Modeling and source apportionment of diesel particulate matter

L.A. Díaz-Robles [a], J.S. Fu [b,*], G.D. Reed [b]

[a] School of Environmental Engineering, Catholic University of Temuco, Temuco, Chile
[b] Department of Civil and Environmental Engineering, University of Tennessee, Knoxville, Tennessee, USA

Abstract

The fine and ultra fine sizes of diesel particulate matter (DPM) are of greatest health concern. The composition of these primary and secondary fine and ultra fine particles is principally elemental carbon (EC) with adsorbed organic compounds, sulfate, nitrate, ammonia, metals, and other trace elements. The purpose of this study was to use an advanced air quality modeling technique to predict and analyze the emissions and the primary and secondary aerosols concentrations that come from diesel-fueled sources (DFS). The National Emissions Inventory for 1999 and a severe southeast ozone episode that occurred between August and September 1999 were used as reference. Five urban areas and one rural area in the Southeastern US were selected to compare the main results. For urban emissions, results showed that DFS contributed ($77.9\% \pm 8.0$) of EC, ($16.8\% \pm 8.2$) of organic aerosols, ($14.3\% \pm 6.2$) of nitrate, and ($8.3\% \pm 6.6$) of sulfate during the selected episodes. For the rural site, these contributions were lower. The highest DFS contribution on EC emissions was allocated in Memphis, due mainly to diesel non-road sources (60.9%). For ambient concentrations, DFS contributed ($69.5\% \pm 6.5$) of EC and ($10.8\% \pm 2.4$) of primary anthropogenic organic aerosols, where the highest DFS contributions on EC were allocated in Nashville and Memphis on that episode. The DFS contributed ($8.3\% \pm 1.2$) of the total ambient $PM_{2.5}$ at the analyzed sites. The maximum primary DPM concentration occurred in Atlanta ($1.44~\mu g/m^3$), which was 3.8 times higher than that from the rural site. Non-linearity issues were encountered and recommendations were made for further research. The results indicated significant geographic variability in the EC contribution from DFS, and the main DPM sources in the Southeastern U.S. were the non-road DFS. The results of this work will be helpful in addressing policy issues targeted at designing control strategies on DFS in the Southeastern U.S. Published by Elsevier Ltd.

Keywords: Diesel particulate matter; CMAQ, Elemental carbon; Modeling, air quality

1. Introduction

Diesel exhaust is emitted from a broad range of diesel engines; the on-road diesel engines of trucks, buses, and cars and the non-road diesel engines that include locomotives, marine vessels, and heavy duty equipment (USEPA, 2002). DPM is part of a complex mixture. The sizes of diesel particulates, which are of greatest health concern, are in the categories of fine, ultra fine, and nano particles. The mixture of these fine, ultra fine, and nano particles is composed mainly of elemental carbon (EC) with adsorbed compounds such as organic carbon (OC), sulfate, nitrate, metals, and other trace elements (Kleeman et al., 2000). The elemental

fraction stems from fuel droplet pyrolysis, while the organic fraction originates from unburned fuel, lubricating oil, and combustion byproducts (Shah et al., 2004). Many carcinogenic and mutagenic compounds have been measured in the organic fraction of DPM, such as polycyclic aromatic hydrocarbons (PAHs) and nitroarenes (Neumann, 2001 and Rosenkranz, 1996). A diesel particle initially consists of an agglomeration of EC particles coated with organic and inorganic compounds that are adsorbed or absorbed at the surface of this agglomerate (Vouitsis et al., 2005, Kim et al., 2002a,b). According with Ning et al. (2004), diesel particles lose their identity rapidly as they coagulate with other particles and act as condensation sites for secondary aerosol species. The DPM composition is variable, which typically has a composition of 25–60% of EC (Seigneur et al., 2003 and Schauer et al., 1999), with estimates ranging from 5 to 90% (Moosmuller et al., 2001), and 20–50% of OC of total mass (Shi et al., 2000). Sulfate and nitrate may account for up to 12%
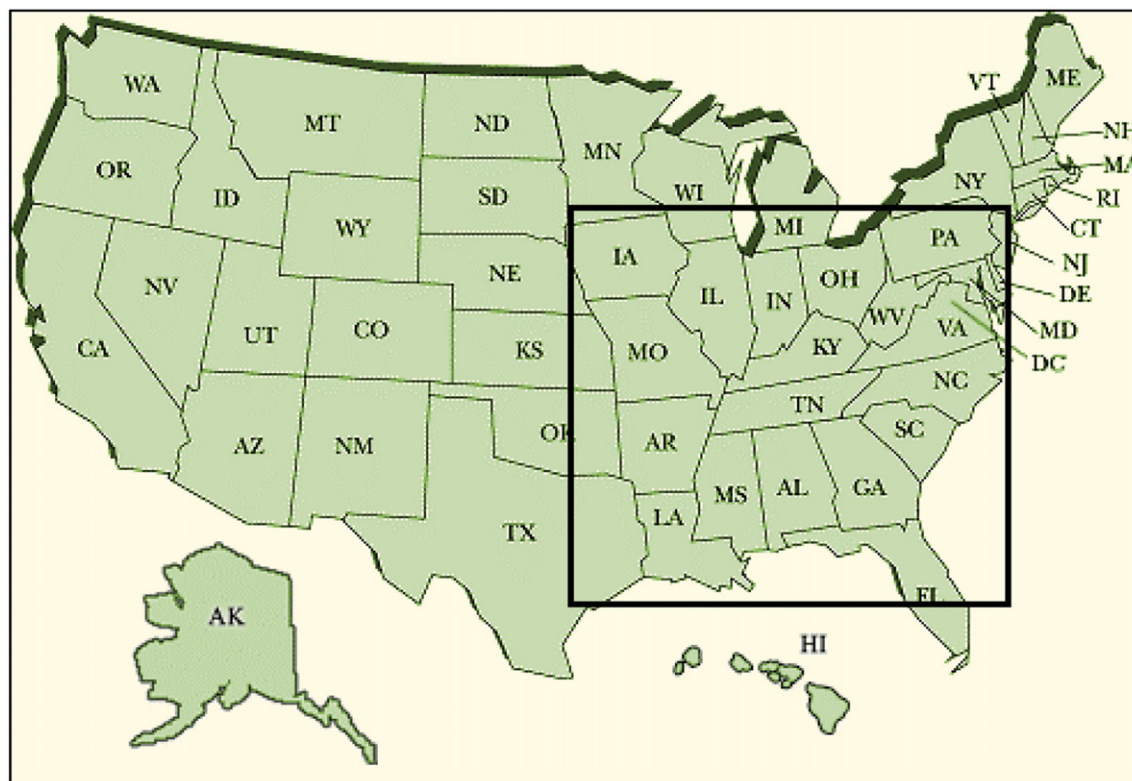
Fig. 1. Grid resolution domain for 36-km.

and 4%, respectively (Shi et al., 2000), depending on the sulfur content in the diesel fuel.

Increased mortality and morbidity in communities with elevated fine particles concentrations has been reported by a variety of studies (Schneider and Hill, 2005, Fruin et al., 2004, and Adonis et al., 2003). 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 (Tainio et al., 2005). According to the Clean Air Task Force, in its modeling study over the 1999 National Emissions Inventory Version 3 (NEI99) (Schneider and Hill, 2005), diesel exhaust posed a cancer risk that was 7.5 times higher than the combined total cancer risk from all other air toxics in the whole nation. 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.

Because DPM is the major source of EC in the atmosphere (Adonis et al., 2003 and Schauer, 2003), EC has been used 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 (Shah et al., 2004, Schauer, 2003, Tamura and Eisinger, 2003, and Birch and Cary, 1996). 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 at different seasons. Thus, this approximation generates important uncertainties, because those studies used an average EC contribution to estimate the DPM concentration in

any place and any season between 50 and 80%. In addition, EC is not a unique tracer for ambient DPM. Efforts to utilize EC as an indicator of DPM must properly address other sources of EC, such as gasoline fueled sources and open burning sources. Finally, using EC as DPM tracer has to have a consistent measurement technique for EC when comparing source and ambient EC measurements to avoid significant biases.

In order to better manage ambient DPM concentrations, it is important to know the sources or source categories that contribute to the DPM concentrations at a particular area or receptor. One possibility is to use receptor models. Although receptor models have been used to analyze $PM_{2.5}$ source apportionment, they do not fully take into account the chemical reactions involved in the formation of secondary fine particles (NRC, 1999, Kim et al., 2004, Kim et al., 2005, Kim and Hopke, 2004a,b, and Kim and Hopke, 2006), and so far there is not an available method to measure ambient DPM (Fruin et al., 2004). It is possible to

Table 1
$PM_{2.5}$ NO_x NH_3 and SO_2 emissions composition of the BC and DFS scenarios

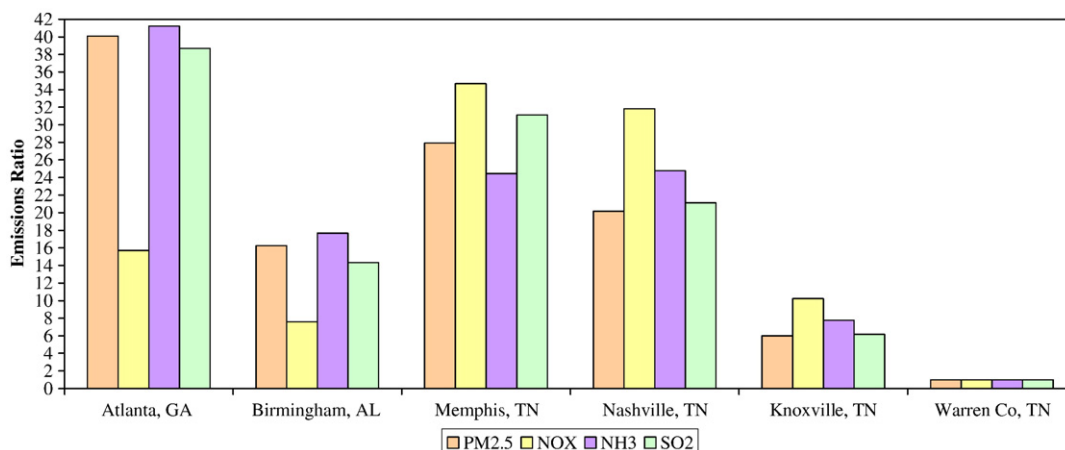| Site	BC%				DFS%			
	$PM_{2.5}$	NO_x	NH_3	SO_2	$PM_{2.5}$	NO_x	NH_3	SO_2
Atlanta	17.3	65.3	2.1	15.3	10.9	77.9	0.3	10.9
Birmingham	24.6	67.5	2.8	5.0	9.6	81.4	0.2	8.8
Nashville	14.4	75.8	4.4	5.5	4.0	91.2	0.1	4.7
Knoxville	11.5	66.9	5.6	16.1	3.3	93.1	0.1	3.5
Memphis	18.5	64.3	9.1	8.1	3.0	93.7	0.1	3.2
Warren Co	14.1	31.8	41.8	12.3	4.9	89.8	0.1	5.1

Fig. 2. Emission ratios to compare DFS emissions by site.

estimate a more realistic ambient DPM concentration by using an air quality modeling.

In this study, the most population growth region—the southeastern states in US (US Census Bureau, 2005) was chosen as the study domain to provide the implications for further health effect study caused by DPM in this region. This study models the source apportionment on $PM_{2.5}$ emissions and concentrations of eliminating diesel emissions in the 1999 National Emission Inventory, since 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 (Mysliwiec and Kleeman, 2002). However; the non-road sources were an important contribution of PM also. The uncertainty to use EC as a tracer was reduced in the present research, because EC and DPM were estimated by eliminating DFS and modeled temporally and spatially over an urban to a regional area through an advanced air quality model. This model predicted emissions, aerosol concentrations, and the source apportionment of primary and secondary aerosols that come from DFS in the Southeastern US for the following five populated urban areas and a rural area: Atlanta GA, Nashville TN, Knoxville TN, Memphis TN, Birmingham AL, and Warren County TN (rural area). The National Emissions Inventory Version 3 for the

year 1999 (NEI99), currently public released, was used in this analysis (USEPA, 2004).

2. Methodology

Diesel aerosols were predicted using the advanced air quality model Community Multi-scale Air Quality (CMAQ) version 4.3 (Byun and Ching, 1999). The emissions were temporal and spatially allocated using the advanced emissions model Sparse Matrix Operator Kernel Emissions (SMOKE) Modeling System version 2.0 (CMAS, 2006) over the NEI99 and the meteorological variables were generated through the mesoscale model (MM5) version 3 from the Pennsylvania State University/National Center for Atmospheric Research (NCAR/PSU, 2005). The MM5 results were processed by the meteorology–chemistry interface processor (MCIP) version 2.2 (CMAS, 2006). The modeling domain consisted of a 36 km domain in Fig. 1.

2.1. Inventory development

The emission inventories are usually categorized into four major categories:

2.1.1. Point sources
This category includes all emission sources that can be attributed to point emitters, usually a stack and include power plants as well. These are identified by latitude and longitude. The 1999 criteria pollutants point source inventory for the state of TN was used, which is the most updated developed by a research group at the University of Tennessee, Knoxville (UTK), (Doraiswamy, 2004). For other states in the domain, the NEI99 version 3.0 was used (USEPA, 2004).
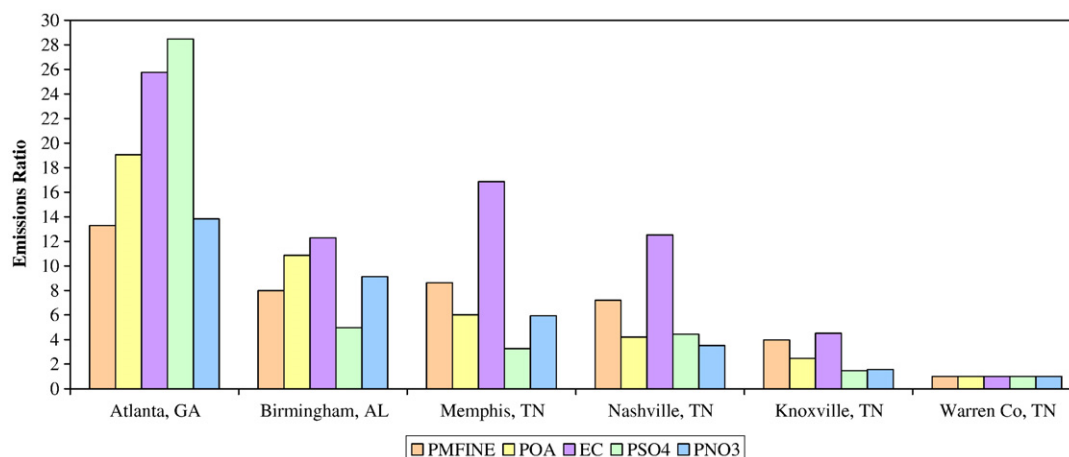

Fig. 3. Emissions ratios to compare $PM_{2.5}$ emissions by site.

Table 2
Speciation of the $PM_{2.5}$ emissions from the BC and DFS scenarios

Site	BC%					DFS%				
	PMFINE	POA	EC	PSO$_4$	PNO$_3$	PMFINE	POA	EC	PSO$_4$	PNO$_3$
Atlanta	62.1	20.9	9.4	7.5	0.2	0.9	23.1	74.0	1.8	0.2
Birmingham	67.7	21.6	8.1	2.4	0.2	1.0	23.1	74.1	1.6	0.2
Nashville	76.4	10.5	10.3	2.7	0.1	0.9	22.7	74.5	1.8	0.2
Knoxville	79.6	11.6	7.0	1.7	0.1	1.0	22.8	74.4	1.6	0.2
Memphis	74.7	12.3	11.4	1.6	0.1	0.6	22.7	74.3	2.3	0.2
Warren Co	72.9	17.1	5.7	4.1	0.2	0.7	22.8	74.2	2.1	0.2

2.1.2. Area sources

This includes emission sources that are spread over an area including many small point sources that are not accounted for in the point source inventory. The 1999 ammonia area source inventory (Kim, 2003) for the state of TN calculated by UTK (Doraiswamy, 2004). For other pollutants in the domain the NEI99 version 3.0 was used (USEPA, 2004).

2.1.3. Mobile sources

This category includes all on-road mobile sources (i.e. cars, trucks etc.). This category also includes non-road mobile sources such as marine vessels, locomotives, etc. The 1999 criteria pollutants on-road mobile source inventory, including fugitive particulate emissions from paved roads for the state of TN, was estimated by UTK (Doraiswamy, 2004 and Davis et al., 2002). For other states in the domain the NEI99 version 3.0 was used (USEPA, 2004).

2.1.4. Biogenic sources

This includes emissions from natural sources such as vegetation. This inventory was created using BEIS 3.09 and SMOKE2.0, base on land use and meteorological data.

2.2. SMOKE2.0 model runs

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

2.2.1. Inventory speciation

The criteria emission inventory typically includes emissions of NO_x, VOC, CO, NH_3, SO_2, PM_{10} and $PM_{2.5}$. 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 chemical mechanism was used in SMOKE 2.0 to run the emission inventory. Because 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. The DPM emissions were estimated considering the addition of the following $PM_{2.5}$ species defined in SMOKE2.0: elemental carbon (EC), primary fine particulate matter (PMFINE), primary nitrate (PNO_3), primary organic aerosols (POA), and primary sulfate (PSO_4).

2.2.2. Spatial allocation of emissions

County-based emissions were allocated to each grid cell based on the spatial surrogates (Doraiswamy, 2004). Spatial surrogates represent the percentage of emissions from each county that are allocated to each grid. Spatial surrogates were developed for the domain using SMOKE tool. For emissions from on-road mobile sources on interstates (within TN), spatial surrogates for gridding were developed (Doraiswamy, 2004). The miles of interstate highways that fell within each grid, within each county were determined and multiplied times the average daily traffic volume. Using that data, the fraction of vehicle miles traveled (VMT) in each grid and 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 SMOKE2.0 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 VMT rather than lane miles as used in SMOKE2.0.

2.2.3. Temporal processing

The emissions in the inventory were annual emissions in tons/year. These were converted to hourly emissions by using appropriate default profiles within the SMOKE2.0 model. The temporal profiles describe the variation in emissions as a 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 in SMOKE2.0.
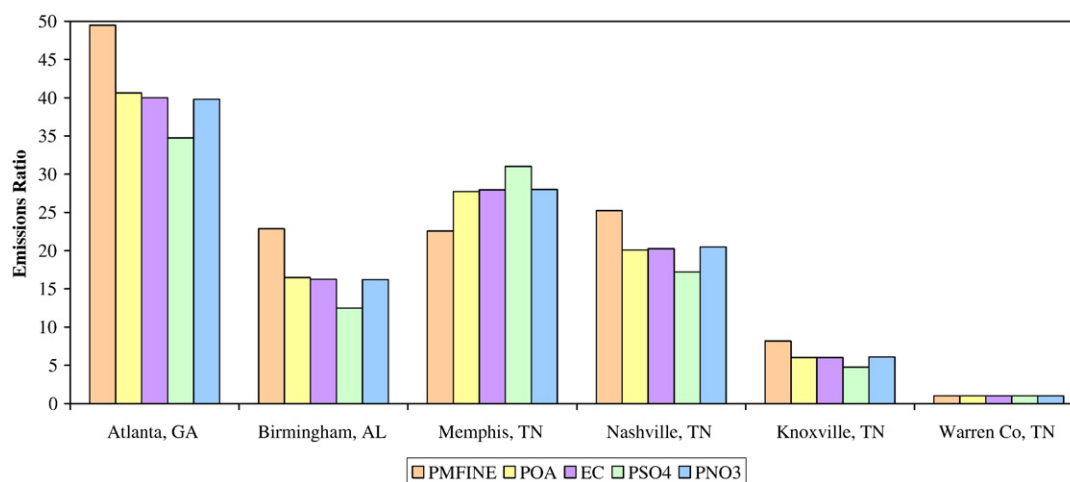

Fig. 4. Emissions ratios to compare diesel $PM_{2.5}$ emissions by site.

Table 3
DFS contribution on NO_x SO_2 $PM_{2.5}$ and NH_3 emissions

Site	NO_x%	SO_2%	$PM_{2.5}$%	NH_3%
Atlanta	20.8	10.9	9.5	2.0
Birmingham	28.2	36.4	7.3	1.6
Nashville	57.2	9.0	11.4	0.6
Knoxville	59.4	15.8	6.4	0.4
Memphis	58.3	15.2	13.4	0.8
Warren Co	30.2	4.6	4.1	0.0

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

2.2.4. Episode and modeling domain

The episode that was chosen for 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 36 km domain, whose grid size was selected due to the available $PM_{2.5}$ monitoring concentrations in the region. Fig. 1 gives a general idea of the region that is covered by the domain.

2.3. CMAQ model runs

The methodology consisted of running the CMAQ model with and without the diesel-fueled emissions. The base case consisted of a run with all sources included. The scenario without the DFS was estimated from the emissions generated in SMOKE2.0. The difference between the BC and the scenario without the DSF were the diesel primary and secondary aerosol concentrations. The default set of boundary and initial conditions available in CMAQ was used for the domain run. Because the first day of the episode under consideration was August 30th, 1999, the model runs were set to start three days earlier (August 27, 1999) to avoid the influence of the initial conditions on the model results.

2.3.1. Aerosols speciation

The $PM_{2.5}$ species in CMAQ are represented by two mode distributions; the Aitken (i) mode, which are particles that have diameters up to 0.1 μm, and the Accumulation (j) mode, which are particles that have diameters between 0.1 and 2.5 μm. The chemical species considered in Aitken and Accumulation modes are: sulfate (ASO_4), nitrate (ANO_3), ammonia (ANH_4), primary organics (AORGPA), secondary anthropogenic organics (AORGA), secondary biogenic organics (AORGB), EC (AEC), and unspecified anthropogenic mass (A25). The primary species considered in the CMAQ module were elemental and primary organic carbon (AEC and AORGPA), dust and other species not further specified (A25). A mix between primary and secondary species considered are sulfate (ASO_4), nitrate (ANO_3), and ammonium (ANH_4). The secondary species considered were organics from precursors of anthropogenic (AORGA) and biogenic (AORGB) sources. This approach did not account for the PM sources that are apportioned between primary and secondary sulfate, ammonia, and nitrate aerosol concentrations, because there currently is no way to determine

how much of the sulfate, ammonia, and nitrate in the Aitken and Accumulative modes of CMAQ are primary and how much are secondary.

Once the base case run was completed, the model results for the BC were compared to the monitoring data of $PM_{2.5}$. As the model performed reasonably well, the specific scenario was modeled. In order to determine the contribution of DFS, the CMAQ run was conducted without DFS emissions. In this case, the ambient DPM concentrations were estimated according to the following equation:

$$DPM = BC_{scenario} - (BC - DFS)_{scenario} \qquad (1)$$

3. Results and discussion

3.1. Emissions

According to SMOKE 2.0 outputs, NO_x emissions from Nashville, Birmingham, and Knoxville had higher contribution over the total analyzed criteria emissions (Table 1) than the other analyzed sites, including all sources. This indicates that DFS could have a higher contribution at those metropolitan areas and important DPM concentrations over those cities, since DFS produce high amounts of NO_x emissions. This contribution can be proved in Tables 1 and 3, where DFS contributed 59.4, 57.2, and 58.3% on the total NO_x emissions in Nashville, Birmingham, and Knoxville, respectively. According to Table 1, it is clear that NO_x is the biggest contributor over the total analyzed emissions on urban areas, with an average contribution of 68.0%. For the rural county, the greatest emissions were the NH_3 emissions, with a 41.8%. These emissions come mainly from area sources.

The maximum $PM_{2.5}$, NH_3, and SO_2 DFS emissions occurred in Atlanta, which were 40, 41, and 39 times higher respectively than those from the rural area Warren County TN on the studied episode (Fig. 2). However, NO_x DFS emissions in Atlanta were not as high as those from Memphis and Nashville. This difference can be explained because in Memphis the non-road DFS contribute with more NO_x emissions than on-road DFS, whereas in Atlanta on-road DFS contribute with

Table 5
Non-road/on-road DFS Ratio on $PM_{2.5}$ emissions

Site	EC	POA	PNO3	PSO4
Atlanta	1.16	0.97	1.07	7.56
Birmingham	0.90	0.81	0.80	6.43
Nashville	1.12	1.08	1.03	8.31
Knoxville	0.90	0.82	0.89	6.79
Memphis	2.36	2.36	2.29	17.73
Warren Co	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

Table 4
DFS contribution on $PM_{2.5}$ emissions

Site	EC%	POA%	PNO3%	PSO4%	PMFINE%
Atlanta	79.7	10.5	10.3	2.4	0.1
Birmingham	69.5	8.3	6.4	5.1	0.1
Nashville	83.9	25.3	21.8	8.0	0.1
Knoxville	69.7	14.4	14.5	6.5	0.1
Memphis	86.8	25.6	18.5	19.5	0.1
Mean	77.9	16.8	14.3	8.3	0.1
DEV	8.0	8.2	6.2	6.6	0.0
Warren Co	52.6	6.9	5.7	4.7	0.0

Table 6
Non-road DFS contribution on $PM_{2.5}$ emissions

Site	%			
	EC	POA	PNO3	PSO4
Atlanta	42.8	5.1	5.3	2.2
Birmingham	32.9	3.7	2.8	4.4
Nashville	44.3	13.1	11.1	7.2
Knoxville	32.9	6.5	6.8	5.7
Memphis	60.9	18.0	12.9	18.5
Warren Co	32.8	4.4	3.6	4.4
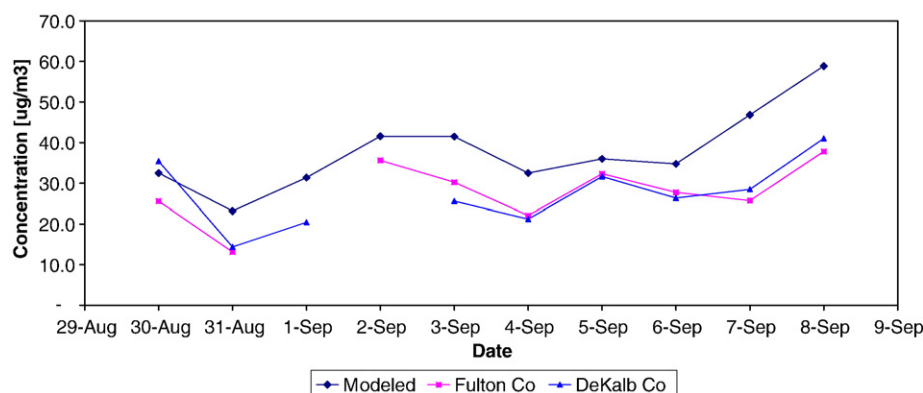
Fig. 5. Modeled vs. monitored 24-h PM$_{2.5}$ concentration in Atlanta, GA.
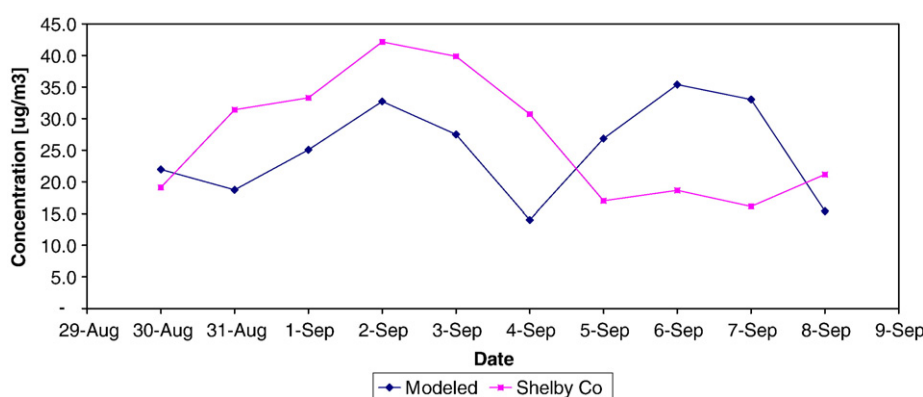
Fig. 6. Modeled vs. monitored 24-h PM$_{2.5}$ concentration in Memphis, TN.

more emissions than non-road DFS sources (Saiyasitpanich et al., 2005).

The NO$_x$ DFS emissions from Nashville, Memphis, and Knoxville, even Warren County had higher contribution over the total analyzed criteria emission (Table 1) than the other sites, which also indicates that the non-road DFS could be important factors for those NO$_x$ emissions as indicated in EPA (USEPA, 2004 and Saiyasitpanich et al., 2005). Finally, it is clear that NO$_x$ is the biggest contributor of the total analyzed DFS emissions with an average of 88%. Memphis, Knoxville, and Nashville showed the highest NO$_x$ contribution over the total

analyzed DFS emission. This result could be because this study used an improved mobile sources inventory for the state of Tennessee. The NH$_3$ emissions were not significant contributors over the total analyzed DFS emissions for all sites. On average, DFS sources contributed around 6% over the total PM$_{2.5}$ emissions, where Atlanta presented the highest contribution with 11% on the studied episode.

SMOKE2.0 generates five PM$_{2.5}$ emission species; fine particulate matter (PMFINE), primary organic aerosols (POA), elemental carbon EC, primary sulfates (PSO$_4$), and primary nitrates (PNO$_3$). The maximum PMFINE, POA, EC, PSO$_4$, and PNO$_3$ emissions occurred in
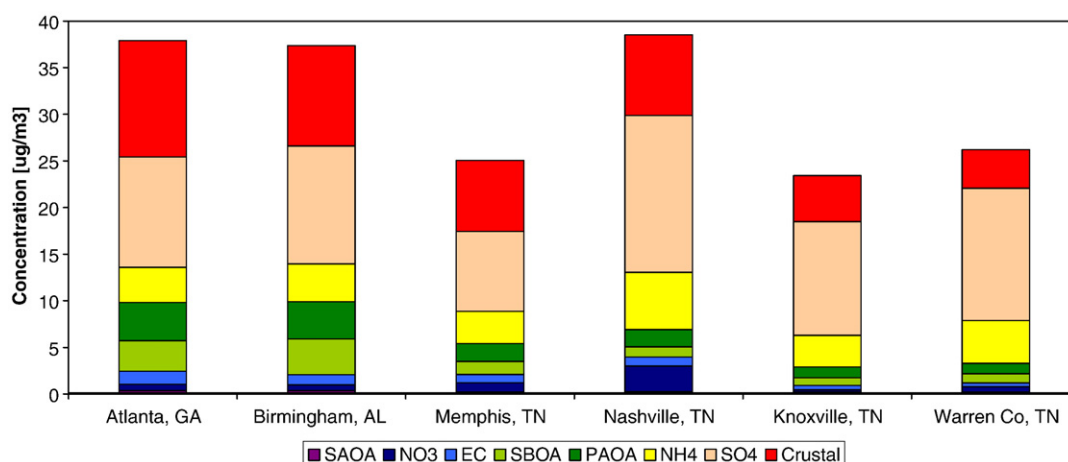

Fig. 7. PM$_{2.5}$ aerosol species by site for the BC from 08/30 to 09/08 1999.

Table 7
Average ambient PM$_{2.5}$ speciation

Site	%							
	Crustal	SO$_4$	PAOA	NH$_4$	SBOA	EC	NO$_3$	SAOA
Atlanta	32.9	31.2	10.8	9.9	8.7	3.7	1.8	1.0
Birmingham	28.9	33.8	10.6	10.9	10.3	2.9	1.7	1.0
Memphis	30.4	34.2	7.6	13.8	5.6	3.5	4.0	0.8
Nashville	22.4	43.7	4.8	16.0	2.9	2.5	7.1	0.7
Knoxville	21.0	52.1	5.0	14.5	3.4	2.1	1.1	0.8
Warren Co	15.8	54.2	4.3	17.4	3.8	1.6	2.2	0.8

Atlanta, which were 13, 19, 26, 29, and 14 times higher than those from the rural area Warren County TN respectively on the studied episode (Fig. 3). EC emissions were significantly higher 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, Nashville, and Memphis had higher contributions over the total analyzed criteria emissions (Table 2) than the other sites; with 9, 10, and 11% respectively. Finally, according to Table 2, it is clear that PMFINE is the biggest contributor over the total analyzed emissions of the PM$_{2.5}$ species, which on average was 72%. The maximum PMFINE, POA, EC, PSO$_4$, and PNO$_3$ DFS emissions occurred in Atlanta, which were 50, 41, 40, 35, and 40 times higher than those from the rural area Warren County TN, respectively on the studied episode (Fig. 4). Those high values were followed by Memphis and Nashville. On the other hand, it is clear that EC was the biggest contributor over the total analyzed diesel PM$_{2.5}$ species, which accounted for 74% on average, followed by POA for each site (Table 2).

For the analyzed sites, DFS contributed from 21 to 59% of the total NO$_x$ emissions (Table 3), whose maximum contribution occurred in Knoxville, followed by Memphis and Nashville. This could be due mainly to the non-road DFS contribution. The maximum DFS contribution on the total SO$_2$ emissions occurred in Birmingham with 36% (Table 3). This could be due to the presence of coal power plants in Birmingham. For PM$_{2.5}$, the maximum DFS contribution was in Memphis and Nashville, with 13 and 11% respectively (Table 3), which could be explained due to the non-road sources.

According to Table 4, DFS were significant contribution sources of the total EC for each analyzed site, which accounted for 53 to 87% of the total EC emissions. This provides evidence of why EC was used as an ambient DPM tracer in several studies (Birch and Cary, 1996; Kim and Hopke, 2006; Kleeman et al., 2000; NCAR/PSU, 2005; NRC, 1999). The maximum contribution occurred in Memphis, followed by Nashville and Atlanta, and the minimum contribution occurred in Warren County. The average urban DFS contribution was 78% of the total EC emissions. On the other hand, the average urban DFS contribution over the total POA was 17%, for PNO$_3$ 14%, for PSO$_4$ 8%, and for PMFINE 0.1%. The maximum DFS contribution on POA, PNO$_3$, and PSO$_4$ emissions occurred in Memphis and Nashville. The ratios between non-road and on-road DFS emission are shown in Table 5, where the non-road DFS sources performed a higher contribution on the total EC emissions than on-road DFS sources in Memphis (2.4), Warren County (1.7), Atlanta (1.2), and Nashville (1.1). For Knoxville and Birmingham the on-road sources were more important than non-road DFS (ratio=0.9). The non-road DFS had the highest contribution on EC emissions in Memphis, more than two times those from on-road DFS. In fact, the highest DFS contribution on EC emissions was allocated in Memphis, due mainly to diesel non-road sources (60.9%) shown in Table 6. These non-road DFS sources could have more sulfur content in the diesel fuel, because the non-road DFS contribution on PSO$_4$ was 17.7 times higher than on-road DSF

shown in Table 5. In effect, according with the Saiyasitpanich et al. (2005) studies, the more sulfur content in the diesel fuel, the more diesel PM$_{2.5}$ emissions from DFS.

3.2. Concentrations

3.2.1. Modeling performance

There is no DPM monitoring data available. The ambient DPM is proportioned of PM$_{2.5}$ mentioned in the earlier section. The model performance will be presented by PM$_{2.5}$. Limited monitored PM$_{2.5}$ data was available for the episode

The model results from the base case run were compared to monitored data for PM$_{2.5}$. In order to compare model predicted concentrations to monitored data, grids of 36 by 36 km, with the cell containing the monitor at the center, were used. This was based on the draft guidance published by EPA for PM$_{2.5}$ (USEPA, 2001). In general, the model appeared to perform reasonably well for PM$_{2.5}$. Plots of predicted (modeled) and observed (monitored) concentrations for PM$_{2.5}$ are shown in Figs. 5 and 6 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.

The model over predicted and followed the 24-hour PM$_{2.5}$ concentration trends at the Atlanta's sites in the episode, and under predicted the Memphis' site before September 4, 1999 and over predicted after September 5, 1999. One of the causes can be the size of the 36 km grid, which assumes an average concentration over that grid in CMAQ. More detailed study is required to determine more causes. Although the model over and under predicted the monitored values, the model performance was acceptable mainly over the trends. In fact, according to the EPA's guideline (USEPA, 2001), the bias [(Predicted−Observed)/ Observed] was within ±30%.

3.2.2. Speciation

CMAQ4.3 generates eight PM$_{2.5}$ species: crustal/unspeciated PM, sulfates (SO$_4$), primary anthropogenic organic aerosols (PAOA), ammonia (NH$_4$), secondary biogenic organic aerosols (SBOA), elemental carbon (EC), nitrates (NO$_3$), and secondary anthropogenic organic
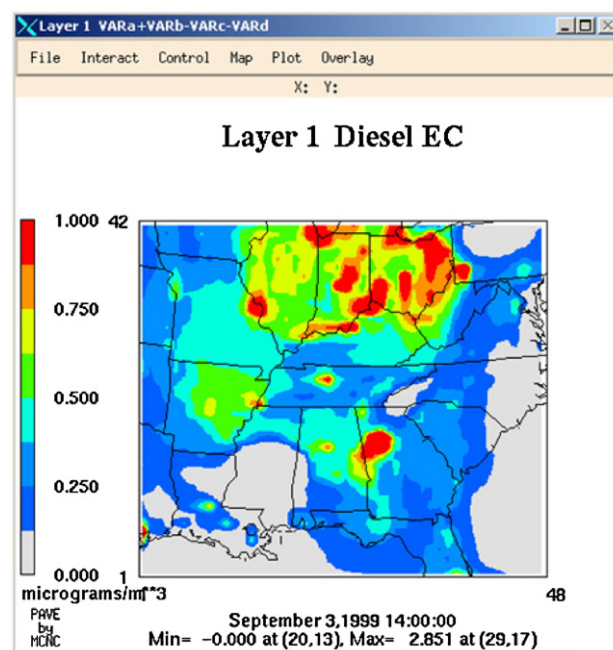

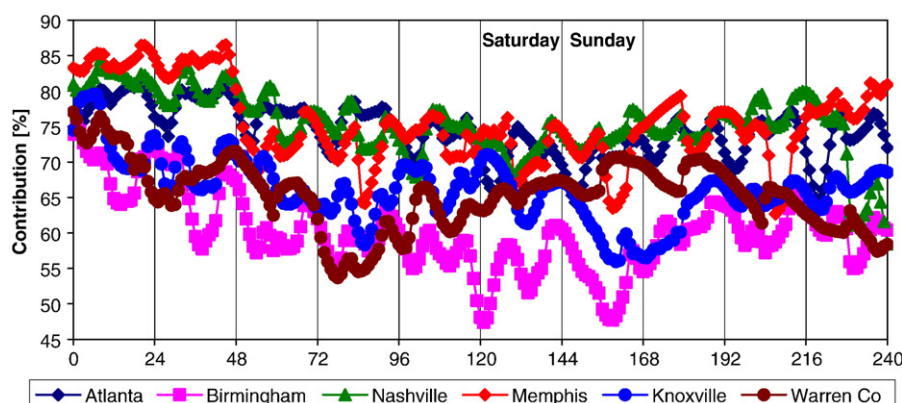Fig. 8. Hourly DFS EC concentrations.

Fig. 9. Contribution of DFS on hourly EC concentrations from 08/30 to 09/08 of 1999. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

aerosols (SAOA). However, CMAQ cannot split sulfates, nitrates, and ammonia between primary and secondary species. CMAQ also track unspeciated mass as crustal/other PM. According to speciation profiles in SMOKE, those crustal/other PM are sources such as road dusts, construction and open burning. The unspeciated $PM_{2.5}$ (crustal and other PM) were modeled as high as 4–12 $\mu g/m^3$ in Fig. 7. The maximum daily average aerosol concentrations occurred in Nashville, Atlanta, and Birmingham, which were 47, 45 and 43% higher than those from the rural area Warren County TN, respectively on the studied episode (Fig. 7). NO_3 was unusually high in Nashville TN, which was 4.8 times higher than the rural area. This could indicate that point and area sources have a significant contribution in Nashville.

In fact, NO_3 concentrations from Nashville had a higher contribution over the total analyzed $PM_{2.5}$ (Table 7) than the other sites with a 7%. Finally, according to Table 7, it is clear that sulfates are the biggest contributors over the total analyzed $PM_{2.5}$ species for each site, mainly in TN, which on average was 42%. This demonstrates that in TN the sulfur contribution from power plants is significant.

3.2.3. DFS sources contribution

The scenario considered was without exhaust DFS emissions. The difference between the base case run and the scenario without DFS emissions gives the DFS contributions as a whole towards the observed concentrations at any receptor. Fig. 8 shows the DFS EC concentration at 2 PM EDT. An animation of the plot suggests higher EC concentrations at night hours and during noon traffic hours, while a lower concentration in the afternoon hours. This suggests that at night and noon there are more goods transportation over the roads. This kind of transportation usually uses diesel fuel. As the day progresses and the mixing layer height increases, the air is more uniformly mixed, there are more kinds 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% of the total EC concentrations in rural regions and as much as 85% in urban areas (Figs. 8 and 9). 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 had lower DFS EC concentrations, while Atlanta area had the highest DFS EC concentrations. Fig. 9 shows the contribution of DFS over the total hourly EC concentrations of the 10 days episode for each site. The DFS for each city contribute with strong variability over the total hourly EC concentrations. There was a little lower contribution on weekends for most sites, especially for Birmingham, where the DFS contributed as low as 47% on Saturday 4th at night and on Sunday 5th about 3 PM.
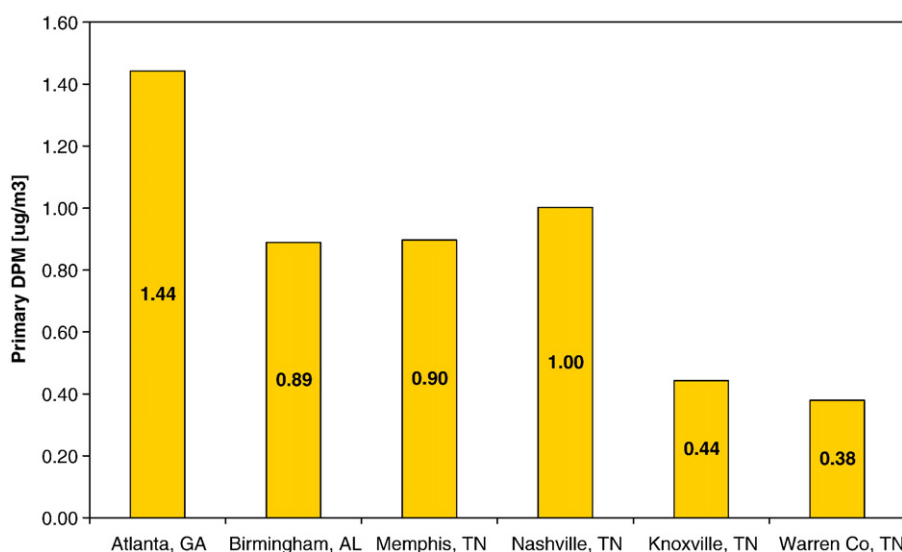

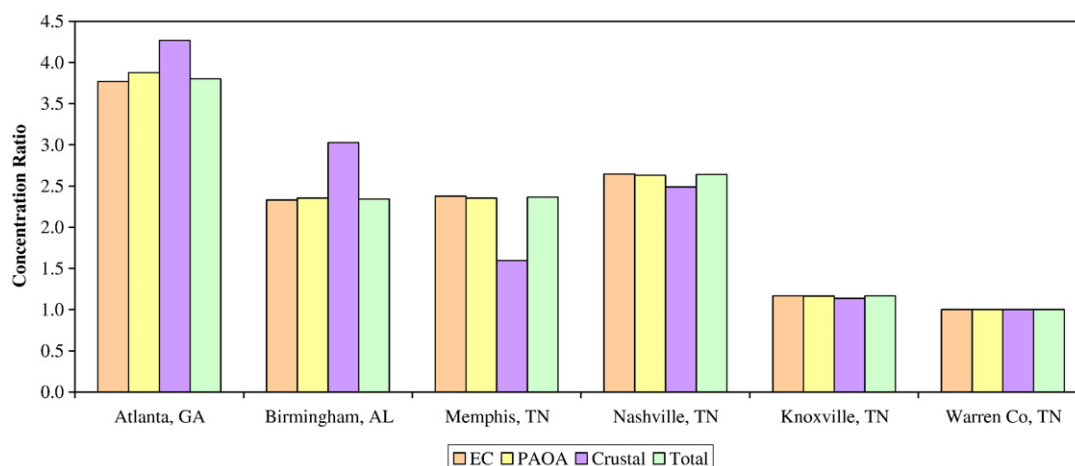Fig. 10. Primary DPM concentration by city from 08/30 to 09/08 1999.

Fig. 11. Concentration ratios to compare primary DPM aerosols by site.

All sites did not show some hourly pattern on the DFS contributions, except Atlanta, where it is possible to see that there are two daily peaks. The highest one is around 8 PM and the second one around 9 AM. Both peaks correspond to the traffic rush hours, mainly for heavy duty vehicles (Fig. 9 dark blue symbol-line). The lowest contributions occurred around 4 and 5 AM, a time where almost no heavy duty vehicles are running. In addition, there is another inflexion point with low contribution, around 11 and noon, when truck drivers are lunching. This Atlanta pattern almost disappeared the weekend of that 10 days episode. For Atlanta, non-road DFS do not influence significantly the total hourly EC concentration patterns. However, for the other sites, non-road DFS affected strongly the total hourly EC concentration patterns. In fact, that pattern had strong variability during the days of the episode and for each hour for those sites (Fig. 9). That variability is due mainly to the effect of the on-road and non-road DFS, but it is due to meteorology and terrain conditions as well. Other sources could contribute too, like gasoline fueled sources, open burning, and others. The variability of the DFS contribution over the total hourly EC concentrations in the Eastern US suggests that using EC concentrations as an ambient DPM tracer is not a good method, producing significant uncertainty.

Primary and secondary aerosols compose DPM; however, the most important part from a health point of view is the primary part. This work used EC, PAOA, and crustal aerosol species to estimate primary DPM because CMAQ cannot split other species to primary and secondary aerosols. Fig. 10 shows the average primary DPM concentrations by cite, where the maximum primary DPM concentra-

tion occurred in Atlanta (1.44 µg/m³), Nashville (1.00 µg/m³), and Memphis (0.90 µg/m³), 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 (Fig. 11). In the other hand, it is clear that EC is the biggest contributor over the total analyzed primary DPM species with an average of 73%, followed by PAOA for each site with 26% in average. Secondary DPM species were not analyzed because there is no monitoring data available and CMAQ does split the primary and secondary aerosols. It is important that future CMAQ versions include a tool to separate effectively primary and secondary aerosols, mainly for DPM.

According to Table 8, DFS were significant contribution sources of the total daily EC concentrations for each analyzed site, which accounted from 60 to 76% of the total daily EC concentrations. The maximum contribution occurred in Nashville, followed by Memphis and Atlanta, and the minimum contribution occurred in Birmingham instead of Warren County. This higher contribution in Warren County can be due to the lack of other sources different from DFS. The average DFS contribution was 70% of the total daily EC concentration. These DFS contributions were not close to the values obtained by Zheng et al. (2002), where the authors employed a molecular marker chemical mass balance model to apportion the sources of atmospheric particulate matter in eight cities in the Southeastern U.S. Their work was for one-month of each season between the spring of 1999 and the winter of 2000. The calculated values for January, April, July, and October were 74, 84, 92, and 85%, respectively. Their results demonstrated the seasonal impact of wood smoke on EC concentrations. The difference

Table 8
Average DFS contribution to each ambient 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

between the results of this study and their results could be due to his method not taking into account the chemical and photochemical reactions of the aerosol precursors, generating significant uncertainty.

In Table 8, it is possible to see that DFS contributed in average 8.3% of the total ambient $PM_{2.5}$ for all analyzed sites, with Memphis the site where DFS contributed the maximum value (10.1%). For Atlanta, the DFS contribution was 6.8%, which was different than the value of 10.5% estimated by Kim et al. (2004) using a positive matrix factorization (PMF) model over 529 samples between August 1998 and August 2000 (Kim et al., 2004). For the Midwest area and using PMF with IMPROVE data between March 2001 and May 2003, Kim et al. (2005) estimated that DFS contributed 2% of the total ambient $PM_{2.5}$. For the Northeastern area and using the same technique the contribution was around 3% (Kim and Hopke, 2006). Finally, for the Great Smoky Mountain National Park and using PMF with IMPROVE data between March 1988 and December 2003, the DFS contribution over the total ambient $PM_{2.5}$ was about 1% (Kim and Hopke, 2006). These receptor results using PMF in contrast with the CMAQ results estimated in this study is that those authors did not take into account the chemical and photochemical reactions of the precursor species of $PM_{2.5}$ aerosols. Those chemical and photochemical mechanisms are included in the CMAQ tools.

The uncertain contribution of the secondary DPM aerosols was mainly over nitrate, ammonia, and sulfate species, because the difference between the base case and the case without DFS does not reflect the non-linear chemical and physical mechanism of the secondary aerosols within the advanced air quality model CMAQ. However, this model does not have a tool to separate some aerosols into primary and secondary species.

4. Conclusions

The maximum $PM_{2.5}$, NH_3, EC, POA, and SO_2 DFS emissions occurred in Atlanta. However, NO_x DFS emissions in Atlanta were not as high as those from Memphis and Nashville. This difference suggests that non-road DFS in Atlanta do not influence significantly the NO_x and DPM emissions as compared with Memphis and Nashville.

Urban DFS emissions contributed (77.9%±8.0) of EC, (16.8%±8.2) of organic aerosols, (14.3%±6.2) of nitrate, and (8.3%±6.6) of sulfate during the selected episode. The highest contributions of EC and sulfate emissions were allocated in Memphis, where there are more non-road sources than the other analyzed sites. TN sites showed more DFS contribution on EC and sulfate emissions mainly due to non-road sources, whose diesel fuel quality is lower in terms of sulfur content than the diesel fuel used to on-road sources. In order to reduce significantly the diesel $PM_{2.5}$ emissions, the government has to generate more restrictive regulations over the non-road diesel fuel quality, mainly on sulfur content and better engine and pollution control technologies.

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, respectively during the studied episode. On the other hand, it is clear that EC is the largest species of the total analyzed primary diesel $PM_{2.5}$ species, with an average value of 73%, followed by PAOA for each site.

DFS contributed (69.5%±6.5) of the total daily EC concentrations, (19.4%±11.2) of nitrate, (10.8%±2.4) of primary anthro-

pogenic 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) had the smaller EC contribution of DFS. The 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. DFS contributed in average 8.3% of the total ambient $PM_{2.5}$ for all analyzed sites, being Memphis the site where DFS contributed with the maximum value (10.1%).

The variability of the DFS contribution over the total hourly EC concentrations in the Southeastern US suggests that using EC concentrations as an ambient DPM tracer is not a good method, producing significant uncertainty.

The contribution over the secondary DPM aerosols was uncertain mainly over some aerosol species. The difference between the base case and the case without DFS does not reflect the non-linearity between chemical and physical mechanism of the secondary aerosols within the advanced air quality model CMAQ. And this model does not have a tool to split nitrate, sulfate, and ammonia aerosols to primary and secondary species.

Acknowledgment

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