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Changes in $PM_{2.5}$ concentrations and their sources in the US from 1990 to 2010

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Abstract

Significant reductions of emissions of SO_2, NO_x, volatile organic compounds (VOCs) and primary particulate matter (PM) took place in the US from 1990 to 2010. We evaluate here our understanding of the links between these emissions changes and corresponding changes in concentrations and health outcomes using a chemical transport model, the Particulate Matter Comprehensive Air Quality Model with Extensions (PMCAMx) with the Particle Source Apportionment Algorithm (PSAT). Results for 1990, 2001 and 2010 are presented. The reductions in SO_2 emissions (64%, mainly from electric generating units) during these 20 years have dominated the reductions in $PM_{2.5}$ leading to a 45% reduction in sulfate levels. The predicted sulfate reductions are in excellent agreement with the available measurements. Also, the reductions in elemental carbon (EC) emissions (mainly from transportation) have led to a 30% reduction of EC concentrations. The most important source of organic aerosol (OA) through the years according to PMCAMx is biomass burning, followed by biogenic secondary organic aerosol (SOA). OA from on-road transport has been reduced by more than a factor of three. On the other hand, changes in biomass burning OA and biogenic SOA have been modest. In 1990, about half of the US population was exposed to annual-average $PM_{2.5}$ concentrations above 20 μg m^{-3}, but by 2010 this fraction had dropped to practically zero. The predicted changes in concentrations are evaluated against the observed changes for 1990, 2001, and 2010,

in order to understand if the model represents reasonably well the corresponding processes caused by the changes in emissions.

1. Introduction

During recent decades, regulations by the US Environmental Protection Agency (EPA) have led to significant reductions of the emissions of SO_2, NO_x, VOCs, and primary PM from electrical utilities, industry, transportation, and other sources. Xing et al. (2013) estimated that, from 1990 to 2010, emissions of SO_2 in the US were reduced by 67%, NO_x by 48%, non-methane VOCs by 49%, and primary $PM_{2.5}$ by 34%. An increase of ammonia emissions by 11% was estimated for this twenty-year period. At the same time, there have been significant observed reductions in the ambient $PM_{2.5}$ 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 $PM_{2.5}$ faces challenges. The available $PM_{2.5}$ composition and mass concentration measurements are sparse in space and are quite limited before 2001. 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 on a number of statistical techniques including land-use regression models to calculate the concentrations of $PM_{2.5}$ over specific areas and periods (Eeftens et al., 2012; Beckerman et al., 2013; Ma et al., 2016; Li et al., 2017a). More recent efforts also include applications of chemical transport models. 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. That study 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 that work. Li et al. (2017a) combined in-situ and satellite observations with the global CTM, GEOS-Chem, to quantify global and regional trends in the chemical composition of $PM_{2.5}$ over 1989–2013. 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 O_3 in the US. The same meteorology and the same natural emissions (including wildfires) were used for all six simulated years. The authors 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 use period-specific meteorological data and source-resolved emissions for every year simulated, to estimate the concentrations, 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. We also quantify trends in population exposure and estimated health outcomes.

2. Model Description

2.1 PMCAMx

PMCAMx (Karydis et al., 2010; Murphy and Pandis, 2010; Tsimpidi et al., 2010; Posner et al., 2019) 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 the aerosol mass distribution. 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 in this application of PMCAMx for gas-phase chemistry calculations. The version of CB5 used here includes 190 reactions of 79 surrogate gas-phase species. For condensation and evaporation of inorganic species, a bulk equilibrium approach was used, assuming equilibrium between the bulk inorganic aerosol and gas phases. The partitioning of

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each semi-volatile inorganic species between the gas and aerosol phases is determined by the ISORROPIA aerosol thermodynamics model (Nenes et al., 1998). The mass transferred between the two phases in each step is distributed to the size sections using weighting factors based on the effective surface area of each size bin (Pandis et al., 1993). Organic aerosols (primary and secondary) are simulated using the volatility basis set approach (Donahue et al., 2006). For primary organic aerosols (POA), 8 volatility bins, ranging from 10^{-1} to 10^{6} μg m^{-3} at 298 K 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} μg m^{-3}) (Murphy and Pandis, 2009). NO_x-dependent yields (Lane et al., 2008) are used. For better representation of the chemistry in NO_x plumes, the Plume-in-Grid modeling approach of Karamchandani et al. (2011) has been used for the major point sources following Zakoura and Pandis (2019).

2.2 Particulate Source Apportionment Technology (PSAT)

The PSAT algorithm (Wagstrom et al., 2008; Wagstrom and Pandis, 2011a, 2011b; Skyllakou et al., 2014; 2017) is an efficient algorithm that tracks and computes the contributions of different sources to pollutant concentrations. The advantages of PSAT are that it runs in parallel with 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, the apportionment of 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 developed by Skyllakou et al. (2017) that is compatible with the Volatility Basis Set to calculate the contribution of each emission source to the concentration of $PM_{2.5}$ and its components.

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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 with horizontal dimensions of 36 km by 36 km (covering an area of 4752 × 2952 km) and 14 layers of varying thickness up to an altitude of approximately 13 km. 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). This coarse resolution introduces errors in areas where there are significant $PM_{2.5}$ gradients in space including California and urban areas in the rest of the western US.

3.1 Meteorology

Meteorological simulations were performed with the Weather Research Forecasting model (WRF v3.6.1) over the CONUS area, with horizontal resolution of 12 x 12 km and 36 vertical (sigma) levels up to a height of about 20 km. The simulations were executed using 3-day reinitialization from observations. Initial and boundary conditions 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 database. 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 Land Surface Model (Xiu and Pleim, 2002) was selected. Other important WRF physics options used in this study include the Rapid Radiative Transfer Model/Dudhia radiation schemes (Iacono et al., 2008), the Asymmetric Convective Model version 2 for the planetary boundary layer (Pleim, 2007a, 2007b), the Morrison double-moment cloud microphysics scheme (Morrison et al., 2008), and version 2 of the Kain–Fritsch cumulus parameterization (John, 2004). The selected WRF configuration is recommended for air quality simulations (Hogrefe et al., 2015; Rogers et al., 2013).

3.2 Emissions

Emissions for the simulations were obtained from the internally consistent, historical 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 the Model of Emissions of Gases and Aerosols from Nature (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 plus initial and boundary conditions which are each tracked separately by the model as different "sources". As a result, the emission source categories used are: 'road' which includes road emissions over the 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 1 depicts the total annual emissions for each source and each year.

Biomass burning (included in the 'other' category) was the dominant source of EC and remained relatively constant during the simulated period. The second most important source of EC was road transport, with the corresponding emissions having been reduced by a factor of 3.5 from 1990 to 2010. The overall reduction of EC emissions was 40%.

Biomass burning and other sources, were the dominant source also for POA, with almost constant contributions. Based on the emissions that Xing et al. (2013) reported in the category 'other', we can estimate that biomass burning was responsible for 46% of the total 'other' POA emissions. This contribution increased to 80% in 2001 and 83% in 2010. The PM emitted from biomass burning, according to the inventory, is similar for these three years (Xing et al., 2013). The second most important source of POA during 1990 was road transport contributing 5%. This emission source was reduced by a factor of 3.5 from 1990 to 2010. Overall POA emissions in the inventory were reduced by 27% from 1990 to 2010.

Emissions of VOCs by on-road sources were reduced by a factor of 3.5 during these 20 years. On the other hand, the VOCs emitted by non-road transport decreased by only 8%. The biogenic VOC emissions varied from year to year based on the prevailing meteorology, but their changes were less than 20%. The total (anthropogenic and biogenic) VOC emissions decreased by 31% from 1990 to 2010.

The emissions of the most important SO_2 source, EGUs, were reduced 33% from 1990 to 2001 and 67% from 1990 to 2010. This resulted in a 64% reduction of the total SO_2 emissions over these 20 years.

For NH_3, the most important source is agriculture (included in the 'other' category), and the corresponding emissions increased by 9% during these 20 years.

Road transportation is one of the major NO_x sources with the corresponding emissions having been reduced by 21% from 1990 to 2001 and 58% from 1990 to 2010. The second most important source for NO_x in 1990, were the EGUs, which emitted 25% less NO_x in 2001 and 66% less in 2010 compared to 1990. Total NO_x emissions in the inventory were 47% lower in 2010 compared to 1990.

4. Results

4.1 Annual-average concentrations and sources

We examine first 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 especially in urban areas in 1990 (Figure 2). The EC concentrations 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 most important source during the simulated period. Long range transport (LRT), which represents the transport from areas outside of the domain, contributed approximately 0.1 μg m^{-3}.

The predicted average total OA levels defined as the sum of POA and SOA are shown in Figure 3. The OA originating from road transport was about 0.7 μg m^{-3} during 1990 over the Eastern US, but it was reduced to less than 0.5 μg m^{-3} during 2010. 'Non-road' transport and 'non-EGU' emission sources had smaller contributions to OA, with less than 0.2 μg m^{-3} in most areas during all years. Biogenic SOA was almost 1 μg m^{-3} over the south-east US both during 1990 and 2001, but during 2010 it had higher concentrations in some areas. Especially in the South due to local meteorology predicted SOA was much higher compared to 1990. In 2010, the biogenic VOC concentrations were on average 15% higher compared to 1990 due

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mainly to the meteorological conditions during these two specific years. This small increase is consistent with the biogenic VOC emissions estimated by Sindelarova et al. (2014). Also, high OA concentrations were predicted to originate from biomass burning during 1990. The average contribution of long-range transport OA was approximately 0.6 μg m^{-3}.

Sulfate was the dominant component of $PM_{2.5}$ in the Eastern US in 1990 and the EGUs were its dominant source contributing more than 5 μg m^{-3} over wide areas of the East (Figure 4). The corresponding sulfate concentrations from EGUs were reduced to 3 μg m^{-3} in 2001 and to 1.5 μg 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 μg m^{-3} or less during all years. Long-range transport contributed approximately 0.9 μg m^{-3} to the sulfate levels during the simulated period.

4.2 Regional contributions of sources to $PM_{2.5}$ components

The US was divided in 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 such as New York, Boston, Philadelphia, Baltimore and Pittsburgh, while the Mideast (ME) includes the Ohio-river valley area with a number of electrical generation units. The Midwest (MW) has significant agricultural activities, while much of the West (WE) is relatively sparsely populated. California (CA) was kept separate from the other western regions. The southern US was split into a southeast region (SE) with significant biogenic emissions and the southwest (SW) with much less vegetation.

Figure 6a shows the predicted average concentrations of EC for each year in each region. The highest concentrations for 1990 were predicted in Northeast, followed by the Mideast and the California. Biomass burning, included in the ‘other’ source, was the dominant source of EC in all regions, with relatively constant concentration through the years, except from CA, where the contribution from this source in 1990 was much higher due to the annual variation in fires. There was significant reduction of the EC levels in all regions except for the West, where the EC originates mainly from biomass burning and long-range transport. The highest reductions were predicted for the eastern US. Figure 6b shows the population exposure (Walker et al., 1999), which is calculated in this work as the product of the average annual concentration of each computational cell times the population living in the cell. The US population distribution was calculated for each year based on the US Census Bureau (2019) data. The population exposure is significant in areas with high population density, for example in CA.

The source contributions to the annual-average concentrations of OA are depicted in Figure 7a. The predicted concentrations of OA in 1990 in the eastern US (NE, SE and ME regions) were almost 3 μg m^{-3} and in the other regions, less than 2.5 μg m^{-3}. OA originating from biomass burning dominated the concentrations of OA during all years and 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 0.5 μg m^{-3} during 1990 and almost 0.2 μg 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 a small increase of the total OA compared to 2001. The population exposure for OA (Figure 7b) is almost the same for Northeast and Mideast during 1990 and it decreased during 2001 and 2010. For the Midwest, West, and Southwest the population exposure to OA remained almost constant though the years. For all regions, the highest population exposure was due to biomass burning and the “other” sources. In addition, 20% of the population exposure was due to road transport during 1990 at the highest populated areas (NE, ME, and CA), but this percentage was reduced to almost 10% during 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 dominant SO_2 source in these areas (Fig. 8a). The drastic reductions of the EGU emissions are predicted to have led 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 from the EGU source are small given that the sulfate there even in the 1990s was relatively low and was dominated on average by long-range transport. Regarding the population exposure for NE and ME, the percentage of population exposure due to EGUs during 1990 was

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58% for the NE and 64% for the ME, but during 2010 these percentages were reduced to 44% and 53% respectively.

The mortality rates caused by total $PM_{2.5}$ were also calculated for the three simulated periods, following the relationships of Tessum et al. (2019) and using the death rates of US population by Murphy et al. (2013). We estimated 861 deaths per 100,000 persons for 1990, 777 for 2001, and 658 for 2010.

4.3 Linking average changes in emissions, concentrations, and exposure

The 72% reduction of emissions of EC from road transport, from 1990 to 2010 according to PMCAMx led to a 72% reduction of EC concentrations and a 70% reduction in human exposure to EC from this source (Table 1). The changes in concentrations are practically the same as those of the emissions because EC is inert and the atmospheric processes that affect it (transport and removal) are close to linear. The small difference between the change in emissions and that of exposure is due to small differences in the spatial distributions of the EC concentrations from road transport and the population density. The differences are small because most road transport emissions are in densely populated areas. The similarity in the fractional change of emissions and concentrations applies as expected to all EC source types (Table 1). However, for all these other sources the reduction in exposure is less than the reduction in emissions (or concentrations). For example, the 44% reduction of EC emissions from non-road transport, was accompanied by a 43% reduction in concentrations, but a 35% reduction of human exposure. This is due to the location of the reductions of these non-road transport emissions. A significant fraction of these reductions took place away from densely populated regions (e.g., in agricultural regions) therefore they resulted in a smaller reduction of human exposure. The situation is a little different for total EC. The 40% reduction in emissions is predicted to have led to a 31% reduction in concentration. The difference here is due to the contribution of long-range transport (sources outside of the US) which are assumed to have remained approximately constant during this period. The predicted reduction in exposure is 33% and is due to the local sources. The changes in EC exposure in each region are depicted in Figure 6b.

The changes in fresh POA are a little more interesting, because it is treated as semi-volatile and reactive in PMCAMx. For all US sources, the reduction in concentrations is a little higher than that of the emissions (Table 1). For example, a 25% reduction of POA emissions of non-road POA, is predicted to have resulted in a 30% reduction of the POA concentrations. This difference is due mostly to the non-linear nature of the partitioning of these emissions between the gas and the particulate phase. As the emissions are reduced, the corresponding OA concentrations are reduced and more of the organic material is transferred to the gas phase to maintain equilibrium. This additional evaporation leads to an additional reduction of the POA concentrations. This is the case for all sources, so the 27% reduction in POA emissions corresponds according to PMCAMx to a 33% average reduction in POA concentrations. The reduction in exposure is, in absolute terms, a little less than that of the concentrations for the same reasons as for EC. This difference is small (-74% versus -71%) for road transport, but more significant for sources located outside urban centers (e.g. for EGU it is -13% for concentrations and -6% for exposure).

The reductions predicted by PMCAMx for SOA (aSOA+bSOA) concentrations are far more complex than those of fresh POA, since the formation of secondary organic species involves non-linear processes such as partitioning, dependence on oxidant levels, NO_x-dependence of the yields, and the complexity of the chemical aging. Overall, PMCAMx predicts that the reductions in exposure are less than the reductions in average concentrations over the US which are also less than the reductions in the emissions of the anthropogenic volatile and intermediate volatility organic compounds. The major reasons for this behavior are the simultaneous decreases in NO_x that have led to increased SOA formation yields and the time required for the formation of this SOA which is often produced away from its sources in high urban density areas. The reasons for this behavior are complex and will be analyzed in detail in future work. However, at least part of the explanation is due to decreases in NO_x concentrations over the same period and associated increases in SOA yields.

The predicted reductions in sulfate concentrations are less than the reductions in emissions due mainly to the non-linearity of the aqueous-phase conversion of SO_2 to sulfate (Seinfeld and Pandis 2016) (Table 1). Taking into account the transport of some of the sulfate from areas outside of the US, the model predicts that the 64% reduction in SO_2 emissions has resulted in a 45% reduction of the sulfate concentration on average. The change in exposure is a little less, -40% on average due mainly to the location of the major SO_2 sources relatively away from urban centers.

4.4 Distribution of population exposure to $PM_{2.5}$ from different sources

We have calculated the percentage of people exposed to different $PM_{2.5}$ concentrations from the major sources ('other', 'EGUs', 'road transport') for the three different periods. Almost half of the US population was exposed to $PM_{2.5}$ concentrations above 20 μg m^{-3} in 1990. A decade later this percentage was less than 20% and close to zero during 2010 (Fig. 9a). During 1990, almost 90% of the US population was exposed to $PM_{2.5}$ concentrations above 10 μg m^{-3}, the suggested annual mean by the World Health Organization (WHO, 2006). This percentage was reduced to 83% in 2001 and 70% in 2010 (Fig. 9a and Fig. S2h).

The predicted distribution of the population exposed to $PM_{2.5}$ from the source 'other' in 1990 covered a wide range extending from approximately 1 to 16 μg m^{-3}. The exposure from these sources was reduced significantly in the following years mainly due to the reductions in the emissions of paved/unpaved road dust, prescribed burning, and industrial emissions (Xing et al., 2013). The average emissions from wildfires did not change appreciably, but this distribution was sharper in 2010, with maximum percentages of people exposed appearing for $PM_{2.5}$ concentrations ranging from 5 to 8 μg m^{-3}. The random spatial variation of biomass burning sources can affect areas with different population density.

The exposure of the population to primary and secondary $PM_{2.5}$ from EGUs has been dramatically decreased (Fig. 9c). In 1990 according to PMCAMx 56% of the US population was exposed to more than 3 μg m^{-3} from this source. This percentage was reduced to 39% in 2001 and to 2% in 2010. For the threshold of 5 μg m^{-3} the reduction was from 18% in 1990, to 1% in 2001 to practically zero in 2010.

Similarly, significant decreases are predicted for road transport $PM_{2.5}$. While in 1990, 79% of the population was exposed to levels exceeding 1 μg m^{-3}, this percentage was 58% in 2001 and 18% in 2010 (Fig. 9d). The corresponding changes for the 2 μg m^{-3} were from 27% (1990) to 8% (2001) to zero (2010).

4.5 Evaluation of the model

The model was evaluated on annual basis against ground level measurements from the IMPROVE and CSN networks (STN U.S. EPA, 2002; IMPROVE, 1995). The metrics used (Fountoukis et al., 2011), 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),

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

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

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

where P_i represents the model-predicted value for site i, O_i is the corresponding observed value and n is the total number of sites. During 1990, there were only 27 measurement sites available from the IMPROVE network, but this number increased dramatically in 2001 and 2010. The results are summarized in Table 2.

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.

According to Morris et al. (2005), the level of the performance of the model would be considered as excellent if it meets the following criteria: FBIAS $\leq \pm$ 15% and FERROR $\leq$ 35%; and is good if FBIAS $\leq \pm$ 30% and FERROR $\leq$ 50%. Based on the above criteria the model performance is excellent for annual averages of $PM_{2.5}$, OA, and ammonium for all years. The EC performance is good to excellent, while that for sulfate it is excellent of 1990 and 2010 but average for 2001. The current version of PMCAMx has difficulties reproducing the nitrate levels with performance that varies from average to good. There several reasons for these problems including the spatial resolution used here, the assumption of bulk equilibrium, etc., that will be analyzed further in future work. PMCAMx has a small tendency towards overprediction of the OA and underprediction of the EC. There is also a tendency towards overprediction of the sulfate and as a result, the ammonium too. The fractional error for nitrate is closer to 0.5 with the model in general underpredicting the observed values.

The predictions for $PM_{2.5}$ concentrations, for which there are many more stations and thus available measurements in 2001 and 2010, are reproduced with fractional bias of 9% and fractional error less than 25%. For 1990, there is little bias, while there is a small tendency towards overprediction in the later years. The performance of the model differs with the region examined (Table S1), for example the model tends to underpredict $PM_{2.5}$ and its components in the West part of US. The coarse resolution used here is not sufficient to represent the gradients observed between some relatively isolated urban areas and the relatively clean background.

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.

4.5.1 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 S3 shows the reductions in EC concentrations from 1990 to 2010. The reductions of the EC emissions resulted in total reductions of the average concentrations of around 30% in the twenty-year period. Reductions above 20% are predicted not only in the large urban areas but also in large regions in both the eastern and the western US.

Average organic aerosol levels were reduced according to PMCAMx by close to 1.5 $\mu g\ m^{-3}$ from 1990 to 2010 in a wide area extending from the Great Lakes to Tennessee, but also in parts of the Eastern seaboard (Fig. S4). These reductions correspond to 35-45% of the OA in both the Northeast and California.

From 1990 to 2010, sulfate was reduced by 50-60% 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 (Fig. S5). These simulations suggest that the Eastern US has benefited more both in an absolute and in a relative sense from these reductions in SO_2 emissions.

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We also compared the predicted and observed concentration changes, using the Pearson's correlation coefficient and the average percentage differences, summarized in Table 3. For the first two cases (1990 to 2001 and 1990 to 2010) there were only a few measurements available for 1990. The model reproduces quite well the predicted changes against the observed for $PM_{2.5}$ and its components (Fig. S6).

For EC, the correlation was high between 1990 and 2001, with r = 0.80; and between 1990 and 2010, with r = 0.91. However, the analysis for the changes up to 2010 is complicated by the change in the EC measurement protocol in several CSN sites in the period from 2007 to 2010. The change from the Thermal Optical Transmittance (TOT) to the Thermal Optical reflectance (TOR) resulted in small increases in the reported EC that were of similar magnitude as the predicted changes due to the emissions reductions. To partially address this issue, we do not include in the analysis the results from 14 CSN sites which reported increases in the EC from 2001 to 2010. Excluding these sites an r = 0.39 is calculated (Table 3). The data points from these sites can be seen in the lower triangle of Fig. S6. The reduced r for the 2001-10 is probably due, at least partially, to this uncertainty of the measured changes.

The predicted average change of OA in the measurement sites from 1990 to 2001 was -13%, in good agreement with the observed -16% in the same locations. The predicted changes were reasonably well correlated (r = 0.68) with the measured ones during this decade. However, the model performance during the next decade (2001-10) deteriorates as it underpredicts on average the changes (predicted -9% versus observed -18%) and the changes are not correlated to each other in space. Additional analysis suggested that, while the model does a reasonable job reproducing the changes in the western half of the country and the northeastern quarter, it overpredicts the OA concentration in 2010 and thus underpredicts the reductions in the southeastern US. Our analysis also suggests that this mainly due to an overprediction of the biogenic SOA in this part of the country. This is consistent with the anomalous predicted increase of biogenic SOA from 2001 to 2010 in the SE US (Figure 7 and Figure S1). This interesting discrepancy regarding the predicted and observed changes of biogenic SOA will be analyzed in detail in a subsequent paper.

For sulfate, the model reproduced well the observed changes for the three comparison periods, with Pearson's correlation coefficient r = 0.88 (from 1990 to

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2001); 0.97, from 1990 to 2010; and 0.92, from 2001 to 2010 (Table 3). Despite the nonlinearity in the behavior of sulfate, the average predicted and observed percentage changes were consistent for the three comparison periods.

Finally, for $PM_{2.5}$ the model reproduces well the observed changes for the three comparison periods with r = 0.81 (from 1990 to 2001); 0.82 (from 1990 to 2010) and 0.61 (from 2001 to 2010). The average percentage changes for the observations and the predictions were close for all the cases (Table 3).

5. Conclusions

The CTM, PMCAMx, was used to simulate the changes in source contributions to $PM_{2.5}$ and its components over two decades accounting for changes in emissions and meteorology with internally consistent methods. Biomass burning and 'other' sources, primarily including construction processes; mining; agriculture; waste disposal, and other miscellaneous sources, contributed approximately half of the total (primary and secondary) $PM_{2.5}$ during the examined 20-year period. The corresponding average $PM_{2.5}$ concentration levels due to this group of sources have been reduced by 33% from 1990 to 2010. EGUs were the second most important source of $PM_{2.5}$; the corresponding ambient $PM_{2.5}$ levels have been reduced by 55% and their contribution to the total from 16% to 11%. On-road transport was the third most important source of $PM_{2.5}$. The total average $PM_{2.5}$ from this source was reduced by 59%, while their contribution to the average $PM_{2.5}$ levels has been reduced from 8% to 5%.

OA was a significant fraction of $PM_{2.5}$. Biomass burning included in the 'other' sources was the most important source of OA with fractional contributions varying from 38% to 52% depending on the region. Biogenic SOA was the second dominant component of OA with contributions ranging from 6% to 22% in the South US.

The reduction in exposure was less than the reduction in emissions (or concentrations) for sources that are located away from densely populated regions (non-road transport and non-EGUs) due to the spatial non-uniformity of the corresponding $PM_{2.5}$ reductions. For example, sulfate human exposure by non-EGU source was reduced by 46% from 1990 to 2010, while the corresponding reduction in emissions was 62%.

From 1990 to 2010, the reduction of human exposure to EC was 33%, to fresh POA 35%, to sulfate 40%, and to SOA (both anthropogenic and biogenic) 8%. The reduction of EC was mostly due to the 72% reduction of on-road EC emissions, while the reduction in sulfate to the 64% reduction of SO_2 emissions from EGUs.

During the 20 year-long examined period, the fraction of the US population exposed to average $PM_{2.5}$ concentrations above 20 μg m^{-3} decreased from approximately 50% to close to zero. In 1990, 12% of the US population was exposed to $PM_{2.5}$ concentrations lower than the suggested annual mean by the WHO (10 μg m^{-3}). This fraction increased to 30% in 2010.

PMCAMx reproduced the annual average concentrations of $PM_{2.5}$ with fractional error less than 30% for the three simulation periods. The corresponding fractional biases were 19% for 1990 and 9% for both 2001 and 2010. The model also reproduces well the average reduction of $PM_{2.5}$ in the measurement sites; the measured reduction was 28% while the model predicts a reduction of 30%. A model weakness that requires additional investigation is its tendency to predict an increase in the biogenic SOA from 2001 to 2010 that appears inconsistent with the observations.

6. Code and data availability

The code and simulation results are available upon request (spyros@chemeng.upatras.gr).

7. Supplement

8. Author contributions

K.S performed the PMCAMx and PSAT simulations, analyzed the results and wrote the manuscript. P.G.R. prepared the anthropogenic emissions and other inputs for the simulations. B.D. performed MEGAN simulations and analyzed the results; E.K. performed and evaluated the WRF simulations; I.K. set-up the WRF simulations and assisted in the preparation of the meteorological inputs. C.H. analyzed the simulation output. S.N.P. and P.J.A. designed and coordinated the study and helped in the writing of the paper. All authors reviewed and commented on the manuscript.

9. Competing interests

The authors declare that they have no conflict of interest.

10. Acknowledgments

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Table 1: Percentage changes in emissions from each source, and corresponding changes in average concentrations and exposure from 1990 to 2010.

	Road	Non-road	EGU	Non-EGU	Biogenic	Other	Total
EC							
1990 to 2010							
Emissions (EC)	-72	-44	-13	-7	-	-17	-40
Concentrations	-72	-43	-13	-8	-	-18	-31
Exposure	-70	-35	-3	4	-	-12	-33
Fresh POA							
1990 to 2010							
Emissions (fresh POA)	-72	-25	-13	-14	-	-25	-27
Concentrations	-74	-30	-13	-20	-	-31	-33
Exposure	-71	-25	-6	-11	-	-32	-35
SOA							
1990 to 2010							
Emissions (IVOCs+VOCs)	-71	-8	-8	-31	15	-34	-31
Concentrations	-71	-17	-11	-21	23	-27	-21
Exposure	-66	-6	1	-8	37	-18	-8
Sulfate							
1990 to 2010							
Emissions (SO_2)	-93	-51	-67	-62	-	-52	-64
Concentrations	-91	-44	-63	-54	-	-38	-45
Exposure	-88	-30	-60	-46	-	-27	-40

Table 2: Evaluation metrics for annual average concentrations of PM$_{2.5}$ and for its major components for each examined year.

	MB (μg m^{-3})	MAGE (μg m^{-3})	NMB	NME	FBIAS	FERROR	Stations	Comment
EC								
1990	-0.02	0.07	-0.07	0.27	0.04	0.28	27	Excellent
2001	0.14	0.19	0.42	0.59	0.28	0.38	104	Good
2010	-0.05	0.15	-0.10	0.34	0.05	0.37	268	Good
OA								
1990	0.01	0.47	0.01	0.26	0.07	0.26	27	Excellent
2001	-0.21	0.60	-0.09	0.25	-0.01	0.27	103	Excellent
2010	0.20	0.50	0.09	0.23	0.09	0.23	269	Excellent
Sulfate								
1990	0.13	0.23	0.09	0.15	0.20	0.23	27	Excellent
2001	0.19	0.40	0.14	0.29	0.31	0.38	101	Average
2010	0.07	0.31	0.04	0.17	0.16	0.25	287	Excellent
Nitrate								
1990	0.01	0.18	0.03	0.65	-0.31	0.59	27	Average
2001	-0.15	0.32	-0.14	0.30	-0.19	0.47	97	Good
2010	-0.25	0.32	-0.26	0.34	-0.34	0.49	282	Average
Ammonium								
1990	-0.04	0.14	-0.06	0.22	0.07	0.24	27	Excellent
2001	0.02	0.20	0.02	0.21	0.10	0.26	96	Excellent
2010	0.09	0.16	0.11	0.20	0.19	0.26	286	Excellent
PM$_{2.5}$								
1990	1.20	1.63	0.23	0.31	0.19	0.26	27	Excellent
2001	1.49	2.72	0.12	0.23	0.09	0.23	951	Excellent
2010	1.10	2.08	0.12	0.22	0.09	0.23	938	Excellent

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Table 3: Average observed and predicted PM percentage changes, and Pearson's correlation coefficient calculated for each comparison case.

	Observed changes (%)	**Predicted changes** (%)	**Pearson's r**	**Number of Sites**
		EC		
1990 to 2001	-19	-12	0.80	21
2001 to 2010	-19	-17	0.39	75[a]
1990 to 2010	-45	-24	**0.91**[b]	21
		OA		
1990 to 2001	-16	-13	0.68	21
2001 to 2010	-18	-9	-0.32	89
1990 to 2010	-33	-23	-0.16	21
		Sulfate		
1990 to 2001	-9	-9	**0.88**	21
2001 to 2010	-35	-22	**0.92**	75
1990 to 2010	-40	-29	**0.97**	21
		$PM_{2.5}$		
1990 to 2001	-10	-14	**0.81**	21
2001 to 2010	-21	-20	**0.61**	636
1990 to 2010	-28	-30	**0.82**	21

[a] 14 CSN sites reporting increases of EC, probably due to the change in the measurement protocol in the 2007-09 period, have been excluded from this analysis.

[b] The correlations in bold are statistically significant for a significance level of 5%.

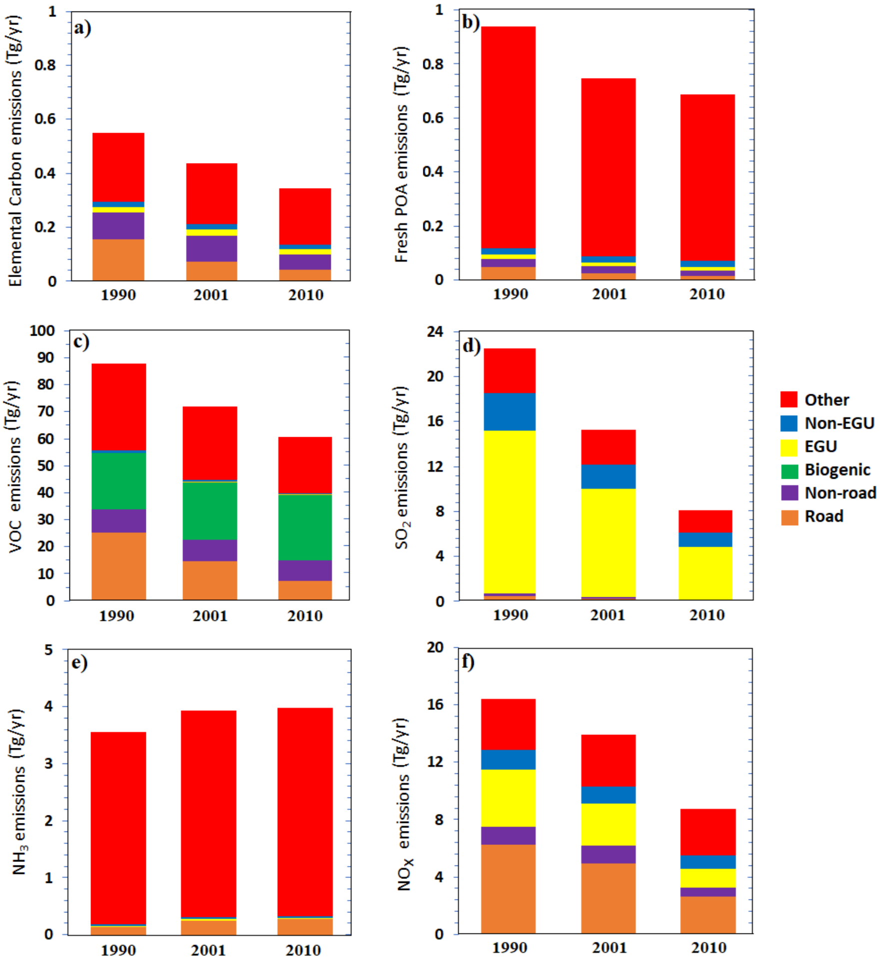

Figure 1: Annual emissions by each source for the whole domain for: a) elemental carbon, b) fresh POA, c) non-methane VOCs, d) SO_2, e) NH_3, and f) NO_x.

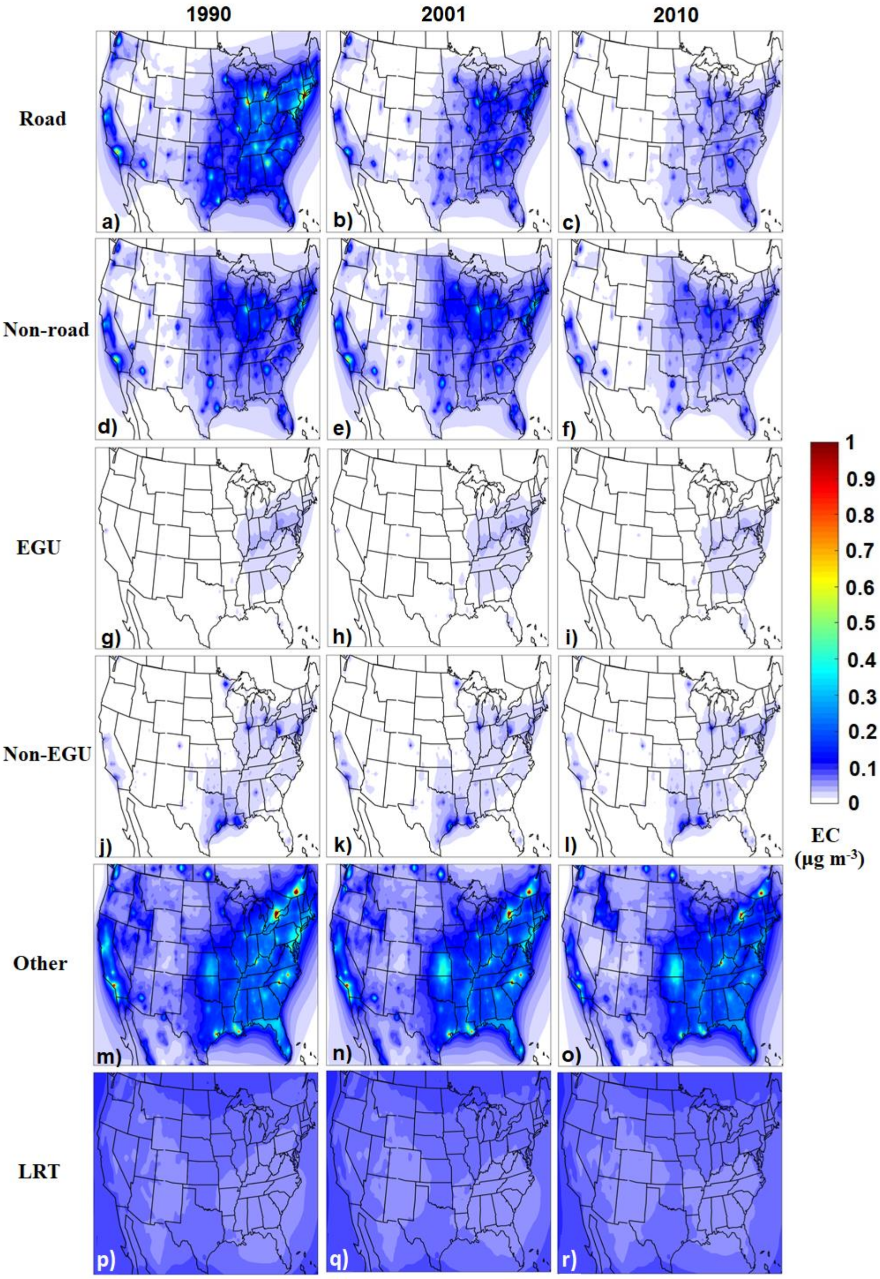

Figure 2: Predicted annual average ground level $PM_{2.5}$ elemental carbon concentrations per source for 1990, 2001, and 2010.

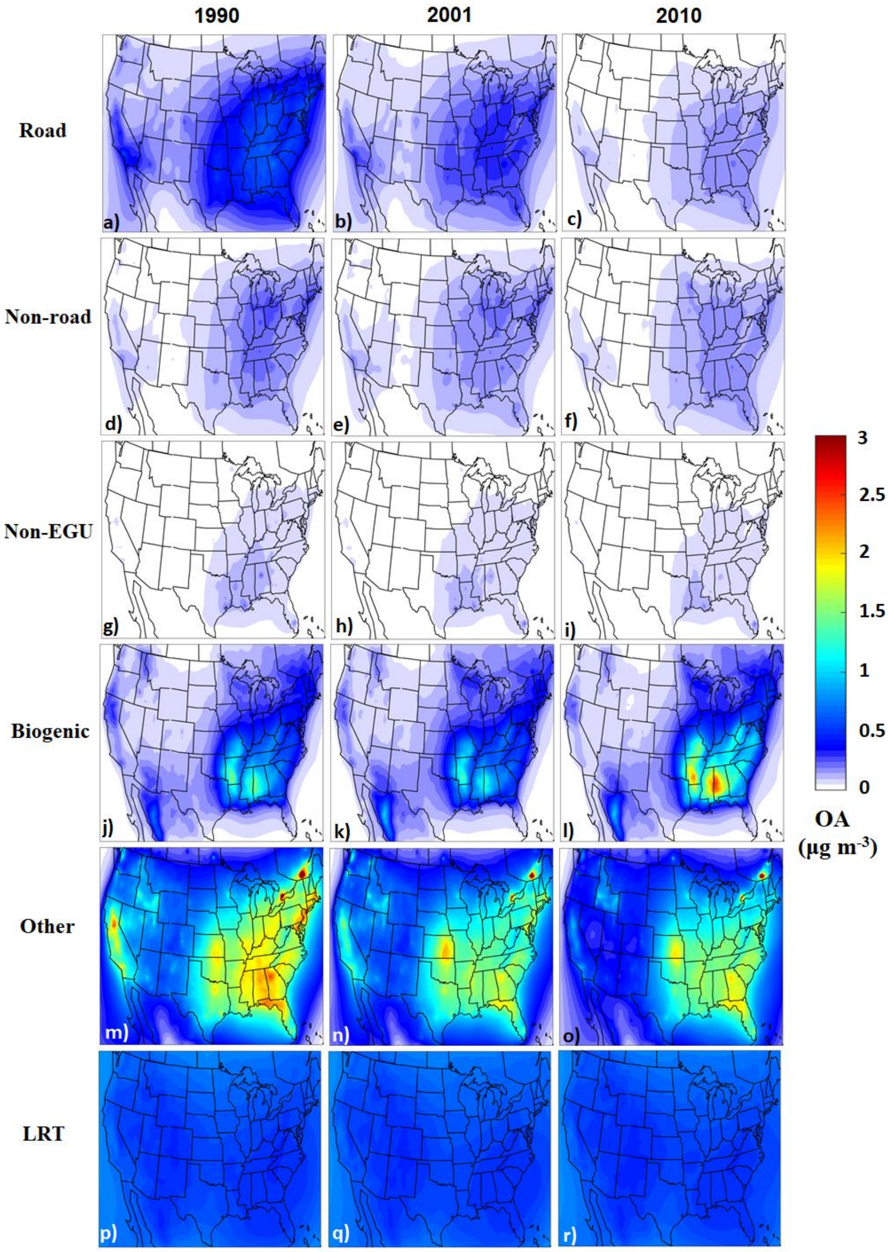

Figure 3: Predicted annual average ground level $PM_{2.5}$ organic (primary plus secondary) aerosol concentrations per source for 1990, 2001, and 2010. The EGU contributions are low and are not shown.

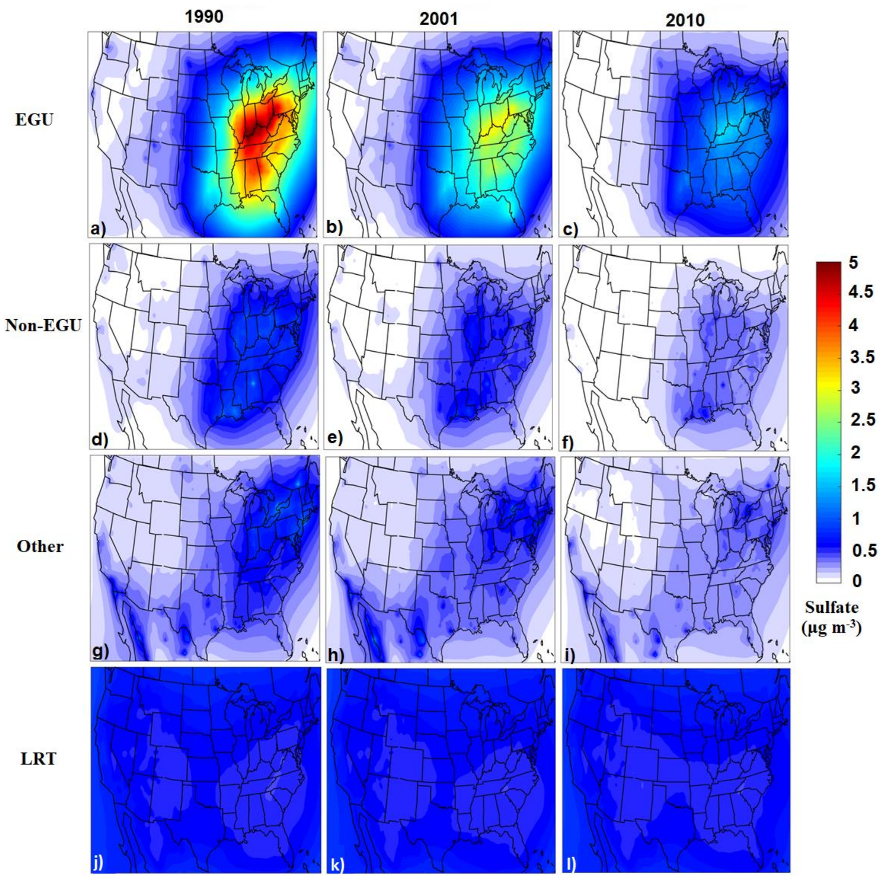

Figure 4: Predicted annual average ground level $PM_{2.5}$ sulfate concentrations per source for 1990, 2001, and 2010. The on-road, non-road, and biogenic contributions are low and are not shown.

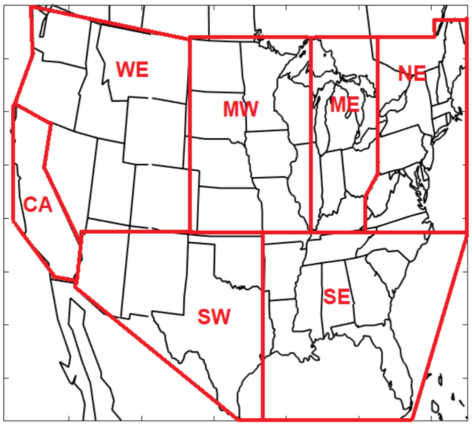

Figure 5: Definition of the 7 regions used in the analysis.

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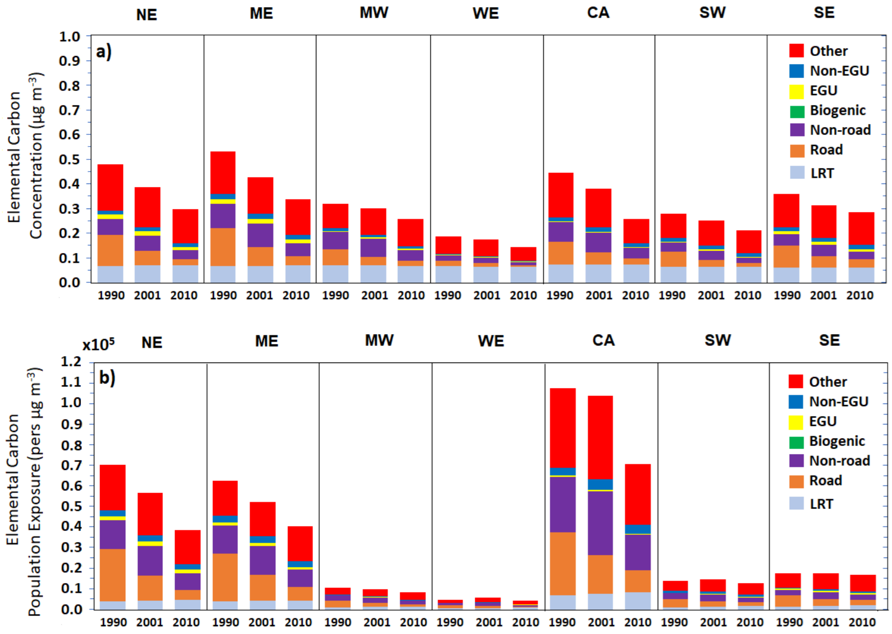

Figure 6: Sources of $PM_{2.5}$ EC for the different regions during 1990, 2001, and 2010 for: a) average concentrations (μg m^{-3}) and b) population exposure (persons μg m^{-3}).

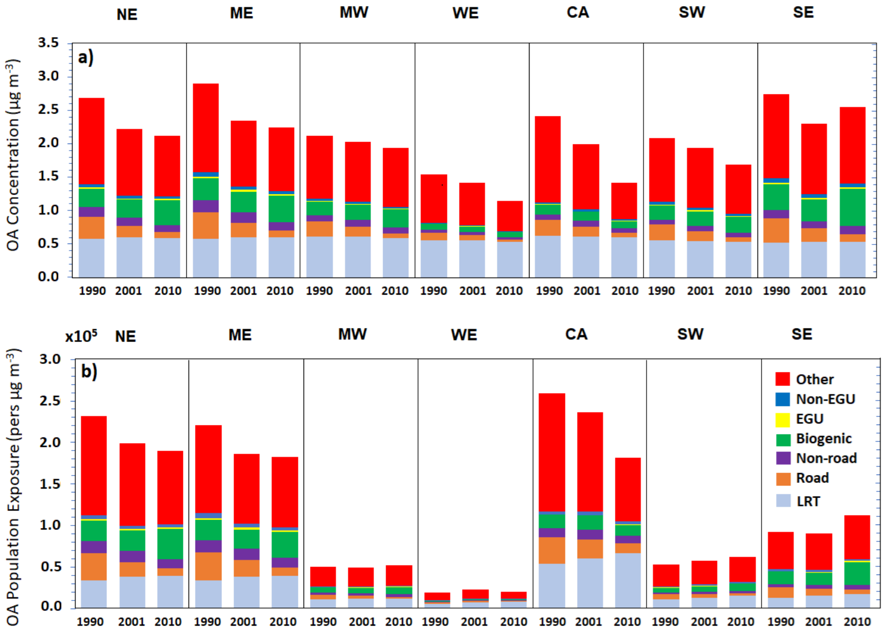

Figure 7: Sources of $PM_{2.5}$ OA for the different regions during 1990, 2001, and 2010 for: a) average concentrations (µg m^{-3}) and b) population exposure (persons µg m^{-3}).

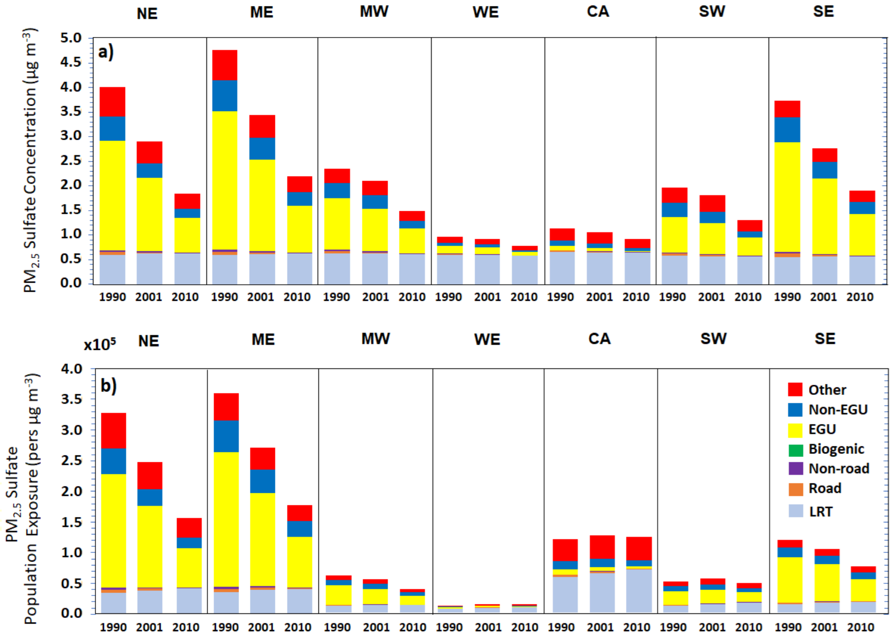

Figure 8: Sources of PM$_{2.5}$ sulfate for the different regions during 1990, 2001, and 2010 for: a) average concentrations (μg m^{-3}) and b) population exposure (persons μg m^{-3}).

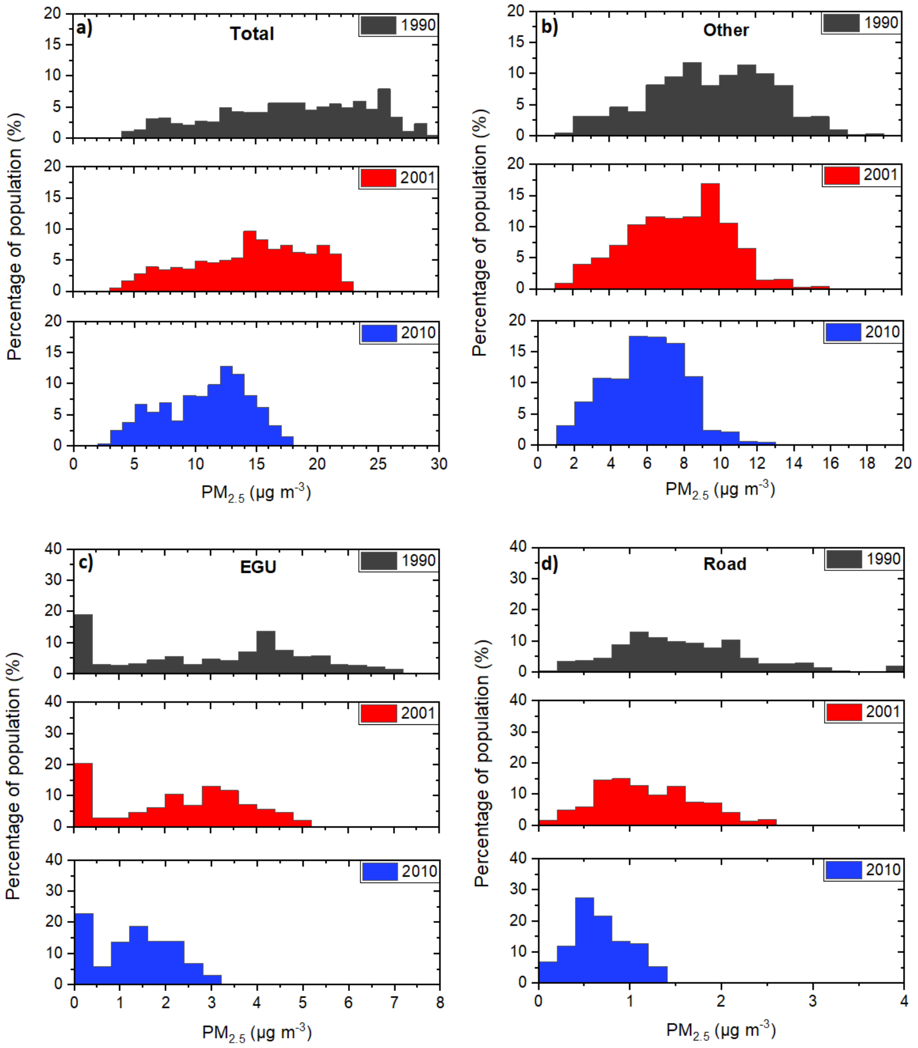

Figure 9: Distributions of population exposed to annual average $PM_{2.5}$ during 1990 (grey), 2001 (red), 2010 (blue); and for the dominant sources of $PM_{2.5}$: a) road transport, b) EGU, c) other, and h) total $PM_{2.5}$.