# 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) for 1990, 2001 and 2010. The use of the Particle Source Apportionment Algorithm (PSAT) allows us to link the concentration reductions to the sources of the corresponding primary and secondary PM. 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 (EPA, 2011). 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). Milando et al. (2016) used positive matrix factorization (PMF) of PM measurements to interpret the observed trends of $PM_{2.5}$ from 2004 to 2011 in Detroit and Chicago. They concluded that as secondary sulfate was declining, emissions from biomass burning, vehicles and metals sources are becoming relatively more important. 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. Jin et al. (2019) combined information from ground-based observations, remote sensing and chemical transport models to estimate that the PM$_{2.5}$-related mortality decreased by 67% in New York State from 2002 to 2012. 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. Three specific years are used as snapshots of US air quality in time. Given that significant emissions changes have taken place over the decades between the examined years, the predicted concentration changes reflect mostly changes in these emissions plus some year to year meteorological variability. 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 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.

## 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 $4752 \times 2952$ 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

169  include the Rapid Radiative Transfer Model/Dudhia radiation schemes (Iacono et al.,

170  2008), the Asymmetric Convective Model version 2 for the planetary boundary layer

171  (Pleim, 2007a, 2007b), the Morrison double-moment cloud microphysics scheme

172  (Morrison et al., 2008), and version 2 of the Kain–Fritsch cumulus parameterization

173  (John et al., 2004). The selected WRF configuration is recommended for air quality

174  simulations (Hogrefe et al., 2015; Rogers et al., 2013).

175

**3.2    Emissions**

176

177  Emissions for the simulations were obtained from the internally consistent, historical

178  emission inventories of Xing et al. (2013) that include source-resolved gas and

179  primary particle emissions. Point source sectors include Electricity Generating Units

180  (EGU) included in the EPA's Integrated Planning Model (IPM); industrial sources not

181  included in the IPM (non-EGU); and all other point sources in Canada and Mexico.

182  Area sources include on-road emissions in the US, Canada and Mexico; off-road

183  emissions for the entire domain; and all remaining non-biogenic sources. We used our

184  WRF meteorology to drive the Model of Emissions of Gases and Aerosols from

185  Nature (MEGAN3) (Jiang et al., 2018) using the default emission factors for all years

186  to generate biogenic emissions for the CONUS domain.

187  In this application of PSAT, we used 6 different emission categories based on

188  those described above plus initial and boundary conditions which are each tracked

189  separately by the model as different "sources". As a result, the emission source

190  categories used are: 'road' which includes road emissions over the US; 'non-road'

191  which includes the off-road emissions of the entire domain; 'EGU'; 'non-EGU' as

192  described above; 'other' which includes the sum of the other point and area sources

193  plus the 'on-road' emissions from Canada and Mexico and finally biogenic emissions.

194  Figure 1 depicts the total annual emissions for each source and each year.

195  Biomass burning (included in the 'other' category) was the dominant source of

196  EC and remained relatively constant during the simulated period. The second most

197  important source of EC was road transport, with the corresponding emissions having

198  been reduced by a factor of 3.5 from 1990 to 2010. The overall reduction of EC

199  emissions was 40%.

200  Biomass burning and other sources, were the dominant source also for POA,

201  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 $\mu g\ m^{-3}$ of EC in all areas during these years. The 'other' source which includes all types of biomass burning was the most important

234 source during the simulated period. Long range transport (LRT), which represents the

235 transport from areas outside of the domain, contributed approximately 0.1 μg m$^{-3}$.

236 The predicted average total OA levels defined as the sum of POA and SOA

237 are shown in Figure 3. The OA originating from road transport was about 0.7 μg m$^{-3}$

238 during 1990 over the Eastern US, but it was reduced to less than 0.5 μg m$^{-3}$ during

239 2010. 'Non-road' transport and 'non-EGU' emission sources had smaller

240 contributions to OA, with less than 0.2 μg m$^{-3}$ in most areas during all years. Biogenic

241 SOA was almost 1 μg m$^{-3}$ over the south-east US both during 1990 and 2001, but

242 during 2010 it had higher concentrations in some areas. Especially in the South due to

243 local meteorology predicted SOA was much higher compared to 1990. In 2010, the

244 biogenic VOC concentrations were on average 15% higher compared to 1990 due

245 mainly to the meteorological conditions during these two specific years. This small

246 increase is consistent with the biogenic VOC emissions estimated by Sindelarova et

247 al. (2014). Also, high OA concentrations were predicted to originate from biomass

248 burning during 1990. The average contribution of long-range transport OA was

249 approximately 0.6 μg m$^{-3}$.

250 Sulfate was the dominant component of PM$_{2.5}$ in the Eastern US in 1990 and

251 the EGUs were its dominant source contributing more than 5 μg m$^{-3}$ over wide areas

252 of the East (Figure 4). The corresponding sulfate concentrations from EGUs were

253 reduced to 3 μg m$^{-3}$ in 2001 and to 1.5 μg m$^{-3}$ in 2010 due to the dramatic reduction of

254 these SO$_2$ emissions over these 20 years. Sulfate concentrations originating from non-

255 EGU and other emission sources were 1 μg m$^{-3}$ or less during all years. Long-range

256 transport contributed approximately 0.9 μg m$^{-3}$ to the sulfate levels during the

257 simulated period.

258

**4.2 Evaluation of the model predictions**

260 The model was evaluated both on a annual and daily basis against ground level

261 measurements from the IMPROVE and CSN networks (STN U.S. EPA, 2002;

262 IMPROVE, 1995). The metrics used in the main analysis, include the normalized

263 mean bias (NMB), the normalized mean error (NME), the mean bias (MB), the mean

264 absolute gross error (MAGE), the fractional bias (FBIAS), and the fractional error

265 (FERROR) (Fountoukis et al., 2011):

266

$$267 \qquad NMB = \sum_{i=1}^{n}(P_i - O_i)\Big/\sum_{i=1}^{n}O_i \qquad\qquad NME = \sum_{i=1}^{n}|P_i - O_i|\Big/\sum_{i=1}^{n}O_i$$

$$268 \qquad MB = \frac{1}{n}\sum_{i=1}^{n}(P_i - O_i) \qquad\qquad MAGE = \frac{1}{n}\sum_{i=1}^{n}|P_i - O_i|$$

$$269 \qquad FBIAS = \frac{2}{n}\sum_{i=1}^{n}\frac{(P_i - O_i)}{(P_i + O_i)} \qquad FERROR = \frac{2}{n}\sum_{i=1}^{n}\frac{|P_i - O_i|}{(P_i + O_i)}$$

270   where $P_i$ represents the model-predicted value for site $i$, $O_i$ is the corresponding

271   observed value and $n$ is the total number of sites. During 1990, there were only 27

272   measurement sites for PM$_{2.5}$ composition, all parts of the IMPROVE network, but this

273   number increased dramatically in 2001 to more than one hundred and 2010 to

274   approximately three hundred stations. There was almost an order of magnitude more

275   measurements and stations for just PM$_{2.5}$ mass concentration. The results for annual

276   evaluation are summarized in Table 1 and for the evaluation based on daily average

277   concentrations in Table 2.

278   According to Morris et al. (2005), the level of the performance of the model

279   for daily resolution is considered excellent if it meets the following criteria: FBIAS ≤

280   ± 0.15 and FERROR ≤ 0.35; good if FBIAS ≤ ± 0.30 and FERROR ≤ 0.50; is average

281   if FBIAS ≤ ± 0.60 and FERROR ≤ 0.75; and is problematic if: FBIAS > ± 0.60,

282   FERROR> 0.75. For simplicity we have adopted the same performance

283   characterization scheme for annual resolution.

284   Based on these criteria, the ability of the model to reproduce the annual

285   average concentrations of the sites is excellent for OA, good to excellent for PM$_{2.5}$,

286   EC, and ammonium, good for sulfate, and average for nitrate. For the daily resolution,

287   the PMCAMx performance is good for PM$_{2.5}$, average for EC, OA, sulfate,

288   ammonium, and problematic for nitrate. The model faced significant problems in

289   reproducing the PM measurements in California, mainly because of the coarse grid

290   resolution used (Table S1). CTMs at this resolution cannot capture the significant PM

291   gradients and high concentrations observed in that area. Excluding the California sites

292   from the evaluation the performance metrics improved significantly (Table S2 and

293   S3). For example, for the annual averages, the performance for PM$_{2.5}$ and ammonium

294   was excellent for all years. There were also improvements in the metrics for all other

295   major PM components. The model also tends to underpredict PM$_{2.5}$ and its

296   components in some urban areas in Western US (Table S1). The coarse resolution

297   used here is not sufficient to represent the gradients observed between some relatively

298    isolated urban areas and the relatively clean background in this part of the country.
299    The daily $PM_{2.5}$ concentrations, for which there are many more stations and
300    measurements in 2001 and 2010, are reproduced with fractional bias of 3 to 13% and
301    fractional error less than 50% (Table 2). For 1990, there is little bias, while there is a
302    small tendency towards overprediction in the later years.

303         The version of PMCAMx used in these simulations has difficulties
304    reproducing the nitrate levels. There several reasons for these problems including the
305    spatial resolution used here, the assumption of bulk equilibrium, etc., that will be
306    analyzed further in future work. PMCAMx has a small tendency towards
307    underprediction of the OA and the EC. There is also a tendency towards
308    overprediction of the sulfate and as a result, the ammonium too.

309         We also followed the approach suggested by Emery et al. (2017) for the
310    characterization of the model performance. This approach relies on the NMB, NME
311    and correlation coefficient (r) as metrics. The results of the corresponding analysis are
312    summarized in Tables S4, S5 and S6 and suggest that the model is acceptable for all
313    components and periods with two exceptions: sulfate during 2010 and ammonium
314    during 2001.

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

319

## 4.3 Regional contributions of sources to $PM_{2.5}$ components

321    The US was divided in seven regions (Fig. 5) to facilitate the spatial analysis of the
322    source contributions and their changes during the simulated period. The Northeast
323    (NE) region includes major cities such as New York, Boston, Philadelphia, Baltimore
324    and Pittsburgh, while the Mideast (ME) includes the Ohio-river valley area with a
325    number of electrical generation units. The Midwest (MW) has significant agricultural
326    activities, while much of the West (WE) is relatively sparsely populated. California
327    (CA) was kept separate from the other western regions. The southern US was split
328    into a southeast region (SE) with significant biogenic emissions and the southwest
329    (SW) with much less vegetation.

330     Figure 6a shows the predicted average concentrations of EC for each year in

331 each region. The highest concentrations for 1990 were predicted in Northeast,

332 followed by the Mideast and the California. Biomass burning, included in the 'other'

333 source, was the dominant source of EC in all regions, with relatively constant

334 concentration through the years, except from CA, where the contribution from this

335 source in 1990 was much higher due to the annual variation in fires. There was

336 significant reduction of the EC levels in all regions except for the West, where the EC

337 originates mainly from biomass burning and long-range transport. The highest

338 reductions were predicted for the eastern US. Figure 6b shows the population

339 exposure (Walker et al., 1999), which is calculated in this work as the product of the

340 average annual concentration of each computational cell times the population living in

341 the cell. The US population distribution was calculated for each year based on the US

342 Census Bureau (2019) data and is different for 1990, 2001 and 2010. The population

343 distribution of 2001 is assumed to be the same with that of 2000. The population

344 exposure is significant in areas with high population density, for example in CA. The

345 US population increased from 1990 to 2010 by almost 24%. This increase would have

346 led to a corresponding increase in total population exposure if the emissions had not

347 changed during this period.

348     The source contributions to the annual-average concentrations of OA are

349 depicted in Figure 7a. The predicted concentrations of OA in 1990 in the eastern US

350 (NE, SE and ME regions) were almost 3 $\mu$g m$^{-3}$ and in the other regions, less than 2.5

351 $\mu$g m$^{-3}$. OA originating from biomass burning dominated the concentrations of OA

352 during all years and regions. Biogenic SOA was the second most significant OA

353 component in the Southeast. OA originating from on-road transport contributed,

354 according to the model, almost 0.5 $\mu$g m$^{-3}$ during 1990 and almost 0.2 $\mu$g m$^{-3}$ during

355 2010 in the eastern US. Significant reductions of OA are predicted for the Northeast,

356 Mideast, and California while moderate reductions for the Midwest, West, and

357 Southwest. The OA in the Southeast has more complex behavior due to the predicted

358 increase of biogenic SOA in 2010 that leads to a small increase of the total OA

359 compared to 2001. The population exposure for OA (Figure 7b) is almost the same for

360 Northeast and Mideast during 1990 and it decreased during 2001 and 2010. For the

361 Midwest, West, and Southwest the population exposure to OA remained almost

362 constant though the years. For all regions, the highest population exposure was due to

363     biomass burning and the "other" sources. In addition, 20% of the population exposure

364     was due to road transport during 1990 at the highest populated areas (NE, ME, and

365     CA), but this percentage was reduced to almost 10% during 2010.

366         The highest concentrations of sulfate for 1990 are predicted in the Eastern US

367     (NE, ME and SE) in regions downwind of the EGUs which are the dominant $SO_2$

368     source in these areas (Fig. 8a). The drastic reductions of the EGU emissions are

369     predicted to have led to major reductions in the sulfate levels in these three regions.

370     More modest, but significant reductions of sulfate are also predicted for the Midwest

371     and the Southwest. The reductions in the West and in California from the EGU source

372     are small given that the sulfate there even in the 1990s was relatively low and was

373     dominated on average by long-range transport. Regarding the population exposure for

374     NE and ME, the percentage of population exposure due to EGUs during 1990 was

375     58% for the NE and 64% for the ME, but during 2010 these percentages were reduced

376     to 44% and 53% respectively.

377         The mortality rates caused by total $PM_{2.5}$ were also calculated for the three

378     simulated periods, following the relationships of Tessum et al. (2019) and using the

379     death rates of US population by Murphy et al. (2013). We estimated 861 deaths per

380     100,000 persons for 1990, 777 for 2001, and 658 for 2010.

381

**382 4.4 Linking average changes in emissions, concentrations, and exposure**

383     The 72% reduction of emissions of EC from road transport, from 1990 to 2010

384     according to PMCAMx led to a 72% reduction of EC concentrations and a 70%

385     reduction in human exposure to EC from this source (Table 3). The changes in

386     concentrations are practically the same as those of the emissions because EC is inert

387     and the atmospheric processes that affect it (transport and removal) are close to linear.

388     The small difference between the change in emissions and that of exposure is due to

389     small differences in the spatial distributions of the EC concentrations from road

390     transport and the population density. The differences are small because most road

391     transport emissions are in densely populated areas. The similarity in the fractional

392     change of emissions and concentrations applies as expected to all EC source types

393     (Table 3). However, for all these other sources the reduction in exposure is less than

394     the reduction in emissions (or concentrations). For example, the 44% reduction of EC

395     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 3). 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. One explanation of this behavior is that the

429    simultaneous decreases in $NO_x$ levels have led to increased SOA formation yields. A

430    second factor is the time required for the formation of SOA especially when multiple

431    generations of reactions are required. The result of this time delay is SOA is often

432    produced away from its sources located in high urban density areas. The reasons for

433    this complex behavior will be analyzed in detail in future work.

434          The predicted reductions in sulfate concentrations are less than the reductions

435    in emissions due mainly to the non-linearity of the aqueous-phase conversion of $SO_2$

436    to sulfate (Seinfeld and Pandis 2016) (Table 3). Such non-linearity has been predicted

437    also in past CTM applications (Karydis et al., 2007; Tsimpidi et al., 2007). Taking

438    into account the transport of some of the sulfate from areas outside of the US, the

439    model predicts that the 64% reduction in $SO_2$ emissions has resulted in a 45%

440    reduction of the sulfate concentration on average. The reduction in exposure is a little

441    less, 40% on average, because both the major sources of $SO_2$ are located and the

442    higher reductions of sulfate take place, according to PMCAMx, away from the major

443    urban centers.

444

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

446    We have calculated the percentage of people exposed to different $PM_{2.5}$

447    concentrations from the major sources ('other', 'EGUs', 'road transport') for the three

448    different periods. Almost half of the US population was exposed to $PM_{2.5}$

449    concentrations above 20 $\mu g\ m^{-3}$ in 1990. A decade later this percentage was less than

450    20% and close to zero during 2010 (Fig. 9a). During 1990, almost 90% of the US

451    population was exposed to $PM_{2.5}$ concentrations above 10 $\mu g\ m^{-3}$, the suggested

452    annual mean by the World Health Organization (WHO, 2006). This percentage was

453    reduced to 83% in 2001 and 70% in 2010 (Fig. 9a and Fig. S2h).

454          The predicted distribution of the population exposed to $PM_{2.5}$ from the source

455    'other' in 1990 covered a wide range extending from approximately 1 to 16 $\mu g\ m^{-3}$.

456    The exposure from these sources was reduced significantly in the following years

457    mainly due to the reductions in the emissions of paved/unpaved road dust, prescribed

458    burning, and industrial emissions (Xing et al., 2013). The average emissions from

459    wildfires did not change appreciably, but this distribution was sharper in 2010, with

460    maximum percentages of people exposed appearing for $PM_{2.5}$ concentrations ranging

461 from 5 to 8 $\mu g\ m^{-3}$. The random spatial variation of biomass burning sources can
462 affect areas with different population density.

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

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

472

473 **4.6 Predicted spatial changes of concentrations**
474 We calculated the predicted changes in annual-average concentrations between 1990
475 and 2010 for the main $PM_{2.5}$ components. Figure S3 shows the reductions in EC
476 concentrations from 1990 to 2010. The reductions of the EC emissions resulted in
477 total reductions of the average concentrations of around 30% in the twenty-year
478 period. Reductions above 20% are predicted not only in the large urban areas but also
479 in large regions in both the eastern and the western US.

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

484       From 1990 to 2010, sulfate was reduced by 50-60% in the part of the country
485 to the east of the Mississippi. The corresponding reductions in the middle of the
486 country and in the western states from 1990 to 2010 were in the 20-30% range for the
487 relatively low sulfate levels in these regions (Fig. S5). These simulations suggest that
488 the Eastern US has benefited more both in an absolute and in a relative sense from
489 these reductions in $SO_2$ emissions.

490       We also compared the predicted and observed concentration changes, using
491 the Pearson's correlation coefficient and the average percentage differences,
492 summarized in Table 4. Also, as for as the exposure changes are concerned, because
493 of the way that exposure is defined (concentration times population) and the

population is measured, the evaluation metrics of our exposure predictions are exactly the same as the evaluation metrics of our concentration predictions. 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 4). 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

527 2001); 0.97, from 1990 to 2010; and 0.92, from 2001 to 2010 (Table 4). Despite the

528 nonlinearity in the behavior of sulfate, the average predicted and observed percentage

529 changes were consistent for the three comparison periods.

530 Finally, for $PM_{2.5}$ the model reproduces well the observed changes for the

531 three comparison periods with r = 0.81 (from 1990 to 2001); 0.82 (from 1990 to 2010)

532 and 0.61 (from 2001 to 2010). The average percentage changes for the observations

533 and the predictions were close for all the cases (Table 4).

534

**5. Conclusions**

536 The CTM, PMCAMx, was used to simulate the changes in source contributions to

537 $PM_{2.5}$ and its components over two decades accounting for changes in emissions and

538 meteorology with internally consistent methods. Biomass burning and 'other' sources,

539 primarily including construction processes; mining; agriculture; waste disposal, and

540 other miscellaneous sources, contributed approximately half of the total (primary and

541 secondary) $PM_{2.5}$ during the examined 20-year period. The corresponding average

542 $PM_{2.5}$ concentration levels due to this group of sources have been reduced by 33%

543 from 1990 to 2010. EGUs were the second most important source of $PM_{2.5}$; the

544 corresponding ambient $PM_{2.5}$ levels have been reduced by 55% and their contribution

545 to the total from 16% to 11%. On-road transport was the third most important source

546 of $PM_{2.5}$. The total average $PM_{2.5}$ from this source was reduced by 59%, while their

547 contribution to the average $PM_{2.5}$ levels has been reduced from 8% to 5%.

548 OA was a significant fraction of $PM_{2.5}$. Biomass burning included in the

549 'other' sources was the most important source of OA with fractional contributions

550 varying from 38% to 52% depending on the region. Biogenic SOA was the second

551 dominant component of OA with contributions ranging from 6% to 22% in the South

552 US.

553 The relationship between the changes in concentrations and changes in

554 exposure is determined by the spatial distributions of these two changes. The more

555 similar these distributions are, the closer the corresponding changes. The reduction in

556 exposure was less than the reduction in emissions (or concentrations) for sources that

557 are located away from densely populated regions (non-road transport and non-EGUs)

558 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.

Considering that the US population increased by almost 24% from 1990 to 2010, the fact that the total population exposure to PM was reduced in most areas indicates that the emission reductions were sufficient to overcome this effect. The decreases in personal exposure have been higher than these of the total population exposure.

During the 20 year-long examined period, the fraction of the US population exposed to average $PM_{2.5}$ concentrations above 20 $\mu g$ $m^{-3}$ 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 $\mu g$ $m^{-3}$). 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 16% for 1990 and 5% 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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778

779

780 **Table 1**: Evaluation metrics for annual average concentrations of PM$_{2.5}$ and for its

781 major components for each examined year.

| | MB (µg m$^{-3}$) | MAGE (µg m$^{-3}$) | NMB | NME | FBIAS | FERROR | Stations | Comment |
|---|---|---|---|---|---|---|---|---|
| **EC** | | | | | | | | |
| **1990** | -0.01 | 0.07 | -0.01 | 0.23 | 0.08 | 0.28 | 33 | Excellent [a] |
| **2001** | 0.13 | 0.18 | 0.39 | 0.56 | 0.28 | 0.39 | 122 | Good |
| **2010** | -0.05 | 0.16 | -0.11 | 0.35 | 0.06 | 0.39 | 304 | Good |
| **OA** | | | | | | | | |
| **1990** | -0.05 | 0.49 | -0.02 | 0.21 | 0.05 | 0.23 | 33 | Excellent |
| **2001** | -0.29 | 0.66 | -0.12 | 0.28 | -0.01 | 0.28 | 121 | Excellent |
| **2010** | 0.05 | 0.60 | 0.02 | 0.27 | 0.05 | 0.26 | 306 | Excellent |
| **Sulfate** | | | | | | | | |
| **1990** | 0.13 | 0.22 | 0.09 | 0.16 | 0.19 | 0.23 | 33 | Good |
| **2001** | 0.17 | 0.38 | 0.13 | 0.30 | 0.28 | 0.37 | 118 | Good |
| **2010** | 0.08 | 0.30 | 0.05 | 0.18 | 0.17 | 0.27 | 327 | Good |
| **Nitrate** | | | | | | | | |
| **1990** | -0.13 | 0.28 | -0.30 | 0.65 | -0.38 | 0.61 | 33 | Average |
| **2001** | -0.26 | 0.40 | -0.24 | 0.37 | -0.28 | 0.54 | 114 | Average |
| **2010** | -0.35 | 0.41 | -0.35 | 0.41 | -0.41 | 0.55 | 321 | Average |
| **Ammonium** | | | | | | | | |
| **1990** | -0.06 | 0.16 | -0.09 | 0.25 | 0.04 | 0.26 | 33 | Excellent |
| **2001** | -0.01 | 0.21 | 0.00 | 0.23 | 0.08 | 0.28 | 113 | Excellent |
| **2010** | 0.06 | 0.18 | 0.08 | 0.23 | 0.17 | 0.29 | 326 | Good |
| **PM$_{2.5}$** | | | | | | | | |
| **1990** | 1.04 | 1.64 | 0.16 | 0.26 | 0.16 | 0.25 | 33 | Good |
| **2001** | 0.94 | 2.92 | 0.08 | 0.24 | 0.05 | 0.24 | 1040 | Excellent |
| **2010** | 0.71 | 2.16 | 0.07 | 0.22 | 0.05 | 0.24 | 1067 | Excellent |

782

783 [a] Following Morris et al. (2005) criteria: Excellent: FBIAS ≤ ± 0.15, FERROR ≤ 0.35;

784 Good: FBIAS ≤ ± 0.30, FERROR ≤ 0.50; Average: FBIAS ≤ ± 0.60, FERROR ≤ 0.

785

786 **Table 2**: Evaluation metrics for daily average concentrations of $PM_{2.5}$ and for its
787 major components for each examined year.

| | MB ($\mu g \ m^{-3}$) | MAGE ($\mu g \ m^{-3}$) | NMB | NME | FBIAS | FERROR | Points | Comment |
|---|---|---|---|---|---|---|---|---|
| **EC** | | | | | | | | |
| **1990** | -0.03 | 0.16 | -0.11 | 0.53 | 0.14 | 0.57 | 2940 | Average [a] |
| **2001** | 0.10 | 0.27 | 0.28 | 0.71 | 0.38 | 0.62 | 18763 | Average |
| **2010** | -0.04 | 0.23 | -0.10 | 0.54 | 0.23 | 0.60 | 29423 | Average |
| **OA** | | | | | | | | |
| **1990** | -0.03 | 0.16 | -0.11 | 0.53 | 0.14 | 0.58 | 2940 | Average |
| **2001** | -0.45 | 1.37 | -0.17 | 0.53 | 0.05 | 0.55 | 18706 | Average |
| **2010** | -0.01 | 1.20 | -0.01 | 0.56 | 0.15 | 0.54 | 29412 | Average |
| **Sulfate** | | | | | | | | |
| **1990** | 0.14 | 0.62 | 0.11 | 0.47 | 0.31 | 0.53 | 3228 | Average |
| **2001** | -0.02 | 0.95 | -0.01 | 0.45 | 0.25 | 0.54 | 18077 | Average |
| **2010** | 0.18 | 0.76 | 0.12 | 0.52 | 0.34 | 0.58 | 33051 | Average |
| **Nitrate** | | | | | | | | |
| **1990** | -0.11 | 0.40 | -0.26 | 0.99 | -0.78 | 1.29 | 2998 | Problematic |
| **2001** | -0.30 | 0.81 | -0.31 | 0.83 | -0.62 | 1.11 | 18019 | Problematic |
| **2010** | -0.33 | 0.66 | -0.34 | 0.68 | -0.74 | 1.13 | 30867 | Problematic |
| **Ammonium** | | | | | | | | |
| **1990** | -0.05 | 0.30 | -0.09 | 0.48 | 0.14 | 0.52 | 2996 | Average |
| **2001** | -0.03 | 0.49 | -0.03 | 0.54 | 0.24 | 0.58 | 17828 | Average |
| **2010** | 0.05 | 0.39 | 0.08 | 0.54 | 0.33 | 0.60 | 30162 | Average |
| **$PM_{2.5}$** | | | | | | | | |
| **1990** | 0.74 | 2.73 | 0.13 | 0.50 | 0.16 | 0.46 | 2706 | Good |
| **2001** | 1.27 | 5.43 | 0.11 | 0.46 | 0.13 | 0.44 | 161909 | Good |
| **2010** | -0.02 | 4.33 | 0.00 | 0.45 | 0.03 | 0.47 | 212899 | Good |

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789 [a] Following Morris et al. (2005) criteria: Good: FBIAS ≤ ± 0.30, FERROR ≤ 0.50;
790 Average: FBIAS ≤ ± 0.60, FERROR ≤ 0.75; Problematic: FBIAS > ± 0.60, FERROR
791 > 0.75

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794 **Table 3**: Percentage changes in emissions from each source, and corresponding

795 changes in average concentrations and exposure from 1990 to 2010.

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| | 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 |

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806 **Table 4**: Average observed and predicted PM percentage changes, and Pearson's

807 correlation coefficient calculated for each comparison case.

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| | 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 |

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811  [a] 14 CSN sites reporting increases of EC, probably due to the change in the

812 measurement protocol in the 2007-09 period, have been excluded from this analysis.

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

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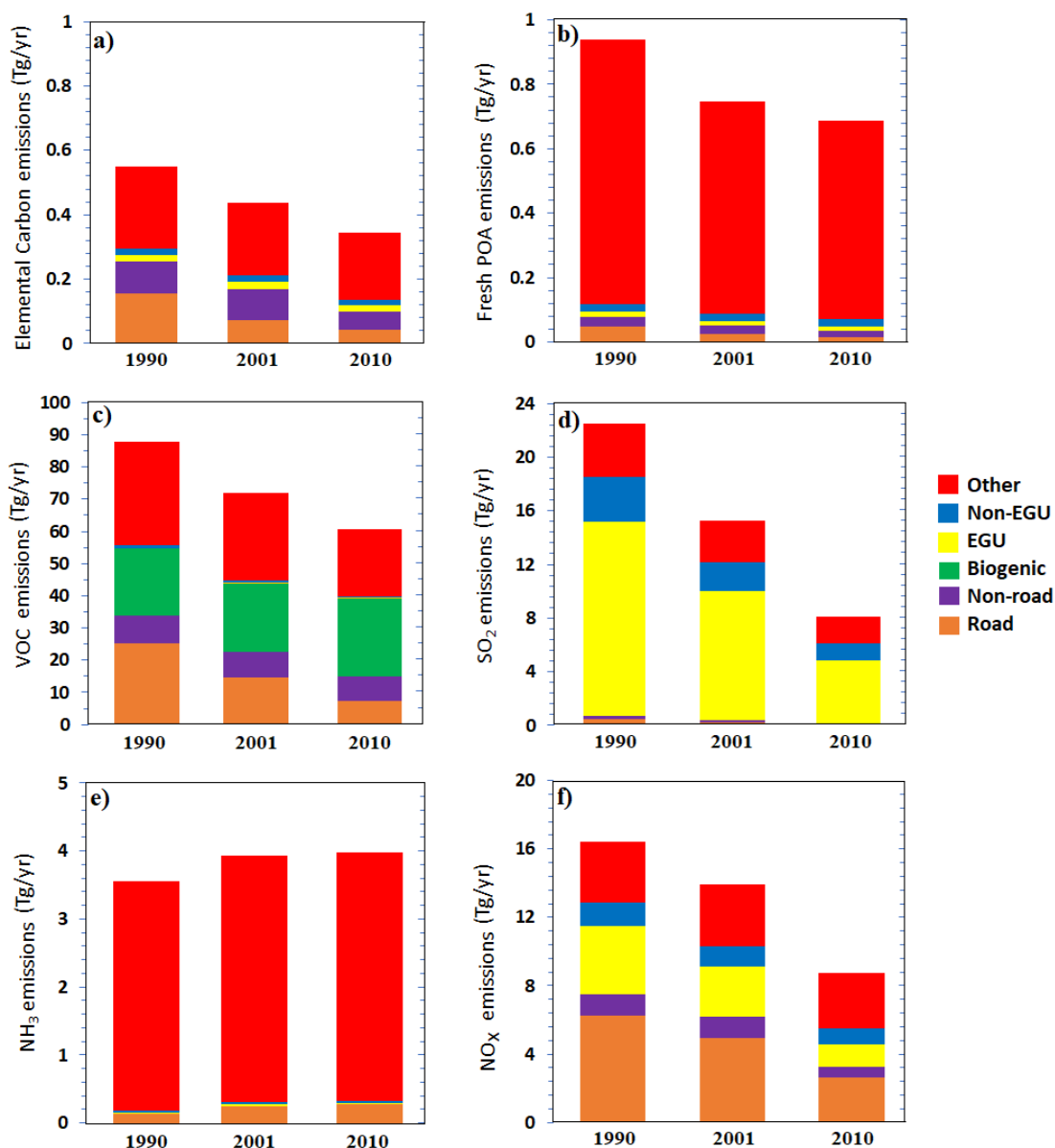
819 **Figure 1**: Annual emissions by each source for the whole domain for: a) elemental

820 carbon, b) fresh POA, c) non-methane VOCs, d) $SO_2$, e) $NH_3$, and f) $NO_x$.

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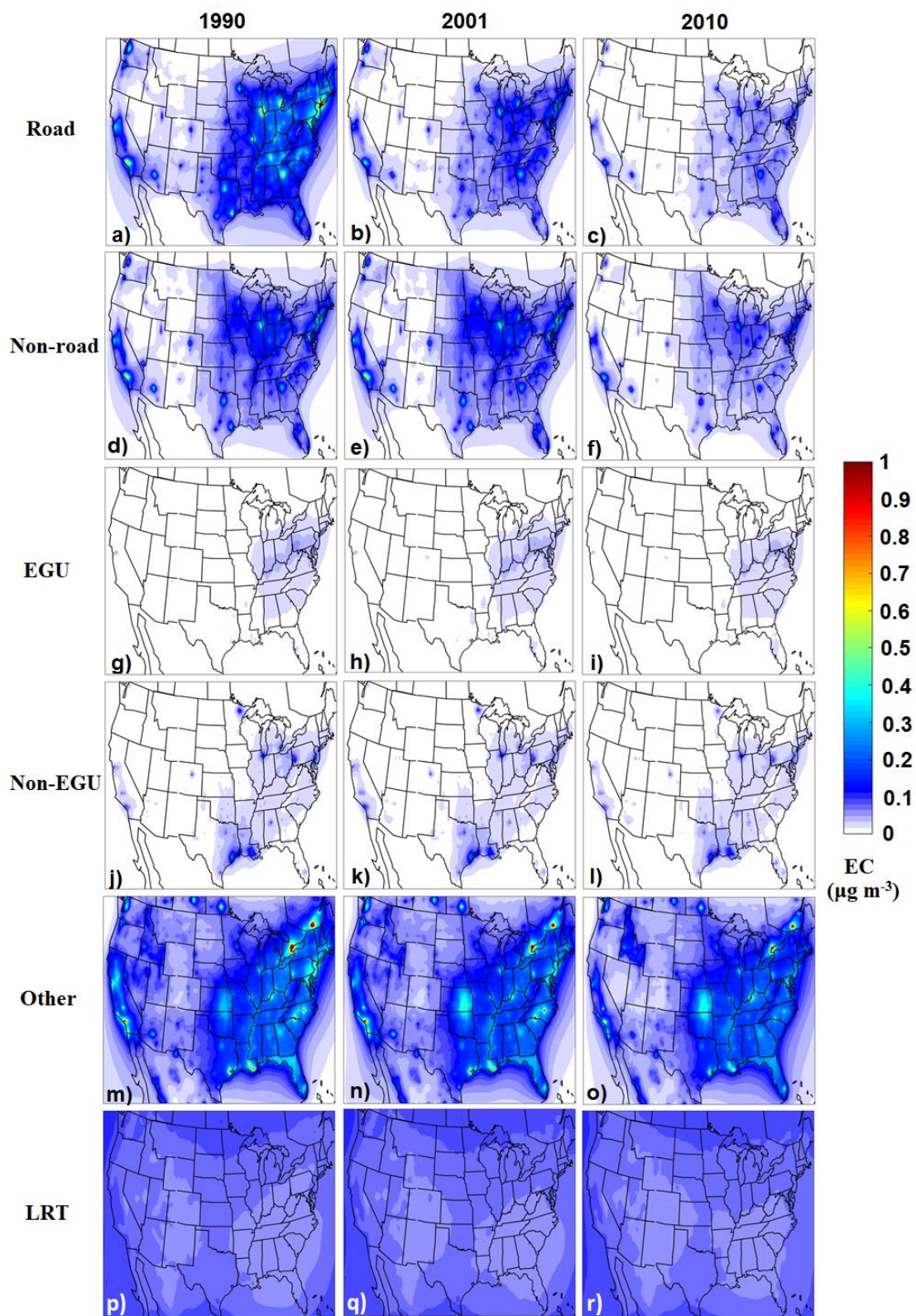
829 **Figure 2:** Predicted annual average ground level PM$_{2.5}$ elemental carbon

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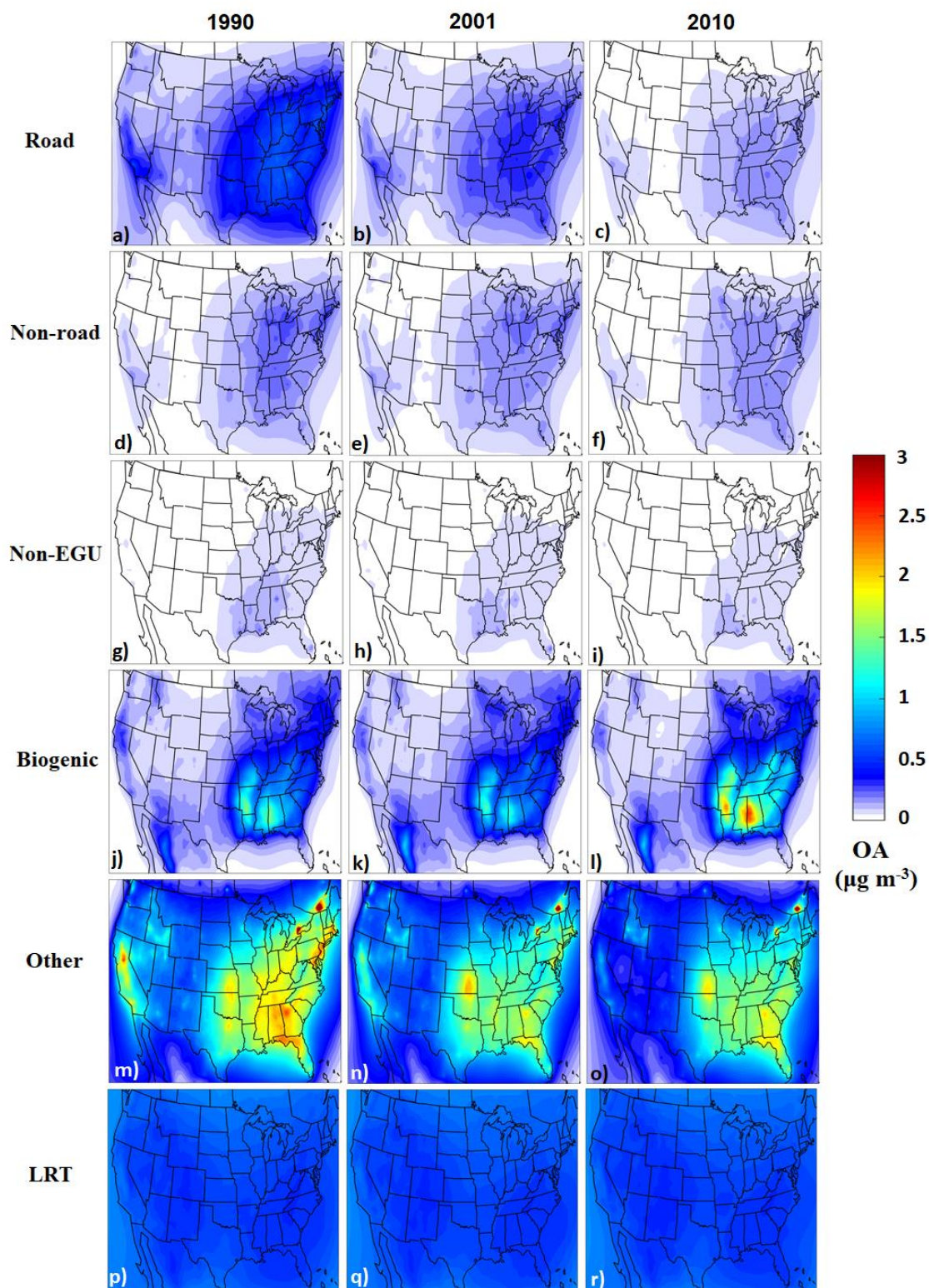
**Figure 3:** Predicted annual average ground level PM$_{2.5}$ organic (primary plus secondary) aerosol concentrations per source for 1990, 2001, and 2010. The EGU contributions are low and are not shown.

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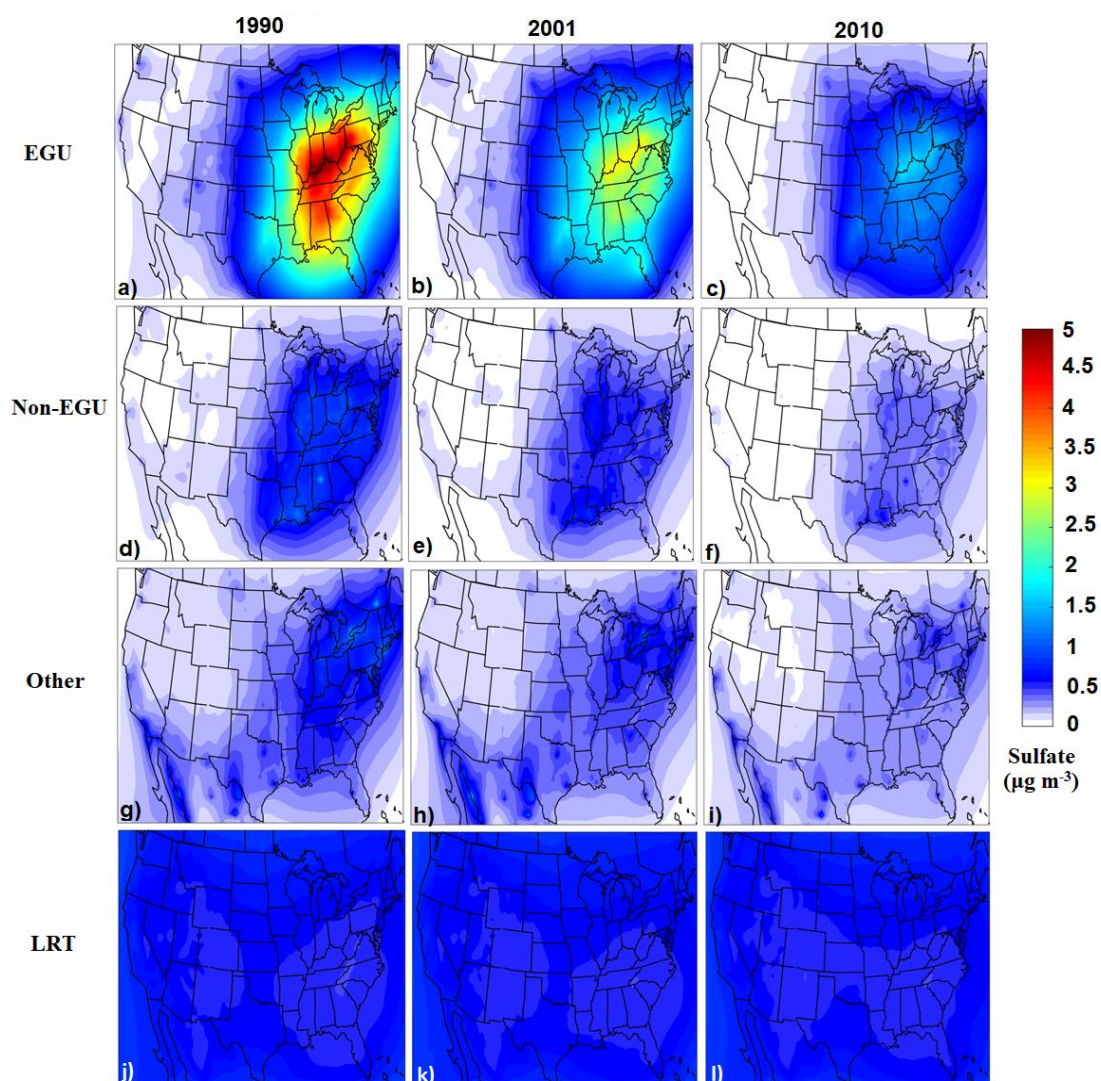
**Figure 4:** Predicted annual average ground level PM$_{2.5}$ sulfate concentrations per source for 1990, 2001, and 2010. The on-road, non-road, and biogenic contributions are low and are not shown.

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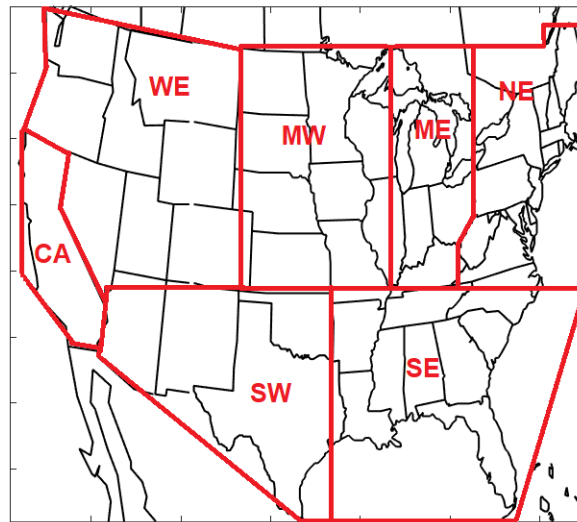
**Figure 5:** Definition of the 7 regions used in the analysis.
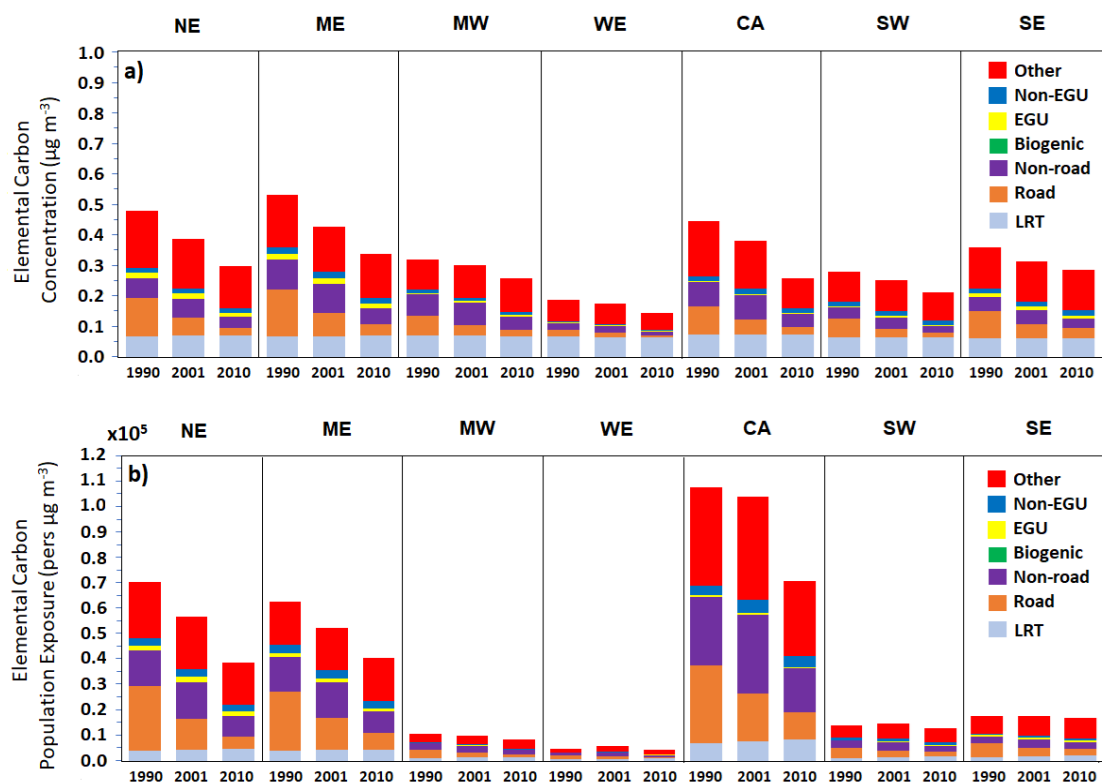
**Figure 6:** Sources of PM$_{2.5}$ EC for the different regions during 1990, 2001, and 2010 for: a) average concentrations (μg m$^{-3}$) and b) population exposure (persons μg m$^{-3}$).
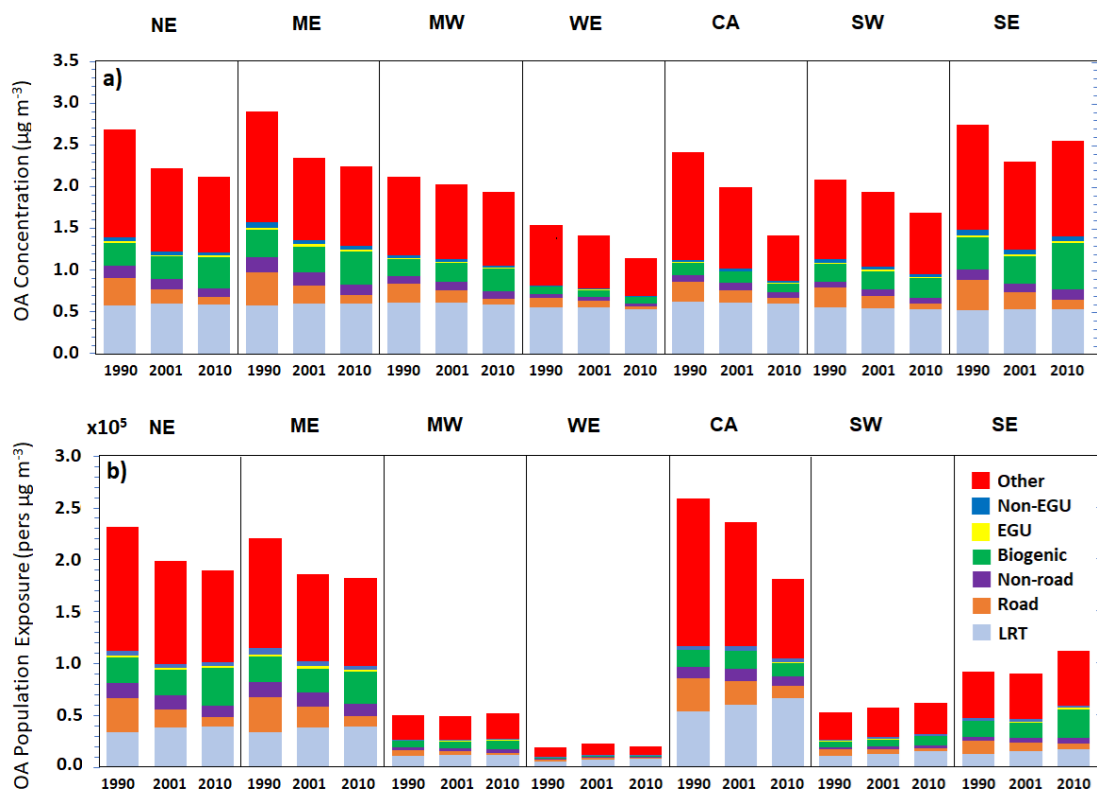
**Figure 7**: Sources of PM$_{2.5}$ OA for the different regions during 1990, 2001, and 2010 for: a) average concentrations (μg m$^{-3}$) and b) population exposure (persons μg m$^{-3}$).

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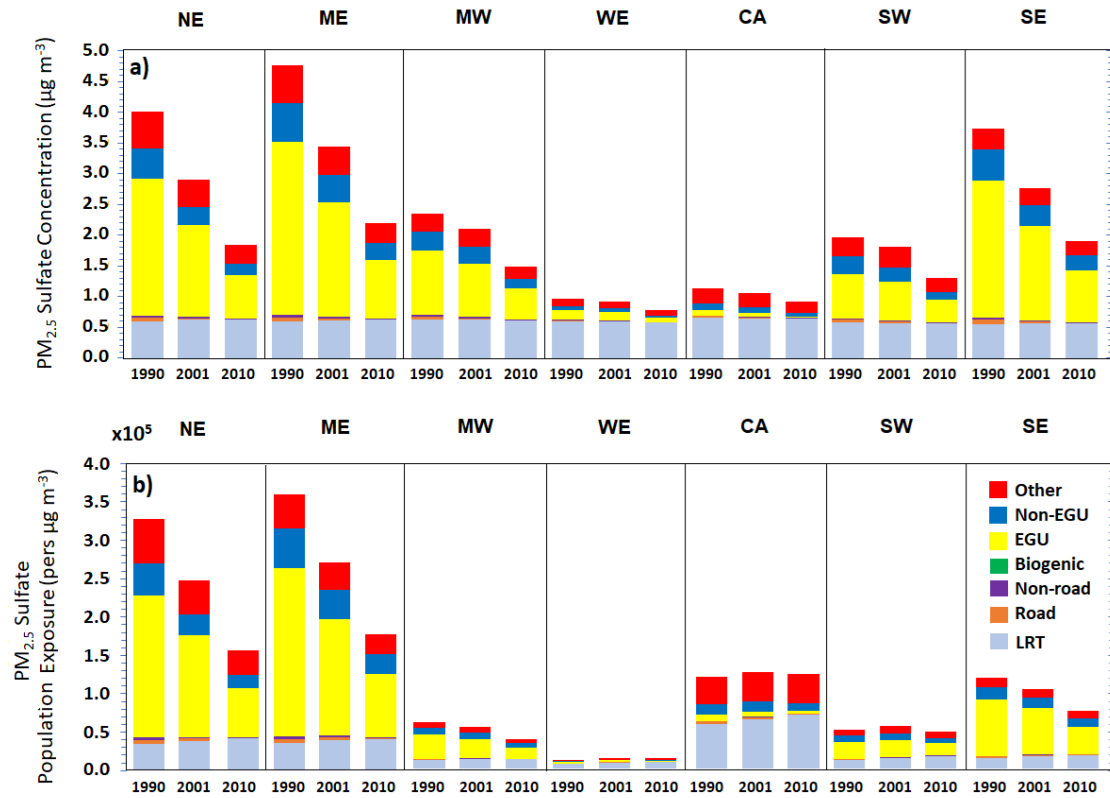
**Figure 8**: Sources of PM2.5 sulfate for the different regions during 1990, 2001, and 2010 for: a) average concentrations (μg m⁻³) and b) population exposure (persons μg m⁻³).

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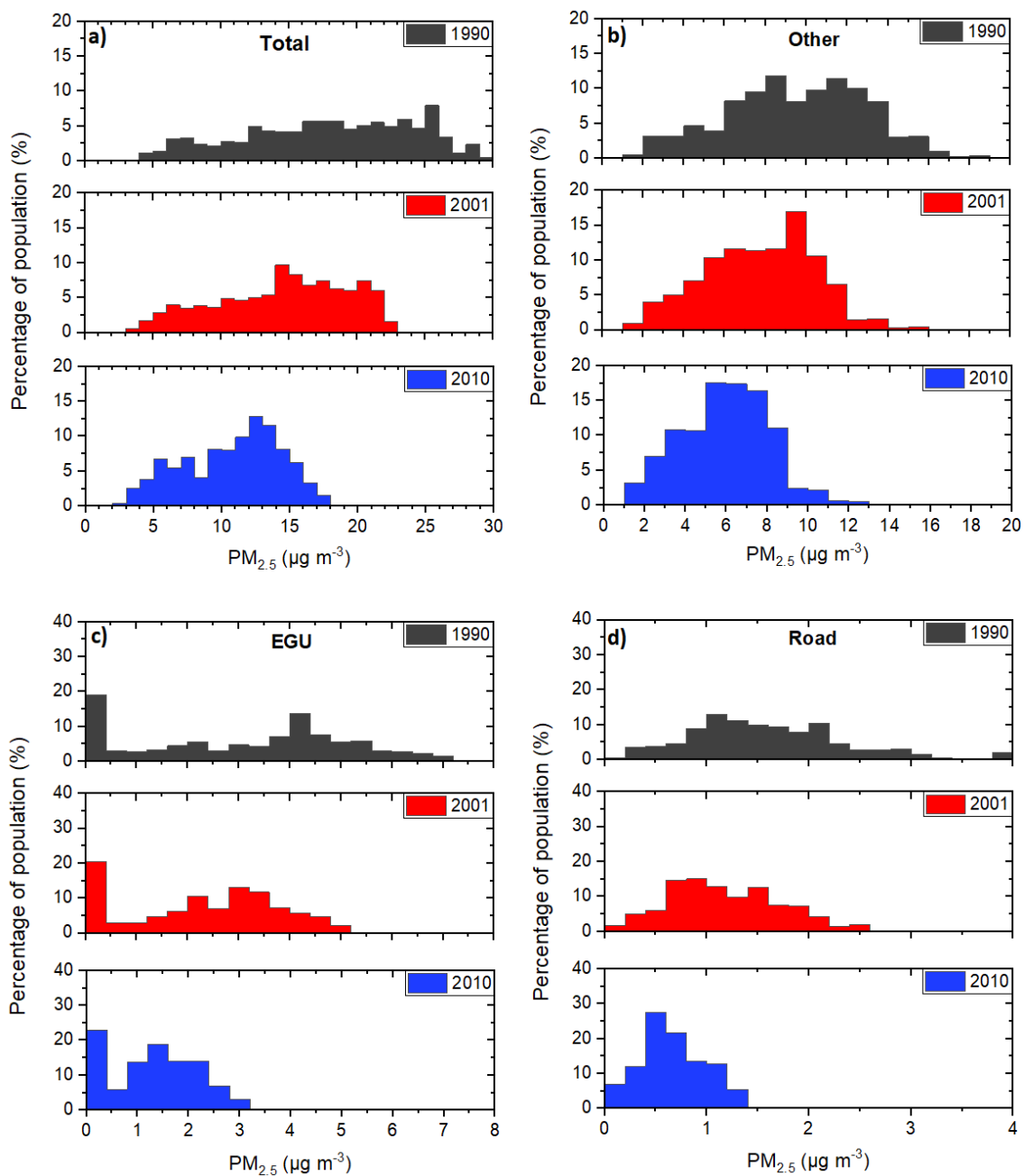
**Figure 9:** Distributions of population exposed to annual average PM$_{2.5}$ during 1990 (grey), 2001 (red), 2010 (blue); and for the dominant sources of PM$_{2.5}$: a) road transport, b) EGU, c) other, and h) total PM$_{2.5}$.

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