14 km southeast of downtown Pittsburgh. Hourly data from Aerosol Mass Spectrometer (AMS) measurements taken at the Carnegie Mellon University campus during winter 2017 was also used along with Positive Matrix Factorization factors of organic aerosol (Gu et al., 2018).

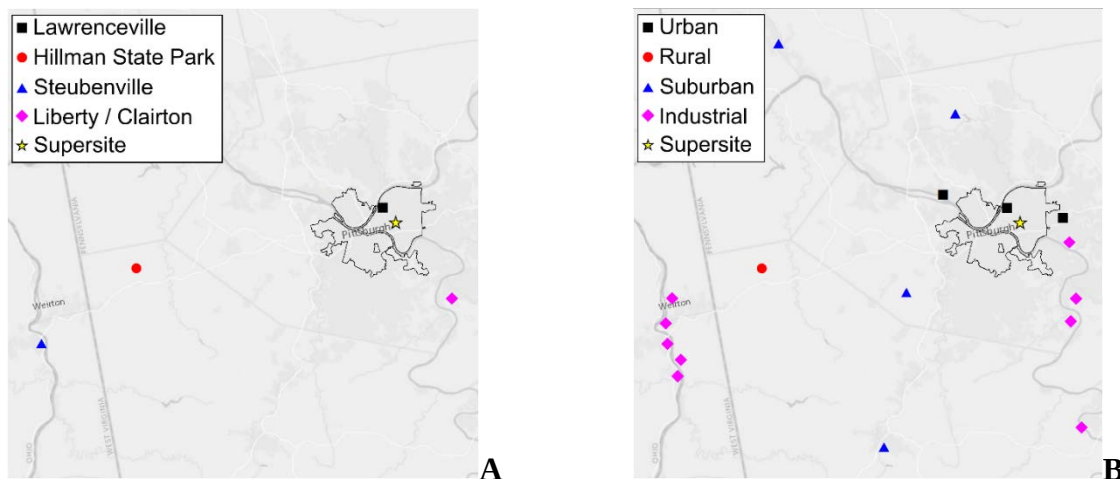


Figure 3-2. Monitoring sites. (A) Particulate matter speciation measurement sites from EPA-CSN. (B) PM_{2.5} measurement sites from EPA AirNow.

Model predictions of PM_{2.5} were compared with measurements from 17 sites in the EPA AirData database (U.S. EPA, 2019). The locations of these sites are shown in Figure 3-2B. The available sites can be classified as: “Urban” sites, near the Pittsburgh downtown, corresponding to the EPA-CSN Lawrenceville site; “Suburban” located in suburban communities in the north-west and south-west of Pittsburgh; “Rural” measuring the remote background, corresponding to the EPA-CSN Hillman State Park site and “Industrial” sites located near the industrial installations and electricity generating units (EGUs) in the Ohio and Monongahela river valleys.

The model performance is assessed in terms of the mean bias (BIAS), the mean error (ERROR), the fractional bias (FBIAS) and the fractional error (ERROR).

$$BIAS = \frac{1}{N} \sum_{i=1}^N P_i - O_i \quad FBIAS = \frac{2}{N} \sum_{i=1}^N \frac{P_i - O_i}{P_i + O_i}$$

$$ERROR = \frac{1}{N} \sum_{i=1}^N |P_i - O_i| \quad FERROR = \frac{2}{N} \sum_{i=1}^N \frac{|P_i - O_i|}{P_i + O_i}$$

where N is the number of valid measurements, P_i is the predicted concentration and O_i is the corresponding observed concentration.

3.5 Model performance evaluation during winter

3.5.1 Evaluation using regulatory measurements

Table 3-2 summarizes the prediction skill metrics of PMCAMx with the EPA-CSN data in the 1 km domain for the winter period. Predictions for sulfate have little fractional bias (7%) with some underestimation at higher measured concentrations in the industrial sites at Liberty / Clairton and Steubenville. Ammonium nitrate is over-predicted in all sites with a bias of $1.66 \mu\text{g m}^{-3}$. The errors are higher during days with lower ammonium nitrate levels with better performance on February 6, where concentrations were higher on all sites.

Table 3-2. Comparison of PMCAMx predictions with daily averages from EPA-CSN during February 2017.

	Sulfate	Nitrate	Ammon.	Elemental Carbon	Organic Aerosol
Measured Avg. ($\mu\text{g m}^{-3}$)	1.92	1.51	0.91	0.94	4.68
Predicted Avg. ($\mu\text{g m}^{-3}$)	1.90	3.17	1.80	0.85	3.70
Error ($\mu\text{g m}^{-3}$)	0.88	1.76	1.16	0.56	2.34
Fractional Error	0.45	0.87	1.01	0.61	0.53
Bias ($\mu\text{g m}^{-3}$)	-0.02	1.66	0.89	-0.08	-0.98
Fractional Bias	0.07	0.85	0.90	-0.03	-0.10

Previous PMCAMx modeling studies (Fountoukis et al., 2011; Trump et al., 2015) have found similar over-predictions on 4 European sites during May 2008. Part of this overprediction was due to the use of coarse-grid resolution (Zakoura and Pandis, 2018), but this cannot be the

cause here. The elemental carbon concentrations were reproduced with negligible fractional bias (-3%). However, predictions at the Lawrenceville are positively biased while in Steubenville and Liberty / Clairton are negatively biased. This may suggest errors in the spatial distribution of the EC emissions in the inventory. Organic aerosol predictions show a low average fractional bias of -10% with an increasing tendency towards under prediction at the higher concentrations measured at the industrial sites of Steubenville and Liberty / Clairton.

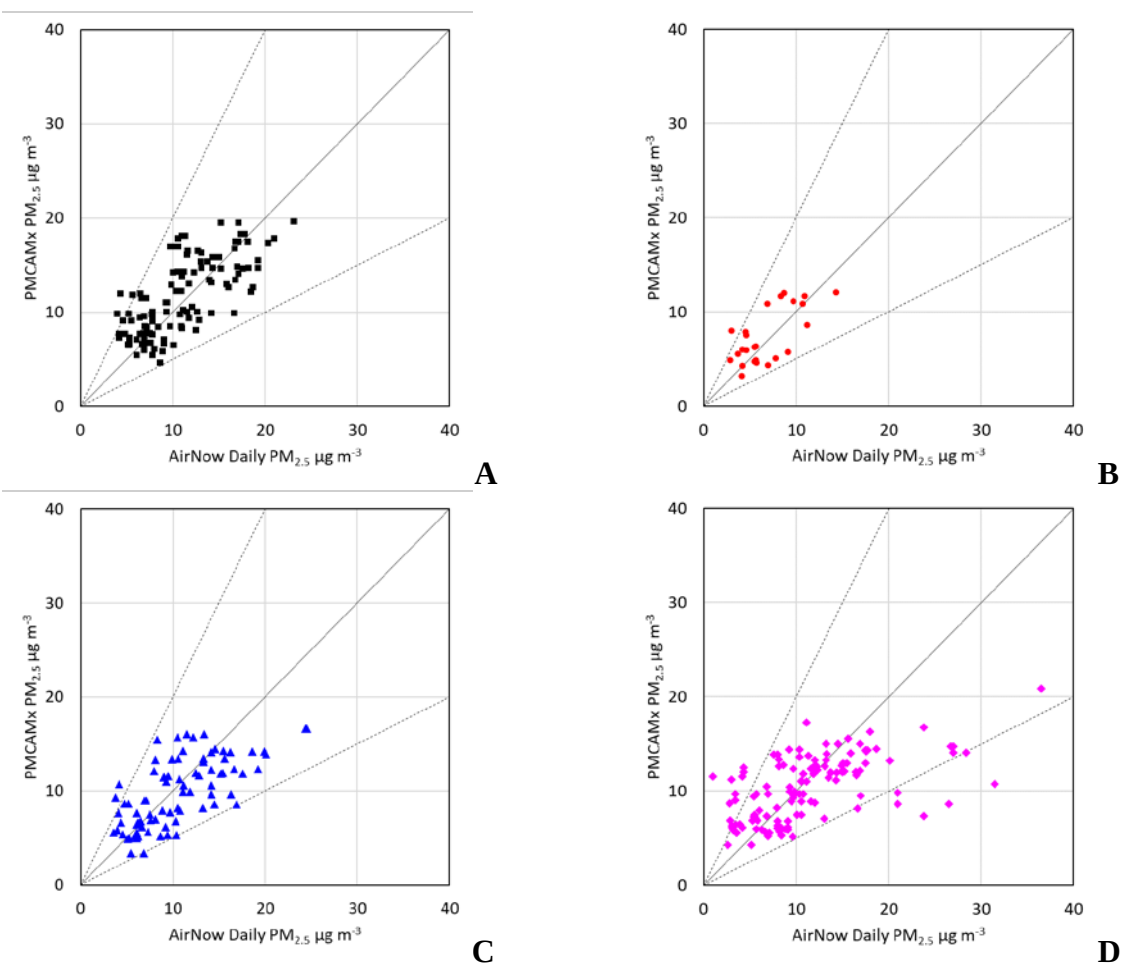


Figure 3-3. Comparison of PMCAMx-predicted $PM_{2.5}$ concentrations during February 2017 with 24-hour averages from (A) 3 urban, (B) 1 rural, (C) 4 suburban and (D) 9 industrial AirNow sites.

At the metropolitan area scale covered by the EPA AirNow $PM_{2.5}$ measurements, PMCAMx predictions have a fractional bias of only 3% (Table 3-3 and Figure 3-3). In the urban and rural sites, the model slightly overpredicts concentrations with fractional biases of 8% and

10% respectively. The concentrations in suburban sites are well reproduced with an average bias of only $-0.16 \mu\text{g m}^{-3}$. At the industrial sites, the fractional bias is also low at 1%, however, the average error is $1.37 \mu\text{g m}^{-3}$ as the model tends to overpredict at low concentrations and to underpredict at high concentrations.

Table 3-3. Comparison of PMCAMx predicted $\text{PM}_{2.5}$ concentrations during February 2017 with 24-hour averages from EPA AirNow sites.

	Urban	Suburban	Rural	Industrial	All
Measured Avg. ($\mu\text{g m}^{-3}$)	11.04	10.59	6.73	11.30	10.72
Predicted Avg. ($\mu\text{g m}^{-3}$)	11.76	9.91	7.36	10.29	10.46
Error ($\mu\text{g m}^{-3}$)	0.88	0.67	0.14	1.37	3.07
Fractional Error	0.25	0.28	0.30	0.36	0.30
Bias ($\mu\text{g m}^{-3}$)	0.23	-0.16	0.05	-0.37	-0.25
Fractional Bias	0.08	-0.04	0.10	0.01	0.03
R	0.71	0.68	0.68	0.58	0.63

The overall performance of PMCAMx for $\text{PM}_{2.5}$ in this period is quite encouraging for the urban, suburban, and rural locations (Figure 3-3), however, the model had difficulties reproducing some of the high concentrations (above $20 \mu\text{g m}^{-3}$) measured only in the sites affected by industrial emissions (Figure 3-3D).

3.5.2 Evaluation using AMS measurements

The absolute concentrations measured by the AMS were quite uncertain due to the uncertainty of the collection efficiency of the instrument during that sampling period. However, the measured composition of the aerosol can be still used for model evaluation purposes.

Comparisons with AMS mass fractions show excellent agreement for sulfate, ammonium, and chlorine, while nitrates are underpredicted and organic aerosol is over predicted somewhat (Figure 3-4A). The underprediction of nitrate in the urban Carnegie Mellon site is not consistent with the tendency of the model to seriously overpredict the $\text{PM}_{2.5}$ nitrate levels in the four sites.

Using positive matrix factorization, Gu et al., (2018) resolved total OA into five factors. Three of them corresponded to primary organic aerosol: hydrocarbon-like OA (HOA), cooking OA(COA) and biomass burning OA (BBOA) and two secondary OA factors: more-oxidized organic aerosol (MOOA) and less-oxidized organic aerosol (LOOA). To compare PMCAMx predictions with the primary PMF factors, two additional simulations were performed in which emissions from biomass burning and commercial cooking were set to zero. The predicted concentrations were then subtracted from the base case to estimate the contribution from each respective source. The remaining primary OA was assigned to HOA. The LOOA and MOOA factors were added together and compared with the PMCAMx SOA predictions.

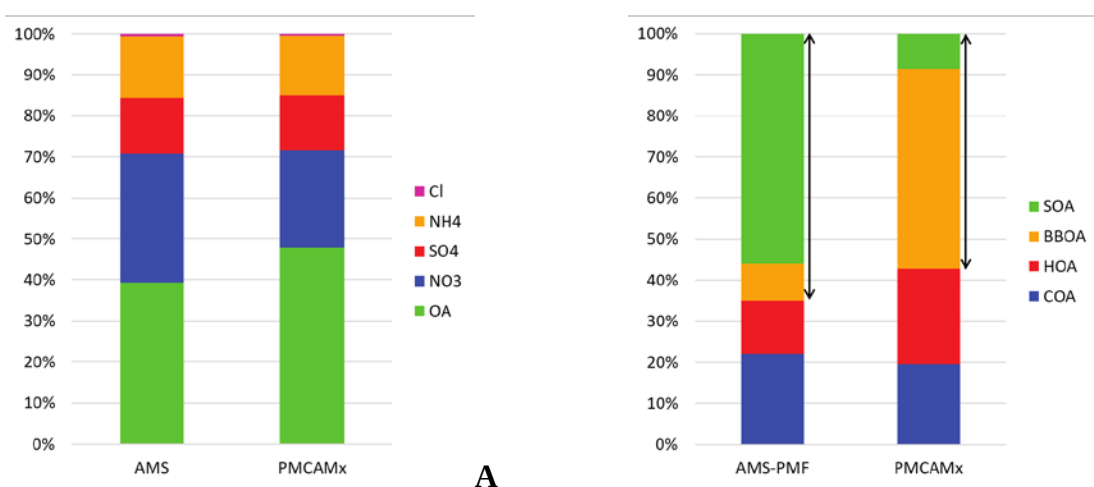


Figure 3-4. (A) Comparison of PMCAMx-predicted fractions of fine PM mass with the corresponding AMS measurements at the CMU Supersite and (B) organic aerosol composition based on the PMF analysis of the AMS measurements and predicted composition. The arrows show the sum of SOA+BBOA which is quite consistent in the AMS measurements and model predictions.

The predicted COA in the CMU site is 20% of the total OA in excellent agreement with the PMF/AMS estimate of 22% (Figure 3-4B). This is encouraging given the small bias of the model for total OA levels. The predicted HOA is higher than measured and the BBOA is almost a factor of 5 more than estimated. The measurements indicate a surprisingly high contribution of OOA (55% of the total OA) during a period with little photochemical activity and low levels of

OH radicals. It is interesting that the model reproduces well the sum of BBOA plus OOA, which was 57% of the total OA compared to the measured 65%. Similar behavior of chemical transport models during winter has been observed in other studies. For example, Tsimpidi et al., (2016) compared the predictions of their global chemical transport model using the VBS with the measurements of 86 campaigns using an AMS. They concluded that while their model did a reasonable job during the three seasons in reproducing the OA levels and composition, it tended to seriously underpredict the OOA during the winter. They suggested that the model was missing an important oxidation process in periods of low photochemical activity.

Our results also strongly suggest that the photochemical conversion of BBOA to OOA currently in PMCAMx cannot explain the rather rapid conversion that is suggested by the measurements. More research is clearly needed in this direction.

3.5.3 Comparison with PM_{2.5} measurements of low-cost sensors

PMCAMx predictions of PM_{2.5} were also compared with measurements taken with a network of Real-time Affordable Multi-Pollutant (RAMP) monitors (Zimmerman et al., 2018) distributed in the city of Pittsburgh. During the winter period measurements at 7 sites were available, all located within the boundaries of the city of Pittsburgh (Figure 3-5). One of the challenges in these comparisons is the significant uncertainty of the RAMP measurements even as daily measurements. However, this is an excellent opportunity to contrast the results of the comparisons of the PM_{2.5} predictions with the quite accurate regulatory measurements and the more uncertain measurements of the low-cost sensors.

In the urban area covered by the low-cost sensor network, the model predictions are on average 23% higher than the measurements of the RAMPs (Figure 3-6). This bias is higher than the 8% determined from the comparison with urban sites of the EPA network. The average

predicted value was $12.4 \mu\text{g m}^{-3}$ compared to $9.9 \mu\text{g m}^{-3}$ for the RAMPs. The average fractional error for the comparison with the RAMPs was 31.7% while it was 25% compared to the regulatory monitors. While these results are encouraging as far as the usefulness of the low-cost sensor as a zeroth-order test of the model predictions, it appears that at least in this application that their measurements have larger discrepancies with the PMCAMx predictions compared to the more accurate measurements.

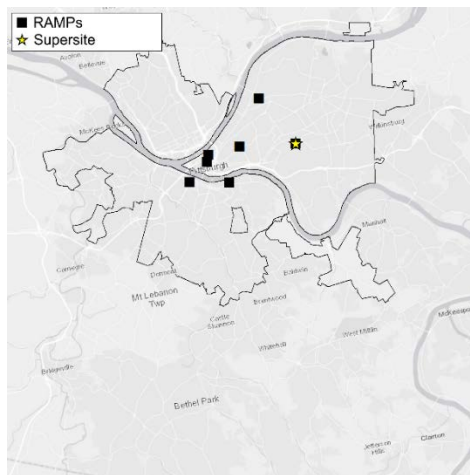


Figure 3-5. PM_{2.5} measurement RAMP sites during February 2017. The CMU Supersite is shown with a star.

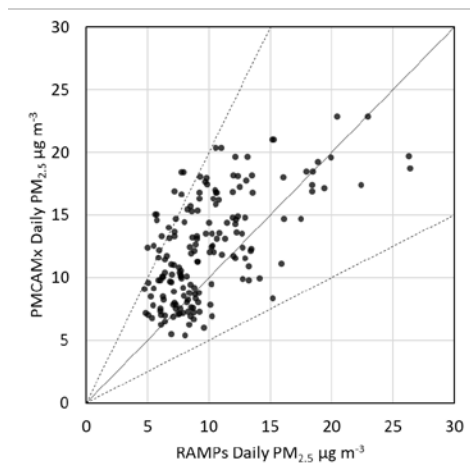


Figure 3-6. Comparison of PMCAMx-predicted daily average PM_{2.5} concentrations with RAMP measurements in 7 sites (172 observations) during February 2017.

3.5.4 Effect of High-Resolution Emission Surrogates

To evaluate the effect of the commercial cooking and traffic spatial surrogates developed for this study, an additional simulation at 1 km resolution was performed with the spatial surrogates provided by EPA with the NEI. In order to isolate and evaluate the model's ability to predict the spatial distribution (as opposed to temporal variability), monthly average $\text{PM}_{2.5}$ measurements from EPA AirNow were compared with PMCAMx predictions for the winter of 2017. The simulation with the CACES surrogates predicts higher $\text{PM}_{2.5}$ by approximately $1 \mu\text{g m}^{-3}$ in the downtown area (Figure 3-7) and values that are $0.1\text{--}0.5 \mu\text{g m}^{-3}$ in much of the urban core and lower values in some of the suburbs.

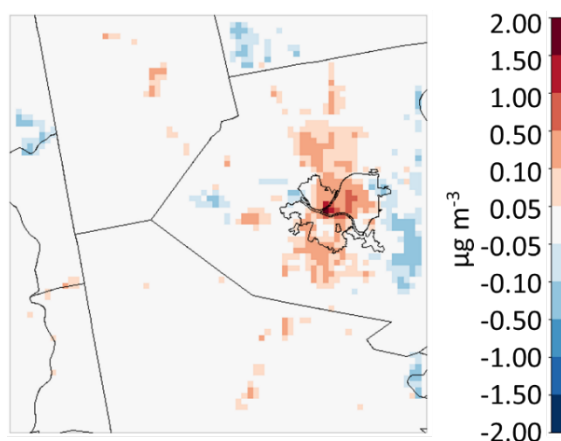


Figure 3-7. Time-averaged concentration differences between simulation with the CACES and EPA NEI default surrogates during February 2017.

The prediction skill metrics for these two simulations are summarized in Table 3-4 where “CACES” denotes the surrogates developed in this study and “EPA” the defaults provided with NEI11. The model performance with both emission surrogates is excellent with very low errors and biases for these comparisons of monthly averages. The contributions of local traffic and cooking OA are modest (40% of the OA which is less than 50% of the $\text{PM}_{2.5}$ in the CMU site,

(Figure 3-4) so the changes of the spatial distributions have a relatively small effect on the total PM_{2.5} predictions in most measurement sites.

Table 3-4. Comparison of PMCAMx predicted PM_{2.5} concentrations during February 2017 with monthly averages from EPA AirNow sites.

	CACES	EPA
Error ($\mu\text{g m}^{-3}$)	1.36	1.33
Fractional Error	0.12	0.12
Bias ($\mu\text{g m}^{-3}$)	0.33	0.35
Fractional Bias	0.04	0.04
R	0.52	0.55
Measured Avg. ($\mu\text{g m}^{-3}$)	10.39	
Predicted Avg. ($\mu\text{g m}^{-3}$)	10.73	10.74
Measured Std. Dev. ($\mu\text{g m}^{-3}$)	2.23	
Predicted Std. Dev. ($\mu\text{g m}^{-3}$)	1.65	1.60

This is expected as the “CACES” surrogates provide the largest change in emissions in the Pittsburgh downtown area causing only the Lawrenceville site to be significantly affected (Figure 3-8). Measurements in the areas of the highest predicted differences between the two simulations (e.g. downtown area) are needed to better evaluate the effect of the CACES surrogates. Also, measurements of COA and HOA concentrations instead of just total PM_{2.5} would be quite useful.

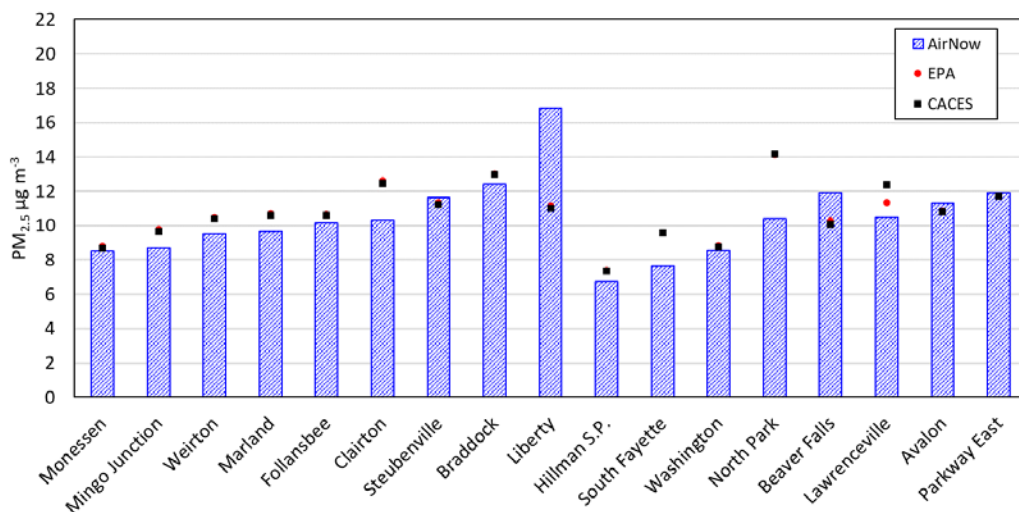


Figure 3-8. Comparison of PMCAMx predicted PM_{2.5} concentrations during February 2017 with monthly averages from 17 EPA AirNow sites using the “CACES” and “EPA” surrogates.

3.6 Effect of Grid Resolution

To determine the effect of grid resolution on the ability of the model to resolve geographical variations in $PM_{2.5}$ concentrations, monthly average measurements from the 17 EPA regulatory sites were compared with PMCAMx predictions from simulations at 36 x 36 km, 12 x 12 km, 4 x 4 km and 1 x 1 km. The PMCAMx prediction skill metrics are summarized in Table 3-5. Increasing grid resolution reduces the average fractional error from 16% at 36 x 36 km to 12% at 1 x 1 km. The average fractional bias was low even at the 36 x 36 master grid at less than 2% so the higher resolution resulted in only a minor improvement.

Examining the performance of the model for different sites, the fractional bias at the rural site at Hillman State Park was reduced from approximately 22% at 36 x 36 km to 7.4% at 12 x 12 km with minimal change at higher resolutions (Figure 3-9).

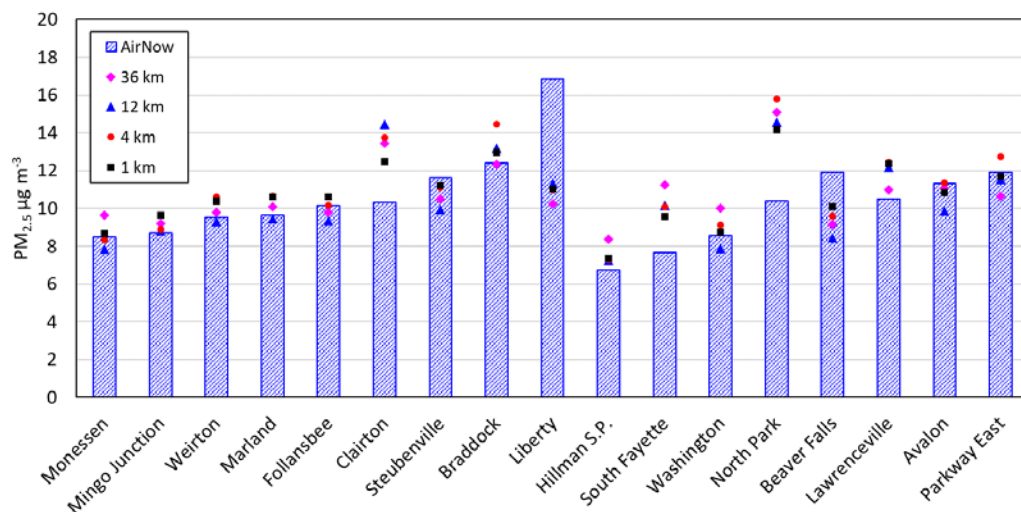


Figure 3-9. Comparison of PMCAMx predicted $PM_{2.5}$ concentrations during February 2017 for 36 x 36 km, 12 x 12 km, 4 x 4 km and 1 x 1 km with monthly averages from 17 EPA AirNow sites.

Similar results were observed by Fountoukis et al. (2013) when comparing PMCAMx predictions with measurements from remote sites in the northeast U.S. during the winter of 2002. The industrial sites in Steubenville and Liberty /Clairton are associated with large point sources

and show small changes in the fractional bias with increasing resolution while the fractional error shows small improvement changing from 12.8% at 4 x 4 km to 11.5% at 1 x 1 km. Increasing the model resolution allows for the more accurate resolution of the plumes from these sources. Previous studies (Zakoura and Pandis, 2019, 2018) showed a similar tendency for nitrate predictions for the northeastern U.S. At suburban sites the fractional error decreases with every increase in resolution from 29% at 36 x 36 km to 18% at 1 x 1 km.

Table 3-5. Comparison of PMCAMx predicted PM_{2.5} concentrations during February 2017 with monthly averages from 17 EPA AirNow sites.

	Urban	Suburban	Rural	Industrial	All
36 x 36 km					
Error ($\mu\text{g m}^{-3}$)	0.66	3.11	1.64	1.51	0.01
Fractional Error	0.06	0.29	0.22	0.13	0.02
Bias ($\mu\text{g m}^{-3}$)	-0.34	1.74	1.64	-0.30	0.07
Fractional Bias	-0.03	0.16	0.22	-0.01	0.02
Measured Avg. ($\mu\text{g m}^{-3}$)	11.23	9.64	6.73	10.86	10.39
Predicted Avg. ($\mu\text{g m}^{-3}$)	10.89	11.37	8.38	10.56	10.68
12 x 12 km					
Error ($\mu\text{g m}^{-3}$)	1.16	2.70	0.51	1.56	0.08
Fractional Error	0.10	0.26	0.07	0.13	0.02
Bias ($\mu\text{g m}^{-3}$)	-0.03	0.63	0.51	-0.45	-0.04
Fractional Bias	-0.01	0.05	0.07	0.04	0.02
Measured Avg. ($\mu\text{g m}^{-3}$)	11.23	9.64	6.73	10.86	10.39
Predicted Avg. ($\mu\text{g m}^{-3}$)	11.20	10.26	7.25	10.41	10.33
4 x 4 km					
Error ($\mu\text{g m}^{-3}$)	0.95	2.67	0.57	1.59	0.00
Fractional Error	0.08	0.24	0.08	0.13	0.01
Bias ($\mu\text{g m}^{-3}$)	0.95	1.52	0.57	0.13	-0.01
Fractional Bias	0.08	0.13	0.08	0.02	0.02
Measured Avg. ($\mu\text{g m}^{-3}$)	11.23	9.64	6.73	10.86	10.39
Predicted Avg. ($\mu\text{g m}^{-3}$)	12.18	11.16	7.30	10.99	11.02
1 x 1 km					
Error ($\mu\text{g m}^{-3}$)	0.85	1.92	0.62	1.37	0.03
Fractional Error	0.08	0.18	0.09	0.11	0.01
Bias ($\mu\text{g m}^{-3}$)	0.39	1.01	0.62	-0.02	0.01
Fractional Bias	0.03	0.10	0.09	0.01	0.01
Measured Avg. ($\mu\text{g m}^{-3}$)	11.23	9.64	6.73	10.86	10.39
Predicted Avg. ($\mu\text{g m}^{-3}$)	11.62	10.64	7.36	10.84	10.73

The improvements in the ability of the model to reproduce the spatial distribution of the observations become evident when one examines the values of the correlation coefficient, R,

between the measurements and the predictions. This starts at 0.2 for the coarse 36x36 km resolution, improves to 0.43 for the intermediate 12x12 km grid, to 0.45 for the fine 4x4 km, and finally to 0.53 for the ultrafine 1x1 km resolution. Another useful metric is the concentration gradient between the urban and rural sites. The measured value is $4.5 \mu\text{g m}^{-3}$. The coarse resolution seriously underpredicts this gradient with a value of $2.5 \mu\text{g m}^{-3}$. The predicted gradient increases to $4 \mu\text{g m}^{-3}$ at the intermediate resolution and to $4.3 \mu\text{g m}^{-3}$ for the finest resolution in very good agreement with the measurements.

Further improvements to model performance at high resolutions could potentially be achieved by modeling large point sources with the Plume in Grid methodology (Zakoura and Pandis, 2019) and by replacing interpolated meteorology with high-resolution data to drive both PMCAMx and the meteorology-dependent emission processors.

3.7 Model performance evaluation during summer

Table 3-6 summarizes the prediction skill metrics of PCMAMx with the EPA-CSN measurements in the 1x1 km domain for the summer period. Predictions of sulfate for the summer period show a similar behavior to winter with a small bias of $-0.3 \mu\text{g m}^{-3}$. Measured nitrate levels in the summer were lower than for the winter period. The model still over-predicts nitrate at low concentrations but by a smaller amount with a bias of approximately $0.3 \mu\text{g m}^{-3}$. Ammonium is also slightly overestimated with an average bias of around $0.3 \mu\text{g m}^{-3}$. Finally, PMCAMx underpredicts EC by approximately $0.2 \mu\text{g m}^{-3}$. While the biases in these predictions are low and expected, the OA is seriously underpredicted with a modeled value of approximately $1.7 \mu\text{g m}^{-3}$ compared to a measured value of around $4.5 \mu\text{g m}^{-3}$.

As a result of the OA underprediction, the PM_{2.5} is also underpredicted. The average measured PM_{2.5} value in the regulatory network in the area was 11.4 µg m⁻³, while the average predicted value was 4.9 µg m⁻³ lower.

Most of the OA during the summer in the modeling domain is secondary and a significant fraction of it is transported to the domain from other areas. Previous PMCAMx modeling studies at medium to high resolutions over the northeastern U.S. (Day and Pandis, 2015; Fountoukis et al., 2013; Zakoura and Pandis, 2018) yielded much better performance for the OA and the PM_{2.5} for summer periods. These studies used larger values for the organic aerosol in the boundary conditions and used MEGAN (Guenther et al., 2006) to model biogenic secondary organic aerosol precursors instead of BEIS (Pierce et al., 1998) used here. Carlton and Baker (2011) found that MEGAN produced less negatively biased results during July of 1998. Improvement of the summertime OA predictions will be the topic of future work.

Table 3-6. Comparison of 24 h average PMCAMx predictions with CSN measurements in July 2017.

	Sulfate	Nitrate	Ammon.	Elemental Carbon	Organic Aerosol
Measured Avg. (µg m ⁻³)	2.04	0.26	0.53	0.74	4.46
Predicted Avg. (µg m ⁻³)	1.77	0.59	0.88	0.56	1.69
Error (µg m ⁻³)	0.93	0.42	0.42	0.41	2.89
Fractional Error	0.47	0.99	0.65	0.63	0.90
Bias (µg m ⁻³)	-0.27	0.33	0.35	-0.18	-2.77
Fractional Bias	-0.10	0.39	0.57	-0.35	-0.86

3.8 Conclusions

We applied the PMCAMx chemical transport model over the city of Pittsburgh during winter using a series of telescoping grids at 36 x 36 km, 12 x 12 km, 4 x 4 km and 1 x 1 km. Emissions were calculated for the relevant grids by using the spatial surrogates provided with

NEI11 for all sectors except commercial cooking and on-road traffic for which 1 x 1 km spatial surrogates were developed.

PMCAMx predicts sulfate, elemental carbon and organic aerosol concentrations well with fractional biases below 10%. Nitrate concentrations are overpredicted following the trend of previous studies in both the US and Europe. Agreement with total PM_{2.5} measurements is also encouraging with a fractional bias of 3%. PMCAMx is also able to reproduce the PM₁ composition as measured by the AMS well. While the cooking OA contribution to OA is reproduced well, the model appears to be missing a mechanism for the rapid conversion of the biomass burning OA to oxygenated OA during the low photochemical conditions of the wintertime. PMCAMx reproduces well the sum of biomass burning OA and oxygenated OA but predicts that most of it is primary while the measurements suggest that it has been oxidized and is secondary.

The use of novel spatial surrogates for commercial cooking and on-road emissions has significant impacts primarily in the downtown Pittsburgh area where the predicted concentrations increase by approximately 1 $\mu\text{g m}^{-3}$ compared to the predictions with the default NEI surrogates. The lack of regulatory measurements in this “hot spot” results in only small changes in the already good model ability to reproduce the monthly average concentrations of fine PM.

Prediction performance improves with increasing resolution reducing the average fractional error from 16% at 36 x 36 km to 12% at 1 x 1 km. The correlation coefficient, R, between fine PM measurements and predictions increases from 0.2 for the coarse 36x36 km resolution to 0.53 for the ultrafine 1x1 km resolution. The predicted concentration gradient between the urban and rural sites increases from 2.5 to 4.3 $\mu\text{g m}^{-3}$ almost matching the measured value of 4.5 $\mu\text{g m}^{-3}$ as the model resolution increases. A lot of the improvement is realized moving from the coarse to the intermediate resolution.

The PMCAMx performance is weaker near the large industrial sites. Further improvements could be achieved by applying the Plume in Grid model to large point sources, increasing the resolution of meteorological data and by further refinements to spatial surrogates.

During a simulated summer period, predictions of total PM_{2.5} are significantly negatively biased driven by the underprediction of organic aerosol. The reasons for this underprediction are under investigation.

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Chapter 4. Changes of PM_{2.5} concentrations and their sources in the US from 1990 to 2010

4.1 Introduction

During the last decades, regulations by the US Environmental Protection Agency (EPA) have led to significant reductions of the emissions of SO₂, NO_x, CO, volatile organic compounds (VOCs), and primary particulate matter (PM) from electrical utilities and other industrial sources, transportation, and other sources. Xing et al., (2013) estimated emissions reductions from 1990 to 2010 of SO₂ by 67%, NO_x by 48%, CO by 60%, non-methane VOCs by 49%, primary PM_{2.5} by 34%. Ammonia emissions have been estimated to increase by 11% during this twenty-year period. At the same time, there have been significant reductions of the PM_{2.5} levels in practically all areas of the US (Meng et al., 2019). However, our ability to link these changes in estimated emissions with the observed changes in PM_{2.5} is uncertain. The available measurements are sparse in space and are quite limited before 2000. Three-dimensional chemical transport models (CTMs) are well suited to help address this problem since they simulate all the major processes that impact PM_{2.5} concentrations and transport.

There have been several efforts to quantify historical changes in PM_{2.5} levels and composition. These rely heavily on measurements (both ground and satellite for the more recent changes) and a number of statistical techniques including land-use regression models to calculate the concentrations of PM_{2.5} over specific areas and periods (Beckerman et al., 2013; Eeftens et al., 2012; Li et al., 2017; Ma et al., 2016). More recent studies include chemical transport models in this effort. For example, Meng et al., (2019) estimated historical PM_{2.5} concentrations over North America from 1981 to 2016 combining the predictions of GEOS-Chem, satellite remote sensing,

and ground-based measurements. They found a good correlation between the estimated PM_{2.5} concentrations and the ground-based measurements. This study is focused on the estimation of total PM_{2.5} levels to assess long-term changes in exposure and associated health risks. The composition of PM_{2.5} and its sources were not analyzed in this work.

Li et al., (2017) combined in-situ and satellite observations with the global CTM GEOS-Chem to quantify global trends in the chemical composition of PM_{2.5} over 1989–2013. The emphasis of the study was on regional trends. They concluded that the predicted average trends for North America were consistent with the available measurements for PM_{2.5}, secondary inorganic aerosols, organic aerosols, and black carbon. Nopmongcol et al., (2017) used CAMx with the Ozone Source Apportionment Technology (OSAT) and Particulate Source Apportionment Technology (PSAT) algorithms for six different years within five decades (1970–2020), to calculate the contributions from different emission sources to PM_{2.5} and O₃ in the US. Constant meteorology and natural emissions (including wildfires) were used for all six simulated years. They concluded that the contribution of electrical generation units (EGUs) and on-road sources to fine PM has declined in most areas while the contributions of sources such as residential, commercial and fugitive dust emissions stand out as making large contributions to PM_{2.5} that are not declining. The use of constant meteorology did not allow the direct evaluation of these predictions.

In this study we used more detailed inputs, such as period-specific meteorological data and source-resolved emissions for every year used, to estimate the concentration, composition, and sources of PM_{2.5} over 20 years in the US. The model predictions are compared with the available measurements. The sources responsible for the PM_{2.5} reductions in various areas of the country are identified and their contribution to the reductions is quantified.

4.2 Model Description

4.2.1 PMCAMx

The Particulate Matter Comprehensive Air Quality Model with Extensions (PMCAMx) (Karydis et al., 2010; Murphy and Pandis, 2010; Posner et al., 2019; Tsimpidi et al., 2009), uses the framework of the CAMx model (Environ, 2006) to describe horizontal and vertical advection and diffusion, wet and dry deposition, and gas and aqueous phase chemistry. A 10-size section (30 nm to 40 μm) aerosol sectional approach is used to dynamically track the evolution of aerosol mass. The aerosol species modeled include sulfate, nitrate, ammonium, sodium, chloride, elemental carbon, mineral dust, and primary and secondary organics. The Carbon Bond 05 (CB5) mechanism (Yarwood et al., 2005) is used for molecularly lumped gas-phase chemistry calculations. The version of CB5 used here includes 190 reactions of 79 surrogate gas-phase species. Transfer of each species between the gas and aerosol phases is determined using the ISORROPIA aerosol thermodynamics model (Nenes et al., 1998) and is then distributed through the size sections using weighting factors based on each section surface area (Pandis et al., 1993). The volatility of organic aerosols is modeled using the volatility basis set approach (Donahue et al., 2006) using NO_x dependent yields (Lane et al., 2008). For primary organic aerosols (POA) 10 volatility bins, ranging from 10^{-3} to 10^6 $\mu\text{g m}^{-3}$ saturation concentration are used. Secondary organic aerosols (SOA) are split between aerosol formed from anthropogenic sources (aSOA) and from biogenic ones (bSOA) and modeled with 4 volatility bins (1, 10, 10^2 , 10^3 $\mu\text{g m}^{-3}$) (Murphy and Pandis, 2009).

4.2.2 Particulate Source Apportionment Technology (PSAT)

The PSAT algorithm (Skylakou et al., 2017, 2011; Wagstrom et al., 2008; Wagstrom and Pandis, 2011a, 2011b) is an efficient algorithm that can track and compute the contribution of

different sources to the concentrations of pollutant concentrations. The advantages of PSAT are that it runs in parallel with the CTM (PMCAMx), so there is no need to modify the CTM for different applications and that it is quite computationally efficient. PSAT takes advantage of the fact that the molecules of each pollutant at each location regardless of their source have the same probability of reacting, depositing or getting transported to avoid repeating the simulations of these processes. For secondary species, it follows the apportionment of their precursor vapors. For example, secondary organic aerosol is based on the apportionment of VOCs or IVOCs, sulfate on SO_2 , nitrate on NO_x , and ammonium on NH_3 .

In this study, we use the version of PSAT that is consistent with the Volatility Basis Set (Skylakou et al., 2017) to calculate the contribution of each emission source to the concentration of $\text{PM}_{2.5}$ and its components.

4.3 Model Application

PMCAMx-PSAT was applied over the continental United States (CONUS) for the years 1990, 2001, and 2010 using a grid of 132 by 82 cells of 36 km by 36 km horizontally (covering an area of 4752×2952 km) and 14 layers of varying thickness up to an altitude of approximately 13 km with a data reporting frequency of 1 hour. We selected this resolution as it has been shown to be a viable option for keeping computational and storage demands manageable while providing sufficient quality for long-term simulations and air quality planning applications (Gan et al., 2016).

4.3.1 Meteorology

Meteorological simulations were performed with WRF v3.6.1 over the CONUS area, with a horizontal resolution of 12 km and 36 vertical (sigma) levels up to a height of about 20 km. The simulations were executed using 3.5-day overlapping run segments. Initial and boundary conditions were generated from the ERA-Interim global climate re-analysis database, together

with the terrestrial datasets for terrain height, land-use, soil categories, etc. from the United States Geological Survey (USGS) database. Model output was recorded every hour. The WRF modeling system was prepared and configured in a similar way as described by Gilliam and Pleim (2010). For the model physical parameterization, the Pleim-Xiu (PX) Land Surface Model (LSM) (Xiu and Pleim, 2002) was selected. Other important WRF physics options include the Rapid Radiative Transfer Model/Dudhia (RRTMG) radiation schemes (Iacono et al., 2008), the Asymmetric Convective Model version 2 (ACM2) for PBL (Pleim, 2007a, 2007b), the Morrison double-moment cloud microphysics scheme (Morrison et al., 2008), and version 2 of the Kain–Fritsch (KF2) cumulus parameterization (John S., 2004). The selected WRF configuration is recommended for air quality simulations (Hogrefe et al., 2015; Rogers et al., 2013).

4.3.2 Emissions

Emissions for the simulations were obtained from the internally consistent, historic emission inventories of Xing et al. (2013) that include source-resolved gas and primary particle emissions. Point source sectors include Electricity Generating Units (EGU), included in the EPA’s Integrated Planning Model (IPM); industrial sources not included in the IPM (non-EGU); and all other point sources in Canada and Mexico. Area sources include on-road emissions in the US, Canada, and Mexico; off-Road emissions for the entire domain; and all remaining non-biogenic sources. We used our WRF meteorology to drive MEGAN3 (Jiang et al., 2018) using the default emission factors for all years to generate biogenic emissions for the CONUS domain.

In this application of PSAT we used 6 different emission categories based on those described above and initial and boundary conditions which can be tracked separately by the model as different sources. The emission sources used, are the following: ‘road’ which includes road emissions over US; ‘non-road’ which includes the off-road emissions of the entire domain; ‘EGU’;

‘non-EGU’ as described above; ‘other’ which includes the sum of the other point and area sources plus the ‘on-road’ emissions from Canada and Mexico and finally biogenic emissions.

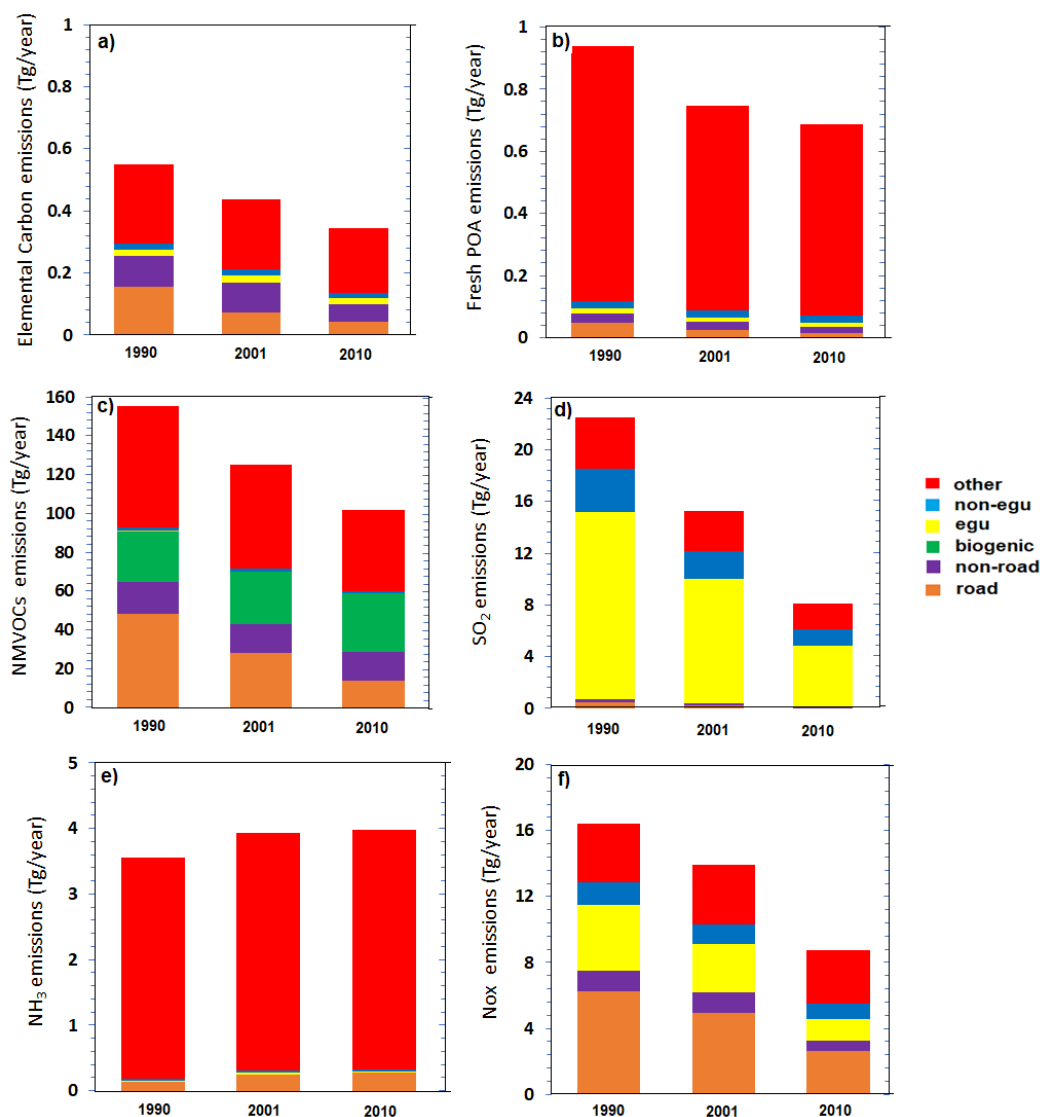


Figure 4-1. Annual emissions by each source for the whole domain for: a) elemental carbon, b) fresh POA, c) non-methane VOCs, d) SO₂, e) NH₃, and f) NO_x.

Figure 4-1 depicts the total annual emissions for each source and each year. For EC and fresh POA, biomass burning (included in the ‘other’ category) was the dominant source and remain relatively constant throughout the years. The second most important source of EC was road

transport, with the corresponding emissions having been reduced by almost 350% from 1990 to 2010, due to the improvement of the corresponding control technologies.

Emissions of VOCs by on-road sources were reduced by a factor of 3.5. On the other hand, the VOCs emitted by non-road transport and biogenic sources changed by less than 10%. The emissions of the most important SO₂ source, EGUs, were reduced 33% from 1990 to 2001 and 67% from 1990 to 2010. For NH₃ the most important source was agriculture (included in the ‘other’ category) and the corresponding emissions increased by 7% during these 20 years. Road transportation was one of the major NO_x sources with the corresponding emissions getting 21% from 1990 to 2001 and 58% from 1990 to 2010. The second most important source for NO_x in 1990, the EGUs, emitted 25% less NO_x in 2001 and 66% less in 2010 compared to 1990.

4.4 Results

4.4.1 Annual average concentrations and sources

We examine here the source apportionment results of PMCAMx-PSAT for the major components of PM_{2.5}, for the three simulated years.

On-road transportation was a major source of EC was a significant source of EC especially in urban areas in 1990 (Figure 4-2). The concentrations of EC originating from this source were reduced by more than a factor of 3 from 1990 to 2010. The industrial sources (EGUs and non-EGU) contributed less than 0.1 µg m⁻³ of EC in all areas during these years. The ‘other’ source which includes all types of biomass burning was the major source during all years. Long-range transport (LRT), which expresses the transport from areas from outside the domain, contributed approximately 0.1 µg m⁻³.

The concentrations of total OA are presented as the sum of POA and SOA in Figure 4-3. The OA originating from on-road transportation was about $1 \mu\text{g m}^{-3}$ during 1990 over the Eastern US, but it was reduced to less than $0.5 \mu\text{g m}^{-3}$ during 2010.

‘Non-road’ transport and ‘non-EGU’ emission sources had smaller contributions to OA, contributing less than $0.2 \mu\text{g m}^{-3}$ in most areas. Biogenic SOA was almost $1 \mu\text{g m}^{-3}$ over the south-east US both during 1990 and 2001, but during 2010 it had much higher concentrations in some areas due to the meteorological conditions in the south during that year. Also, high OA concentrations were predicted to originate from biomass burning during 1990. The contribution of long-range transport OA was approximately constant during the simulated years, at around $0.6 \mu\text{g m}^{-3}$.

Sulfate was the dominant component of $\text{PM}_{2.5}$ in the Eastern US in 1990 and the EGUs were the dominant source contributing more than $5 \mu\text{g m}^{-3}$ over wide areas of the Eastern US (Figure 4-4). The corresponding sulfate concentrations from EGUs were reduced to $3 \mu\text{g m}^{-3}$ in 2001 and to $1.5 \mu\text{g m}^{-3}$ in 2010 due to the dramatic reduction of these SO_2 emissions over these 20 years. Sulfate concentrations originating from non-EGU and other emission sources were $1 \mu\text{g m}^{-3}$ or less during all the years. Long-range transport contributed approximately $0.9 \mu\text{g m}^{-3}$ to the sulfate levels during the simulated period.

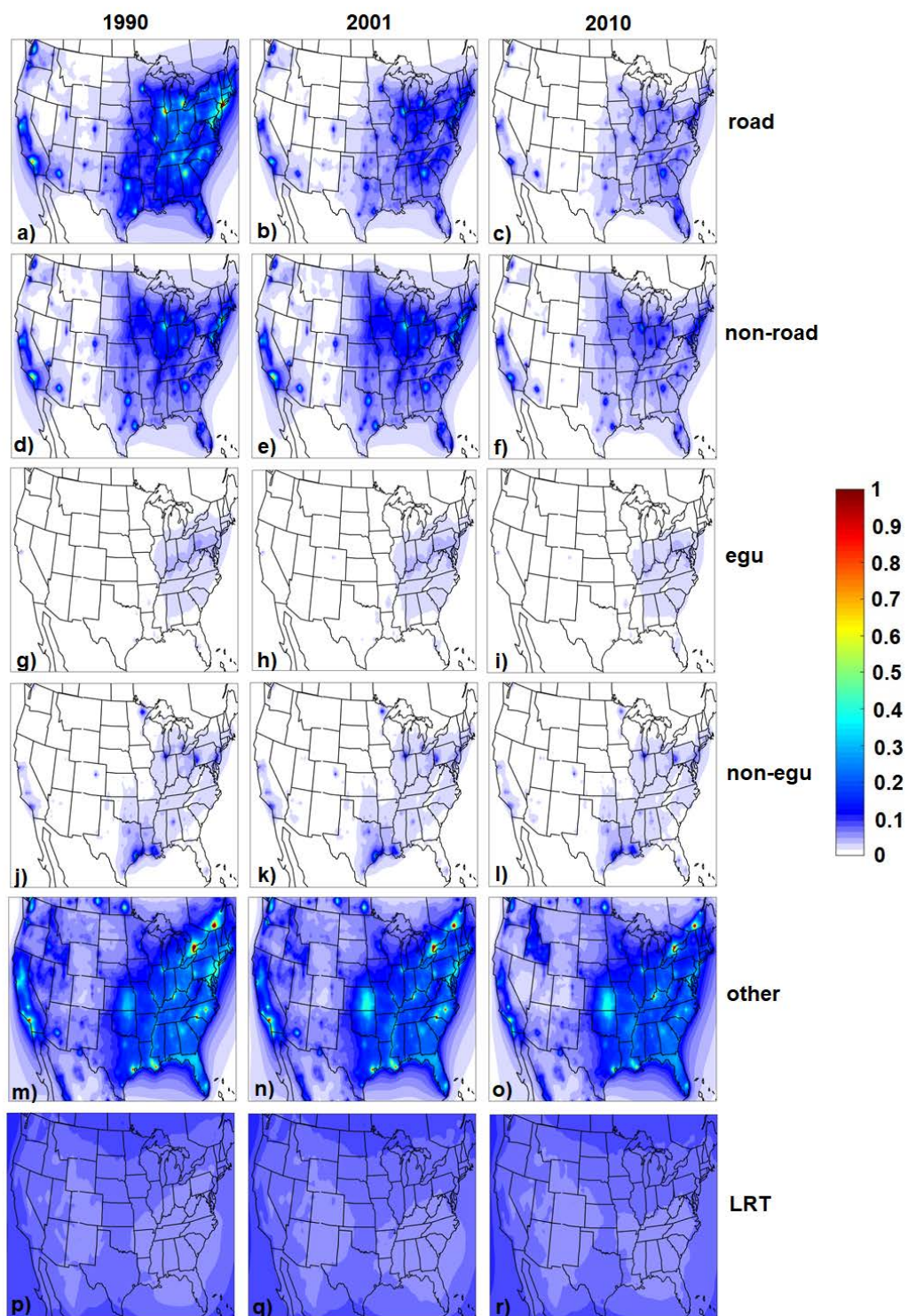


Figure 4-2. Predicted annual average ground level PM_{2.5} elemental carbon concentrations per source in $\mu\text{g m}^{-3}$ for 1990, 2001, and 2010.

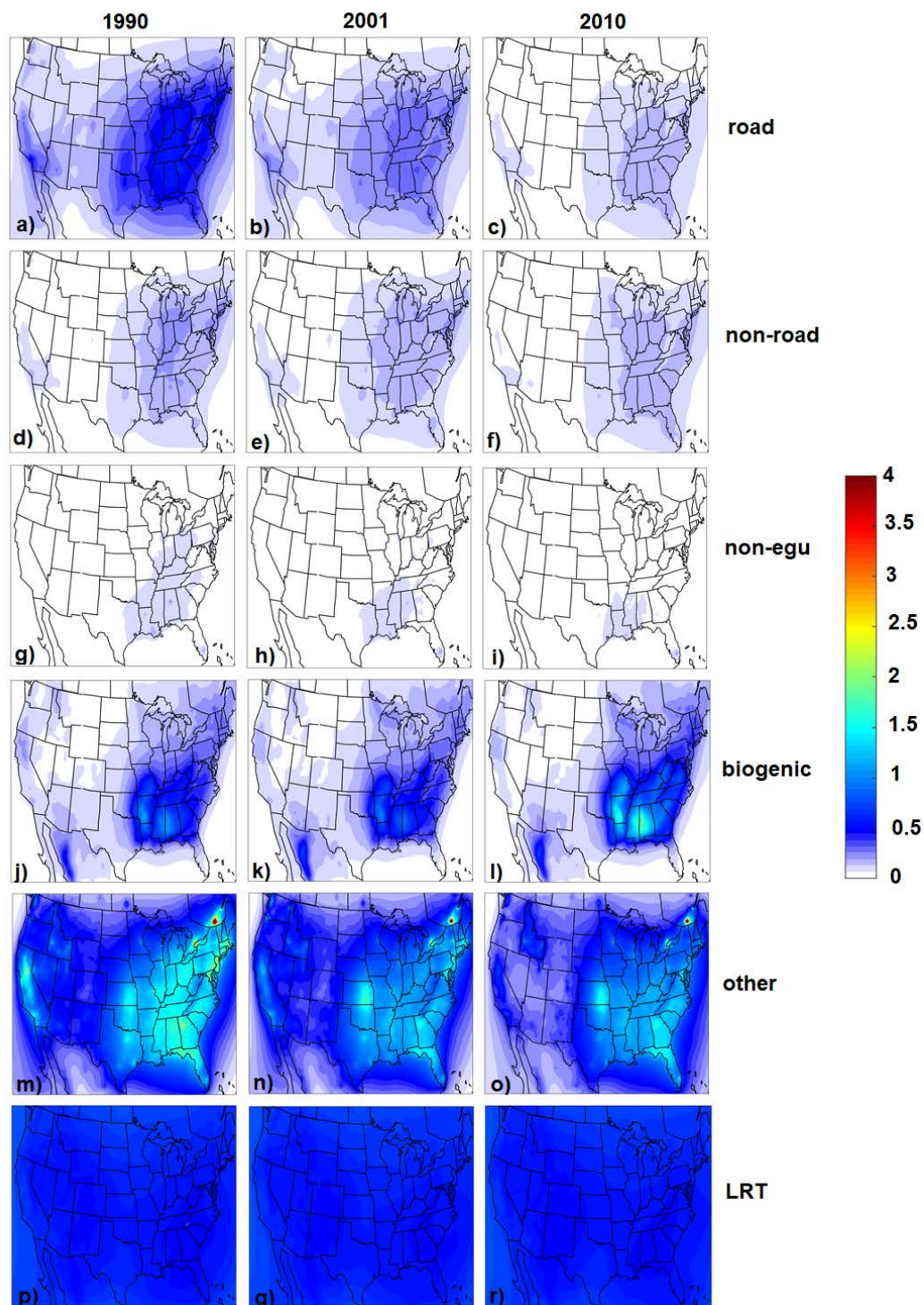


Figure 4-3. Predicted annual average ground level PM_{2.5} organic aerosol concentrations per source in $\mu\text{g m}^{-3}$ for 1990, 2001, and 2010.

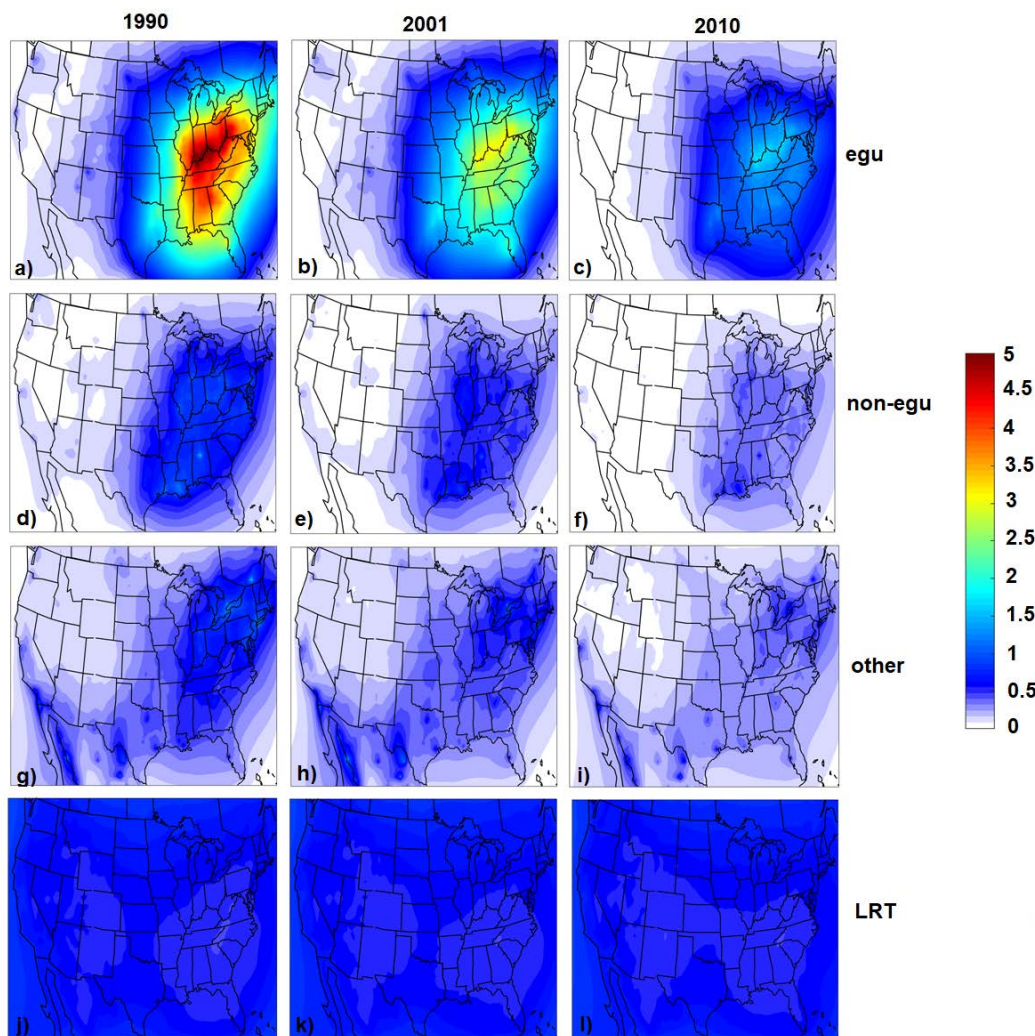


Figure 4-4. Predicted annual average ground level PM_{2.5} sulfate concentrations per source in $\mu\text{g m}^{-3}$ for 1990, 2001, and 2010.

4.4.2 Regional contributions of sources to PM_{2.5} components

The US was separated into seven regions (Fig. 5) to facilitate the spatial analysis of the source contributions and their changes during the simulated period. The Northeast (NE) region includes major cities like New York, Boston, Philadelphia, Baltimore, and Pittsburgh, while the Mideast (ME) includes the Ohio-river area with a lot of the Electrical Generation Units. The Midwest (MW) has significant agricultural activities, while the West (WE) is relatively sparsely populated. California (CA) was kept separate from the other western regions. The south US was

split into a southeast region (SE) with significant biogenic emissions and the southwest (SW) with much less vegetation.

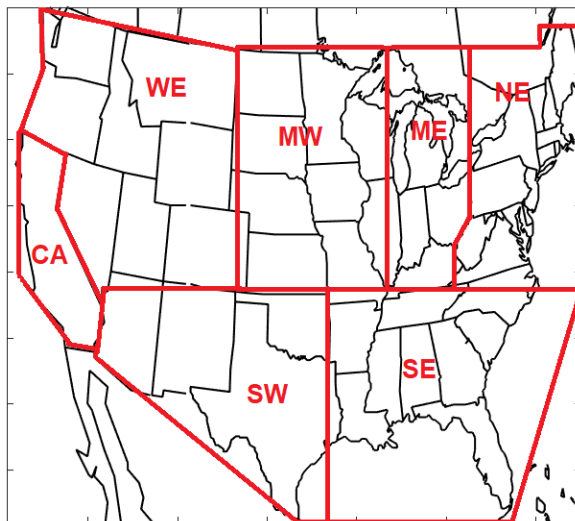


Figure 4-5. Definition of the 7 US regions used in the analysis.

Figure 4-6 shows the average concentrations of EC for each year in each region. The highest concentrations for 1990 were predicted in California, followed by the Mideast and the Northeast. Biomass burning was the dominant source of EC during all years and regions, with relatively constant concentration through the years, except from CA, where the contribution from wildfires in 1990 was much higher. There was a significant reduction of the EC levels in all regions with the exception of the West where the EC is mainly originating from biomass burning and long-range transport. The higher reductions are predicted in the eastern US.

The annual average concentrations of OA are depicted in Figure 4-7. The predicted concentrations of OA in 1990 in the eastern US (NE, SE and ME regions) and California were almost $2.5 \mu\text{g m}^{-3}$ and in the other regions less than $2 \mu\text{g m}^{-3}$. OA concentrations originating from biomass burning dominated the concentrations of OA during all the years and all regions. Biogenic SOA was the second most significant OA component in the Southeast. OA originating from on-

road transport contributed, according to the model, almost $0.3 \mu\text{g m}^{-3}$ during 1990 and almost $0.1 \mu\text{g m}^{-3}$ during 2010 in the eastern US. Significant reductions of OA are predicted for the Northeast, Mideast, and California while moderate reductions for the Midwest, West, and Southwest. The OA in the Southeast has more complex behavior due to the predicted increase of biogenic SOA in 2010 that leads to an increase of the total OA compared to 2001.

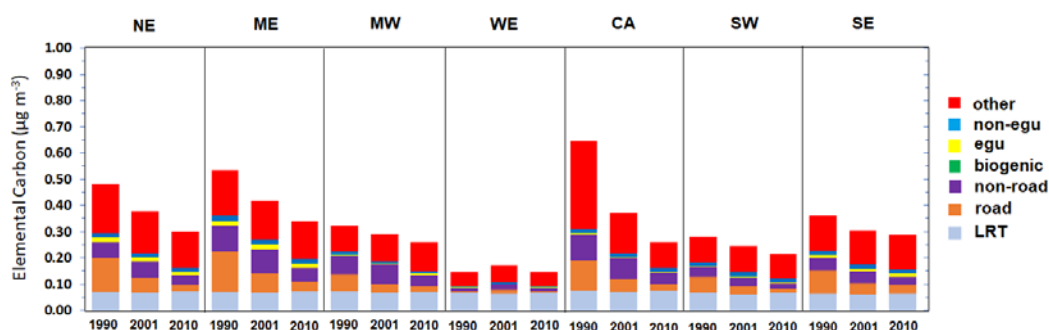


Figure 4-6. Average concentrations and sources of $\text{PM}_{2.5}$ EC for the different regions during 1990, 2001, and 2010.

The highest concentrations of sulfate for 1990 are predicted in the Eastern US (NE, ME and SE) in regions downwind of the EGUs which are the major source in these areas. The dramatic reductions of the EGU emissions are predicted to lead to major reductions in the sulfate levels in these three regions. More modest, but significant reductions of sulfate are also predicted for the Midwest and the Southwest. The reductions in the West and in California are small given that the sulfate there even in the 1990s is predicted to be dominated on average by long-range transport.

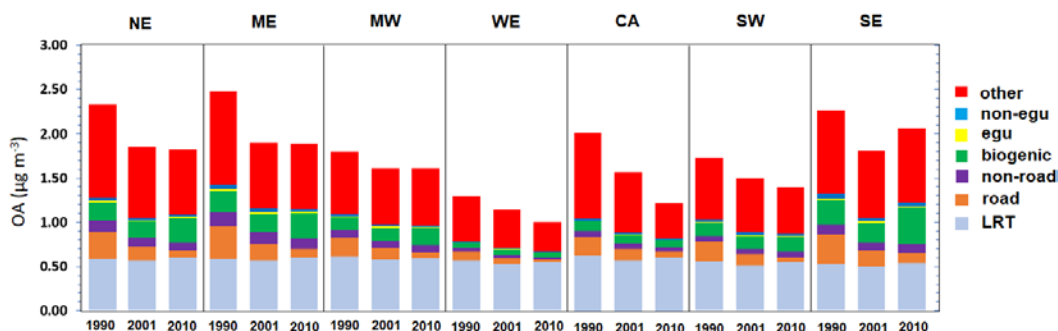


Figure 4-7. Average concentrations and sources of PM_{2.5} OA for the different regions during 1990, 2001, and 2010.

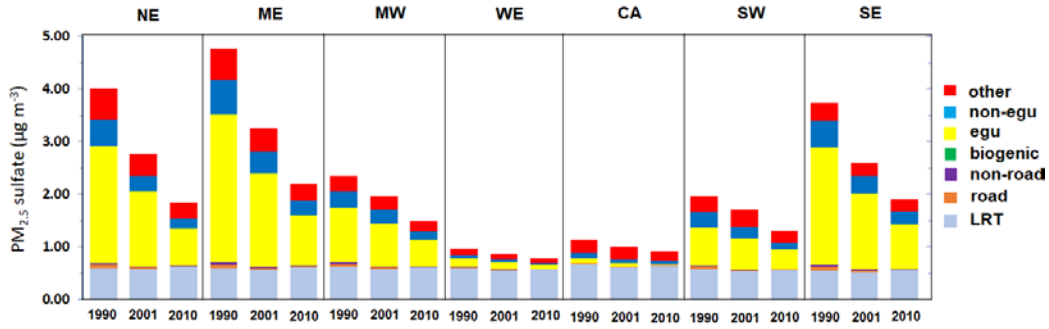


Figure 4-8. Average concentrations and sources of PM_{2.5} sulfate for the different regions during 1990, 2001, and 2010.

4.4.3 Model Evaluation

The model was evaluated against ground-level measurements from IMPROVE and CSN networks (IMPROVE, 1995; U.S. EPA, 2006). The metrics used include the normalized mean bias (NMB), the normalized mean error (NME), the mean bias (MB), the mean absolute gross error (MAGE), the fractional bias (FBIAS), and the fractional error (FERROR),

$$NMB = \sum_{i=1}^n (P_i - O_i) / \sum_{i=1}^n O_i \quad NME = \sum_{i=1}^n |P_i - O_i| / \sum_{i=1}^n O_i$$

$$MB = 1/n \sum_{i=1}^n (P_i - O_i) \quad MAGE = 1/n \sum_{i=1}^n |P_i - O_i|$$

$$FBIAS = 2/n \sum_{i=1}^n (P_i - O_i) / (P_i + O_i) \quad FERROR = 2/n \sum_{i=1}^n |P_i - O_i| / (P_i + O_i)$$

where P_i represents the model predicted value for data point i , O_i is the corresponding observed value and n is the total number of data points. The results are summarized in Table 4-1. We have excluded the region of California from this analysis because the coarse resolution used in this application does not allow PMCAMx to capture the significant gradients and high concentrations observed in that area. During 1990 there were only 25 measurement sites available from the IMPROVE network available, but this number increased dramatically in 2001 and 2010.

Table 4-1. Evaluation metrics for each year and each major PM_{2.5} component.

	MB ($\mu\text{g m}^{-3}$)	MAGE ($\mu\text{g m}^{-3}$)	NMB	NME	FBIAS	FERROR	Stations
EC							
1990	-0.02	0.07	-0.07	0.25	0.02	0.26	25
2001	0.12	0.17	0.35	0.49	0.26	0.37	126
2010	-0.04	0.15	-0.09	0.03	0.06	0.37	270
OA							
1990	-0.25	0.36	-0.14	0.20	-0.10	0.18	27
2001	-0.69	0.85	-0.27	0.33	-0.17	0.30	122
2010	0.04	0.39	0.02	0.19	0.01	0.20	270
Sulfate							
1990	-0.02	0.07	-0.08	0.25	0.16	0.26	33
2001	0.10	0.34	0.05	0.15	0.16	0.23	115
2010	0.12	0.28	0.07	0.16	0.18	0.23	285
Nitrate							
1990	0.02	0.19	0.09	0.67	-0.26	0.56	27
2001	-0.06	0.32	-0.07	0.39	-0.10	0.53	114
2010	-0.23	0.32	-0.25	0.33	-0.32	0.47	285
Ammonium							
1990	-0.02	0.14	-0.04	0.21	0.09	0.24	26
2001	0.07	0.21	0.07	0.21	0.13	0.26	134
2010	0.11	0.17	0.14	0.21	0.21	0.28	290
PM_{2.5}							
1990	0.25	1.07	0.04	0.19	-0.01	0.15	33
2001	1.31	2.70	0.11	0.22	0.07	0.23	976
2010	0.88	1.96	0.09	0.21	0.07	0.23	869

The model reproduces well the EC, OA, sulfate, and ammonium annual average concentrations with fractional bias and fractional error less than 0.3 for almost all years. PMCAMx has a small tendency towards overprediction of the EC and underprediction of the OA. There is also a tendency towards overprediction of the sulfate and as a result of the ammonium too. The fractional error for nitrate is a little higher and closer to 0.5 with the model in general underpredicting the observed values. The predictions for PM_{2.5} concentrations, for which there are

almost a thousand measurements in 2001 and 2010, is reproduced with fractional bias less than 10% and fractional error less than 25%. For 1990 there is little bias, while there is a small tendency towards overprediction in the later years.

One of the important results of this evaluation is the relatively consistent performance of PMCAMx during the different years. The use of a consistent emission inventory, consistent meteorology and measurements have probably contributed to this outcome.

4.4.4 Predicted spatial changes of concentrations

We calculated the predicted changes in annual average concentrations between 1990 and 2010 for the main PM_{2.5} components. Figure 4-9 shows the reductions in EC concentrations from 1990 to 2001 and from 1990 to 2010, both absolute and as a percentage. EC concentrations were reduced by almost 0.5 $\mu\text{g m}^{-3}$ in major cities from 1990 to 2001, which corresponds to a 25-30% reduction. The continuing reductions of the EC emissions in the next decade resulted in total reductions of around 50% in the twenty-year period in both large cities but also extended areas of the Northeastern and Mideastern US and California. Significant reductions are also predicted for the Southeast, Texas, Western coast, etc.

From 1990 to 2001, sulfate was reduced about by 2.5 $\mu\text{g m}^{-3}$ in southern Indiana and by about 2 $\mu\text{g m}^{-3}$ in Ohio, Illinois, and Kentucky (Figure 4-11). The predicted reductions during this decade are in the 30-35% range for the Eastern US. These reductions continued during the second decade of the simulated period reaching 50-60% of the 1990 levels in the part of the country to the east of the Mississippi. The corresponding reductions in the middle of the country and in the western states from 1990 to 2010 were in the 20-30% range for the relatively low sulfate levels in these regions.

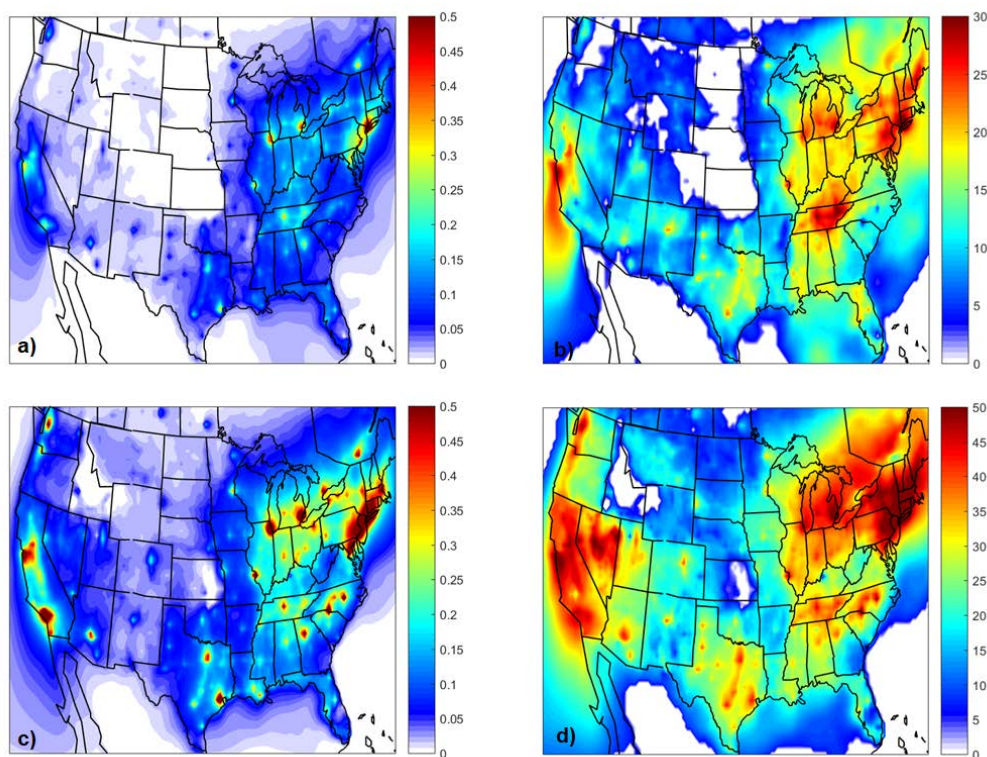


Figure 4-9. Reductions in PM_{2.5} elemental carbon: absolute ($\mu\text{g m}^{-3}$) from 1990 to 2001 (a) and from 1990 to 2010 (c) and percent (%) from 1990 to 2001 (b) and from 1990 to 2010 (d).

These simulations suggest that the Eastern US has benefited more both in an absolute and in a relative sense from these reductions in SO₂ emissions.

4.4.5 Evaluation of the predicted PM reductions

We calculated the changes from 1990 to 2001, from 1990 to 2010, and from 2001 to 2010 and compared them to the corresponding observed changes. For the first two cases, there were only a few measurements available for 1990.

For sulfate, the model reproduced very well the observed changes for the three comparison periods with Pearson's correlation coefficient $r = 0.91$ (from 1990 to 2001); 0.97 (from 1990 to 2010) and 0.95 (from 2001 to 2010).

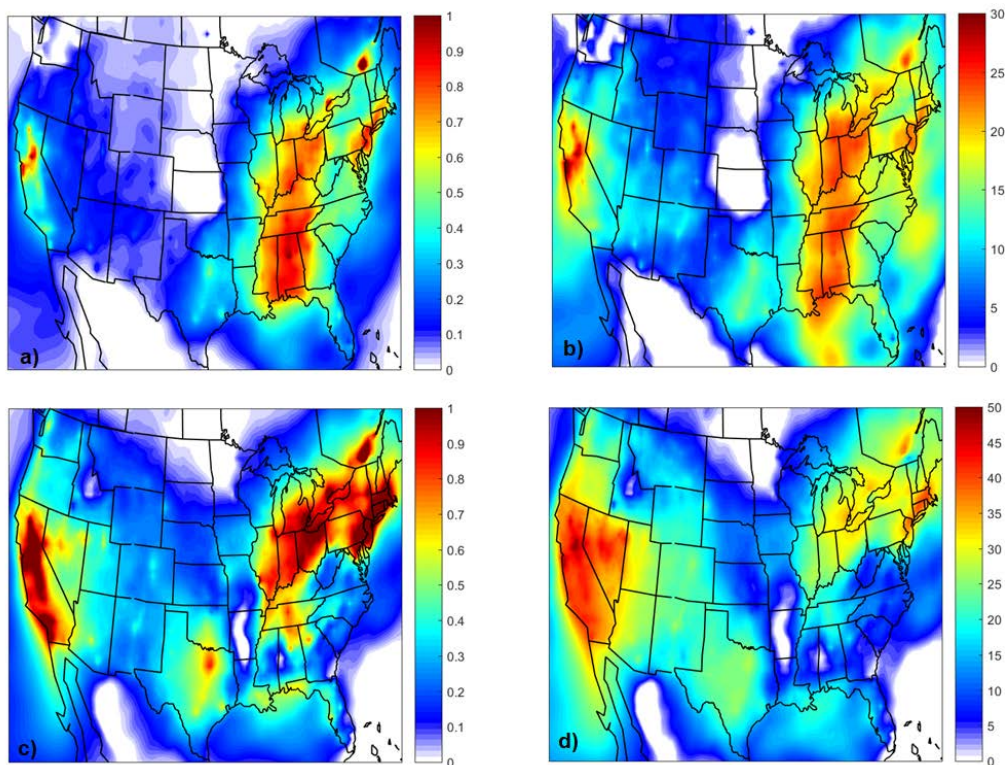


Figure 4-10. Reductions in PM_{2.5} OA: absolute ($\mu\text{g m}^{-3}$) from 1990 to 2001 (a) and from 1990 to 2010 (c) and percent (%) from 1990 to 2001 (b) and from 1990 to 2010 (d).

For EC the performance was quite good between 1990 and 2010 ($r = 0.77$) and between 2001 and 2010 ($r=0.64$) but weaker during the period from 1990 to 2001 ($r=0.39$).

For OA the model responded reasonably for changes between 1990 and 2001 ($r = 0.48$) and between 1990 to 2010 ($r = 0.31$), but not so well for changes between 2001 and 2010 ($r = 0.1$). There was a general tendency of the model to underpredict the reductions in OA in some areas. This issue needs to be examined in future work.

Finally, for PM_{2.5} the model reproduces well the changes between 1990 and 2010 with $r = 0.83$ and not as well the other changes ($r = 0.26$ from 1990 to 2001 and $r = 0.31$ from 2001 to 2010).

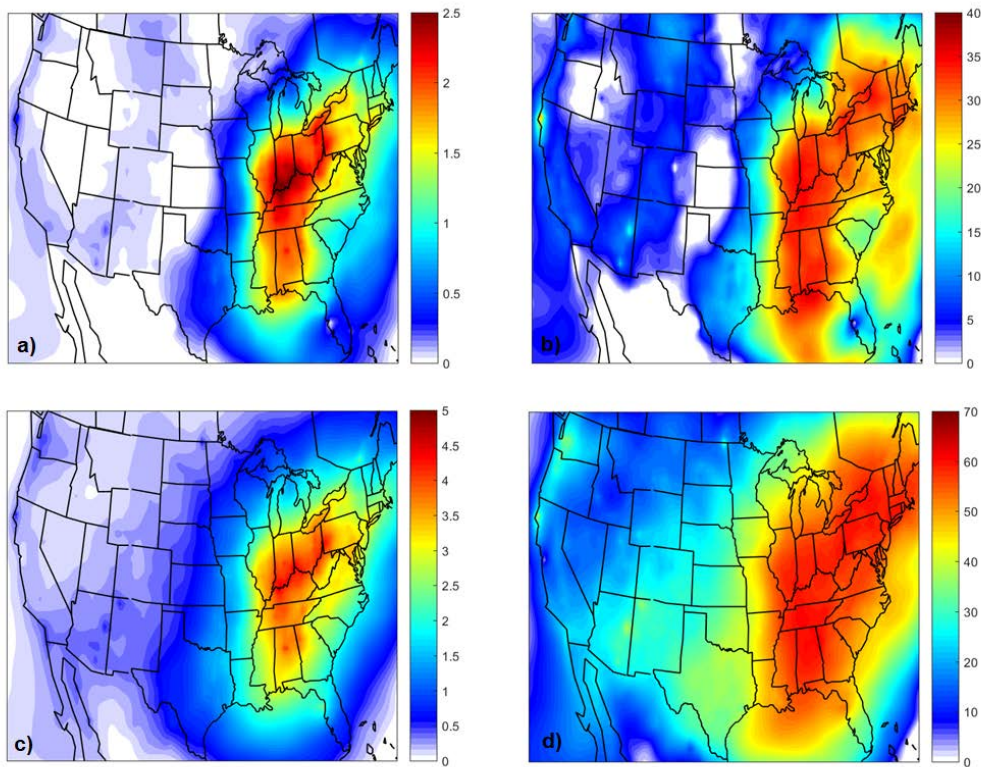


Figure 4-11. Reductions in PM_{2.5} sulfate: absolute ($\mu\text{g m}^{-3}$) from 1990 to 2001 (a) and from 1990 to 2010 (c) and percent (%) from 1990 to 2001 (b) and from 1990 to 2010 (d).

4.5 Conclusions

The CTM PMCAMx using consistent emissions and meteorology was used to simulate the changes in source contributions over two decades. The performance of the model was similar to those of its previous evaluation exercises in the same domain. PMCAMx reproduces the annual average concentrations of PM_{2.5} and its components from 1990 to 2010 with fractional errors of less than 30 %.

Biomass burning the most important source for OA during this 20-year period with approximately constant average contribution. Biogenic SOA is the second most important OA component, while OA coming from on-road transport decreased almost 3 times from 1990 to 2010.

For EC, 37% average reduction in emissions from 1990 to 2010 caused a reduction of 23% in concentrations, while the average reduction of 63% in SO₂ emissions due to the reduction of SO₂ coming from EGUs caused an average reduction of almost 40% in sulfate and higher (60%) in specific areas like NE and SE part of the US.

The predicted changes by the model seem reasonable compared with the observed changes giving perfect comparisons for changes between 1990 and 2010 for EC ($r = 0.77$), sulfate ($r = 0.97$) and PM_{2.5} ($r = 0.83$).

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Chapter 5. Conclusions and future work

5.1 Conclusions

We applied the PMCAMx chemical transport model over the city of Pittsburgh using a series of telescoping grids at 36 x 36 km, 12 x 12 km, 4 x 4 km and 1 x 1 km. Emissions were calculated with the EPA NEI11 using the provided 2017 projections (Eyth and Vukovich, 2016). The provided spatial surrogates were used for all grids and sectors (Adelman, 2015). For commercial cooking, a new spatial surrogate based on freely available restaurant location data was built for the finest grid, while for on-road traffic a traffic model was used (Ma et al., 2019).

At the finest resolution, the model successfully resolved intra-urban variations and individual roadways. Pollutants with significant local emissions such as elemental and organic carbon have gradients that can only be resolved at the finest resolution. Biomass burning has significant emissions during the winter period as well as the largest variability while during the winter period its contribution is negligible. During both periods the most important source was long-range transport from outside the domain.

Increasing the grid resolution from 36 x 36 to 12 x 12 km improves the model ability to resolve the PM_{2.5} exposure distribution for concentrations below 9.6 $\mu\text{g m}^{-3}$. At 1 x 1 km the distribution for higher concentrations is resolved and the effect of hotspots can be observed. During winter, biomass burning is the most important local source for PM_{2.5} exposure.

PMCAMx predictions at various grid resolutions were then compared with measurements of PM_{2.5} concentration and composition. PMCAMx predicts sulfate, elemental carbon and organic aerosol concentrations well with fractional biases below 10%. Nitrate concentrations are overpredicted following the trend of previous studies in both the US and Europe. Agreement with

total PM_{2.5} measurements is also encouraging with a fractional bias of 3%. PMCAMx is also able to reproduce the PM₁ composition as measured by the AMS well.

The novel spatial surrogates developed in this work for commercial cooking and on-road emissions have significant impacts in downtown Pittsburgh where the predicted concentration increases by $\sim 1 \mu\text{g m}^{-3}$. As there are no regulatory monitors in this “hot spot” very little change in the model ability to predict the monthly average concentration is observed. Prediction performance improves with increasing resolution reducing the average fractional error from 16% at 36 x 36 km to 12% at 1 x 1 km. The predicted concentration gradient between the urban and rural sites increases from 2.5 to 4.3 $\mu\text{g m}^{-3}$ almost matching the measured value of 4.5 $\mu\text{g m}^{-3}$ as the model resolution increases.

Lastly, PMCAMx was used to simulate the changes in source distributions from 1990 to 2010 using consistent emissions and meteorology. Model performance was evaluated and found to be similar to previous modeling exercises in the same domain. PMCAMx reproduces the concentration of PM_{2.5} and its components during the period with a fractional error of less than 30%. Biomass burning was identified as the main source for OA during this period, followed by biogenic SOA. Significant reductions in OA from on-road traffic were observed.

EC concentrations reduced by 23% due to a 37% reduction on emissions from 1990 to 2010. SO₂ emissions were reduced by 63% causing a large reduction of sulfate concentrations in the northeast of the U.S. A comparison between the predicted and observed reductions of EC, sulfate, and PM_{2.5} showed excellent correlations.

5.2 Future work

For the simulations in Chapters 2 and 3, PMCAMx was used in a base configuration. One of the main advantages of PMCAMx is its modularity and extensibility. The use of PMCAMx

extensions comes at the cost of additional computational burden, data storage, and input complexity.

To improve the prediction of the contribution of long-range transport aerosol in the $PM_{2.5}$ concentrations in the inner, high-resolution grids, a two-way nesting approach can be used (Fountoukis et al., 2013). In this approach, each grid can exchange pollutants with its parent grid at every time step. In this work, PMCAMx performance is weaker near the large industrial and power generation sites. Zakoura and Pandis, (2019) have shown improvements in PMCAMx predictive performance for nitrate by applying the Plume in Grid model to large point sources.

In chapters 2 and 3 of this work, source contributions were calculated using a sensitivity simulation approach. In chapter 4 the PSAT algorithm (Skylakou et al., 2017) was used to track the contribution of different sources to pollutant concentrations. Using the PSAT algorithm for future high-resolution simulations could improve the prediction of local source contributions. For the 1 x 1 km grid, long range transport is the largest source of $PM_{2.5}$. Use of the PSAT approach for all grids would resolve the source distribution of the concentrations from outside the finest grid which then can be added to the local source contributions for comparison with AMS measurements of cooking and biomass burning organic aerosols.

In this work, we use WRF metrology calculated at a resolution of 12 x 12 km. The use of metrology calculated higher resolutions could improve the model ability to predict local concentration gradients. In chapters 2 and 3 of this work biogenic emissions were calculated with the BEIS model as included in the NEI. Previous studies with PMCAMx have shown good performance in the prediction of secondary organic aerosols using the MEGAN model of biogenic emissions. This approach was followed for the historical simulations with good results. Further simulations at high resolutions would possibly benefit from the higher biogenic organic aerosol

precursor emissions generated by MEGAN. The effect of this change is expected to be more pronounced during the summer period where biogenic emissions are larger.

The exposure distributions presented in this work use the residential population for exposure calculations. However, in urban areas like Pittsburgh, there are significant amounts of commuter populations that are registered in the census as residing in suburban areas but spend much of their time exposed to the higher concentrations observed in the city center. Further estimations of exposure could be improved by calculating exposure distributions with estimations of the commuting population. The contribution to exposure of sources that are associated with large population densities like commercial cooking and on-road traffic could be better determined by limiting the exposure distribution analysis to areas above a population density threshold.

5.3 References

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Appendix A. Additional Results from Chapter 3

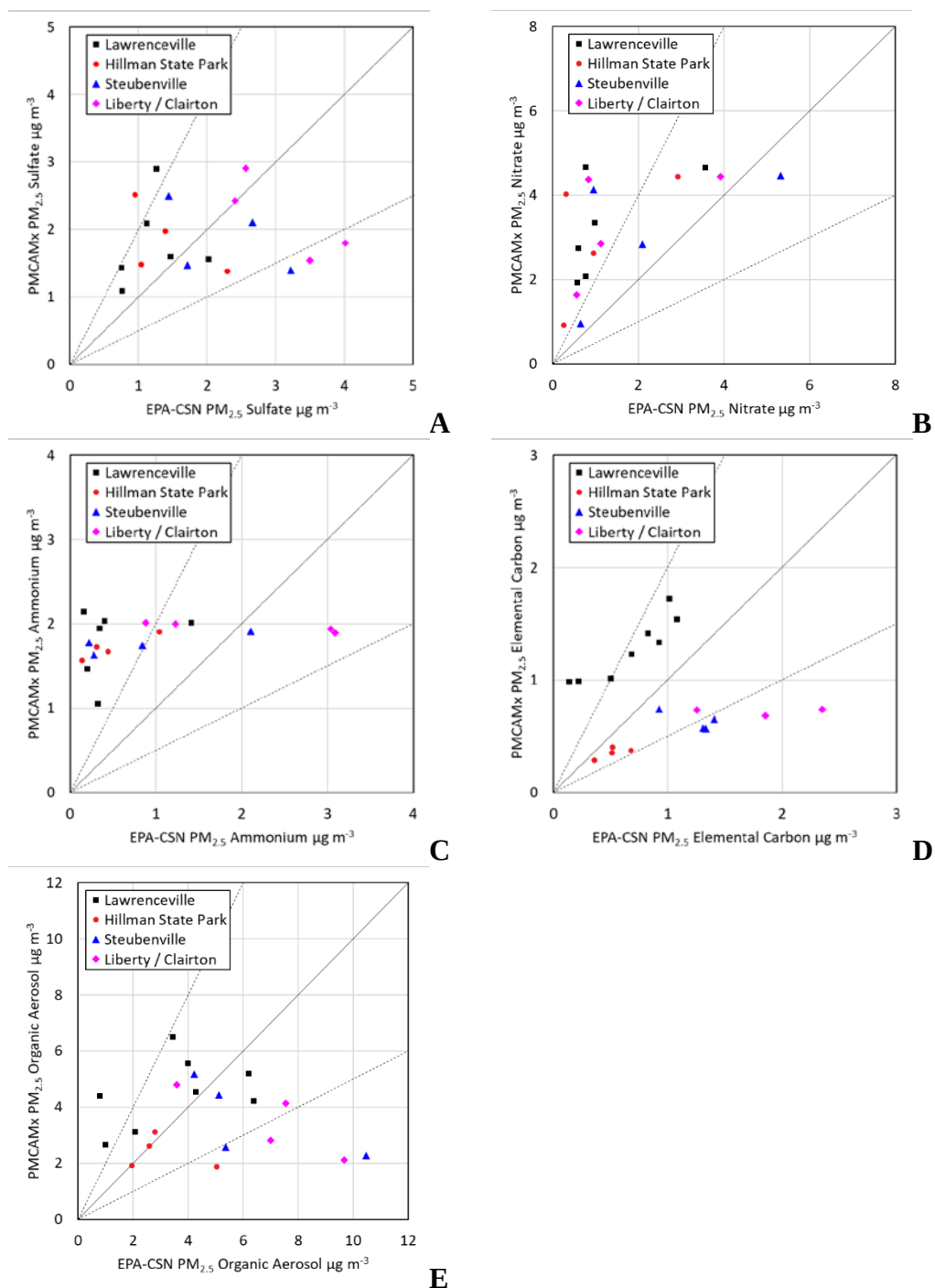


Figure A-1. Comparison of PMCAMx predicted concentrations of (A) sulfate, (B) nitrate, (C) ammonium, (D) elemental carbon and (E) organic aerosol to 24-hour measurements from 4 EPA-CSN sites during February 2017.

Table A-1. Comparison of PMCAMx sulfate predictions with daily averages of from EPA-CSN during February 2017.

	Lawrenceville	Hillman State Park	Steubenville	Liberty / Clairton	All
ERROR ($\mu\text{g m}^{-3}$)	0.70	0.87	0.92	1.13	0.88
FERROR	45%	52%	43%	42%	45%
BIAS ($\mu\text{g m}^{-3}$)	0.55	0.42	-0.39	-0.95	-0.02
FBIAS	37%	28%	-16%	-35%	7%
R	0.18	-0.61	-0.50	-0.82	-0.03
Meas. Avg. ($\mu\text{g m}^{-3}$)	1.23	1.42	2.26	3.12	1.92
Pred Avg. ($\mu\text{g m}^{-3}$)	1.78	1.84	1.87	2.17	1.90

Table A-2. Comparison of PMCAMx nitrate predictions with daily averages of from EPA-CSN during February 2017.

	Lawrenceville	Hillman State Park	Steubenville	Liberty / Clairton	All
ERROR ($\mu\text{g m}^{-3}$)	2.03	1.89	1.27	1.71	1.76
FERROR	101%	104%	53%	83%	87%
BIAS ($\mu\text{g m}^{-3}$)	2.03	1.89	0.85	1.71	1.66
FBIAS	101%	104%	44%	83%	85%
R	0.61	0.61	0.62	0.60	0.57
Meas. Avg. ($\mu\text{g m}^{-3}$)	1.21	1.11	2.26	1.61	1.51
Pred Avg. ($\mu\text{g m}^{-3}$)	3.24	3.00	3.10	3.32	3.17

Table A-3. Comparison of PMCAMx ammonium predictions with daily averages of from EPA-CSN during February 2017.

	Lawrenceville	Hillman State Park	Steubenville	Liberty / Clairton	All
ERROR ($\mu\text{g m}^{-3}$)	1.30	1.23	1.00	1.05	1.16
FERROR	123%	120%	94%	54%	101%
BIAS ($\mu\text{g m}^{-3}$)	1.30	1.23	0.90	-0.10	0.89
FBIAS	123%	120%	89%	8%	90%
R	0.26	0.94	0.84	-0.94	0.35
Meas. Avg. ($\mu\text{g m}^{-3}$)	0.47	0.48	0.86	2.06	0.91
Pred Avg. ($\mu\text{g m}^{-3}$)	1.78	1.72	1.77	1.96	1.80

Table A-4. Comparison of PMCAMx elemental carbon predictions with daily averages of from EPA-CSN during February 2017.

	Lawrenceville	Hillman State Park	Steubenville	Liberty / Clairton	All
ERROR ($\mu\text{g m}^{-3}$)	0.61	0.16	0.61	0.83	0.56
FERROR	72%	35%	63%	62%	61%
BIAS ($\mu\text{g m}^{-3}$)	0.61	-0.16	-0.61	-0.83	-0.08
FBIAS	72%	-35%	-63%	-62%	-3%
R	0.91	0.73	-0.78	0.05	-0.02
Meas. Avg. ($\mu\text{g m}^{-3}$)	0.67	0.52	1.24	1.82	0.94
Pred Avg. ($\mu\text{g m}^{-3}$)	1.28	0.36	0.64	0.72	0.85

Table A-5. Comparison of PMCAMx organic aerosol predictions with daily averages of from EPA-CSN during February 2017.

	Lawrenceville	Hillman State Park	Steubenville	Liberty / Clairton	All
ERROR ($\mu\text{g m}^{-3}$)	1.79	0.89	3.15	4.08	2.34
FERROR	53%	26%	58%	75%	53%
BIAS ($\mu\text{g m}^{-3}$)	0.99	-0.71	-2.68	-3.49	-0.98
FBIAS	39%	-20%	-48%	-61%	-10%
R	0.45	-0.34	-0.74	-0.84	-0.16
Meas. Avg. ($\mu\text{g m}^{-3}$)	3.53	3.09	6.30	6.96	4.68
Pred Avg. ($\mu\text{g m}^{-3}$)	4.52	2.38	3.61	3.47	3.70

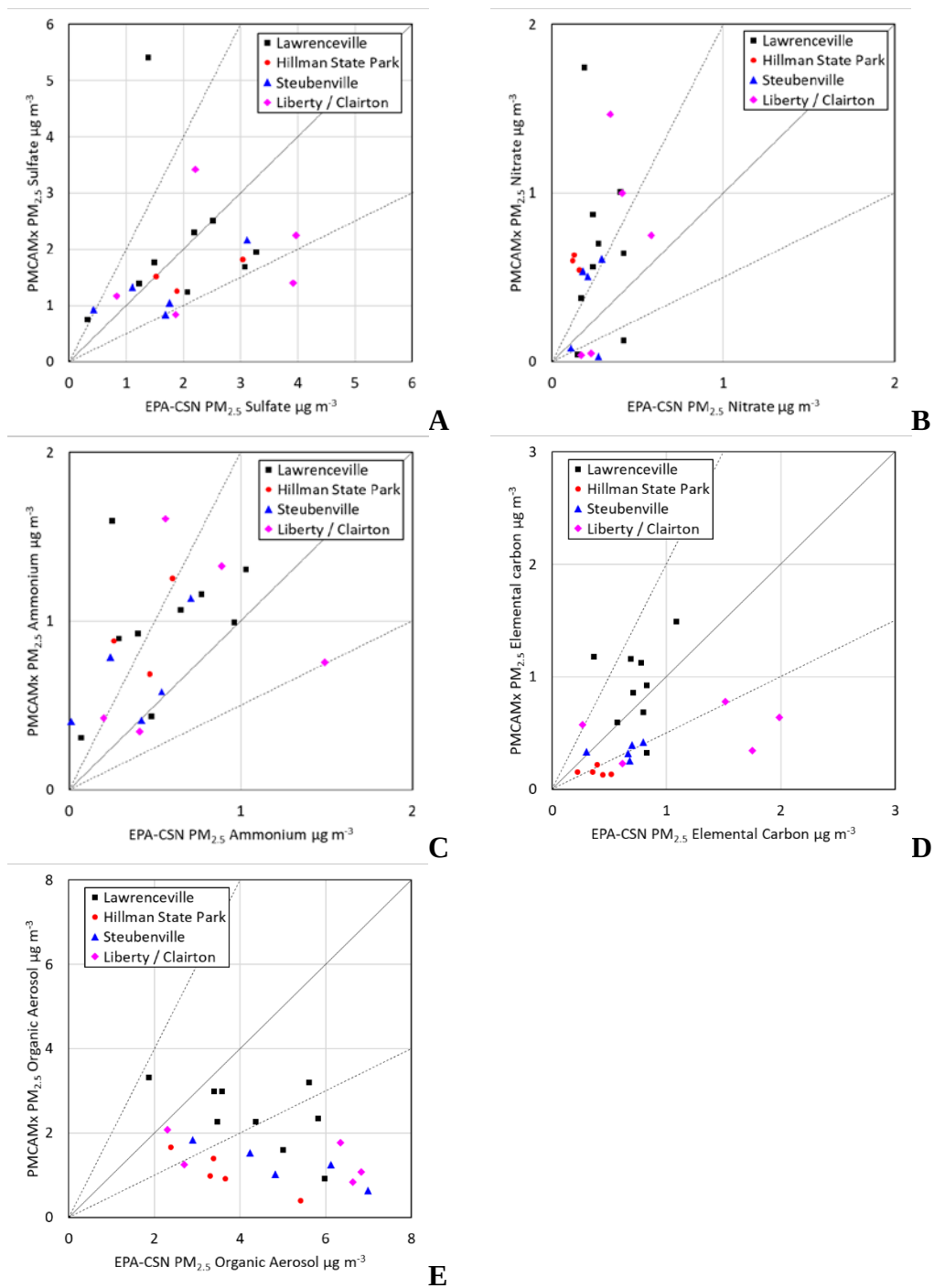


Figure A-2 Comparison of PMCAMx predicted concentrations of (A) sulfate, (B) nitrate, (C) ammonium, (D) elemental carbon and (E) organic aerosol to 24-hour measurements from 4 EPA-CSN sites during July 2017.

Table A-6. Comparison of PMCAMx sulfate predictions with daily averages of from EPA-CSN during July 2017.

	Lawrenceville	Hillman State Park	Steubenville	Liberty / Clairton	All
ERROR ($\mu\text{g m}^{-3}$)	0.95	0.61	0.64	1.36	0.93
FERROR	44%	30%	49%	61%	47%
BIAS ($\mu\text{g m}^{-3}$)	0.16	-0.61	-0.36	-0.74	-0.27
FBIAS	8%	-30%	-12%	-30%	-10%
R	0.05	0.76	0.78	0.23	0.21
Meas. Avg. ($\mu\text{g m}^{-3}$)	1.95	2.14	1.62	2.56	2.04
Pred Avg. ($\mu\text{g m}^{-3}$)	2.11	1.53	1.26	1.81	1.77

Table A-7. Comparison of PMCAMx nitrate predictions with daily averages of from EPA-CSN during July 2017.

	Lawrenceville	Hillman State Park	Steubenville	Liberty / Clairton	All
ERROR ($\mu\text{g m}^{-3}$)	0.49	0.45	0.25	0.44	0.42
FERROR	96%	125%	88%	98%	99%
BIAS ($\mu\text{g m}^{-3}$)	0.40	0.45	0.14	0.32	0.33
FBIAS	47%	125%	13%	-4%	39%
R	-0.06	-0.82	0.29	0.55	0.27
Meas. Avg. ($\mu\text{g m}^{-3}$)	0.28	0.14	0.21	0.35	0.26
Pred Avg. ($\mu\text{g m}^{-3}$)	0.67	0.59	0.35	0.66	0.59

Table A-8. Comparison of PMCAMx ammonium predictions with daily averages of from EPA-CSN during July 2017.

	Lawrenceville	Hillman State Park	Steubenville	Liberty / Clairton	All
ERROR ($\mu\text{g m}^{-3}$)	0.43	0.50	0.28	0.50	0.42
FERROR	64%	72%	70%	58%	65%
BIAS ($\mu\text{g m}^{-3}$)	0.42	0.50	0.28	0.18	0.35
FBIAS	62%	72%	70%	25%	57%
R	0.39	0.54	0.64	0.24	0.38
Meas. Avg. ($\mu\text{g m}^{-3}$)	0.54	0.44	0.38	0.71	0.53
Pred Avg. ($\mu\text{g m}^{-3}$)	0.97	0.94	0.66	0.89	0.88

Table A-9. Comparison of PMCAMx elemental carbon predictions with daily averages of from EPA-CSN during July 2017.

	Lawrenceville	Hillman State Park	Steubenville	Liberty / Clairton	All
ERROR ($\mu\text{g m}^{-3}$)	0.33	0.23	0.30	0.84	0.41
FERROR	40%	81%	58%	93%	63%
BIAS ($\mu\text{g m}^{-3}$)	0.19	-0.23	-0.28	-0.71	-0.18
FBIAS	17%	-81%	-54%	-64%	-35%
R	0.15	-0.21	0.27	0.29	0.25
Meas. Avg. ($\mu\text{g m}^{-3}$)	0.74	0.39	0.63	1.23	0.74
Pred Avg. ($\mu\text{g m}^{-3}$)	0.93	0.16	0.34	0.51	0.56

Table A-10. Comparison of PMCAMx organic aerosol predictions with daily averages of from EPA-CSN during July 2017.

	Lawrenceville	Hillman State Park	Steubenville	Liberty / Clairton	All
ERROR ($\mu\text{g m}^{-3}$)	2.24	2.56	3.76	3.56	2.89
FERROR	65%	104%	113%	99%	90%
BIAS ($\mu\text{g m}^{-3}$)	-1.92	-2.56	-3.76	-3.56	-2.77
FBIAS	-52%	-104%	-113%	-99%	-86%
R	-0.59	-0.93	-0.89	-0.53	-0.41
Meas. Avg. ($\mu\text{g m}^{-3}$)	4.35	3.63	5.01	4.96	4.46
Pred Avg. ($\mu\text{g m}^{-3}$)	2.43	1.07	1.26	1.40	1.69

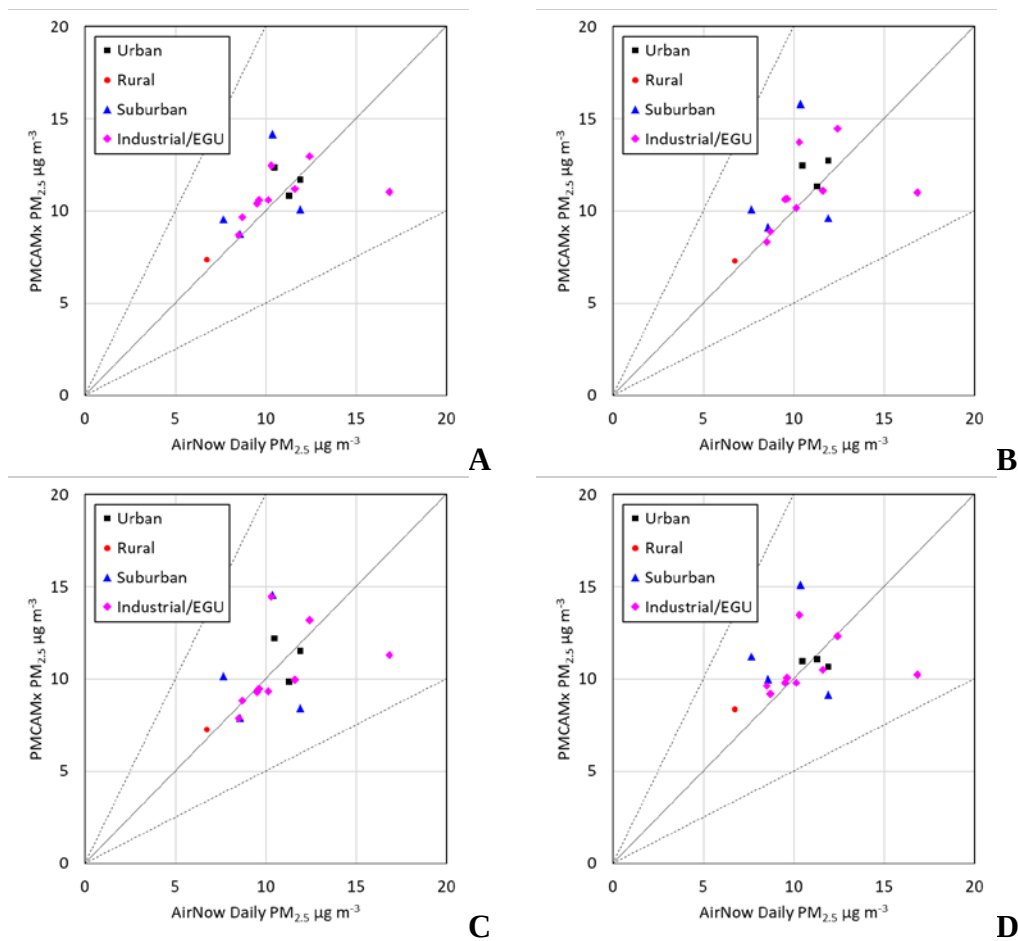


Figure A-3 Comparison of PMCAMx predicted $PM_{2.5}$ concentrations during February 2017 for (A) 36 x 36 km, (B) 12 x 12 km, (C) 4 x 4 km and (D) 1 x 1 km with monthly averages from 17 EPA AirNow sites.

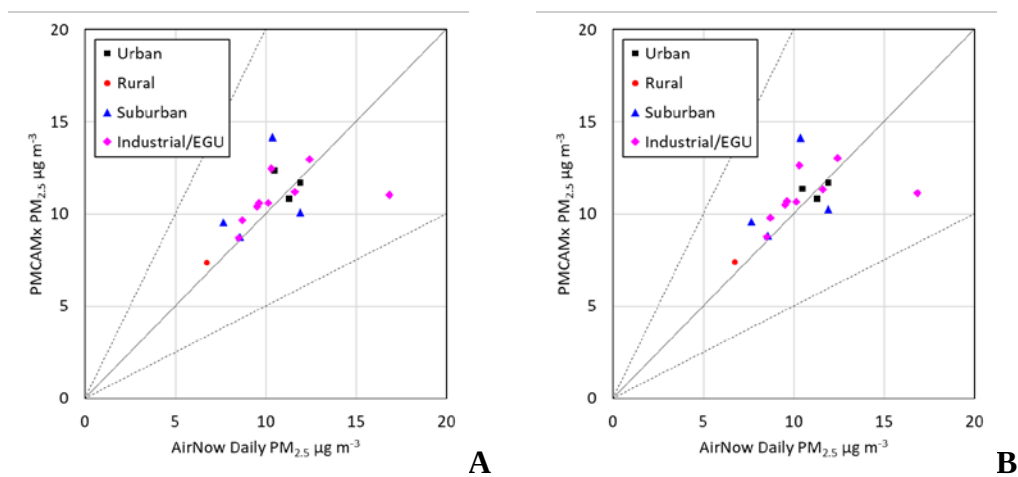


Figure A-4 Comparison of PMCAMx predicted $PM_{2.5}$ concentrations during February 2017 with monthly averages from 17 EPA AirNow sites using the (A) CACES and (B) EPA surrogates.

Appendix B. Additional Results from Chapter 4

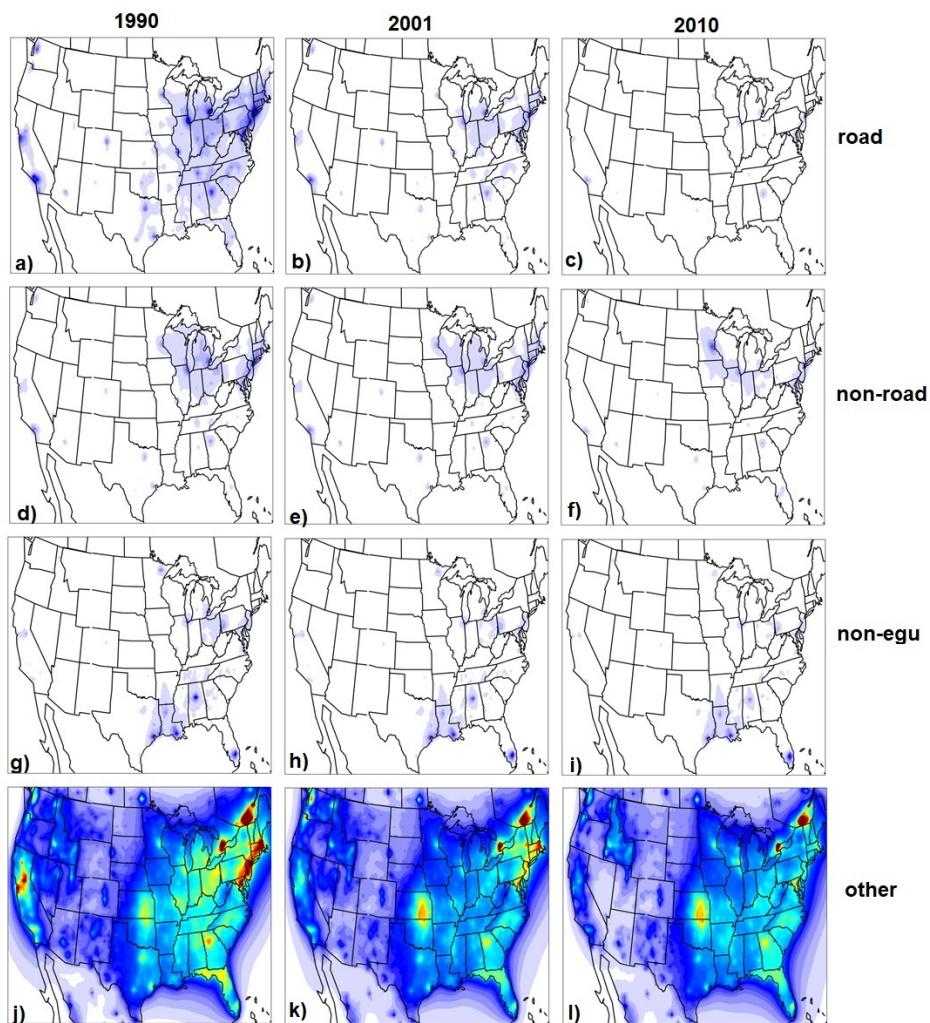


Figure B-5 Annual averaged predicted ground-level PM_{2.5} fresh POA concentrations per source in $\mu\text{g m}^{-3}$ for simulations of three different years, 1990, 2001, 2010.

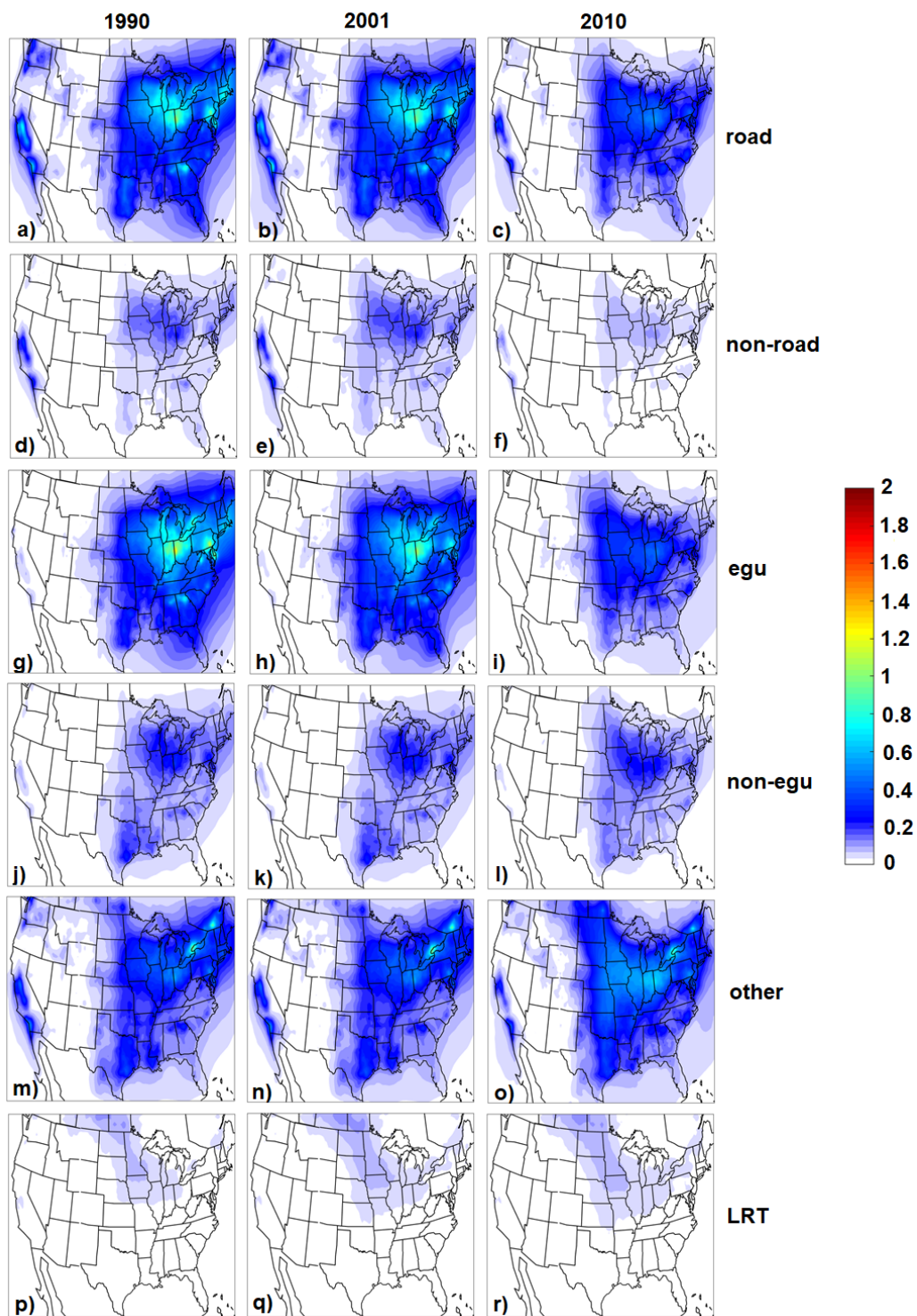


Figure B-6 Annual averaged predicted ground-level PM_{2.5} nitrate concentrations per source in $\mu\text{g m}^{-3}$ for simulations of three different years, 1990, 2001, 2010.

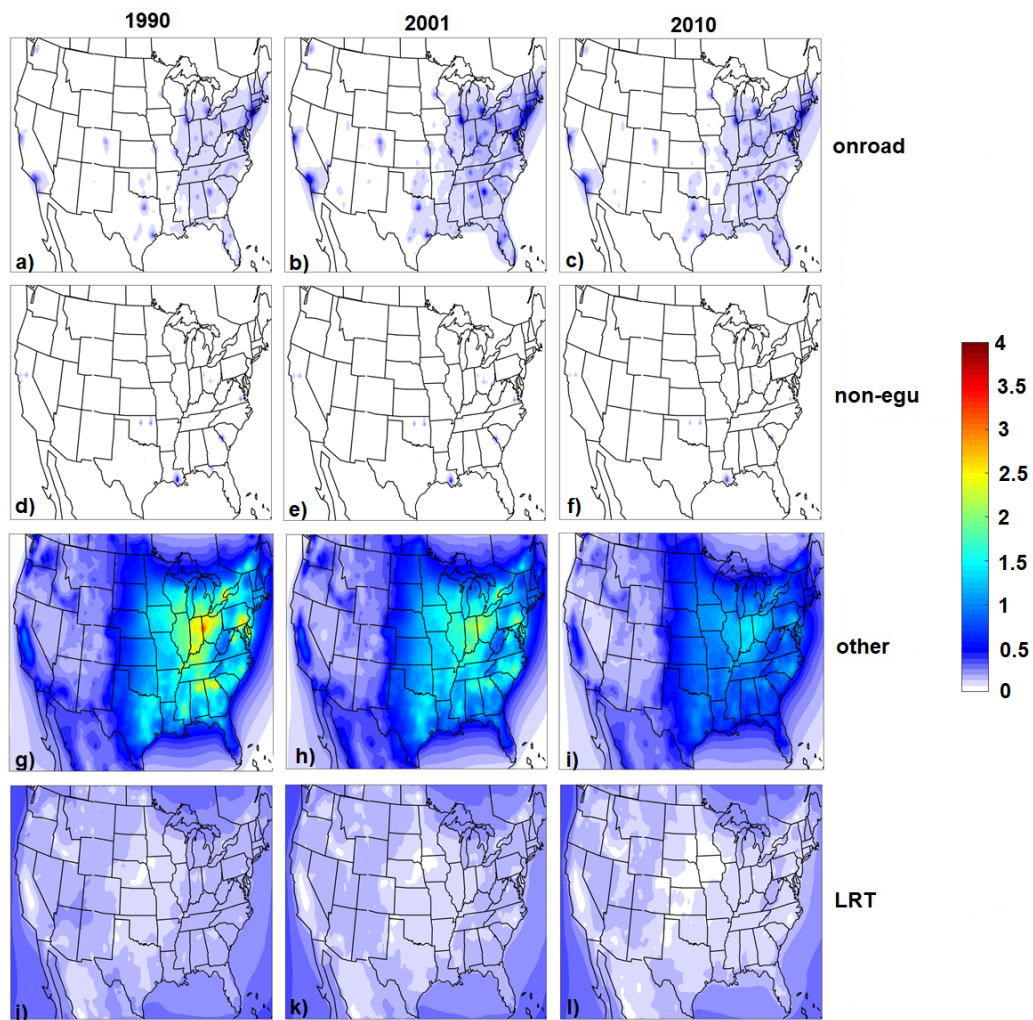


Figure B-7 Annual averaged predicted ground-level PM_{2.5} ammonium concentrations per source in $\mu\text{g m}^{-3}$ for simulations of three different years, 1990, 2001, 2010.

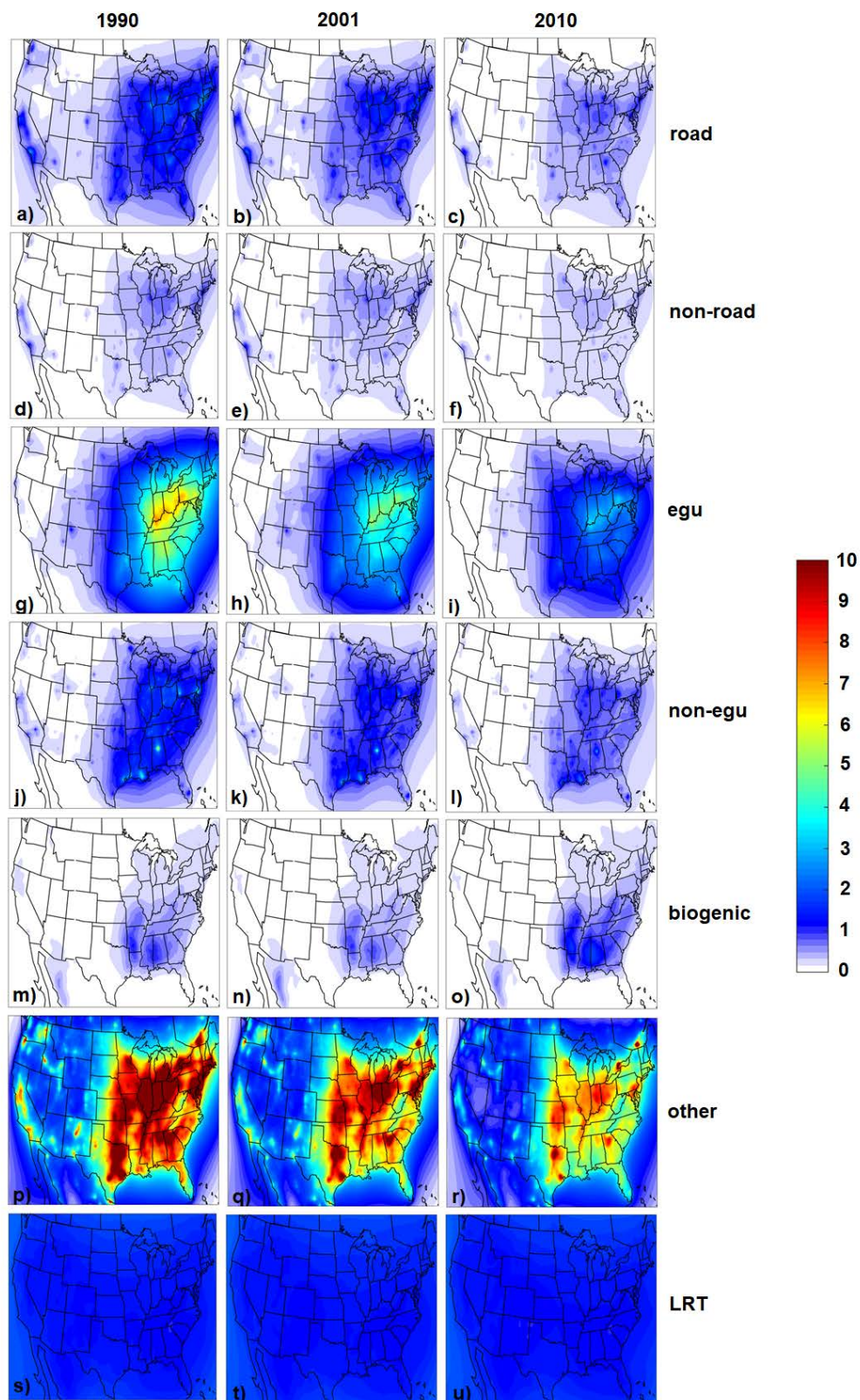


Figure B-8 Annual averaged predicted ground-level total $PM_{2.5}$ concentrations per source in $\mu g m^{-3}$ for simulations of three different years, 1990, 2001, 2010.

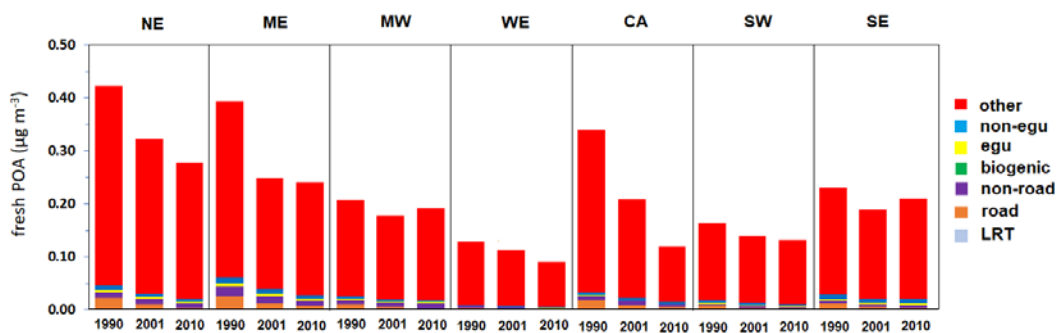


Figure B-9 Annual source concentration of fresh POA for seven different regions in the US and for three different years, 1990, 2001, 2010.

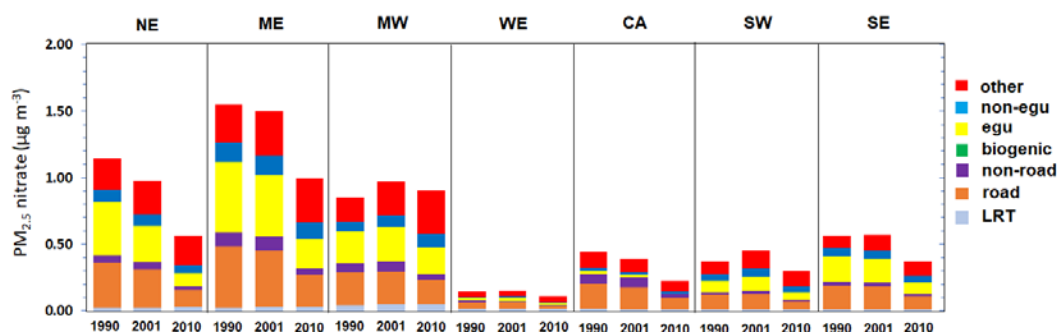


Figure B-10 Annual source concentration of nitrate for seven different regions in the US and for three different years, 1990, 2001, 2010.

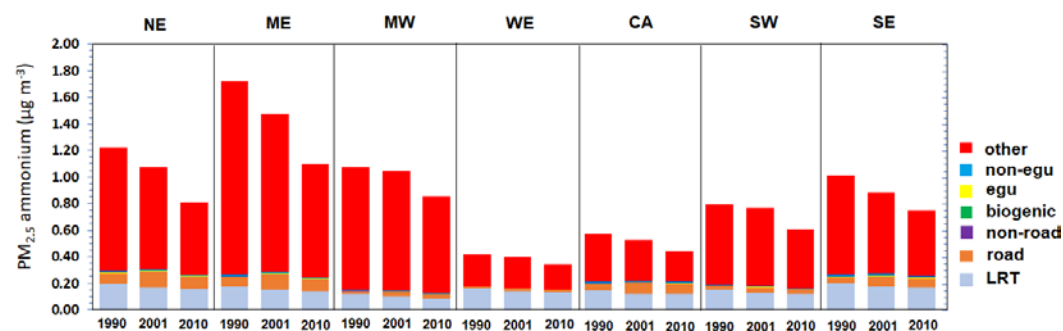


Figure B-11 Annual source concentration of ammonium for seven different regions in the US and for three different years, 1990, 2001, 2010.

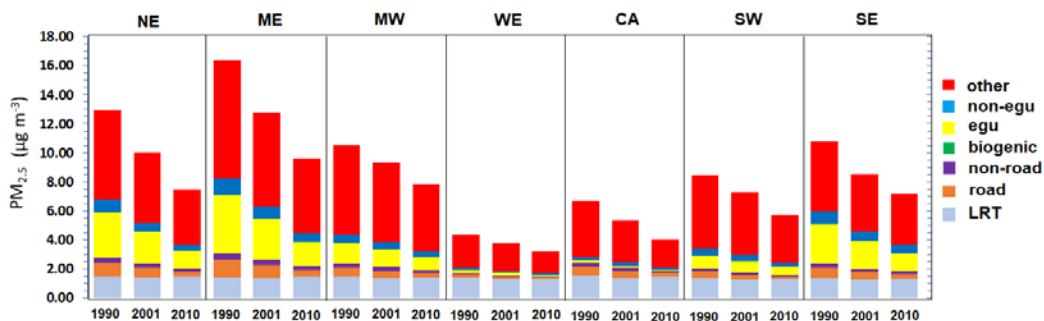


Figure B-12 Annual source concentration of total PM_{2.5} for seven different regions in the US and for three different years, 1990, 2001, 2010.

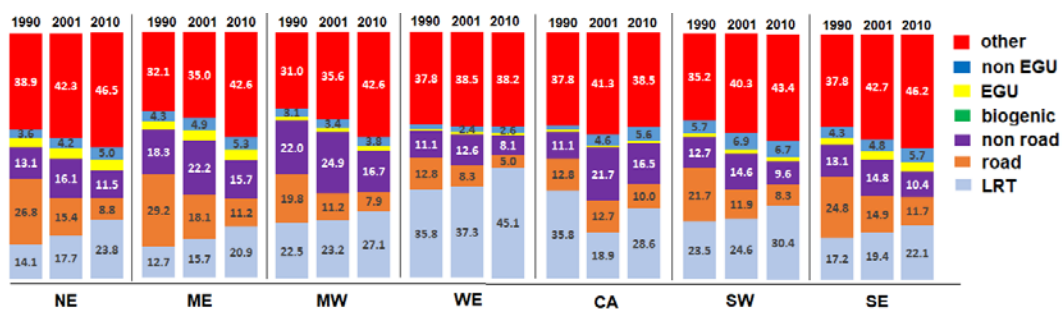


Figure B-13 Annual source percent contributions to the concentration of Elemental Carbon for seven different regions in the US and for three different years, 1990, 2001, 2010.

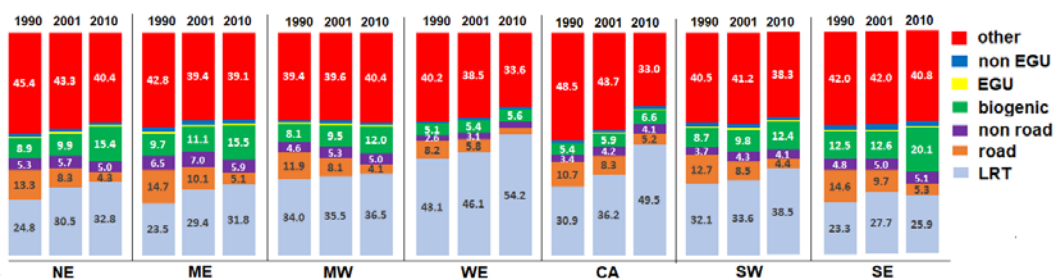


Figure B-14 Annual source percent contributions to the concentration of OA for seven different regions in the US and for three different years, 1990, 2001, 2010.

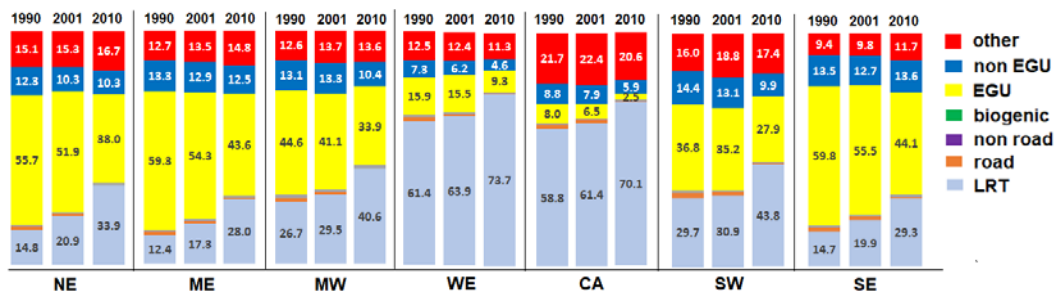


Figure B-15 Annual source percent contributions to the concentration of PM_{2.5} sulfate for seven different regions in the US and for three different years, 1990, 2001, 2010.

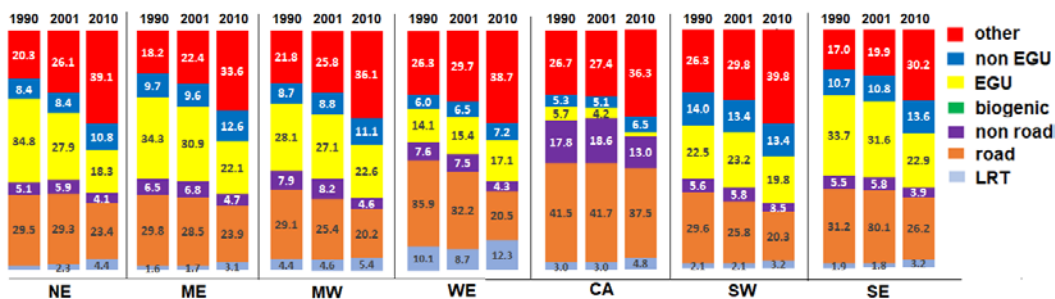


Figure B-16 Annual source percent contributions to the concentration of PM_{2.5} nitrate for seven different regions in the US and for three different years, 1990, 2001, 2010.

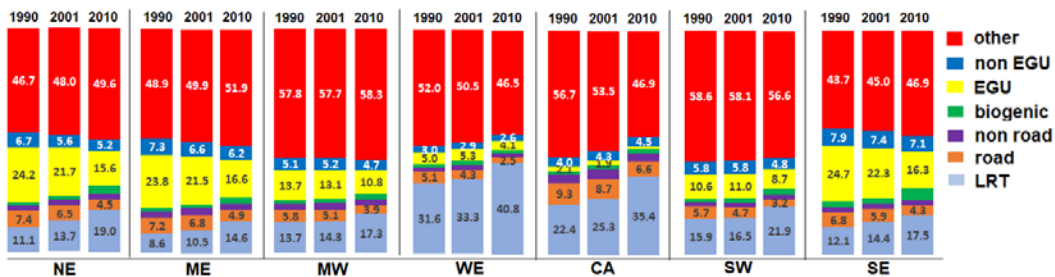


Figure B-17 Annual source percent contributions to the concentration of total PM_{2.5} for seven different regions in the US and for three different years, 1990, 2001, 2010.

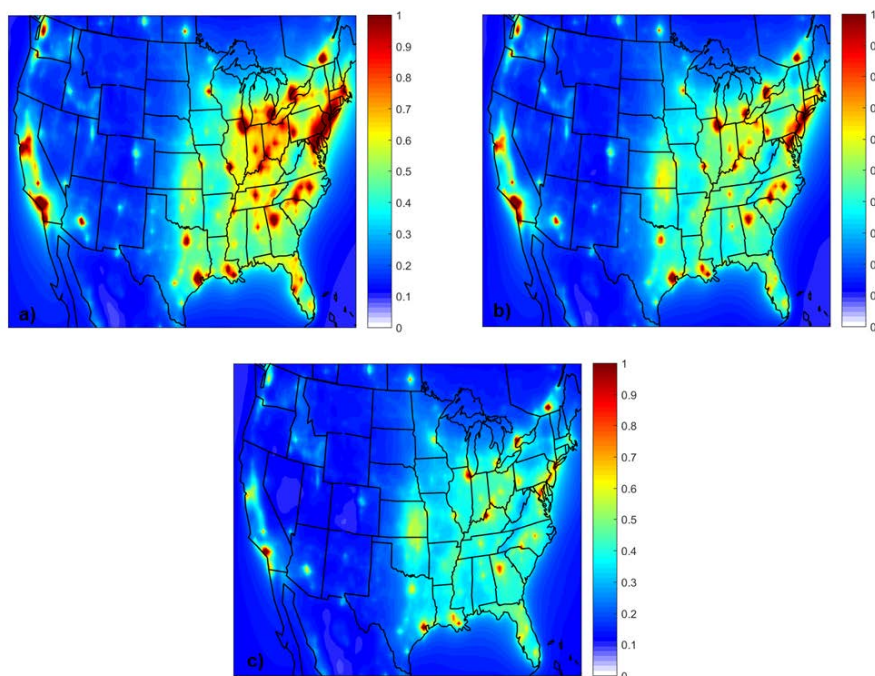


Figure B-18 Annual ground level predicted concentrations of PM_{2.5} Elemental Carbon for three different years, (a) 1990, (b) 2001 and (c) 2010.

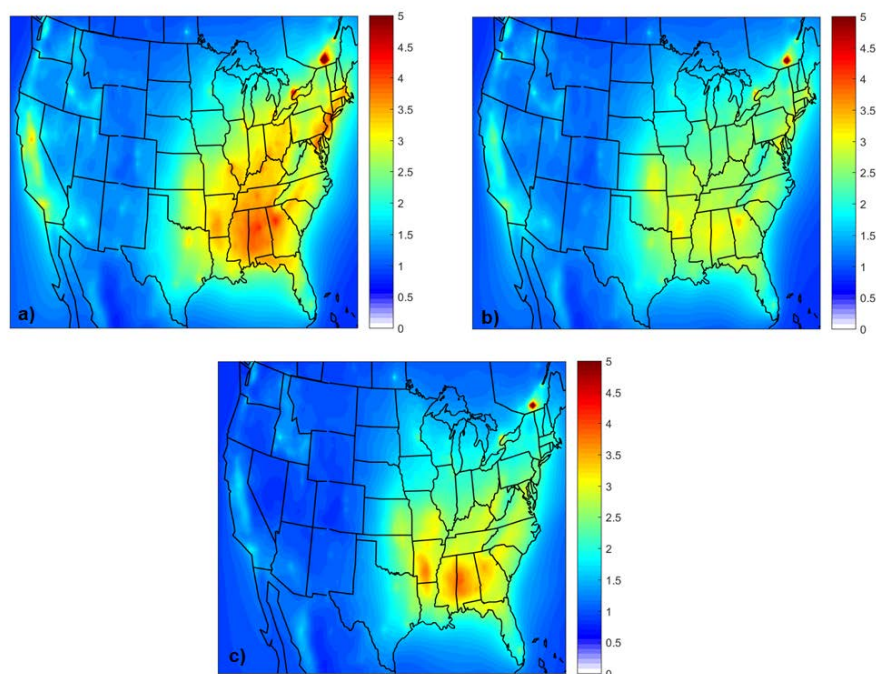


Figure B-19 Annual ground level predicted concentrations of PM_{2.5} OA for three different years, (a) 1990, (b) 2001 and (c) 2010.

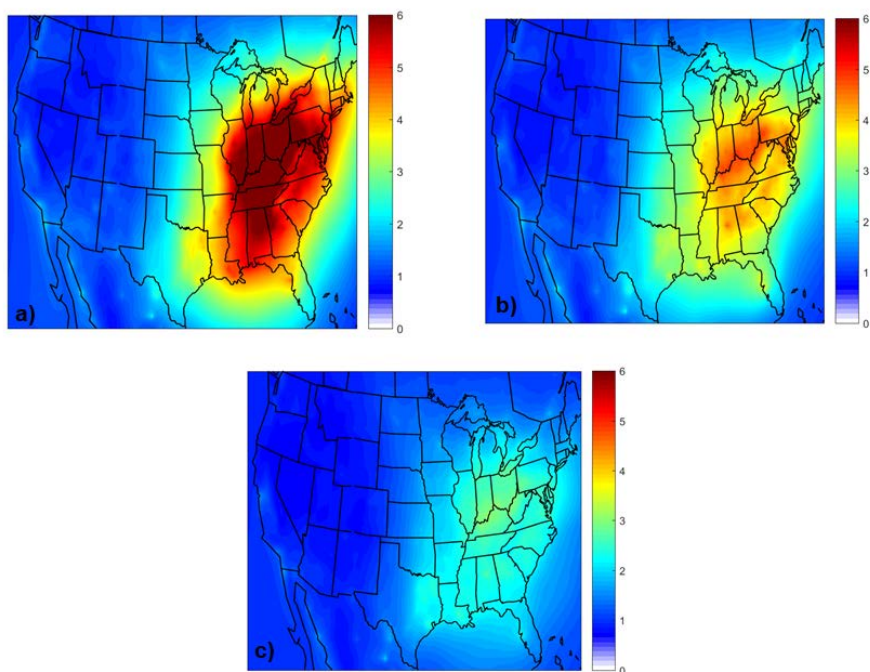


Figure B-20 Annual ground level predicted concentrations of PM_{2.5} sulfate for three different years, (a) 1990, (b) 2001 and (c) 2010.

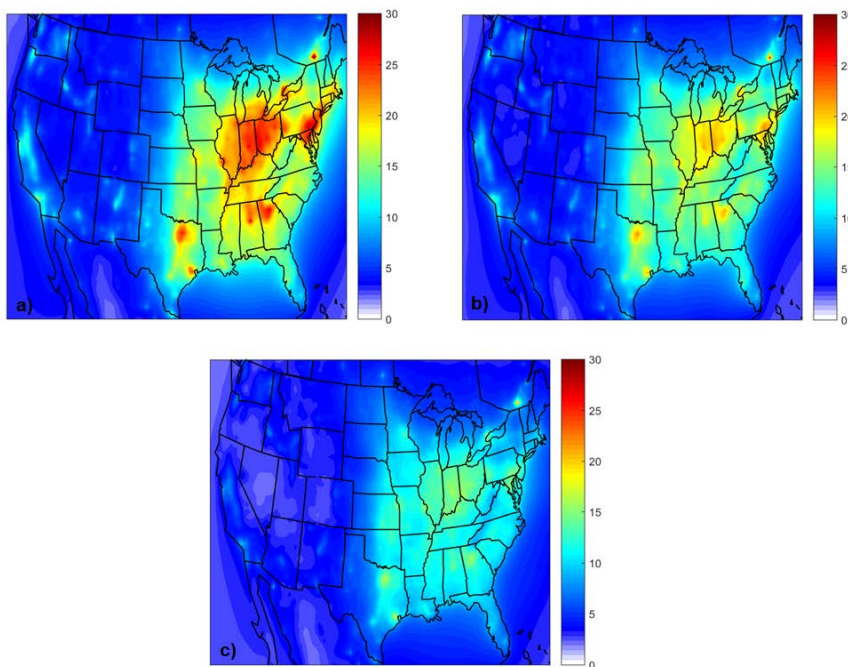


Figure B-21 Annual ground level predicted concentrations of total PM_{2.5} for three different years, (a) 1990, (b) 2001 and (c) 2010.

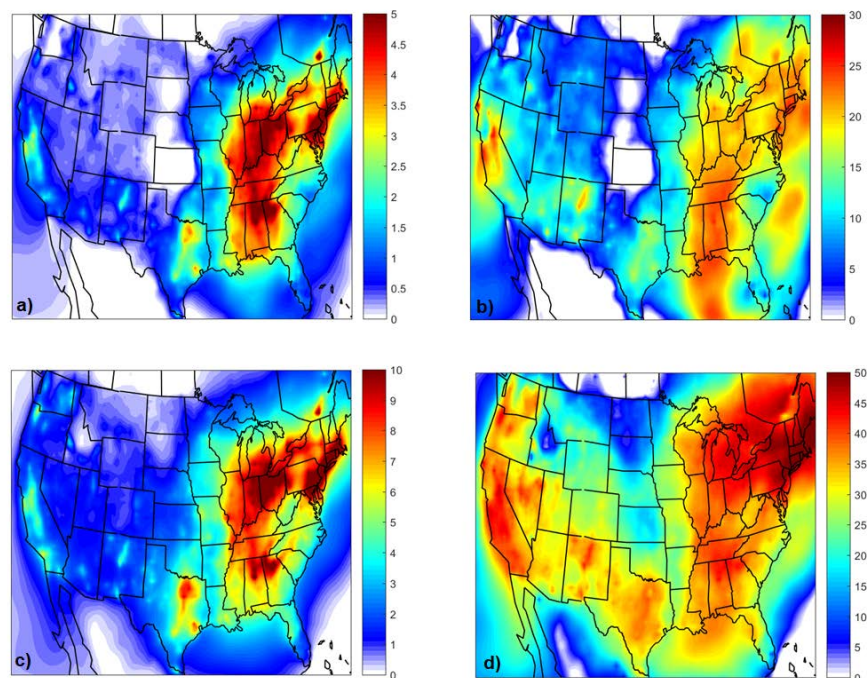


Figure B-22 Reductions in total PM_{2.5}: absolute ($\mu\text{g m}^{-3}$) from 1990 to 2001 (a) and from 1990 to 2010 (c) and percent (%) from 1990 to 2001 (b) and from 1990 to 2010 (d).

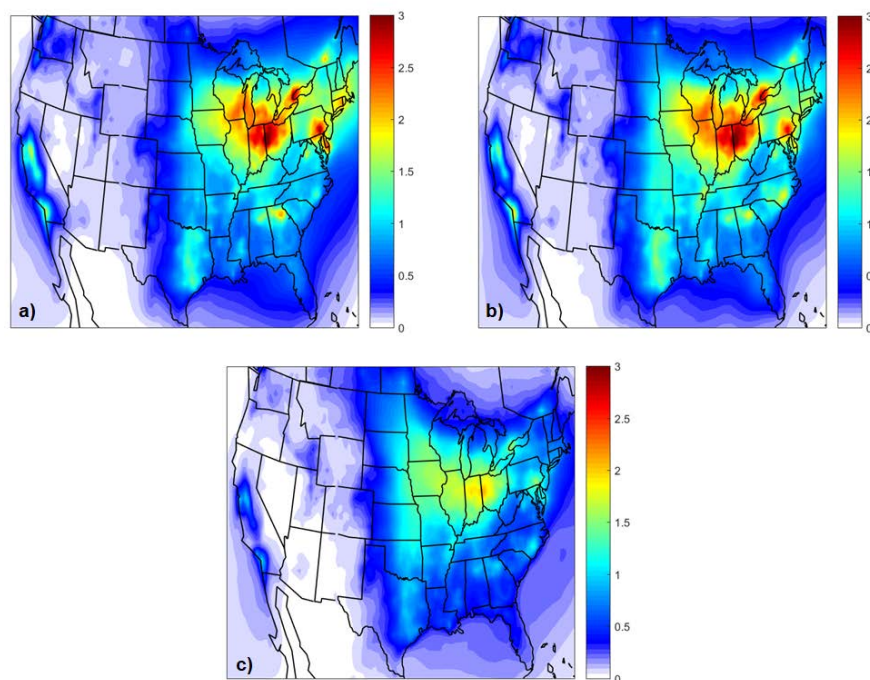


Figure B-23 Annual ground level predicted concentrations of PM_{2.5} nitrate for three different years, (a) 1990, (b) 2001 and (c) 2010.

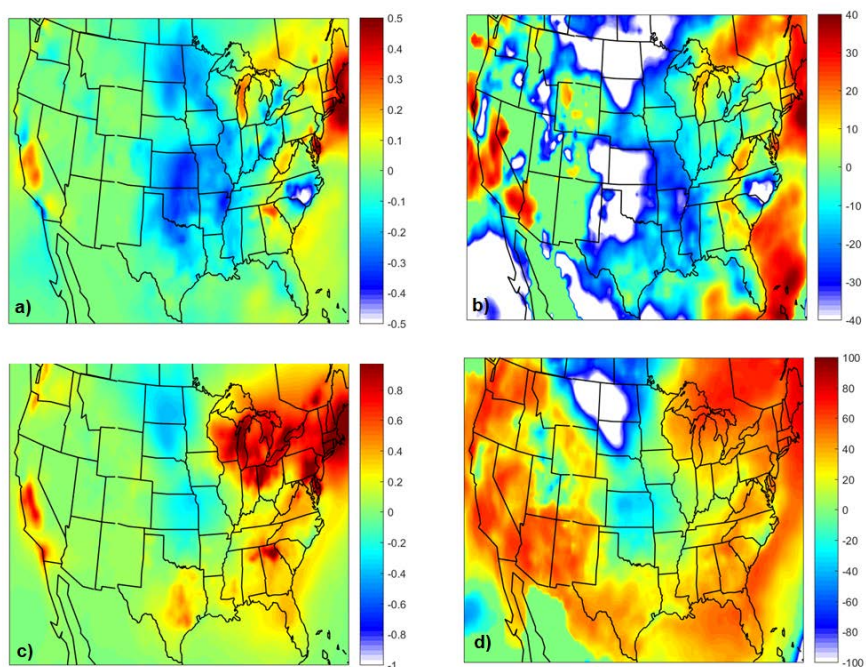


Figure B-24 Differences in PM_{2.5} nitrate: absolute ($\mu\text{g m}^{-3}$) from 1990 to 2001 (a) and from 1990 to 2010 (c) and percent (%) from 1990 to 2001 (b) and from 1990 to 2010 (d).

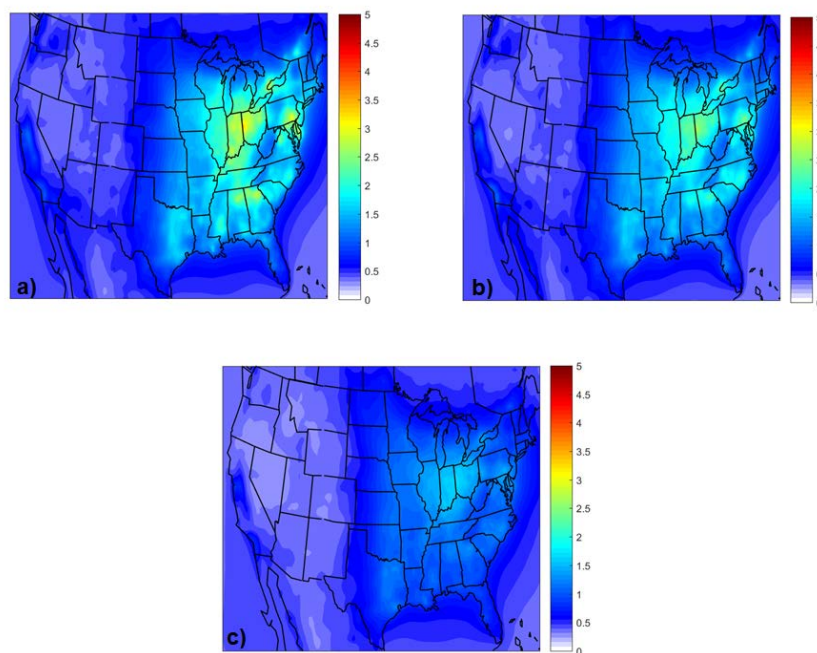


Figure B-25 Annual ground level predicted concentrations of PM_{2.5} ammonium for three different years, (a) 1990, (b) 2001 and (c) 2010.

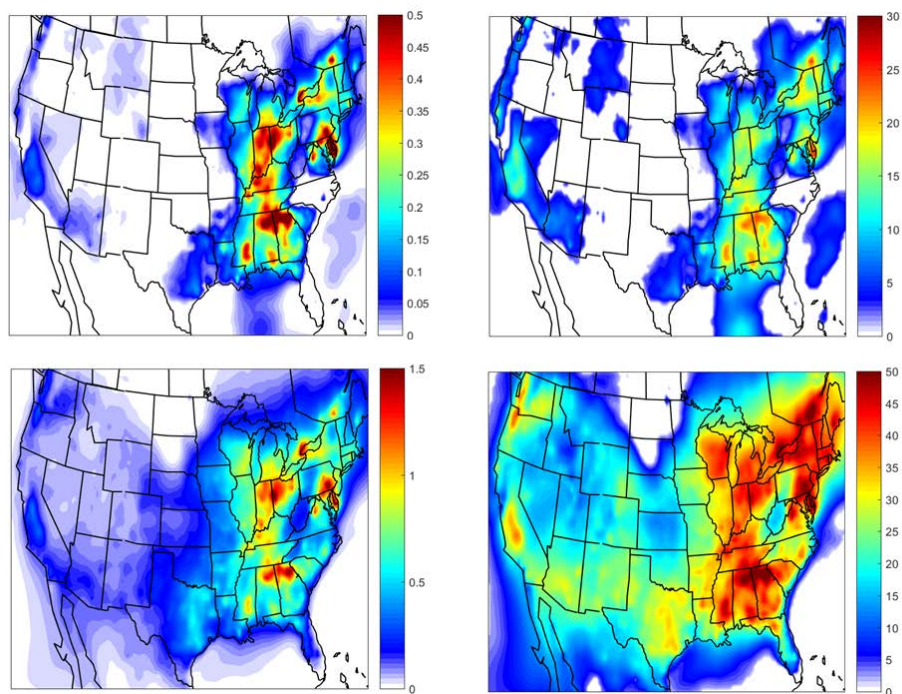


Figure B-26 Reductions in PM_{2.5} ammonium: absolute ($\mu\text{g m}^{-3}$) from 1990 to 2001 (a) and from 1990 to 2010 (c) and percent (%) from 1990 to 2001 (b) and from 1990 to 2010 (d).