Source Apportionment of Diesel Particulate Matter in the Southeastern United States Using Models3/CMAQ

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ABSTRACT

Source apportionment of fine particulate matter is important to identify the sources that are responsible for the ambient concentrations observed in a particular area. The fine and ultra fine sizes of diesel particulate matter (DPM) are of greatest health concern, which significantly contributes to the overall cancer risk from air toxics. The composition of these fine and ultra fine particles is composed principally by elemental carbon (EC) with adsorbed compounds such as VOCs, sulfate, nitrate, ammonia, metals, and other trace elements. So far, EC has been used as a marker for DPM in the environment, which can be modeled temporally and spatially over an urban to a regional area. The purpose of this project was to use EPA's Models3/CMAQ version 4.3 to predict aerosol concentrations and the source apportionment of primary and secondary aerosols that come from diesel-fueled sources (DFS) with a focus on EC in the South East US by linking the MM5v3 meteorological model, the Sparse Matrix Operator Kernel Emissions (SMOKE 2.0) model, and Mobile6.2. The national emissions inventory version 3 for the year 1999 (NEI99) was used in this analysis. The modeling domain consisted of a 36 km domain. Five urban areas and one rural area were selected in the domain to compare the main results. A severe southeast ozone episode between August and September 1999 was used as a reference. For emissions, results showed that DFS contributed by (73.7 % ± 12.6) of EC, (15.2 % ± 8.3) of organic aerosols, (12.9 % ± 6.5) of nitrate, and (7.7 % ± 6.1) of sulfate during the selected episode, where the highest contribution of EC was allocated in Memphis TN. On the other hand, for ambient concentrations, DFS contributed by (69.5% ± 6.5) of EC, (19.4% ± 11.2) of nitrate, (10.8 % ± 2.4) of primary anthropogenic organic aerosols, (8.9% ± 1.5) of total organic aerosols, (7.1% ± 1.1) of secondary anthropogenic organic aerosols, (6.9 % ± 1.3) of ammonia, (5.8% ± 0.9) of sulfate (4.4% ± 1.2) of secondary biogenic organic aerosols, and (0.08% ± 0.01) of crustal, where the highest contribution of EC due to DFS was allocated in Nashville TN. The rural site (Warren County TN) performed the smaller EC contribution of DFS. The maximum primary DPM concentrations occurred in Atlanta, Memphis, and Nashville, which were 3.8, 2.6, and 2.3 times higher than those from the rural area Warren County TN respectively. Our results indicate significant geographic variability in the EC contribution from DFS. The contribution over the secondary DPM aerosols was uncertain mainly over nitrate and sulfate species.

INTRODUCTION

Diesel exhaust is emitted from a broad range of diesel engines; the on road diesel engines of trucks, buses, and cars and the off road diesel engines that include locomotives, marine vessels, and heavy duty equipment [1]. DPM is part of a complex mixture. The sizes of diesel particulates, which are of greatest health concern, are in the categories of fine, and ultra fine particles. The mixture of these fine and ultra fine particles is composed of elemental carbon (EC) with adsorbed compounds such as organic carbon (OC), sulfate, nitrate, metals, and other trace elements [2]. The elemental fraction stems from fuel droplet pyrolysis, while the organic fraction originates from unburned fuel, lubricating oil, and combustion byproducts [3]. Many carcinogenic and mutagenic compounds have been measured in the organic fraction of DPM. A diesel particle initially consists of an agglomeration of EC spheres coated with organic and inorganic compounds that are adsorbed or absorbed at the surface of this agglomerate. Diesel particles lose their identity rapidly as they coagulate with other particles and act as condensation sites for secondary aerosol species [4]. The DPM composition is variable, which typically has a composition of 25-60% of EC [5], with estimates ranging from 5 to 90% [6], and 20-50% of OC of total mass [7]. Sulfate and nitrate may account for up to 12% and 4%, respectively, of total mass [7].

Increased mortality and morbidity in communities with elevated DPM concentrations has been reported by a variety of studies [8, 9, and 10]. Adverse effects also are observed when breathing airborne particles in controlled acute human exposure studies, including cough, respiratory symptoms of asthmatics, and reduced lung function. According to the Clean Air Task Force, in its modeling study over the 1999 National Emissions Inventory Version 3 (NEI99) [8]**,** diesel exhaust poses a cancer risk that is 7.5 times higher than the combined total cancer risk from all other air toxics in the whole nation. Fine particle pollution from diesels shortens the lives of nearly 21,000 people each year. This includes almost 3,000 early deaths from lung cancer. Finally, this study indicated that tens of thousands of Americans suffer each year from asthma attacks (over 400,000), heart attacks (27,000), and respiratory problems associated with fine particles from diesel vehicles [8]. These illnesses result in thousands of emergency room visits, hospitalizations, and lost work days. This important report did not estimate secondary formation of PM that may occur from gaseous diesel exhaust, such as sulfur or nitrogen compounds; instead, it used directly-emitted DPM.

Since DPM is the major source of EC in the atmosphere [10]. This has led to the use of EC as a marker for assessing human exposure to diesel exhaust, for determining the contribution of diesel engines to ambient particulate concentrations, and as a surrogate for DPM [3, 11, 12, and 13]. The ability to accurately use EC as a tracer for DPM in either the environmental or occupational setting critically relies on a clear understanding of relative contributions of other sources to EC concentrations, however, it approximation generates important uncertainty, since those studies used an average EC contribution to come up the DPM concentration in any place between 50 and 80%. In addition, EC is not a unique tracer for ambient DPM and efforts to utilize EC as an indicator of DPM must properly address other sources of EC as well as utilize a consistent measurement

technique for EC when comparing source and ambient EC measurements to avoid significant biases.

In order to better manage air quality, it is important to know the sources or source categories that contribute to the concentrations of DPM at a particular area or receptor. Although receptor models have been used to do PM2.5 source apportionment, they do not fully take into account the chemical reactions involved in the formation of secondary fine particles [14] and so far there is not an available method to measure ambient DPM. Diesel on-road sources are believed to be a major contributor to fine particles. It has been shown that transportation related sources dominate the size distribution of ambient PM in the South Coast Air Basin [15].

This report estimates the source apportionment on PM2.5 emissions and concentrations of eliminating diesel emissions in 1999. The uncertainty to use EC as a tracer was reduced in the present research, since EC and DPM were estimated eliminating diesel-fueled sources and modeled temporally and spatially over an urban to a regional area using an advanced air quality model to predict emissions, aerosol concentrations, and the source apportionment of primary and secondary aerosols that come from DFS with a focus on EC in the South East US by linking the MM5v3 meteorological model for the following urban and rural areas: Atlanta GA, Nashville TN, Knoxville TN, Memphis TN, Birmingham AL, and Warren County TN. The national emissions inventory version 3 for the year 1999 (NEI99) was used in this analysis

APROACH

In our study, diesel aerosols were predicted using the advanced air quality model Community Multi-scale Air Quality (CMAQ) version 4.3 and the emissions were temporal and spatially allocated using the advanced emissions model Sparse Matrix Operator Kernel Emissions (SMOKE) Modeling System version 2.0 over the NEI99. The chosen episode was August 27th to September 9th, 1999. This episode was one of the worst ozone episodes that occurred in the southeast U.S. between 1997 and 2000, and has also been chosen as one of the episodes to be modeled for non-attainment purposes in the Arkansas, Tennessee, and Mississippi Ozone Study (ATMOS). The modeling domain consisted of a nested 36 km domain.

Inventory Development

Point Source Inventory. The criteria pollutants point source inventory for the state of TN was developed by the research group at the University of Tennessee, Knoxville (UTK). This is an outcome of the ongoing contract with the Tennessee Department of Environment and Conservation (TDEC). For other states in the domain, the NEI99 version 3.0 was used. The emission inventory was carefully checked for errors and corrected, particularly, the SO_2 emissions for plants in Ohio (OH) and PM emissions for two plants in Georgia (GA). For electric utility plants, data from the continuous emissions monitoring systems (CEMS) were used. The corrected emission inventory was used for this study.

Area Source Inventory. The 1999 NEI version 2.0 data was used for all area sources in the domain for criteria pollutants. Since ammonia emissions play an important role in secondary formation of PM, they were estimated for the state of TN [16] and were used in preference to the ammonia emissions in the NEI database for TN. Fugitive particulate emissions from paved roads in TN were estimated based on the latest version of guidance released at that time [17]. Vehicle weight was needed to estimate fugitive particulate emissions from roads. Data from an interstate truck weight station was used to estimate the distribution of truck weights. Loaded vehicle weights (LVW) for heavy-duty trucks were found to be ~70% of the high end Gross Vehicle Weight Rating (GVWR). This percentage was applied to other vehicle categories as well. An average loaded weight of 2 tons was used for light duty vehicles. Silt loadings recommended in the document for "Normal Conditions" were used. High average daily traffic (ADT) conditions were assumed for Interstate and Arterial roadway classifications and low ADT conditions were assumed for Collector and Local roadway classifications.

On-Road Source Inventory. The 1999 criteria pollutants on-road mobile source inventory for the state of TN was estimated using the latest version of the mobile source emission factor model available at the time of preparation of the inventory. MOBILE6 was used to estimate emissions of NO_x, VOC and CO. Emissions were estimated for each county based on locality specific inputs. The emission factors were multiplied by daily vehicle miles traveled to obtain typical summer day emission rates. More information is available elsewhere [18]. The draft version of MOBILE6.2 was used to estimate emissions of PM_{10}, $PM_{2.5}$, SO_2 and NH_3. The gasoline sulfur content was set to default values in the model. The diesel sulfur content for 1999 was set to be 500 ppm. The on-road mobile source emissions for other states were based on the 1996 National Emissions Trends (NET96) database, adjusted to a 1999 MOBILE6 based emission inventory. The NET96 emissions for each state was multiplied by the ratio

$$\mathrm{R1} = \frac{1999\,Tier-I\,On-Road\,Mobile\,Source\,Emissions}{NET96\,Emissions}$$

The Tier-I on-road mobile source emissions were those published on the U.S.EPA air data website (http://www.epa.gov/air/data/). The results from this step consisted of a 1996 inventory adjusted to 1999 accounting for the state specific growth rate and any emission controls modeled by MOBILE5b. The next step was to convert from MOBILE5b based emissions to MOBILE6 based emissions. This was done using the ratio:

$$\mathrm{R2} = \frac{TN\,MOBILE6\,Emissions\,estimated\,by\,UTK}{1999\,TN\,Tier-I\,On-Road\,Mobile\,Source\,Emissions}$$

and applying ratio R2 to all the other states to convert to a MOBILE6 based 1999 emission inventory. On the other hand, the 1999 NEI air toxics draft version 3.0 was used for all states in the domain, without any adjustment.

Biogenic Inventory. This inventory was created using BEIS 3.09 version, base on land use and meteorological data.

SMOKE2.0 Model Runs

The methodology consisted of running the SMOKE2.0 model with and without the DFS. The base case run consisted of a run with all sources included. The scenario without the DFS was estimated through a control matrix for each source; point, area, and mobile source. The difference between the base case scenario (BC) and the "without DFS" WODFS were the DPM emissions. Once the base case run was completed, the model results were plotted in order to determine the contribution of each DFS for each area analyzed on the modeling domain.

Inventory speciation. The criteria emission inventory typically includes emissions of NO_x, VOC, CO, NH_3, SO_2, PM_{10} and $PM_{2.5}$ and the air toxics inventory includes 188 species. The VOC classification is an umbrella for all organic compounds in the criteria pollutants inventory, therefore, it is important avoid double counting when those inventories are merged. Similarly, NO_x is the sum of NO and NO_2 emissions in the criteria pollutants inventory. These aggregate emissions need to be broken down into the constituent species for the model to process them appropriately in the chemical reactions. The Carbon Bond IV Air Toxics Version 1.0 (CB4tx1) chemical mechanism was used in SMOKE 2.0 to develop the emission inventory. Since the chemical mechanism requires input of total organic gases (TOG), the VOC emissions in the inventory that are representative of reactive organic gases (ROG), were converted to TOG by using the default conversion factors in the SMOKE model.

Spatial allocation of emissions. County-based emissions were allocated to each grid cell (spatial allocation) based on the spatial surrogates. Spatial surrogates represent the percentage of emissions from each county that are allocated to each grid. Spatial surrogates were developed for the domain using USEPA's SMOKE Tool. For emissions from on-road mobile sources on interstates (within TN), spatial surrogates for gridding were developed. The miles of interstate highways that fell within each grid, within each county were determined and multiplied times the average daily traffic volume. The yielded vehicle miles traveled (VMT) on interstates for each grid. Using that data, the fraction of VMT in each grid in each county was determined. These values were used as spatial surrogates to apportion county-based interstate emissions to each grid. These spatial surrogates were used instead of the surrogates generated by SMOKE Tool for on-road mobile source emissions on interstates in TN. This enabled more accurate apportioning of emissions to each grid cell (within TN) based on vehicle miles traveled (VMT) rather than lane miles as used in SMOKE Tool.

Temporal processing. The emissions in the inventory were annual emissions in tons/year. These were converted to hourly emissions by use of appropriate profiles within the SMOKE model. The temporal profiles describe the variation in emissions as function of time-period for each source category. Profiles are available for month of the year, day of the week and hour of the day periods.

The final processed inventory contained hourly emissions for each grid cell in the domain. This was used as input to the CMAQ model.

Episode and Modeling Domain The episode that was chosen for the purpose of modeling was August 27th to September 9th, 1999. This episode was one of the worst ozone episodes that occurred in the Southeast U.S. between 1997 and 2000, and has also been chosen as one of the episodes to be modeled for non-attainment purposes in the Arkansas, Tennessee, and Mississippi Ozone Study (ATMOS). The modeling domain consisted of a nested 36 km domain, whose grid size was selected due to the available EC monitoring concentrations in the region. Figure 1 gives a general idea of the region that is covered by the domain.

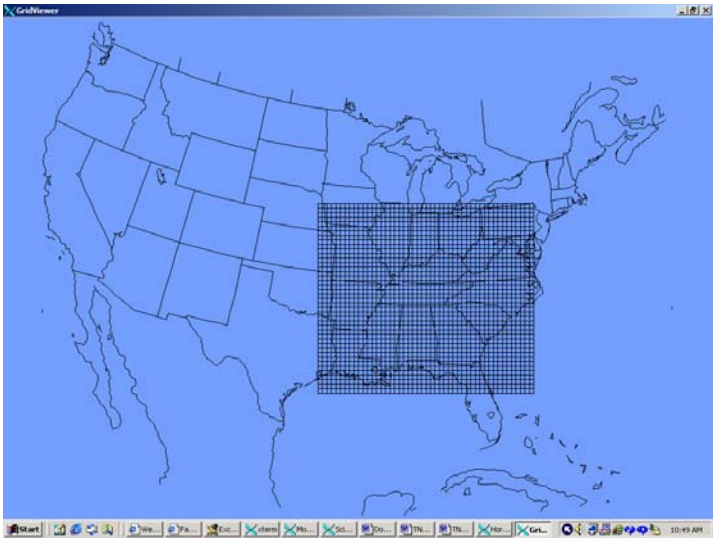

Figure 136 km Grid Resolution Domain

CMAQ Model Runs

The inventory processing resulted in hourly speciated emissions for each grid cell. Speciation of emissions was done according to the carbon bond IV (CB-IV) mechanism. Version 4.3 of the CMAQ model was used for the model runs. The meteorology inputs were processed by the meteorology-chemistry interface processor (MCIP) version 2. The methodology consisted of running the CMAQ model with and without the diesel fueled emissions. The base case run consisted of a run with all sources included. The scenario without the DFS was estimated from the emissions of the SMOKE2.0's WODFS scenario. The difference between the BC and the WODFS scenarios were the diesel primary and secondary aerosols. The default set of boundary and initial conditions

available in CMAQ was used for the 36 km domain run. Since the first day of the episode under consideration is August 30th, 1999, the model runs were set to start three days earlier (August 27, 1999) to allow for the "spin-up" period. This is to avoid the influence of the initial conditions on the model results.

Once the base case run was completed, the model results were compared to the monitoring data for EC and $PM_{2.5}$. As the model performed reasonably well, the specific scenario was modeled. In order to determine the contribution of diesel-fueled sources, the CMAQ run was conducted without diesel-fueled source emissions.

RESULTS AND DISCUSSION

Emissions

According to SMOKE 2.0 outputs, the maximum PM2.5, NOx, and SO2 emissions occurred in Atlanta, which were 15.6, 26.3, and 15.9 times respectively higher than those from the rural area Warren County TN on the studied episode (Figure 2), however, NH3 emissions in Atlanta were 40% less than those from the rural county. The highest ammonia emissions occurred in Nashville TN, which were 3.5 times higher than the smallest emissions occurred in Birmingham AL. The ammonia emissions in Nashville are contributed mainly for area sources. NOx emissions were significantly high in the metropolitan areas of Atlanta GA, Memphis TN, and Nashville TN, where the mobile sources have a significant NOx contribution [19].

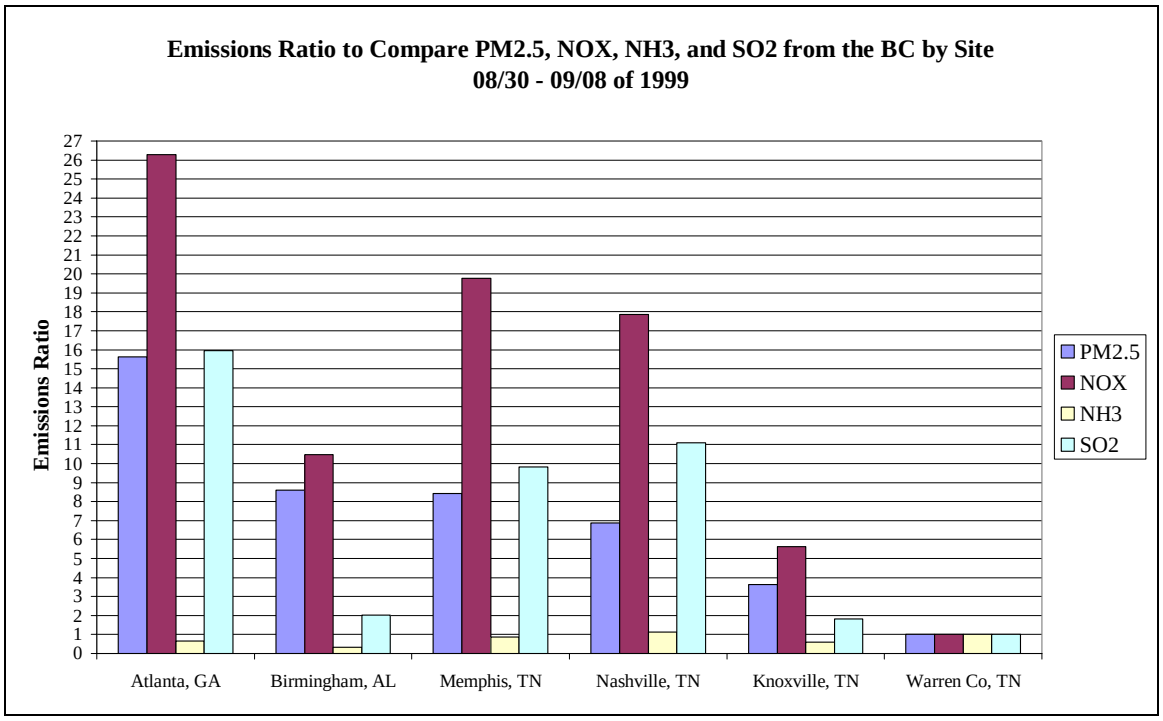

Figure 2 Emissions Ratio to Compare PM2.5, NOx, NH3, and SO2 from the BC by Site

On the other hand, NOx emissions from Nashville, Memphis, and Atlanta had higher contribution over the total analyzed criteria emission (Table 1) than the other sites, which also indicates that DFS could have a bigger contribution at those metropolitan areas and important DPM concentrations over those cities. According to Table 1, it is clear that PM2.5 is the biggest contributor over the total analyzed criteria pollutants, which in average accounted by 87.2%.

Table 1. PM2.5, NOx, NH_3, and SO_2 Emissions Distribution for the BC scenario

Site	PM2.5	NOX	NH3	SO2
Atlanta, GA	90.0%	8.1%	0.6%	1.2%
Nashville, TN	84.1%	11.7%	2.4%	1.8%
Knoxville, TN	89.4%	7.4%	2.6%	0.6%
Memphis, TN	86.2%	10.8%	1.6%	1.4%
Birmingham, AL	93.0%	6.1%	0.6%	0.3%
Warren Co, TN	80.6%	4.3%	14.0%	1.1%

According to Figure 3, the maximum PM2.5, NH3, and SO2 DFS emissions occurred in Atlanta, which were 40.1, 41.2, and 38.7 times higher respectively than those from the rural area Warren County TN on the studied episode. However, NOX DFS emissions in Atlanta were not as high as those from Memphis and Nashville. This difference can be explained since in Memphis the off-road DFS contribute with more emissions than on-road DFS, whereas in Atlanta on-road DFS contribute with more emissions then off-road DFS sources [20]. In addition, speed limits on urban interstates in all TN is 70 MPH instead of 65 in AL and GA, which could be the main answer why NOX DFS emissions were higher over those areas. Finally, Knoxville presented higher NOX DFS emissions than Birmingham, although, PM2.5, NH3, and SO2 were higher in Birmingham than Knoxville.

The NOx DFS emissions from Nashville, Memphis, and Knoxville, even Warren County had higher contribution over the total analyzed criteria emission (Table 2) than the other sites, which also indicates that the off-road DFS and truck speed could be important factors for those NOx emissions as indicated in [19 and 20]. Finally, it is clear that PM2.5 is the biggest contributor over the total analyzed DFS criteria pollutants, which in average accounted by 69.2%. Atlanta and Birmingham showed the highest PM2.5 contribution over the total analyzed DFS criteria pollutants. NH3 and SO2 were not significant contributors over the total analyzed DFS criteria pollutants for all sites.

Table 2. PM2.5, NOx, NH_3, and SO_2 Emissions Distribution for DFS

Site	PM2.5	NOX	NH3	SO2
Atlanta, GA	84.3%	14.3%	0.1%	1.3%
Nashville, TN	58.8%	40.1%	0.1%	1.0%
Knoxville, TN	57.0%	42.0%	0.1%	0.9%
Memphis, TN	64.3%	34.5%	0.1%	1.2%
Birmingham, AL	82.2%	16.6%	0.1%	1.2%
Warren Co, TN	69.0%	29.8%	0.1%	1.1%

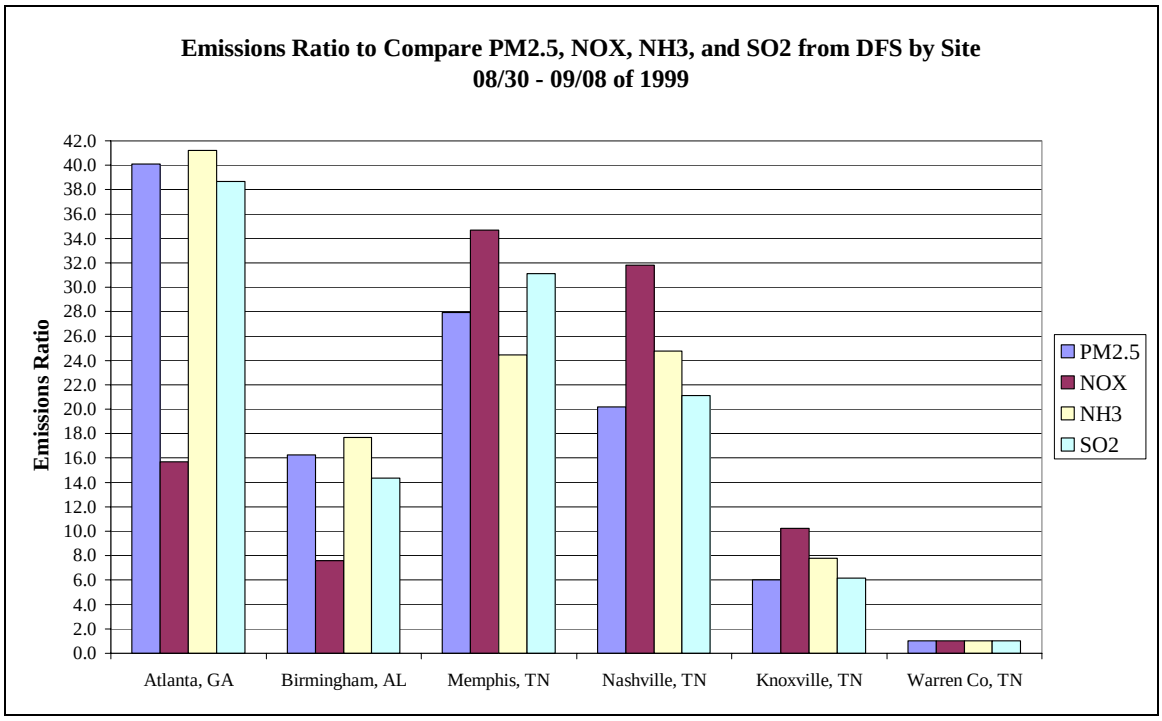

Figure 3 Emissions Ratio to Compare PM2.5, NOx, NH3, and SO2 from DFS by Site

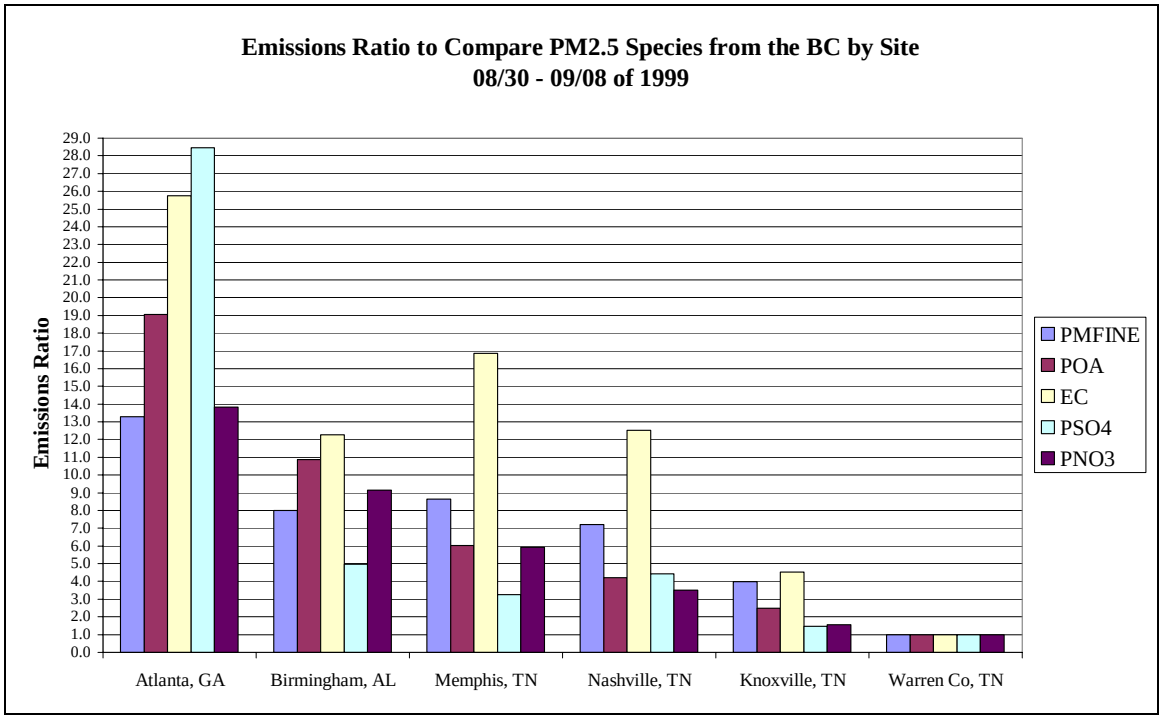

Figure 4 Emissions Ratio to Compare PM2.5 species from the BC by Site

SMOKE2.0 generates five PM2.5 species; fine particulate matter (PMFINE), primary organic aerosols (POA), elemental carbon EC, Primary sulfates (PSO4), and primary

nitrates (PNO3). The maximum PMFINE, POA, EC, PSO4, and PNO3 emissions occurred in Atlanta, which were 13.3, 19.0, 25.8, 28.5, and 13.8 times higher than those from the rural area Warren County TN respectively on the studied episode (Figure 4). EC emissions were significantly high in Memphis and Nashville TN also, which were 16.9 and 12.5 times higher than the rural area respectively, which indicates that diesel mobile sources have a significant contribution in Atlanta, Memphis, and Nashville.

In fact, EC emissions from Atlanta, Memphis, and Nashville had higher contributions over the total analyzed criteria emission (Table 3) than the other sites, accounting by 9.4, 10.3, and 11.4% respectively. This evidence indicates important DPM concentrations over those cities. Finally, according to Table 3, it is clear that PMFINE is the biggest contributor over the total analyzed PM2.5 speciation, which in average accounted by 72.2%.

Table 3. Speciation of Total PM2.5 Emissions on the BC scenario

Site	PMFINE	POA	EC	PSO4	PNO3
Atlanta, GA	62.1%	20.9%	9.4%	7.5%	0.2%
Nashville, TN	76.4%	10.5%	10.3%	2.7%	0.1%
Knoxville, TN	79.6%	11.6%	7.0%	1.7%	0.1%
Memphis, TN	74.7%	12.3%	11.4%	1.6%	0.1%
Birmingham, AL	67.7%	21.6%	8.1%	2.4%	0.2%
Warren Co, TN	72.9%	17.1%	5.7%	4.1%	0.2%

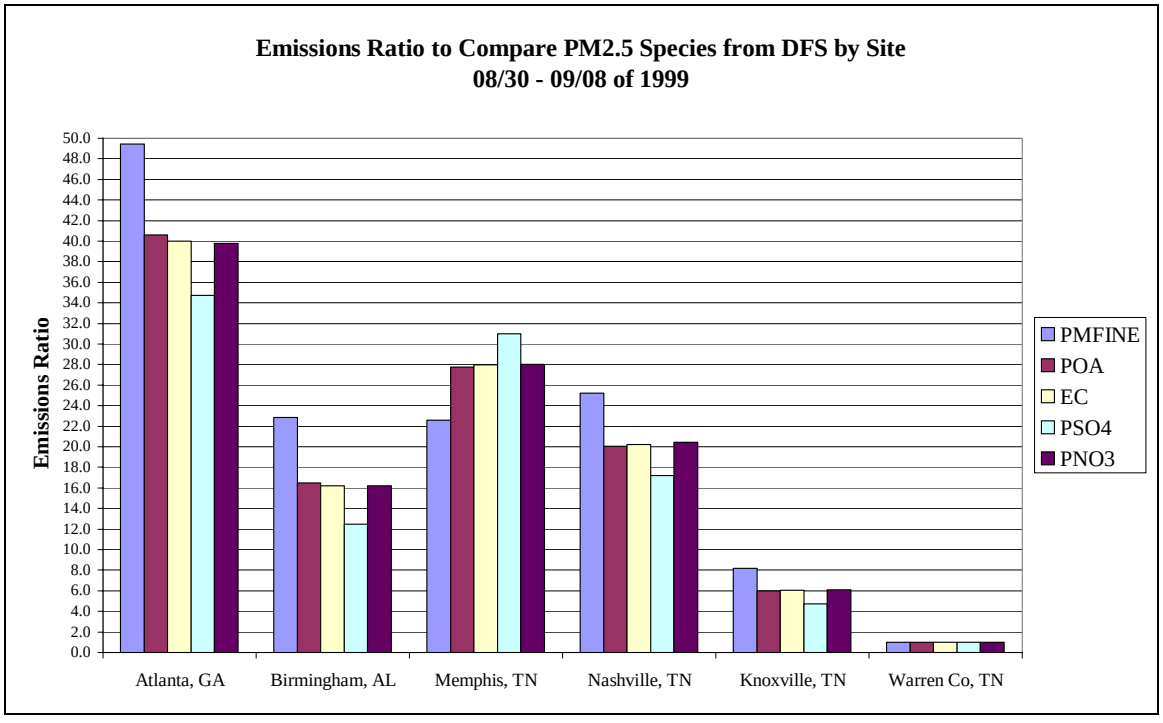

Figure 5 Emissions Ratio to Compare PM2.5 species from DFS by Site

According to Figure 5, the maximum PMFINE, POA, EC, PSO4, and PNO3 DFS emissions occurred in Atlanta, which were 49.5, 40.6, 40.0, 34.8, and 39.8 times higher than those from the rural area Warren County TN respectively on the studied episode, followed by Memphis and Nashville. On the other hand, it is clear that EC is the biggest contributor over the total analyzed diesel PM2.5 speciation, which on average accounted for 74.2%, followed by POA for each site (Table 4). Finally the distribution of the diesel PM2.5 was very similar for each site analyzed, which is speciated by SMOKE2.0.

Table 4. Speciation of PM2.5 Emissions for DFS

Site	PMFINE	POA	EC	PSO4	PNO3
Atlanta, GA	0.9%	23.1%	74.0%	1.8%	0.161%
Nashville, TN	0.9%	22.7%	74.5%	1.8%	0.164%
Knoxville, TN	1.0%	22.8%	74.4%	1.6%	0.164%
Memphis, TN	0.6%	22.7%	74.3%	2.3%	0.162%
Birmingham, AL	1.0%	23.1%	74.1%	1.6%	0.161%
Warren Co, TN	0.7%	22.8%	74.2%	2.1%	0.162%

For our analyzed sites, DFS contributed from 20.8 to 59.4% of the total NOx emissions (Table 5), whose maximum contribution occurred in Knoxville, followed by Memphis and Nashville, and the minimum occurred in Atlanta, it could be due mainly to the off-road DFS contribution and the high truck speed on urban interstates in TN. The maximum DFS contribution on the total SO_2 emissions occurred in Birmingham with 36.4% (Table 5). It could be due to the diesel sulfur content in Birmingham being higher than the other sites. For PM2.5, the maximum DFS contribution was is Memphis and Nashville, with 13.4 and 11.4 % respectively.

Table 5. DFS Contribution on NOx, SO2, PM2.5, and NH3 Emissions

Site	NOx	SO2	PM2.5	NH3
Atlanta, GA	20.8%	10.9%	9.5%	2.0%
Nashville, TN	57.2%	9.0%	11.4%	0.6%
Knoxville, TN	59.4%	15.8%	6.4%	0.4%
Memphis, TN	58.3%	15.2%	13.4%	0.8%
Birmingham, AL	28.2%	36.4%	7.3%	1.6%
Warren Co, TN	30.2%	4.6%	4.1%	0.0%

According to the Table 6, DFS were significant contribution sources of the total EC for each analyzed site, which accounted from 52.6 to 86.8% of the total EC emissions, showing evidences that EC was used as DPM tracer in several studies [2, 4, 9, 11, and 13]. The maximum contribution occurred in Memphis, followed by Nashville and Atlanta, and the minimum contribution occurred in Warren County. The average DFS contribution was 73.7% of the total EC. On the other hand, the average DFS contribution on the total POA was 15.2%, PNO3 12.9%, PSO4 7.7%, and PMFINE 0.1%. The maximum DFS contribution on POA, PNO3, and PSO4 occurred in Memphis and Nashville. The On-Road DFS contributions are shown in the Table 7, where the average on-road DFS contribution on EC was 32.6% and therefore the off-road DFS contribution on the total EC was 41.1%. Thus off-road DFS sources performed a higher contribution

on the total EC than on-road DFS sources by 35% (Table 8). The maximum on-road DFS contribution on the total EC was in Nashville and the minimum in Warren County.

Table 6. DFS Contribution on PM2.5 Emissions

Site	EC	POA	PNO3	PSO4	PMFINE
Atlanta, GA	79.7%	10.5%	10.3%	2.4%	0.1%
Nashville, TN	83.9%	25.3%	21.8%	8.0%	0.1%
Knoxville, TN	69.7%	14.4%	14.5%	6.5%	0.1%
Memphis, TN	86.8%	25.6%	18.5%	19.5%	0.1%
Birmingham, AL	69.5%	8.3%	6.4%	5.1%	0.1%
Warren Co, TN	52.6%	6.9%	5.7%	4.7%	0.0%
Mean	73.7%	15.2%	12.9%	7.7%	0.1%
DEV	12.6%	8.3 %	6.5 %	6.1%	0.0%

Table 7. On-Road DFS Contribution on PM2.5 Emissions

Site	EC	POA	PNO3	PSO4	PMFINE
Atlanta, GA	36.9%	5.3%	5.0%	0.3%	0.1%
Nashville, TN	39.6%	12.2%	10.7%	0.9%	0.1%
Knoxville, TN	36.7%	7.9%	7.7%	0.8%	0.1%
Memphis, TN	25.8%	7.6%	5.6%	1.0%	0.1%
Birmingham, AL	36.6%	4.6%	3.5%	0.7%	0.1%
Warren Co, TN	19.8%	2.5%	2.1%	0.3%	0.0%
Mean	32.6%	6.7%	5.8%	0.7%	0.1%
DEV	7.9%	3.3%	3.1%	0.3%	0.0%

In Memphis the off-road DFS had the highest contribution on EC, more than two times those from on-road DFS, which could explain why NOx emissions in Memphis were the highest among our analyzed sites. In addition, those off-road DFS sources could have more diesel sulfur content, since the off-road DFS contribution on PSO4 is 17.73 times higher than on-road DSF (Table 8). This behavior in Memphis can be seen also in the daily DFS EC emissions plot (Figure 6), where all sites have the same trend and shape, except Memphis. The highest DFS EC emissions occurred between 5:00 and 6:00 PM each day in the episode.

Table 8. Off-Road/On-road DFS Ratio on PM2.5 Emissions

Site	EC	POA	PNO3	PSO4
Atlanta, GA	1.16	0.97	1.07	7.56
Nashville, TN	1.12	1.08	1.03	8.31
Knoxville, TN	0.90	0.82	0.89	6.79
Memphis, TN	2.36	2.36	2.29	17.73
Birmingham, AL	0.90	0.81	0.80	6.43
Warren Co, TN	1.66	1.72	1.73	14.22
Mean	1.35	1.29	1.30	10.17
DEV	0.57	0.62	0.58	4.67

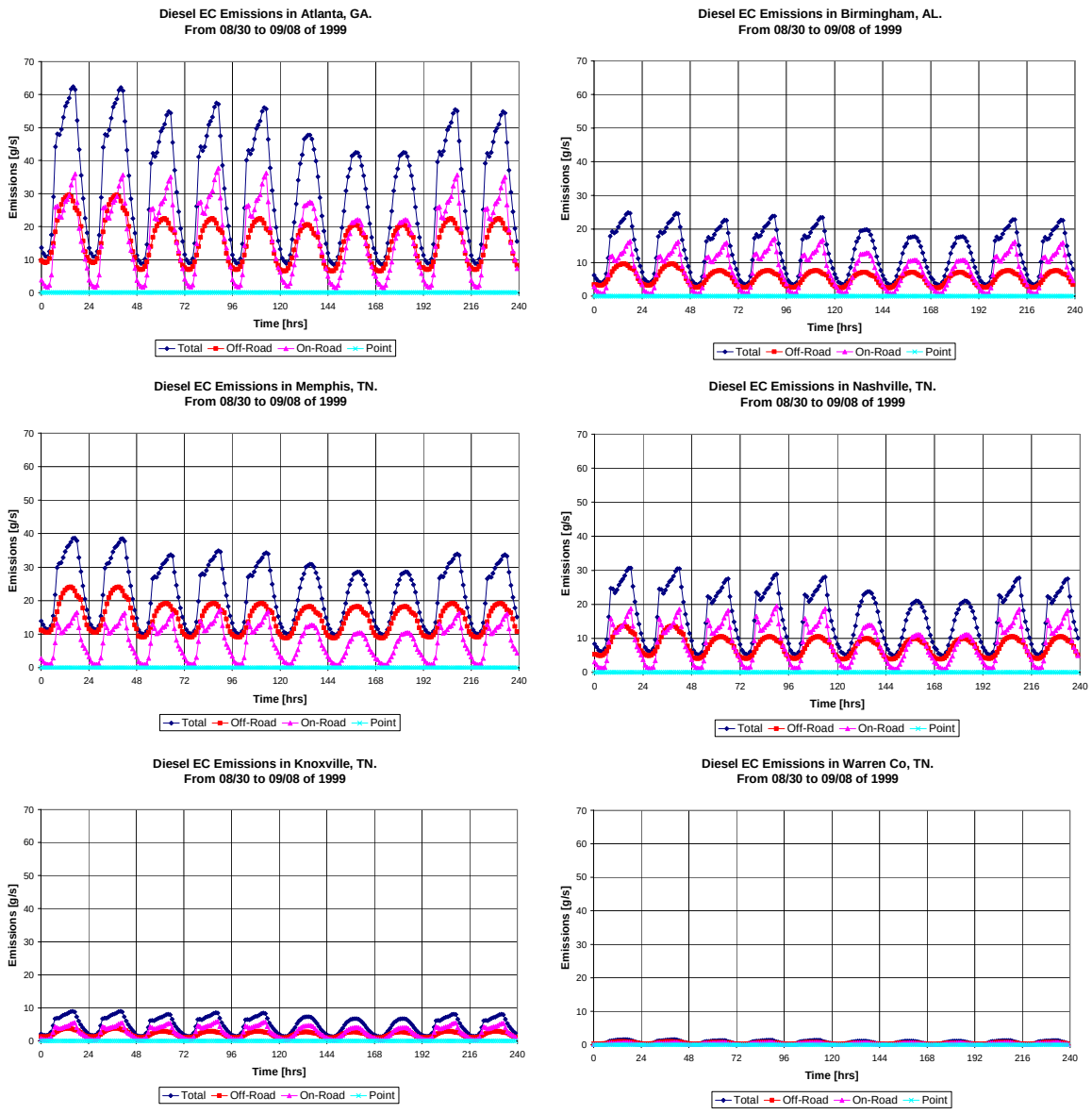

Figure 6 EC emissions that come from DFS by site

Concentrations

Model Performance. The model results from the base case run were compared to monitored data for PM2.5. For purpose of comparing model predicted concentrations to monitored data, grid of 36 by 36 kms, with the cell containing the monitor at the center, was used. This was based on the draft guidance published by EPA for PM2.5 [20]. In general, the model appeared to perform reasonably well for PM2.5. Plots of predicted (modeled) and observed (monitored) concentrations for PM2.5 shown in Figure 7 and Figure 8 for selected sites. The Fulton and DeKalb Counties (Atlanta GA) sites are in the northwest of Georgia, the Shelby County (Memphis) site is in the furthermost southwest corner of Tennessee.

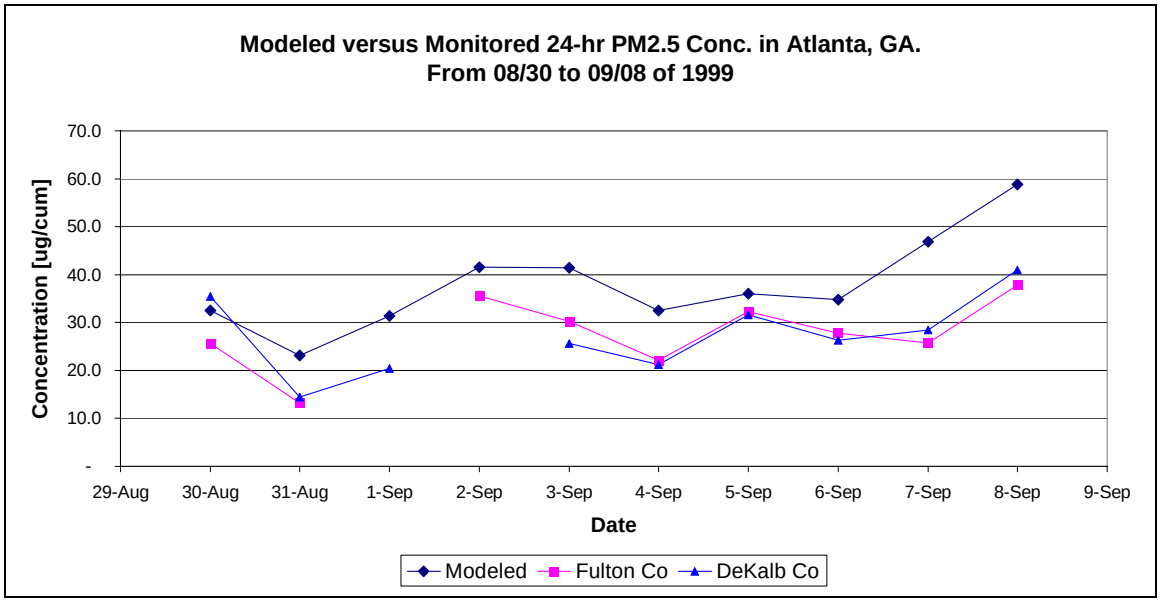

Figure 7 Modeled vs. monitored 24-hr PM2.5 Concentration in Atlanta, GA.

The model over predicted the Atlanta's sites in the episode and under predicted the Memphis' site September 4, 1999 and over predicted after September 5, 1999. More detailed study is required to determine the causes. Although the model over and under predicted the monitored values, the model performance was acceptable mainly over the trends. The bias [(Predicted – Observed)/ Observed] was within ±30%.

PM2.5 Speciation. CMAQ4.3 generates eight PM2.5 species; crustal, sulfates (SO4), primary anthropogenic organic aerosols (PAOA), ammonia (NH4), secondary biogenic organic aerosols (SBOA), elemental carbon (EC), nitrates (NO3), and secondary anthropogenic organic aerosols (SAOA). The maximum aerosols concentrations occurred in Atlanta and Birmingham, which were 45 and 42% higher than those from the rural area Warren County TN respectively on the studied episode (Figure 9). NO3 was unusually high in Nashville TN, which was 4.8 times higher than the rural area, which indicates that point and area sources have a significant contribution in Nashville.

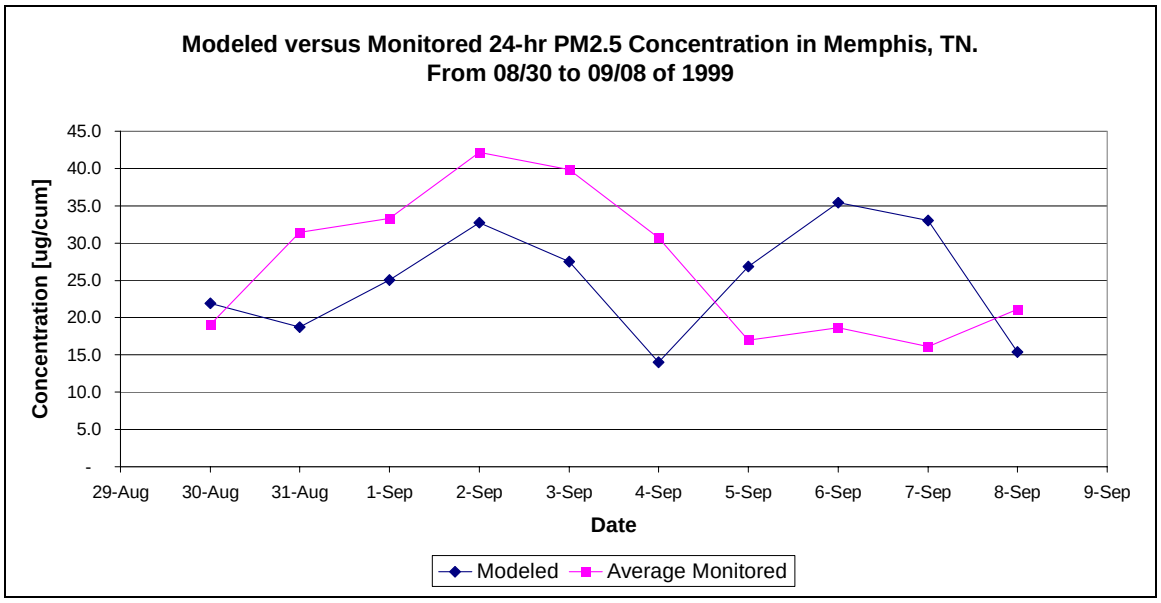

Figure 8 Modeled vs. monitored 24-hr PM2.5 Concentration in Memphis, TN

In fact, NO3 concentration from Nashville had higher contribution over the total analyzed PM2.5 (Table 9) than the other sites, accounting by 7.1%. Finally, according to Table 9, it is clear that PSO4 is the biggest contributor over the total analyzed PM2.5 speciation for each site, mainly in TN, which in average accounted by 41.5%. It demonstrates that in TN the sulfur contribution from power plants is significant.

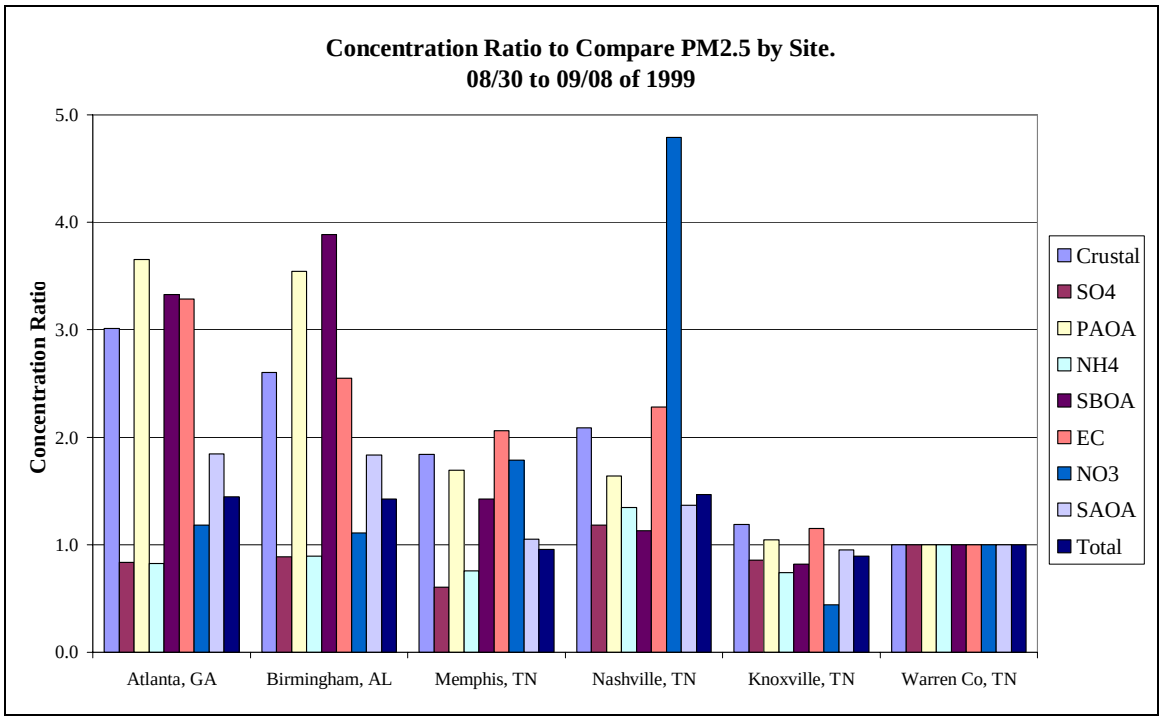

Figure 9 Concentration Ratio to Compare PM2.5 by Site

Table 9. Average PM2.5 Speciation

Site	Crustal	SO4	PAOA	NH4	SBOA	EC	NO3	SAOA
Atlanta, GA	32.9%	31.2%	10.8%	9.9%	8.7%	3.7%	1.8%	1.0%
Birmingham, AL	28.9%	33.8%	10.6%	10.9%	10.3%	2.9%	1.7%	1.0%
Memphis, TN	30.4%	34.2%	7.6%	13.8%	5.6%	3.5%	4.0%	0.8%
Nashville, TN	22.4%	43.7%	4.8%	16.0%	2.9%	2.5%	7.1%	0.7%
Knoxville, TN	21.0%	52.1%	5.0%	14.5%	3.4%	2.1%	1.1%	0.8%
Warren Co, TN	15.8%	54.2%	4.3%	17.4%	3.8%	1.6%	2.2%	0.8%

DFS Sources Contribution. The scenario considered was without exhaust DFS emissions. The difference between the base case run and the scenario gives the contribution of DFS sources as a whole towards the observed concentrations at any receptor. Figure 10 shows a difference plot of the DFS EC concentration at 2 pm EDT. An animation of the difference plot suggests higher differences in EC concentrations at night hours and during noon traffic hours, while a lower difference in the afternoon hours. This suggests that at night and noon there is more goods transportation over the roads. This kind of transportation usually use diesel. As the day progresses and the mixing layer height increases, the air is more uniformly mixed, there are more kind of vehicles types on the roads, and DFS EC concentrations decrease. It appears that, during peak traffic hours the DFS sources might contribute about 65% in rural regions and as much as 90% in urban areas (Figure 10). A gradual trend may be observed where the urban areas show a higher difference (red color), while outer regions show relatively lower and lower difference (gray color). The Great Smoky Mountains Area showed low DFS EC concentrations, however, Atlanta and the Chicago area showed the highest DFS EC concentrations.

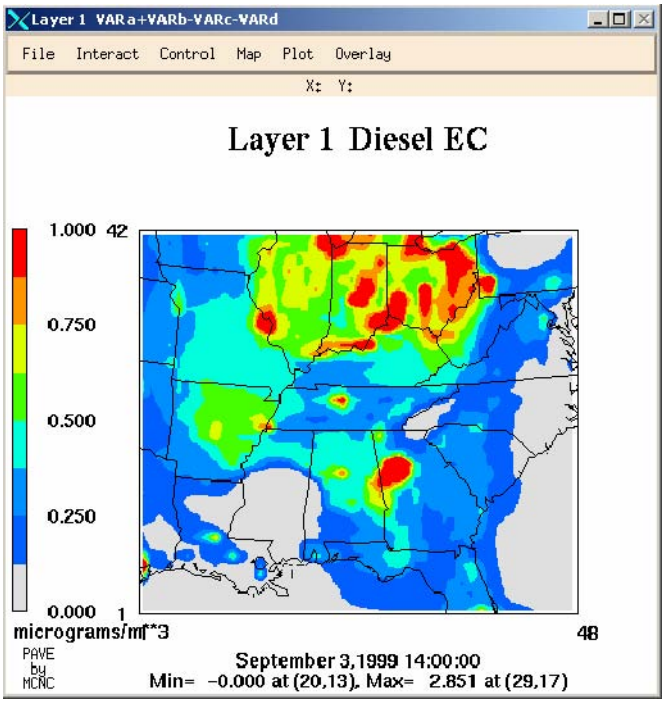

Figure 10 Hourly DFS EC concentration

Primary and secondary aerosols compose DPM, however, the most important part from a health point of view is the primary part. According to Figure 11 and 12, the maximum primary DPM concentrations occurred in Atlanta, Memphis, and Nashville, which were 3.8, 2.6, and 2.3 times higher than those from the rural area Warren County TN respectively on the studied episode. In the other hand, it is clear that EC is the biggest contributor over the total analyzed primary diesel PM2.5 speciation, which in average accounted by 72.9%, followed by PAOA for each site (Table 10).

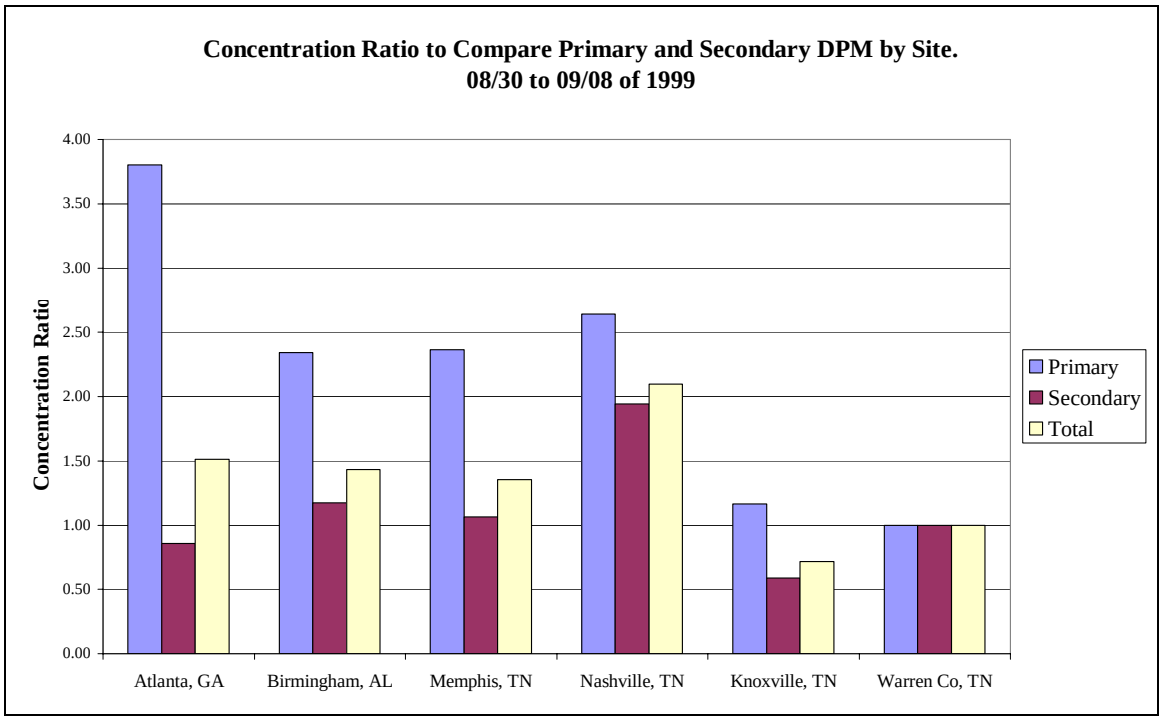

Figure 11 Concentration Ratio to Compare Primary and Secondary DPM by Site

Table 10. Average Primary Diesel PM2.5 Speciation

Site	EC	PAOA	Crustal
Atlanta, GA	72.4%	26.7%	0.9%
Birmingham, AL	72.6%	26.3%	1.0%
Memphis, TN	73.4%	26.1%	0.5%
Nashville, TN	73.1%	26.1%	0.8%
Knoxville, TN	73.1%	26.1%	0.8%
Warren Co, TN	73.0%	26.2%	0.8%
Mean	72.9%	26.3%	0.8%
DEV	0.4%	0.2%	0.2%

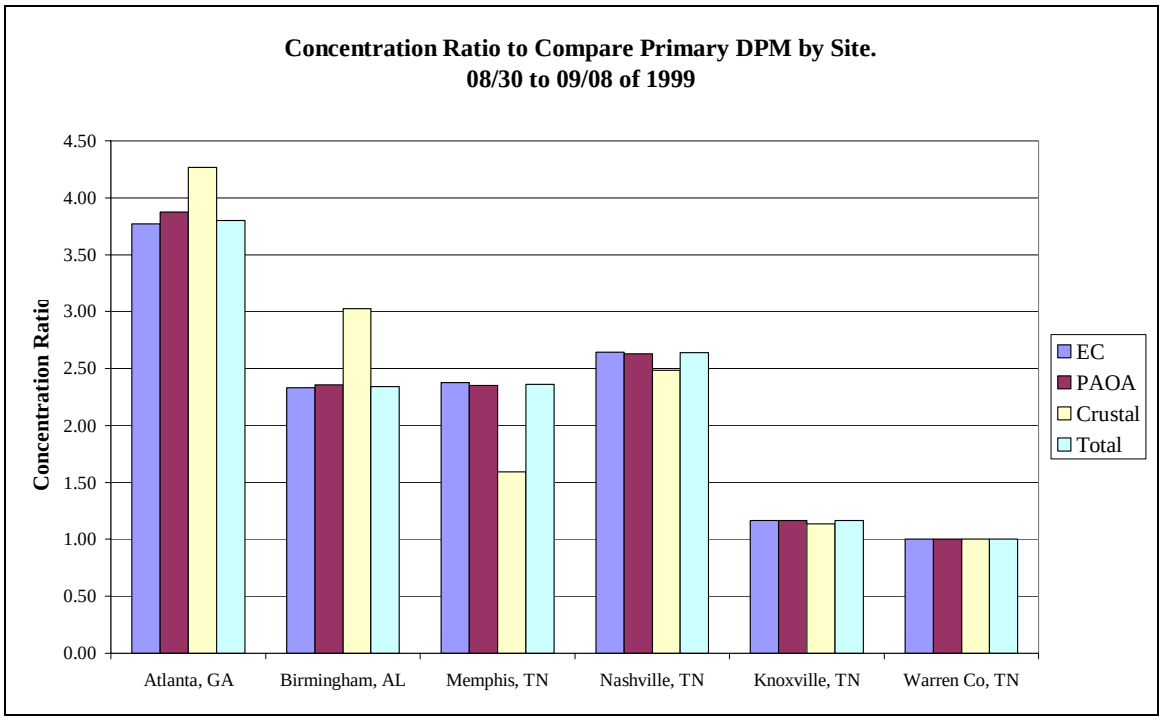

Figure 12 Concentration Ratio to Compare Primary DPM Aerosols by Site

According to the Table 12, DFS were significant contribution sources of the total EC concentration for each analyzed site, which accounted from 60.2 to 75.6% of the total EC concentrations. The maximum contribution occurred in Nashville, followed by Memphis and Atlanta, and the minimum contribution occurred in Birmingham instead of Warren County, it high contribution in Warren County can be due to aerosols transportation. The average DFS contribution was 69.5% of the total EC concentration. These DFS contributions are close to the values obtained in [21], where the author employed a molecular marker chemical mass balance model to apportion the sources of atmospheric particulate matter in eight cities in the Southeastern U.S. for on-month of each season between the spring of 1999 and the winter of 2000. The calculated value for January, April, July, and October were 74, 84, 92, and 85% respectively. His results demonstrated the seasonal impact of wood smoke on EC concentrations.

Table 12. Average DFS Contribution to Each Aerosol Species

Site	EC	NO3	PAOA	TOA	PM2.5	SAOA	NH4	SO4	SBOA	Crustal
Atlanta	74.4%	12.9%	9.6%	7.0%	6.8%	6.6%	5.9%	5.7%	3.3%	0.1%
Birmingham	60.2%	15.8%	8.6%	7.7%	7.3%	6.7%	6.2%	4.9%	3.3%	0.1%
Knoxville	66.2%	11.5%	10.0%	8.6%	8.2%	6.0%	5.4%	4.4%	3.6%	0.1%
Memphis	75.5%	38.2%	13.1%	10.3%	10.1%	8.9%	8.8%	6.5%	5.8%	0.1%
Nashville	75.6%	27.8%	14.6%	11.0%	8.9%	8.0%	7.9%	6.7%	4.7%	0.1%
Warren Co	65.4%	10.0%	9.1%	8.7%	8.3%	8.1%	7.2%	6.3%	5.9%	0.1%
Mean	69.5%	19.4%	10.8%	8.9%	8.3%	7.4%	6.9%	5.8%	4.4%	0.1%
DEV	6.5%	11.2%	2.4%	1.5%	1.2%	1.1%	1.3%	0.9%	1.2%	0.0%

The contribution over the secondary DPM aerosols was uncertain mainly over nitrate and sulfate species, since the difference between the base case and the case without DFS does not reflex the non-linear chemical and physical mechanism of the secondary aerosols within the advanced air quality model.

CONCLUSIONS

The maximum PM2.5, NH3, and SO2 DFS emissions occurred in Atlanta, which were 40.1, 41.2, and 38.7 times respectively higher than those from the rural area Warren County TN on the studied episode. However, NOX DFS emissions in Atlanta were not as high as those from Memphis and Nashville.

The maximum diesel EC and POA emissions occurred in Atlanta, which were 40.0 and 40.6 times higher than those from the rural area Warren County TN respectively on the studied episode. DFS emissions contributed by (73.7 % ± 12.6) of EC, (15.2 % ± 8.3) of organic aerosols, (12.9 % ± 6.5) of nitrate, and (7.7 % ± 6.1) of sulfate during the selected episode, where the highest contribution of EC was allocated in Memphis TN, where there are more off-road sources than the other analyzed sites. TN sites showed more DFS contribution on EC mainly due to truck speed on urban interstates, which are higher than AL and GA.

For ambient concentrations, the maximum primary DPM concentrations occurred in Atlanta, Memphis, and Nashville, which were 3.8, 2.6, and 2.3 times higher than those from the rural area Warren County TN respectively on the studied episode. In the other hand, it is clear that EC is the biggest concentration over the total analyzed primary diesel PM2.5 speciation, which in average accounted by 72.9%, followed by PAOA for each site.

DFS contributed by (69.5% ± 6.5) of the total EC concentration, (19.4% ± 11.2) of nitrate, (10.8 % ± 2.4) of primary anthropogenic organic aerosols, (8.9% ± 1.5) of total organic aerosols, (7.1% ± 1.1) of secondary anthropogenic organic aerosols, (6.9 % ± 1.3) of ammonia, (5.8% ± 0.9) of sulfate (4.4% ± 1.2) of secondary biogenic organic aerosols, and (0.08% ± 0.01) of crustal, where the highest contribution of EC due to DFS was allocated in Nashville TN. The rural site (Warren County TN) performed the smaller EC contribution of DFS. Our results indicate significant geographic variability in the EC contribution from DFS. The contribution over the secondary DPM aerosols was uncertain mainly over nitrate and sulfate species.

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