ASSESSMENT OF THE SOURCES OF ORGANIC CARBON AT MONITORING SITES IN THE SOUTHEASTERN UNITED STATES USING RECEPTOR AND DETERMINISTIC MODELS

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1. INTRODUCTION

Organic Carbon Mass (OCM) is the second largest component of fine particulate matter ($PM_{2.5}$) and visibility impairment at urban and Class I areas in the southeastern United States (ammonium sulfate is the largest component). (Brewer, Holman and Hornback,2003) There are numerous sources of OCM including primary OCM emitted directly from combustion of fossil fuels, biomass burning, vegetative detritus and meat cooking as well as Secondary Organic Aerosols (SOA) that are formed from gaseous organic compound precursors that can be either anthropogenic or biogenic in origin. The source contributions for OCM in the southeastern U.S. have been estimated in several recent studies using the Chemical Mass Balance (CMB) receptor model that attributes a large fraction of the OCM to vegetative burning and mobile sources, but the third largest fraction is unexplained OCM that is presumed to be secondary in orgin. (Zheng, Cass, Schaurer and Edgerton, 2002; Yu, Dennis, Bhave and Eder, 2002; and Sangil, Russell and Baumann, 2007) The spatial and seasonal variations in the OCM source contributions are large and the composition and the source of the unexplained fraction is not well understood.

The Visibility Improvements State and Tribal Association of the Southeast (VISTAS) is one of five Regional Planning Organizations (RPOs) that are addressing the technical requirements of the Regional Haze Rule (RHR). VISTAS initiated a special monitoring study to provide a better understanding of the contributions to particulate Carbon in the southeastern U.S. $PM_{2.5}$ samples were collected on quartz fiber filters at four Class I areas and a suburban site in the southeastern U.S. during April 2004 to May 2005 and analyzed for chemical composition as well as for ^{14}C isotope to determine the fraction of total Carbon (i.e., organic carbon mass plus elemental carbon) due to modern versus fossil carbon:

- Great Smoky Mountains National Park (GRSM), NC and TN;
- Mammoth Cave National Park (MACA), KY;
- Shenandoah National Park (SHEN), VA;
- Cape Romain National Wildlife Refuge (ROMA), SC; and
- Millbrook Station (MILL) in Raleigh, NC.

Given the importance of particulate Carbon on $PM_{2.5}$ and visibility in the southeastern U.S. and the uncertainties associated with the sources of Carbon and Carbon emissions, VISTAS initiated a two pronged approach for performing source apportionment: (1) performing CMB receptor modeling by the Desert Research Institute (DRI) (Fujita, Campbell, Engelbrecht and Zielinski, 2009) to identify the Carbon source category contributions to the Carbon samples collected at the five monitoring sites; and (2) performing deterministic (i.e., emissions based modeling) PM source apportionment modeling using three dimensional photochemical grid models to estimate the source contributions to total Carbon in the southeastern U.S. This paper presents the methodology for the deterministic Carbon source apportionment modeling and comparison of the Carbon source apportionment with the CMB receptor modeling and ^{14}C dating.

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2. METHOD

2.1 Approach

The deterministic Carbon source apportionment modeling was performed using the Comprehensive Air-quality Model with extensions (CAMx) (ENVIRON International Corporation, 2008) PM Source Apportionment Technology (PSAT) using the VISTAS 2002 36 km continental U.S. modeling database. (Morris, Koo, Piyachaturawat, McNally, Loomis, Chien and Tonnesen, 2009) The emissions inventory was split into several source categories for PSAT source apportionment modeling that enabled the model to obtain the separate Carbon contributions to the following source categories:

- Primary Carbon from gasoline combustion;
- Primary Carbon from diesel combustion;
- Primary Carbon from biomass burning;
- Primary Carbon from point sources;
- Primary Carbon from area sources;
- Secondary Carbon from anthropogenic sources (SOAA); and
- Secondary Carbon from biogenic sources (SOAB).

The CAMx/PSAT Carbon source apportionment modeling was performed for the 2002 calendar year. The Carbon source apportionment modeling results were then extracted at the five monitoring sites and processed into seasonal average Carbon contributions. The seasonal average Carbon source contributions at the five sites were then compared against the DRI CMB receptor modeling and ^{14}C isotope analysis. The CMB receptor modeling estimated seasonal average Carbon source apportionment at the five monitoring sites for the following source categories:

- Gasoline combustion;
- Diesel combustion;
- Vegetative burning (separately for hardwood and softwood);
- Meat cooking;
- Vegetative detritus; and
- Unexplained.

The CAMx/PSAT and CMB seasonal average Carbon source apportionment were compared for the five sites. The gasoline, diesel and vegetative burning primary Carbon apportionment categories are the same in the CMB and CAMx/PSAT source apportionment results. The CMB meat cooking and vegetative detritus and CAMx/PSAT point and area source Carbon source apportionment results were grouped into an "other" category for comparison with each other.

2.2 Results

Example comparisons of the primary Carbon source apportionment results using CMB and CAMx/PSAT at the five monitoring sites for the Fall season are shown in Figure 1. The CMB Carbon contributions display the seasonal average contributions (square symbol) with the range representing the potential error of the CMB fit. The CAMx/PSAT results present the seasonal average Carbon source contributions using a large symbol, with the 24-hour contributions during the Fall season using smaller symbols that indicate the variability in the source contributions in the deterministic modeling results. CAMx/PSAT estimates substantially less Carbon due to gasoline combustion than CMB, particularly at the more urban MILL site in Raleigh. Across the four Class I areas and averaged across the four seasons the average CMB gasoline combustion contribution to total Carbon (1.47 $\mu g/m^3$) is approximately five times that estimated by CAMx/PSAT (0.31 $\mu g/m^3$). At the more urban MILL monitoring site, the CMB gasoline contribution to Carbon (2.68 $\mu g/m^3$) is approximately 7 times that estimated by CAMx/PSAT (0.38 $\mu g/m^3$). Better agreement between the two models is seen for Carbon due to diesel: the average contribution due to diesel across the four Class I areas estimated by CMB (2.16 $\mu g/m^3$) is approximately a factor of two greater than estimated by CAMx/PSAT (1.16 $\mu g/m^3$) with the CMB contribution at the MILL site (3.23 $\mu g/m^3$) being a little more than a factor of two greater that CAMx/PSAT (1.43 $\mu g/m^3$). The fire Carbon contributions are also in agreement between the two models with fairly good agreement also seen between the other emissions source category, with the exception of the MILL site where CMB is higher than PSAT. The reason why CMB is estimating higher Carbon contributions due to gasoline, diesel and other primary Carbon sources than CAMx/PSAT at the MILL site than the Class I area sites is likely partly due to the 36 km grid resolution used in the CAMx/PSAT modeling that dilutes the urban/suburban emissions in the Raleigh

area thereby understating their contributions at the MILL site.

The observed contributions of modern versus fossil Carbon at GRSM in the summer and winter from the ^{14}C isotope analysis are compared with the CMB and CAMx/PSAT Carbon source apportionment in Figure 2. The CMB and PSAT both do a good job in estimating the amount of Carbon due to fossil sources and the PSAT modern Carbon contribution also agrees well with the ^{14}C analysis. The combination of the CMB modern primary carbon plus unexplained carbon agrees very well with the ^{14}C total modern carbon providing evidence that the CMB unexplained carbon is likely mainly SOA due to biogenic sources.

Figure 3 displays the relative contributions to the seasonal average Carbon concentrations at GRSM estimated by CMB and CAMx/PSAT for the Winter and Summer seasons. In the winter, CMB (50%) and PSAT (52%) agree that half of the Carbon at GRSM is due to biomass burning sources. CMB estimates that mobile sources contributes more to the Carbon than PSAT (33% versus 21%) with the diesel contributions (24% versus 17%) agreeing better than the gasoline contribution (9% versus 4%). The CMB Winter unexplained Carbon due to modern sources (UCm; 11%) agrees very well with the PSAT contribution due to secondary carbon due to biogenics (SOAB; 12%), suggesting that the CMB unexplained Carbon component is secondary in origin. In the Summer, PSAT estimates that 75% of the Carbon is due to SOA from biogenic sources, whereas the CMB unexplained fraction is only ~50% of the total Carbon. CMB (32%) estimates three times as much carbon due to mobile sources at GRSM in the Summer compared to PSAT (11%).

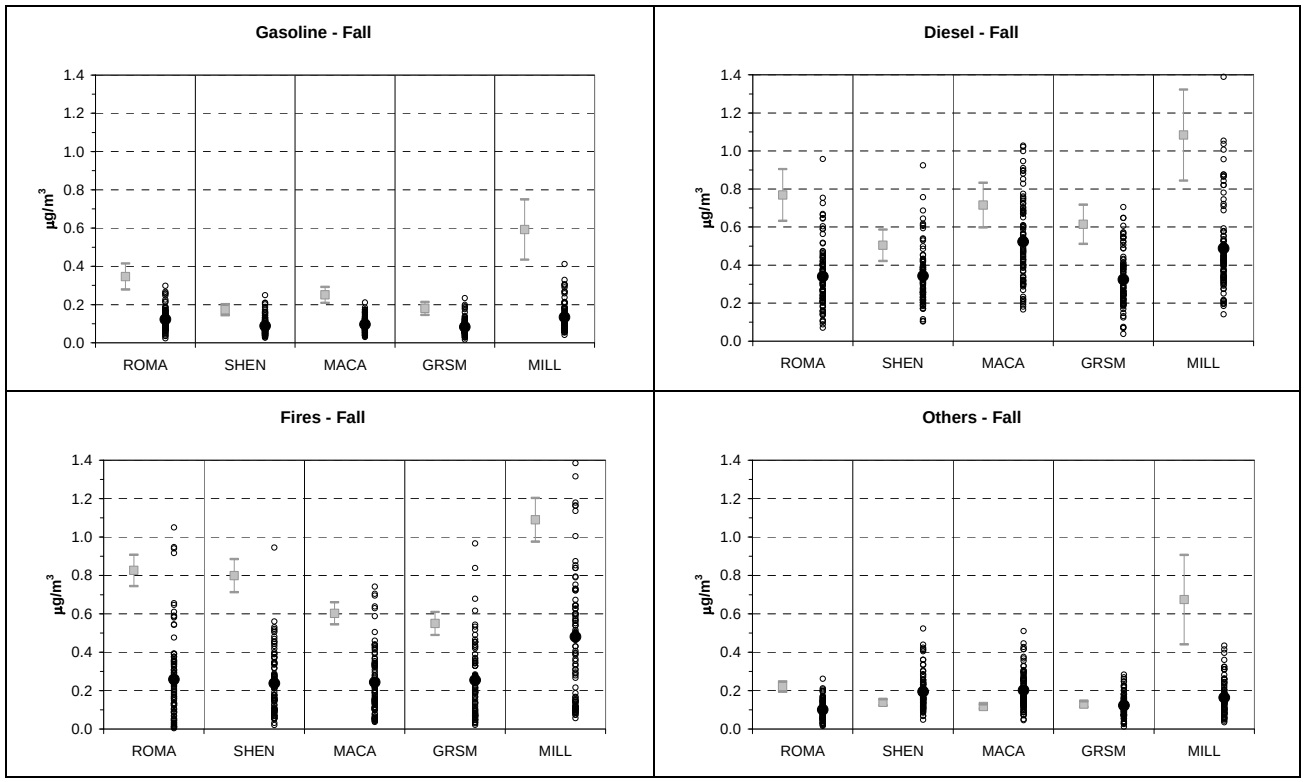

Fig. 1. Comparison of CMB (left) and CAMx/PSAT (right) seasonal average total Carbon (OCM+EC) contributions by source category at the five monitoring sites with the error in the CMB fit and variability in the CAMx/PSAT results by shown the 24-hour average Carbon contributions,

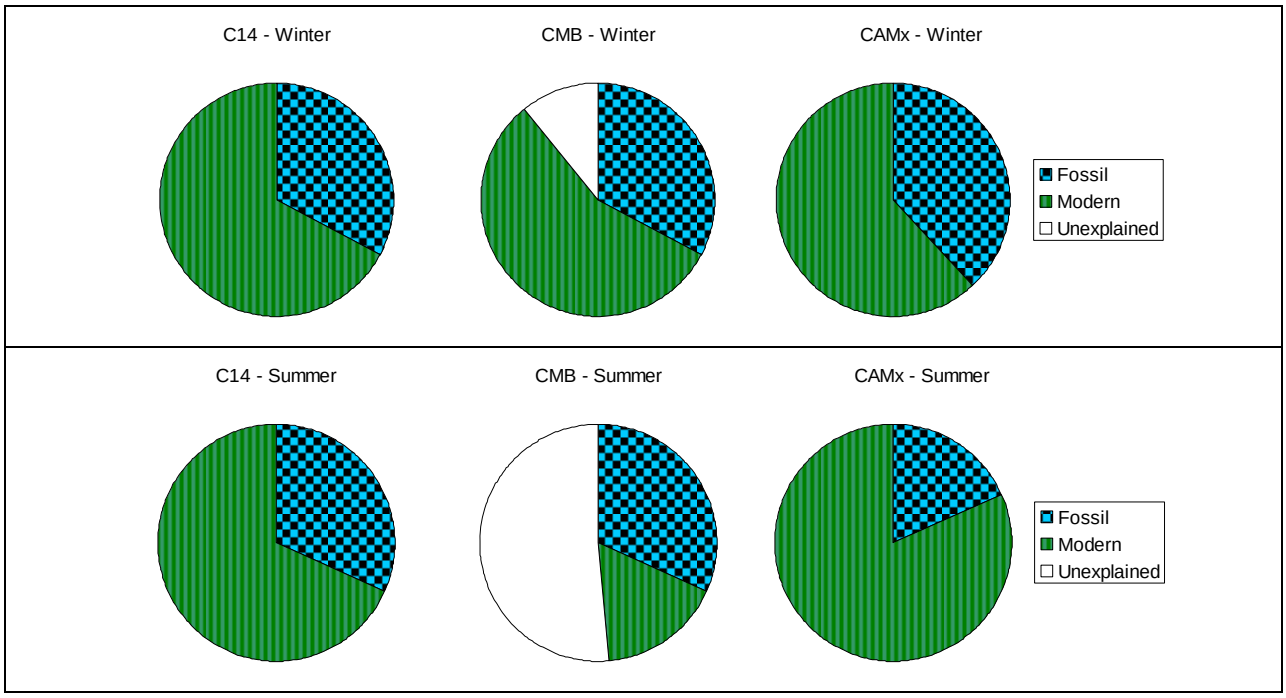

Fig. 2. Comparison of ^{14}C isotope modern and fossil Carbon at GRSM during the summer with CAMx/PSAT estimates of modern and fossil Carbon and CMB estimates of primary modern and fossil Carbon plus unexplained Carbon.

3. SUMMARY

Carbon source apportionment modeling was carried out using the CMB receptor and CAMx/PSAT emissions based deterministic models and analyzed for 5 sites in the southeastern U.S.. The two Carbon source apportionment methods agreed well on the contributions of biomass burning to total Carbon at the five sites. However, the CMB attributed a much larger component of the Carbon to mobile sources than CAMx/PSAT. Both methods exhibited a strong seasonal variation of contributions, with the relative contribution of SOA being much higher in the summer than winter. The CMB and CAMx/PSAT Carbon source apportionment results were compared against ^{14}C isotope analysis and, if you assume that the unexplained component of the CMB source apportionment is SOA due to biogenic sources, then the CMB and CAMx/PSAT agree very well with the ^{14}C analysis on the relative contributions of Carbon due to modern (e.g., biogenic and biomass burning emissions) versus fossil (e.g., mobile and point sources) Carbon.

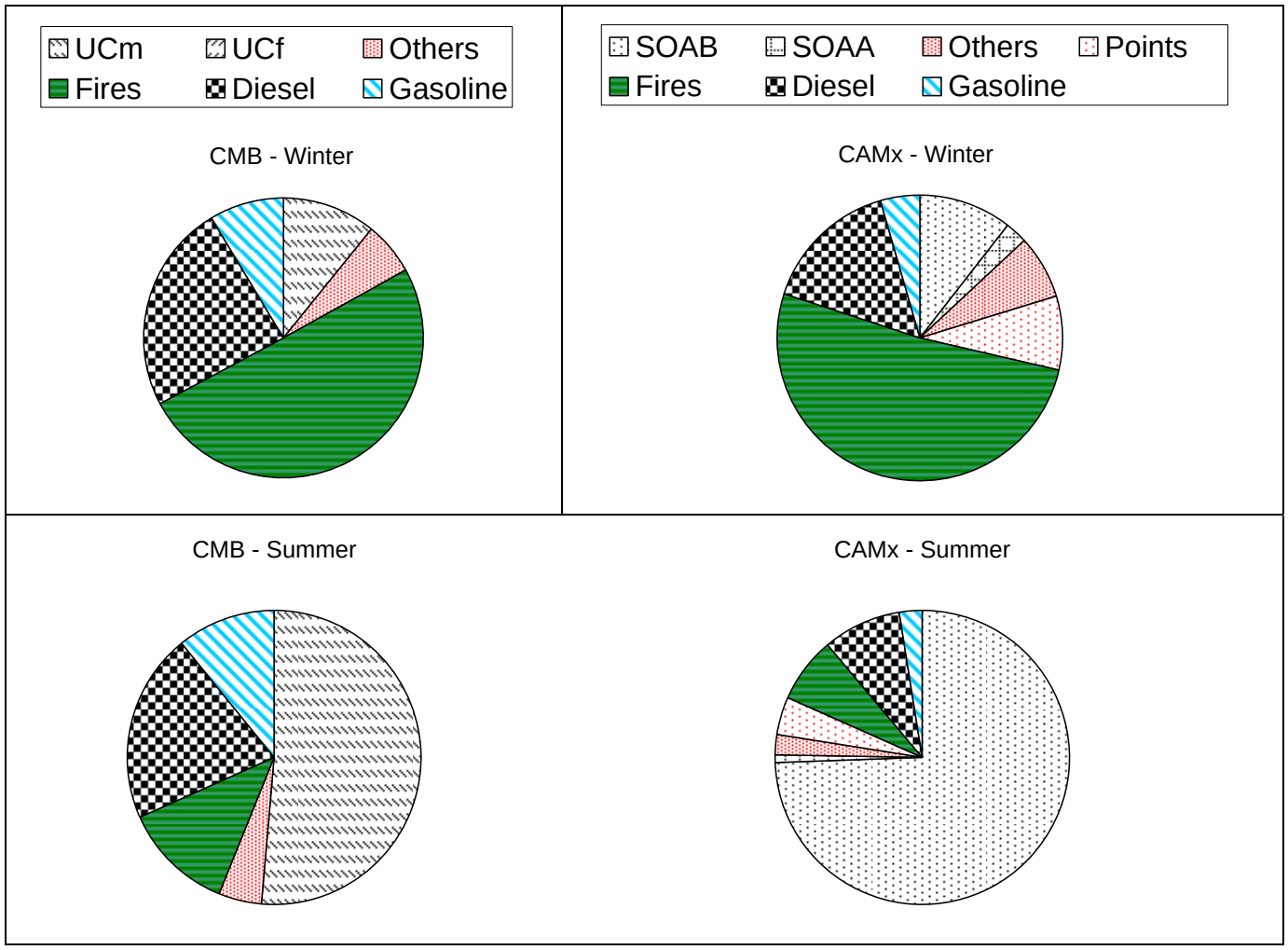

Fig. 3. Relative contributions of source categories to seasonal average total Carbon (OCM+EC) concentrations estimated by CMB (left) and CAMx/PSAT (right) at Great Smoky Mountains national Park (GRSM) for Winter (top) and Summer (bottom).

The biggest differences between the CMB and CAMx/PSAT Carbon source apportionment is for mobile sources, with the CMB estimating much more Carbon associated with mobile sources than the CAMx/PSAT. In particular, CMB estimates a much higher Carbon contribution due to gasoline combustion than CAMx/PSAT. This discrepancy is greater for the MILL suburban site than the five Class I areas that are more rural. One of the major reasons for the lower mobile source Carbon emissions in the CAMx/PSAT is due to deficiencies in the MOBILE6 mobile sources emissions model. Recent research (Lindhjem and Fujita, 2009) has found two areas where the MOBILE6 mobile source emissions are deficient in characterizing Carbon emissions from motor vehicles:

- The OCM and EC particulate matter emission rates in MOBILE6 are out of date and fail to account for temperature and speed effects that are now known to be important.
- MOBILE6 does not account for semi-volatile organic carbon (SVOC) emissions from mobile sources that are emitted as gases and can volatilize into carbon particles.

Although it is difficult to characterize the effects of these deficiencies on the primary Carbon emissions, the lack of including SVOC emissions in the MOBILE6 emissions would result in an underestimation bias in the CAMx/PSAT Carbon estimates associated with

mobile sources. Recent light duty gasoline vehicle emission measurements estimate that the SVOC emissions were over three times the primary Carbon emissions.(Lindhjem and Fujita, 2009) If just a third of the SVOC condensed to particulate Carbon, that would double the amount of Carbon associated with mobile sources in the CAMx/PSAT modeling and improve the agreement between the CAMx./PSAT and CMB Carbon due to gasoline vehicles.

4. ACKNOWLEDGEMENTS

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5. REFERENCES

Brewer, P., S. Holman and J. Hornback. 2003. "Vistas Analyses of Regional Haze in the Southeastern United States." Presented at Annual Air and Waste Management Association Meeting and Exhibition, San Diego, CA. June.

ENVIRON International Corporation. 2008. "User's Guide Comprehensive Air Quality Model with Extensions (CAMx) Version 4.50." Novato, CA. (www.camx.com).

Fujita, E., D. Campbell, J. Engelbrecht and B. Zielinski. 2009. Characterization of Fine Particle Mass Using Particle-Phase Organic Compounds as Tracer. Dessert Research Institute, Reno, Nevada. January.

Lindhjem, C. and E. Fujita. 2009. Development of Modeling Inventory Factors for Mobile Source Particulate Organic Carbon and Semi-Volatile Organic Compound. ENVIRON International Corporation, Novato, California. March.

Morris, R., B. Koo, S.G. Piyachaturawat, D. McNally, C. Loomis, C-J. Chien and G. Tonnesen. 2009. Technical Support Document for VISTAS Emissions and Air Quality Modeling to Support Regional Haze State Implementation Plans. ENVIRON International Corporation, Novato, California. March.

Sangil, L., A.G. Russell and K. Baumann. 2007. Source apportionment of fine particulate matter in the southeastern United States. *J. Air & Waste Manag. Assoc.* **57**, 1123-1135.

Yu, S., R.L. Dennis, P.V. Bhave and B.K. Eder. 2002. Primary and secondary organic aerosols over the United States: estimates on the basis of observed organic carbon (OC) and elemental carbon (EC) and air quality modeling primary OC/EC ratios. *Atmos. Env.* **38**, 5257-5268.

Zheng, M., G. Cass, J.J. Schaurer and E.S. Edgerton. 2002. Source Apportionment of PM2.5 in the southeastern United States using solvent-extractable organic compounds as tracers. *Env. Sci. Technol.* **36**,2361-2371.