Preliminary Analysis of ^{14}C Data for VISTAS 5-Site Network, 2004-2005

Final

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Introduction

During the period of April, 2004 through May, 2005, VISTAS funded the collection of every-third day $PM_{2.5}$ HiVol samples at five sites in the VISTAS region. Desert Research Institute (DRI) was contracted by VISTAS provide laboratory support for this 5-site monitoring network which focused on the origins of fine particulate carbon. In addition to preparing, shipping and storing the samples collected on pre-cleaned quartz filters, DRI determined the collected mass concentrations of the samples, and shipped selected samples to Woods Hole Oceanographic Institute's National Oceanographic Sciences Accelerator Mass Spectrometry (hereafter, NOSAMS) facility for determination of the ^{14}C content and the $^{13}C/^{12}C$ ratios of the aerosol carbon contained in each sample. DRI was also contracted to analyze selected samples using gas chromatography/mass spectrometry, and to apply Chemical Mass Balance analyses to interpret sources of primary carbonaceous material and infer upper limits of secondary carbon in the aerosol samples. The results of this portion of the study are still pending, as well as plans to compare the VISTAS results with those obtained from the CACHE study collection of HiVol samples from four of the 8 SEARCH network sites. Results from the NOSAMS carbon isotopic analysis of selected ¼-filter portions of samples from the 5-site network are analyzed in this report.

Description of Sites

Samples were collected during the period of April, 2004 through May, 2005, on an every-third-day schedule at five sites in the VISTAS region. These included the 3 focus sites at which speciated aerosol sampling was performed: by TVA at the Look Rock, TN, site; by ARA, Inc. at the Millbrook, NC, site in collaboration with the North Carolina Division of Air Quality (DAQ); and by the South Carolina Dept of Health and Environmental Conservation (DHEC) at Cape Romain, SC. Samples were also collected at IMPROVE sites located in Mammoth Cave National Park, KY, and Shenandoah National Park, VA. Conventional high volume (HiVol) samplers, retrofitted with 40-cfm $PM_{2.5}$ inlet heads, were used to collect the HiVol samples on pre-fired, 8x10-in quartz filters. The site details are given in Table 1.

Description of sampling methods and handling procedures

Sampling protocols were developed in which filters were pre-cleaned by DRI to lower the organic blank, shipped to each site operator in clean, sealed aluminum pans, then loaded into filter holders and sent to the sampling site at ~4°C in sealed plastic bags. Within 24 h after sampling, the collected samples were removed in their filter holders and replaced by a new filter, then filter samples were returned to the laboratory for repackaging and shipment back to DRI . Filters were stored at -20°C until shipped, and shipments included a min/max thermometer for QA/QC purposes. Each group of 10 samples also contained a trip blank (filter never removed from the sealed Al container during its trip to and from the site) and a dynamic field blank for which a filter was loaded and unloaded in the sampler, but experienced no air flow and was promptly returned to storage.

Table 1. Location and Elevation of HiVol Sampling Sites

Site	Latitude	Longitude	Elevation, m (MSL)
Cape Romain NWR	32.9408°N	79.6569°W	3 m
Great Smoky Mountains NP	35.6314°N	83.9436°W	815 m
Millbrook, NC	35.8561°N	78.5742°W	100 m
Mammoth Cave NP	37.1315°N	86.1477°W	248 m
Shenandoah NP	38.5229°N	78.4347°W	1098 m

Filters were weighed before and after sampling to determine the collected mass. Calibrated flows and sampling conditions (temperature and pressure) were provided to DRI by the site operators for conversion of mass concentrations to standard conditions as required.

Selection process for ^{14}C and $\delta^{13}C$ analysis by NOSAMS

A group of interested stakeholders, under the leadership of Larry Garrison, formerly the Manager of Technical Services Branch, Kentucky Division for Air Quality, developed the basic selection criteria for which of the collected samples would undergo carbon isotope and CMB source allocation analyses. The following criteria were adopted*:*

- Availability of a valid sample from all 5 VISTAS sites
- Availability of a valid sample from the SEARCH sites
- Use of mass/concentration to enable selection of samples with high and low values
- Use of supplemental data from TEOMs, carbon analyzers, nephelometers, etc.
- Targeted events such as forest fires and ‘leaf-outs’.
- Use of other info such as satellite imagery, etc.

Explanation of these considerations include the following. Since the CMB model works best if the data set is variable, samples were selected to reflect a variety of atmospheric conditions. The intent was to make consistent selections on a quarterly basis, with the limitation that a total not to exceed 250 samples could be analyzed and that total needed to include lab, trip, and field blanks. The intent in comparing days with valid samples at all 5 VISTAS sites with equivalent SEARCH network data was to maximize the number of days with full coverage in both networks, but not to exclude coverage of VISTAS network days of high interest.

There has been extensive correspondence concerning an intercomparison of the chemical analysis techniques and of the CMB source allocation approaches by DRI and Georgia Tech. This relates to the ^{14}C and $^{13}C/^{12}C$ results reported herein as follows. The samples which were selected for isotopic analyses include most (225 of 250, according to the author’s notes) of the samples which are undergoing CMB analysis by DRI. All samples from both SEARCH and VISTAS networks were analyzed for carbon isotopic composition by the NOSAMS group at WHOI. Only the results from the VISTAS samples are presented in this report.

Description of ^{14}C and $\delta^{13}C$ analysis procedures used by NOSAMS

A ¼-portion of each of the selected 8x10-in filters was submitted by DRI for analysis by staff of Woods Hole Oceanographic Institute's (WHOI's) NOSAMS facility. A procedure was used in which the organic aerosol collected on the filter is combusted to CO_2 to quantify the amount of carbon on the filter, the $^{13}C/^{12}C$ ratio is measured, and the remaining sample is converted into a solid pellet for ^{14}C measurement by accelerator mass spectrometry (McNichol et al., 1994; Vogel et al., 1987). The filter sample is placed in a pre-combusted quartz tube containing approximately 2 g of CuO and 100 mg Ag powder. The tube is evacuated on a vacuum line to a pressure of less than 3 mTorr, sealed with a torch, placed in a muffle furnace, heated to 850°C for 5 hours and then cooled. Each tube is then cracked on a vacuum line where the CO_2 is purified, collected, quantified and divided. One portion is transferred to a graphite reaction vessel for ^{14}C measurement, and another, much smaller portion is transferred to a stable isotope ratio mass spectrometer for determination of the $^{13}C/^{12}C$ ratio.

The observed ^{14}C content is compared to that of a standard containing a ^{14}C content similar to ambient $^{14}CO_2$ levels, and the fraction of modern carbon, f_m, determined as the ratio, $(^{14}C/^{12}C)_{obs}/(^{14}C/^{12}C)_{std}$ (Stuiver and Polach, 1977; Donahue et al., 1991). Two primary standards are used during all ^{14}C measurements: NBS Oxalic Acid I (NIST-SRM-4990) and Oxalic Acid II (NIST-SRM-4990C). The ^{14}C activity ratio of Oxalic Acid II ($\delta^{13}C = -17.3$ per mil) to Oxalic Acid I ($\delta^{13}C = -19.0$ per mil) is taken to be 1.293. Every group of samples processed includes an appropriate blank, which is analyzed concurrently with the group. Process blank materials include IAEA C-1 Carrara marble for inorganic carbon and gas samples; a Johnson-Mathey 99.9999% graphite powder for organic carbon samples; and a commercial tank of ^{14}C-free CO_2 for seawater samples. The µmoles of carbon released as CO_2 during the filter sample processing are reported along with the isotopic data..

Summary of data by site

I report in Appendices A1 to A5 a summary of the data from the study, listing the fraction of modern carbon, f_m, compared to the 1948 (pre-bomb carbon) value, the $^{13}C^{12}C$ ratio, $\delta^{13}C$, in parts per mil units compared to the standard, the concentration of aerosol carbon derived from the µmoles of CO_2 evolved from the sample portion, and finally, the $PM_{2.5}$ mass concentrations derived from DRI's 'before and after' filter weighing and the sample volume reported by the site operators. The all-study averages of these parameters are shown in Table 2, both the averages for all days in which all four parameters (f_m, $\delta^{13}C$, AMS [C], and $PM_{2.5}$ mass) were valid (top) and the averages for the 36 days in which all listed parameters at all sites were valid (bottom). These two average data sets are not significantly different for any parameter and the 36-day data sets show the following trends:

Table 2. Averages of All Carbon Isotope, Carbon, and $PM_{2.5}$ Mass Data by Site

Site	N of f_m Values	Fraction Modern C, f_m	$\delta^{13}C$, °%	AMS C, μg/m3	$PM_{2.5}$ Mass, μg/m3
All valid days:					
CARO	47	0.718	-26.43	3.57	12.3
GRSM	45	0.731	-26.59	3.15	13.1
MACA	48	0.734	-26.21	3.39	10.6
MILL	46	0.698	-26.53	5.46	15.0
SHEN	47	0.671	-26.45	3.27	11.5
All common days:					
CARO	36	0.712	-26.49	3.55	12.1
GRSM	36	0.734	-26.64	3.17	12.3
MACA	36	0.745	-26.23	3.21	9.9
MILL	36	0.671	-26.54	5.51	14.6
SHEN	36	0.661	-26.54	3.20	12.0

- f_m decreases in the order: MACA,GRSM > CARO > MILL, SHEN;

- average $\delta^{13}C$ in a narrow range between -26.2 and -26.7, with no significant inter-site differences but with a few outliers;

- AMS [C] decreases in the order: MILL >> CARO > GRSM,MACA,SHEN;

- $PM_{2.5}$ mass decreases in the order: MILL > GRSM,CARO,SHEN > MACA

The trends at these sites for data from all seasons (but with a preponderance of spring season data) show that the fine mass is largest at the sole urban/suburban site, and is so because the carbonaceous aerosol levels are higher at that site. The $PM_{2.5}$ mass at GRSM, CARO, and SHEN are about the same but the AMS [C] is a larger fraction (and other components a smaller fraction) of fine mass at the coastal site. Although there are no significant differences in $^{13}C/^{12}C$ ratios between the sites, the fractions of modern carbon at MILL and SHEN are on average lower than at CARO, with the highest average values observed at the forested MACA and GRSM sites.

Relationship of f_m to other measured parameters.

The fraction of modern carbon in the carbonaceous portion of ambient aerosol samples was plotted vs. other measured parameters to assist in understanding its temporal and spatial variability. Plots of f_m vs. $\delta^{13}C$ for all samples and for each site (Figure 1) showed no relationship. There were a few outliers as low as -33 and as high as -15 °%, and 5 of 6 outliers were at the MILL and SHEN sites. In general, though, the values were tightly clustered in the range of -27.5 to -24.5 °%, and were independent of season. This cluster of values about -26 °% is consistent with our understanding that $^{13}C/^{12}C$ ratios derive from a combination of sources including fossil fuel combustion and conversion of C4 plant material to atmospheric aerosols (*ref.—look this up*).

The plot of f_m from all sites vs. quartz filter estimates of $PM_{2.5}$ (Figure 2) showed a very weak **upward** trend with $PM_{2.5}$ mass with a slope not significantly >0. Plotting all data for individual sites (Figures 3a-e) indicated that this trend is stronger for easterly sites (SHEN, CARO), less strong for MILL, and barely discernable for GRSM and MACA. This trend was somewhat puzzling, since conventional wisdom would suggest that the high $PM_{2.5}$ mass values should be associated with more stagnant conditions and possibly higher contributions from secondary anthropogenically derived aerosols (i.e., lower f_m values). So next we segregated the data and plotted f_m vs. $PM_{2.5}$ mass concentration for all sites by season, as shown in Figures 4a-d. It is clear from the plots that, only in the summer season does the significant upward trend in f_m with increasing $PM_{2.5}$ mass concentrations persist; there is no trend in autumn and winter. For the largest data set, spring, no trend is seen except for the most northeasterly SHEN site, which actually shows a **downward** trend consistent with significant anthropogenic influence at high $PM_{2.5}$ mass. It appears, however, that the trend in the summer season is best explained by biogenic emissions being converted to secondary organic aerosols in the more stagnant, slow-moving, photochemically active summertime air masses. Emissions from the dense vegetation of the southeast U.S. appear to dominate over anthropogenic VOC emissions regionally, and thus conditions leading to high $PM_{2.5}$ mass levels produce organic aerosols with higher modern carbon content in summer compared to other seasons.

This hypothesis was tested by also plotting f_m values vs. the AMS-measured carbon concentrations, as shown in Figure 5. The results are not definitive for the ‘all sites, all seasons’ data set, with a weak upward slope with increasing [C] ($r^2 = 0.15$). However, it appears that the increase of f_m with [C] may level off at about 5 $\mu g/m^3$. Plotting all data by site (Figures 6a-e) yields results which are consistent with Figure 5, show a moderate increase in f_m with carbon concentration. The r^2 values are very modest for GRSM, MACA, and MILL (not shown) largely because of outliers, but the r^2 values for CARO and SHEN (0.42 and 0.43, respectively) are significant, although a leveling off of the plots at higher carbon concentrations is not as evident. Plotting the data by season does not facilitate interpretation significantly compared to the site-by-site f_m vs. $PM_{2.5}$ plot, showing a weak upward trend in all seasons (except for the GRSM data), with a large amount of scatter. Summarizing the results from all of these plots indicates that there is a consistent increase at most sites of the f_m as carbon concentrations increase at all sites and all seasons, and an increase in f_m with fine particle mass which is significant only during the summer season. This indicates that meteorological conditions that lead to high mass generally lead to high carbon concentrations, and that under those conditions the fraction of modern carbon is increased compared to conditions in which mass and C concentrations are low.

Comparison of f_m results in the network on individual days

An all-site comparison of the f_m results from various sampling days was made to determine if there is a consistent pattern between the sites, to determine whether some sites were consistently lower or higher for all days and/or days in which the sites were in the same synoptic air mass. Data for days in which valid f_m values were available for all sites are shown in Table 3, arranged by season (see Appendices A1-A5 for the raw data from each site). There were several days with valid samples data for all sites in which there was good agreement among all but one of the sites, with that site have much larger or smaller fraction of modern carbon. For example, SHEN f_m is much lower than at other sites on 8/31/04 and 10/21/04, and MILL f_m is much lower on 6/2/04 and 12/08/04; in contrast CARO f_m was much higher than at other sites on 11/17/04 and 2/9/05.

Trajectory analyses were conducted for 11 days in which valid samples were available from all sites to confirm whether the similarities or single site differences in f_m and/or TC levels indicated that the sites had experience transport (or not) within the same air mass. Trajectories for 4/27/04, for which both TC levels and f_m values were uniformly high, are all in continental, high pressure air masses with strong subsidence and with relatively slow transport (Figure 7). Trajectories for 9/21/04, for which TC levels are lower and more variable (MILL> MACA>GRSM>CARO>SHEN) and for which f_m values are relatively constant but lower (0.6 range), are faster moving with the air mass transported from the northeast US and eastern Canada in less than 2 days (Figure 8). Contrast this with sample days 7/17/04 and 2/9/05 for which the fraction of modern carbon at CARO was much lower and much higher, respectively than at the other sites, and during which the back trajectories indicate that transport to the sites was within distinctly different air masses. On 7/17/04, back trajectories for the four other sites were entirely continental and slow-moving within regions with relatively high biogenic emissions, whereas CARO back-trajectories were less stagnant with substantial portion of the previous 72 hours over the Gulf of Mexico and the coastal Atlantic (Figure 9), apparently resulting in both the lowest TC level in the network and the lowest f_m value. On 2/9/05, CARO had the highest TC and f_m values with trajectories that were circling along the southeast coast (Figure 10). The trajectories for the other 3 sites (no f_m value was available from MILL) indicated transport from inland areas of the southeast. It is not clear why the 2/9/05 coastal trajectory for CARO resulted in a high f_m compared to those for the inland sites (with back-trajectories largely over rural areas). However, it is tempting to conclude from the full body of ^{14}C network data, both the f_m vs. carbon concentration plots and the trajectory analyses, that similar trajectories through regions of moderate to high biogenic emissions lead to high fractions of modern carbon, at least during the spring through early fall period.

Changes in f_m during ‘leafing-out’

I also looked at the spring data from both 2004 and 2005 to see if increasing f_m levels in the spring season could be attributed to ‘leafing out’ at forested sites. Figure 11 shows a plot of f_m as a time series for all of the spring data from both years. There does appear to be a very modest increase in f_m in samples collected at the GRSM and MACA sites in the late April period when the deciduous trees are leafing out in the region. There is no

Table 3. Sampling Days With All Sites With Valid Samples

Run date	f_m Value Rank	f_m at Sites Similar?(Y/N)	f_m Range	Comments
Spring				
04/27/2004	High	Y	0.83-0.91	*
04/30/2004	Med-High	Y	0.69-0.79	
05/09/2004	Med-High	N	0.66-0.82	CARO value << other sites
05/24/2004	Med-High	N	0.54-0.87	
06/02/2004	Med-High	N	0.66-0.81	MILL value << other sites
06/08/2004	Low-High	N	0.46-0.84	* CARO value << other sites
06/11/2004	Med-High	N	0.59-0.80	SHEN value < other sites
03/23/2005	Medium	N	0.54-0.72	SHEN value (0.027) is outlier, not included
04/07/2005	Med-High	N	0.57-0.81	
04/13/2005	Med-High	N	0.51-0.81	
04/16/2005	Med-High	N	0.57-0.84	
04/25/2005	Med-v High	N	0.51-1.09	* lrg range, SHEN<<GRSM
04/28/2005	Med-High	N	0.63-0.79	
05/01/2005	Med-High	N	0.52-0.71	*
05/10/2005	Med-High	N	0.60-0.79	
Summer				
07/08/2004	Med-v High	N	0.64-1.08	
07/17/2004	Med-v High	N	0.66-1.02	* all high xc CARO
07/20/2004	Med-High	Y	0.58-0.82	
08/04/2004	High	Y	0.73-0.83	* MILL sl < high range.
08/07/2004	Med-High	Y	0.68-0.84	
08/13/2004	Med	Y	0.57-0.66	
08/16/2004	(High) Med	N	0.64-0.76	
08/19/2004	High	Y	0.76-0.86	
08/22/2004	Med-High	Y	0.64-0.78	
08/31/2004	Low-Med	N	0.38-0.73	* SHEN value << other sites
Autumn				
09/21/2004	Med	Y	0.60-0.66	*
10/06/2004	Med	N	0.53-0.71	
10/12/2004	Low-Med	N	0.34-0.69	SHEN value << other sites
10/21/2004	(High) Med	Y	0.56-0.77	range 0.70-0.77 excl MACA
10/27/2004	Med-High	N	0.60-0.84	
10/30/2004	Med-High	Y	0.72-0.80	
11/02/2004	Low-High	N	0.41-0.77	CARO, GRSM << other 3 sites
11/17/2004	Med-High	N	0.50-0.80	* CARO value >> other sites
11/20/2004	Med	Y	0.50-0.72	range 0.68-0.72 excl SHEN
12/02/2004	Med-High	N	0.53-0.81	
12/08/2004	Low-Med	N	0.32-0.76	MILL value << other sites
Winter				
12/29/2004	Med-High	N	0.66-0.80	*
01/31/2005	Medium	N	0.61-0.75	included tho GRSM missing
02/09/2005	Med-High	N	0.52-0.90	MILL missing, CARO>>others
02/24/2005	Med	N	0.54-0.66	included tho SHEN missing
03/20/2005	High	Y/N	0.78-1.77	* range 0.78-0.93 excl MACA (outlier high)

* indicates back-trajectories obtained.

indication of an increase for the other forested site, SHEN, or at the MILL or coastal CARO site. It does not appear that the sampling protocol can unequivocally detect increases in f_m during leafing-out even at forested sites, probably due in part to the substantial day-to-day synoptic variability in air masses reaching the sites.

Summary

This preliminary analysis of the ^{14}C and $^{13}C/^{12}C$ ratio data from high volume samples taken in the VISTAS region show that biogenic sources of carbonaceous aerosol—both primary and secondary—are important contributors to aerosol fine mass at all sites and in all seasons, generally exceeding the contributions from fossil sources of aerosol ($f_m > 0.5$, on average). When combined with CMB source apportionment data based on analyses of organic tracers, this information may provide important guidance in the development of effective haze abatement strategies in the southeastern USA.

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Figure 1. Fraction Modern Carbon vs. $\delta^{13}C$

All Sites

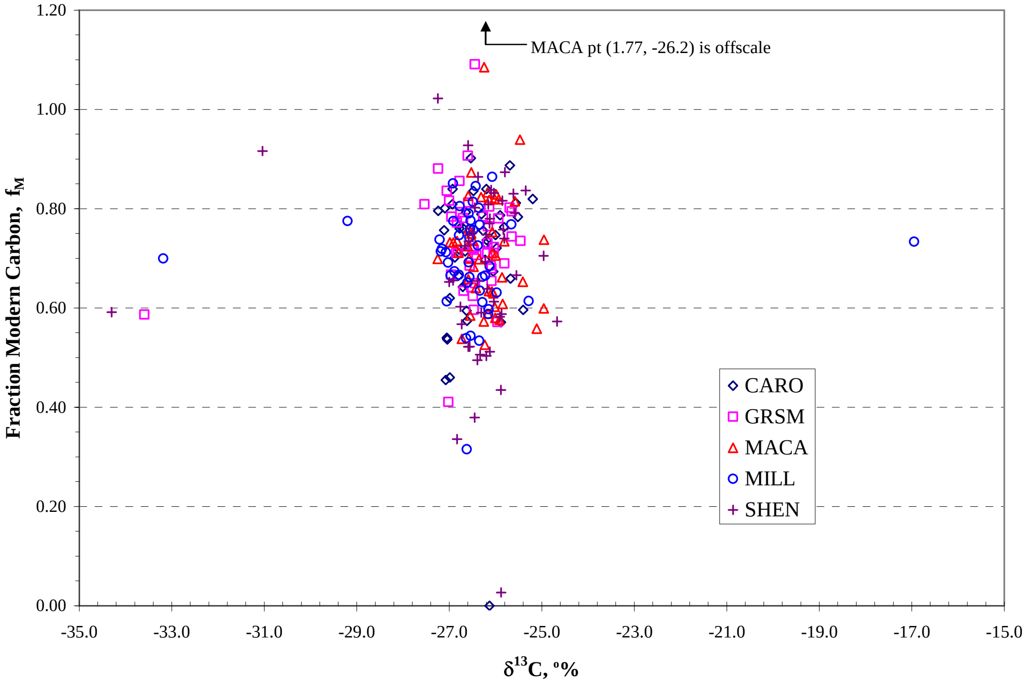


Figure 2. Fraction Modern Carbon vs. PM2.5 Mass

All Sites, All Data

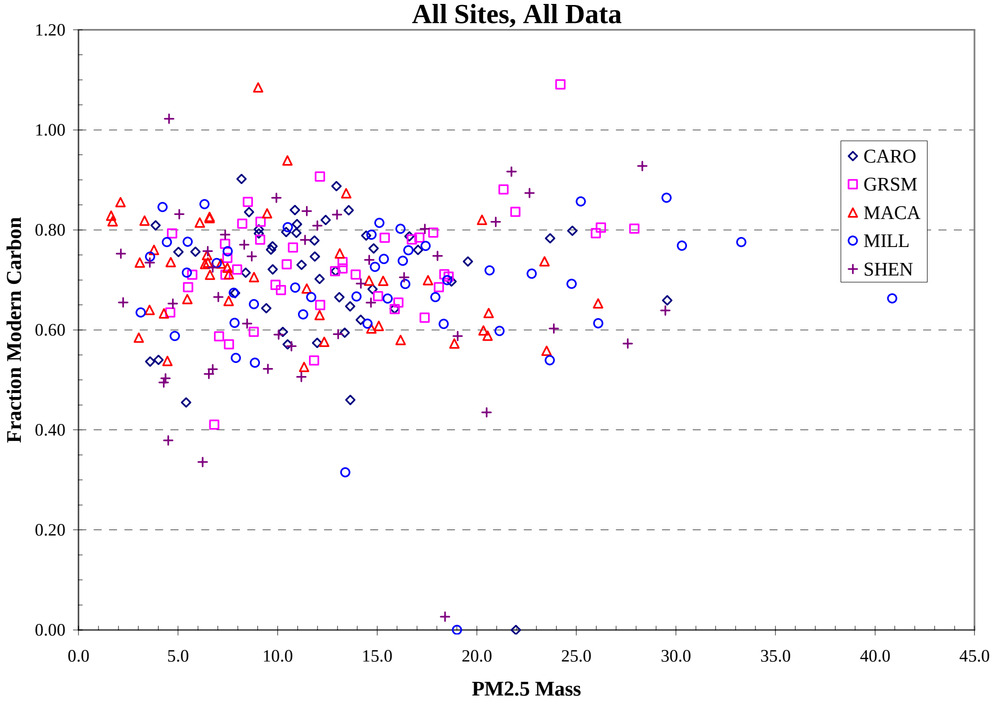


Figure 3a. Fraction Modern C vs. $PM_{2.5}$ Mass

Cape Romain Site, All Data

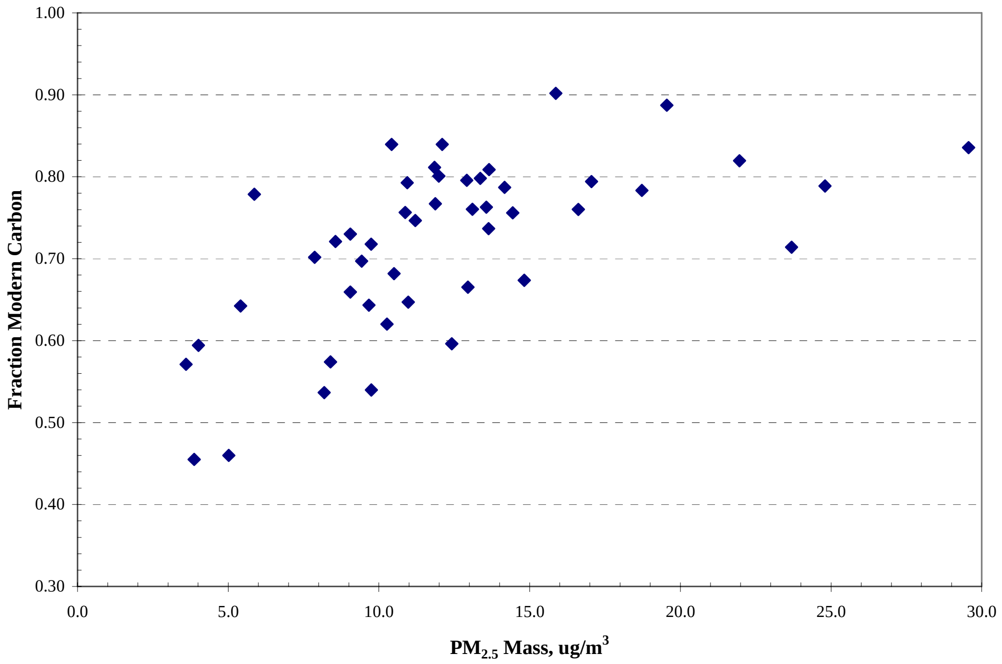


Figure 3b. Fraction Modern Carbon vs. $PM_{2.5}$ Mass

Great Smoky Mountains Site, All Data

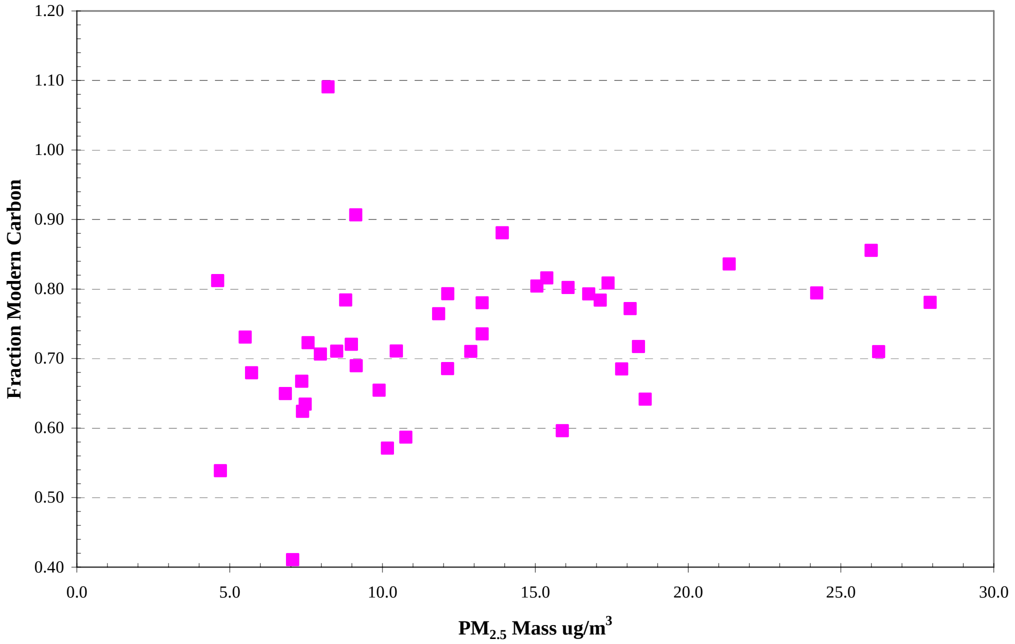
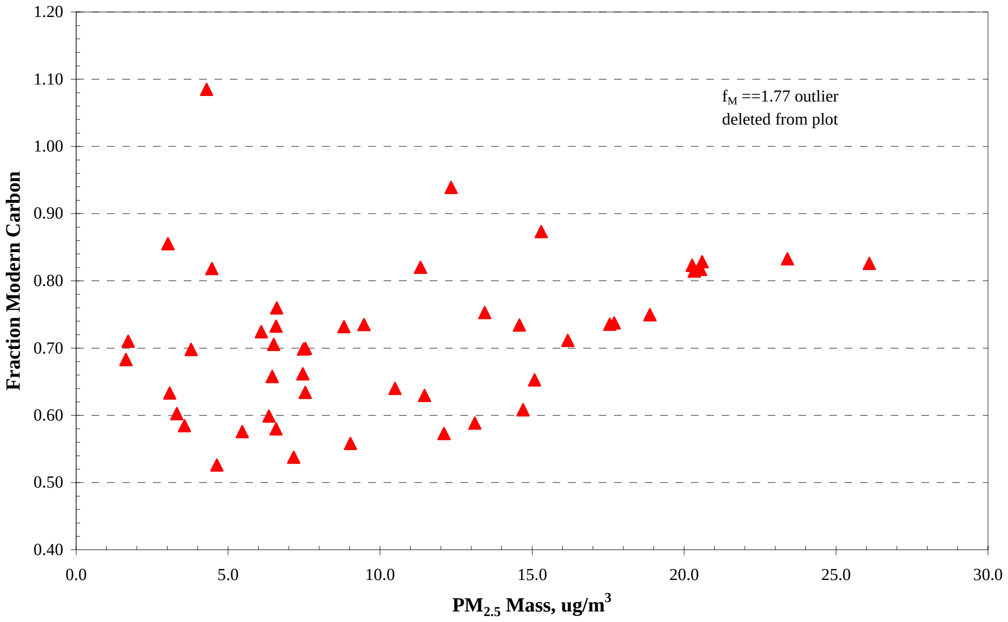


Figure 3c. Fraction Modern Carbon vs. $PM_{2.5}$ Mass

Mammoth Cave Site, All Data



f_M ==1.77 outlier
deleted from plot

Figure 3d. Fraction Modern Carbon vs. $PM_{2.5}$ Mass

Millbrook Site, All Data

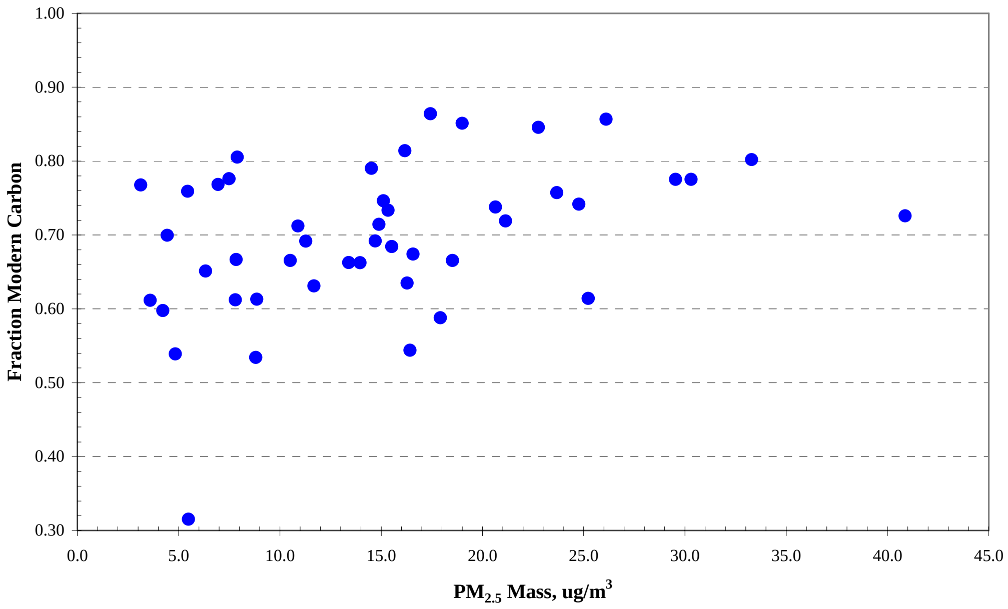


Figure 3e. Fraction Modern Carbon vs. $PM_{2.5}$ Mass

Shenandoah Site, All Data

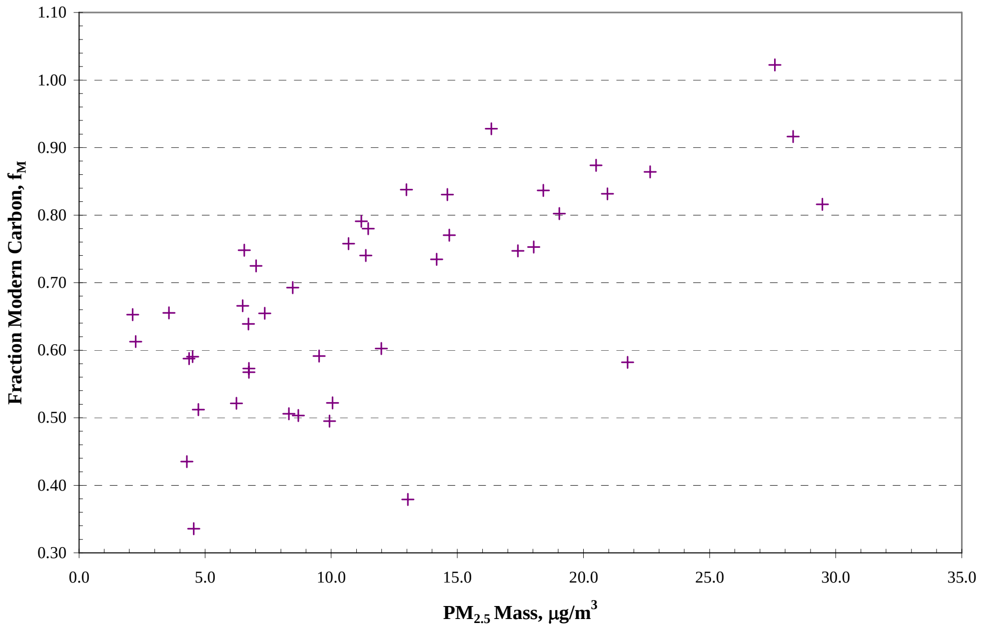


Figure 4a. Spring Fraction Modern Carbon vs. $PM_{2.5}$ Mass

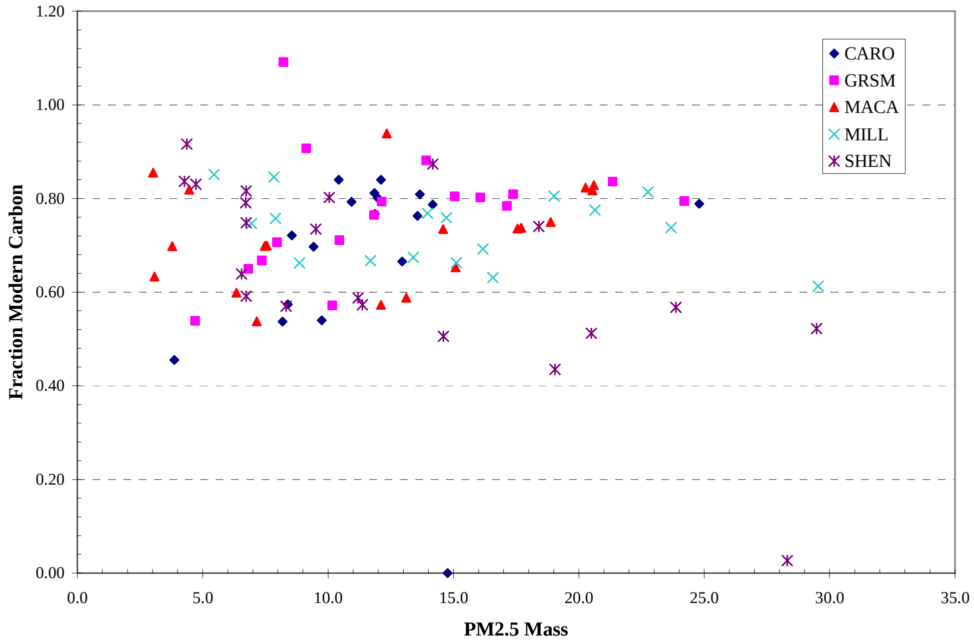


Figure 4b. Summer Fraction Modern Carbon vs. $PM_{2.5}$ Mass

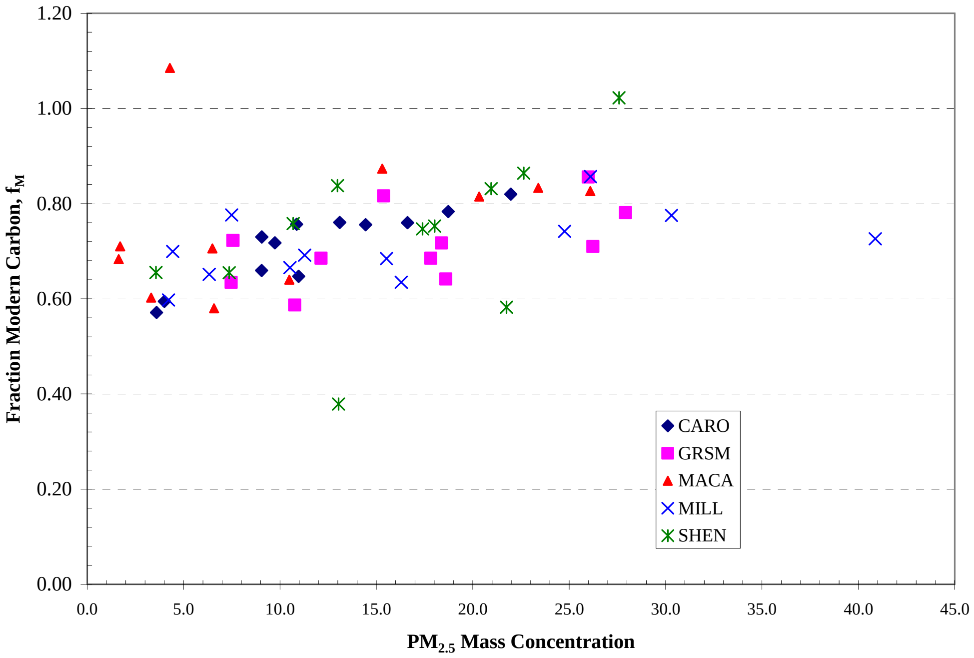


Figure 4c. Autumn Fraction Modern Carbon vs. $PM_{2.5}$ Mass

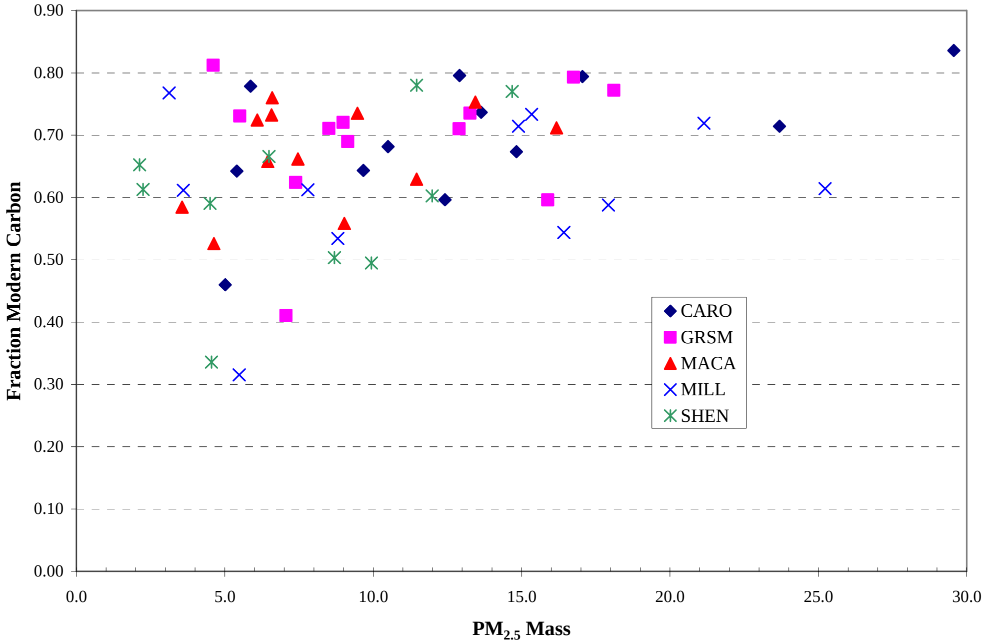


Figure 4d. Winter Fraction Modern Carbon vs. $PM_{2.5}$ Mass

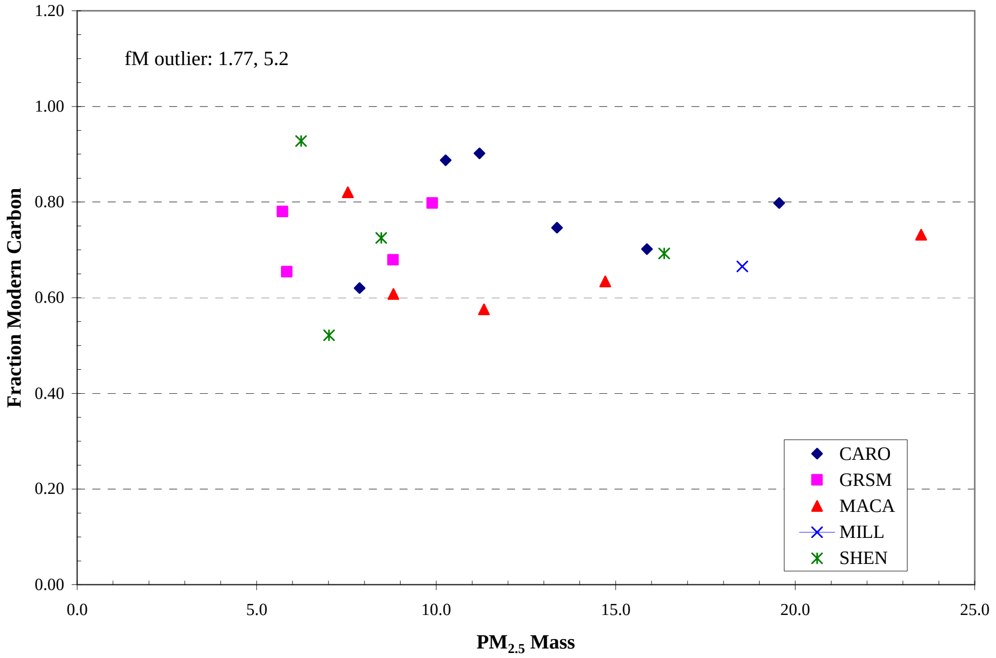


Figure 5. Fraction Modern Carbon vs. Aerosol Carbon
All Sites, All Seasons

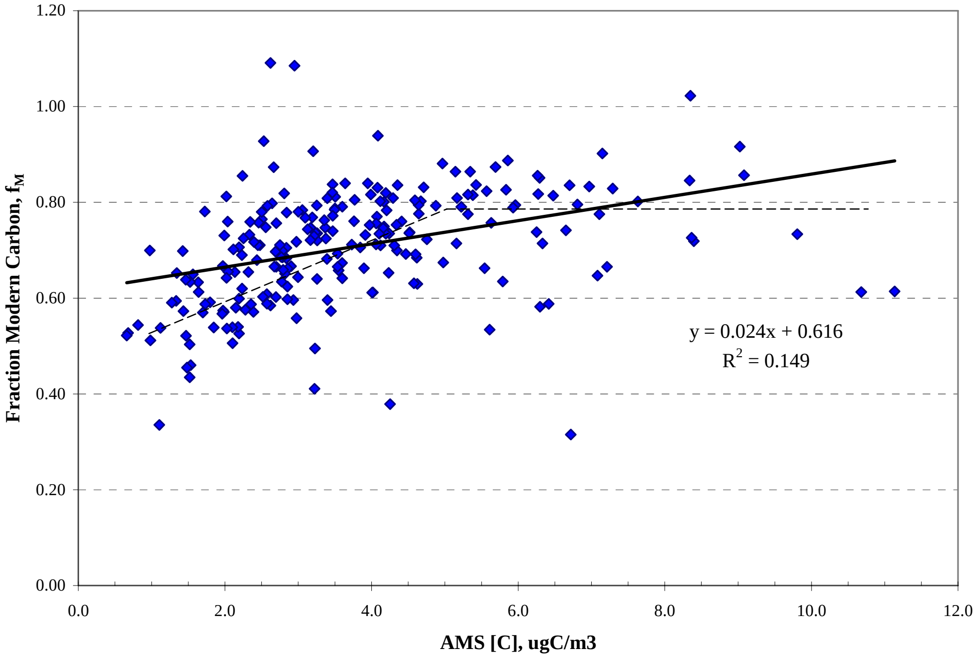


Figure 6a. Fraction Modern Carbon vs. AMS [C]
CARO, All Seasons

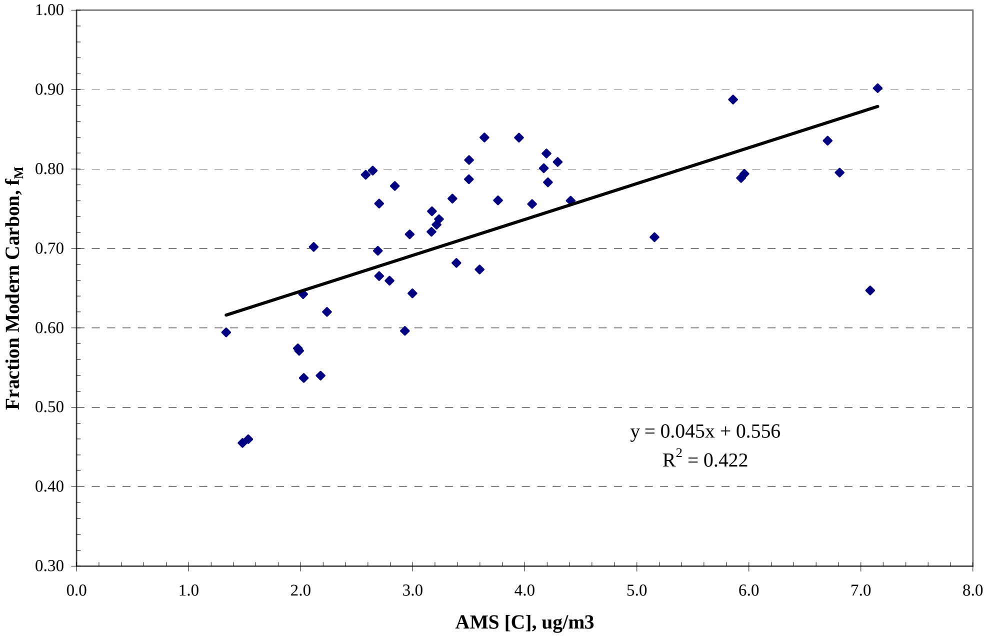


Figure 6b. Fraction Modern Carbon vs. AMS [C]

GRSM, All Seasons

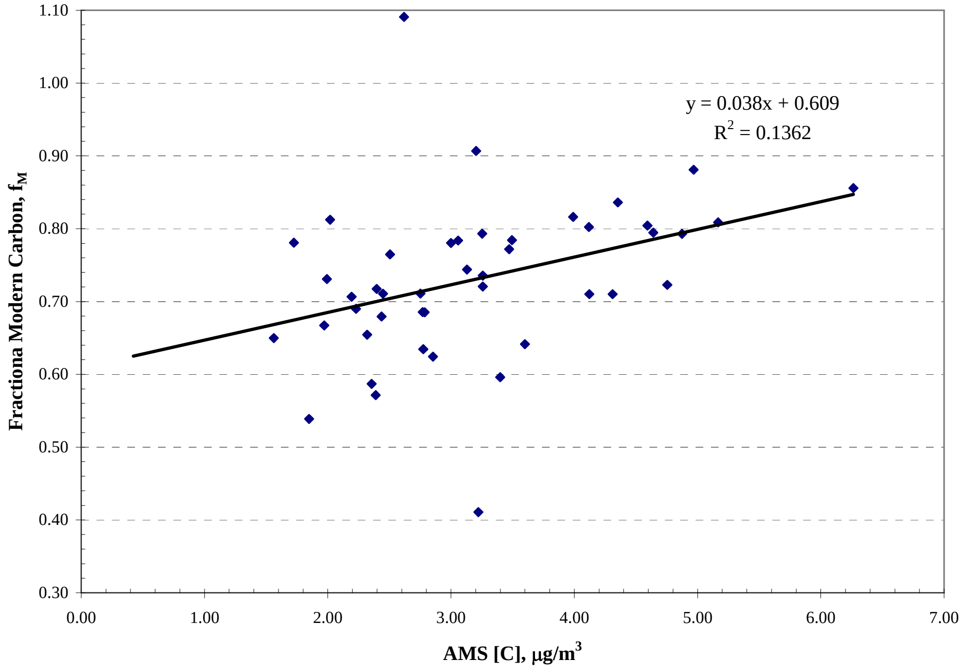


Figure 6c. Fraction Modern Carbon vs. AMS [C]

MACA, All Seasons

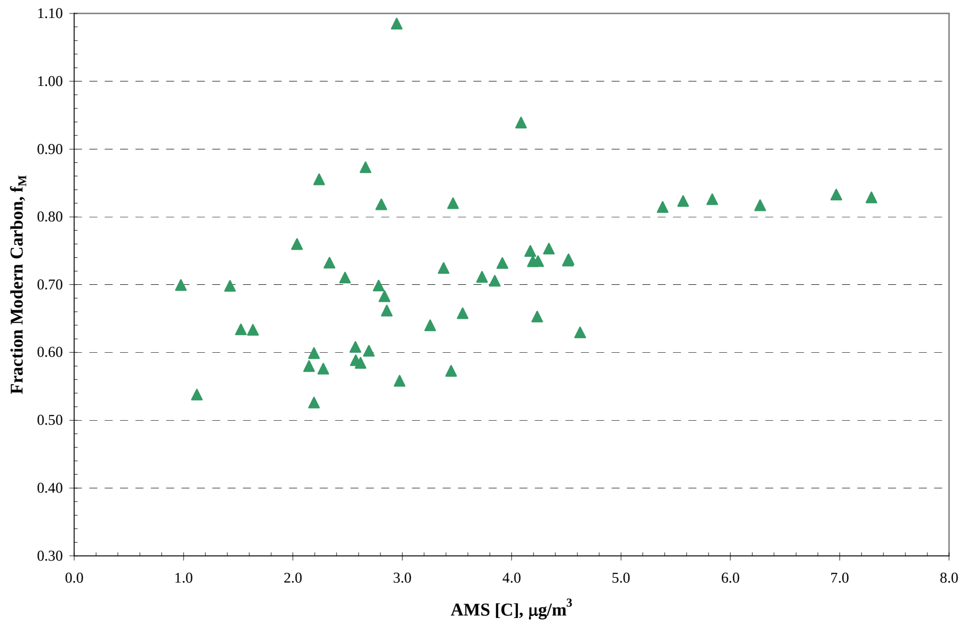


Figure 6d. Fraction Modern Carbon vs. AMS [C]

MILL, All Seasons

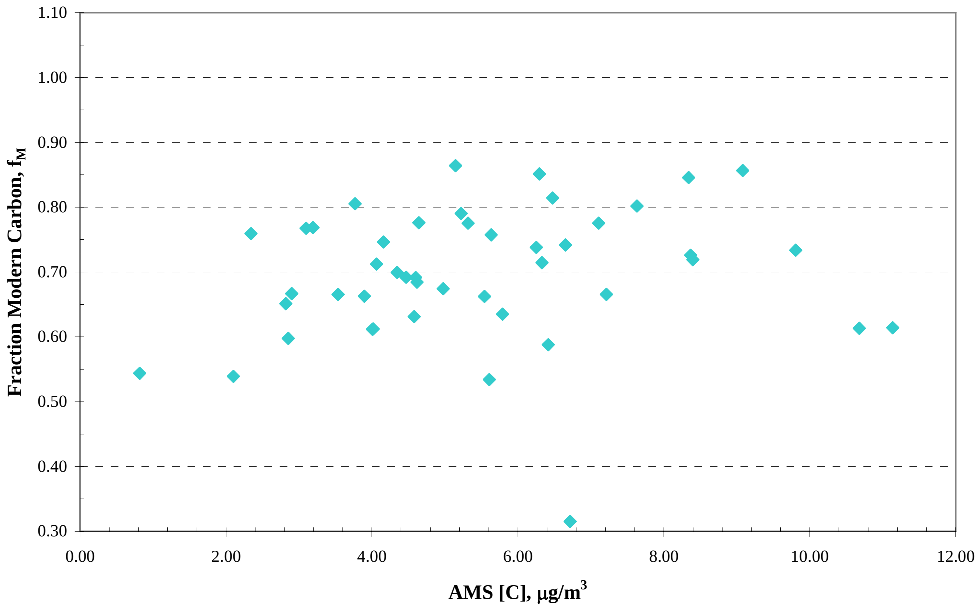


Figure 6e. Fraction Modern Carbon vs. AMS [C]

SHEN, All Seasons

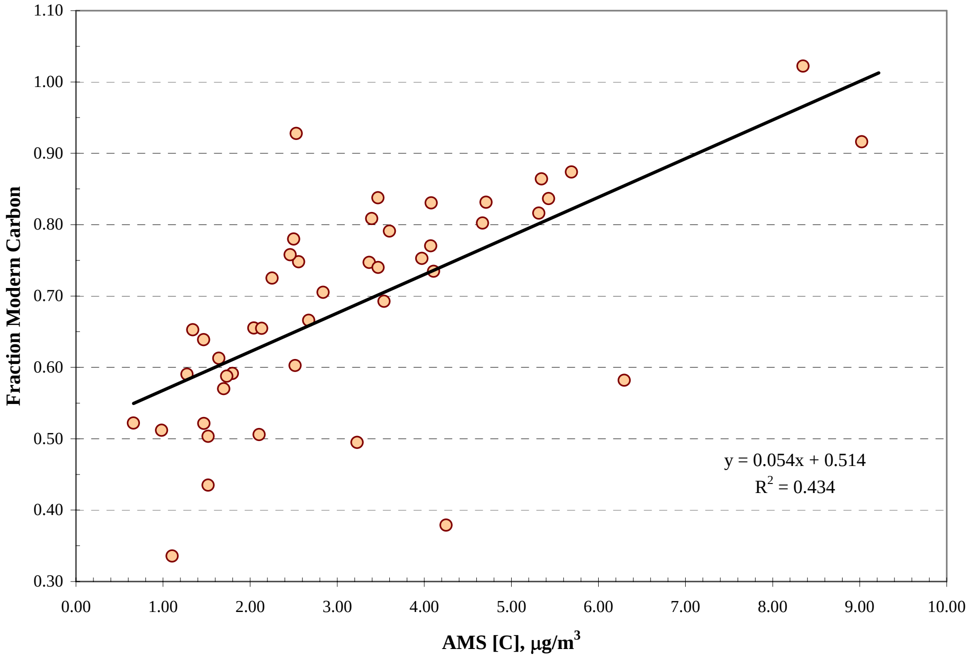
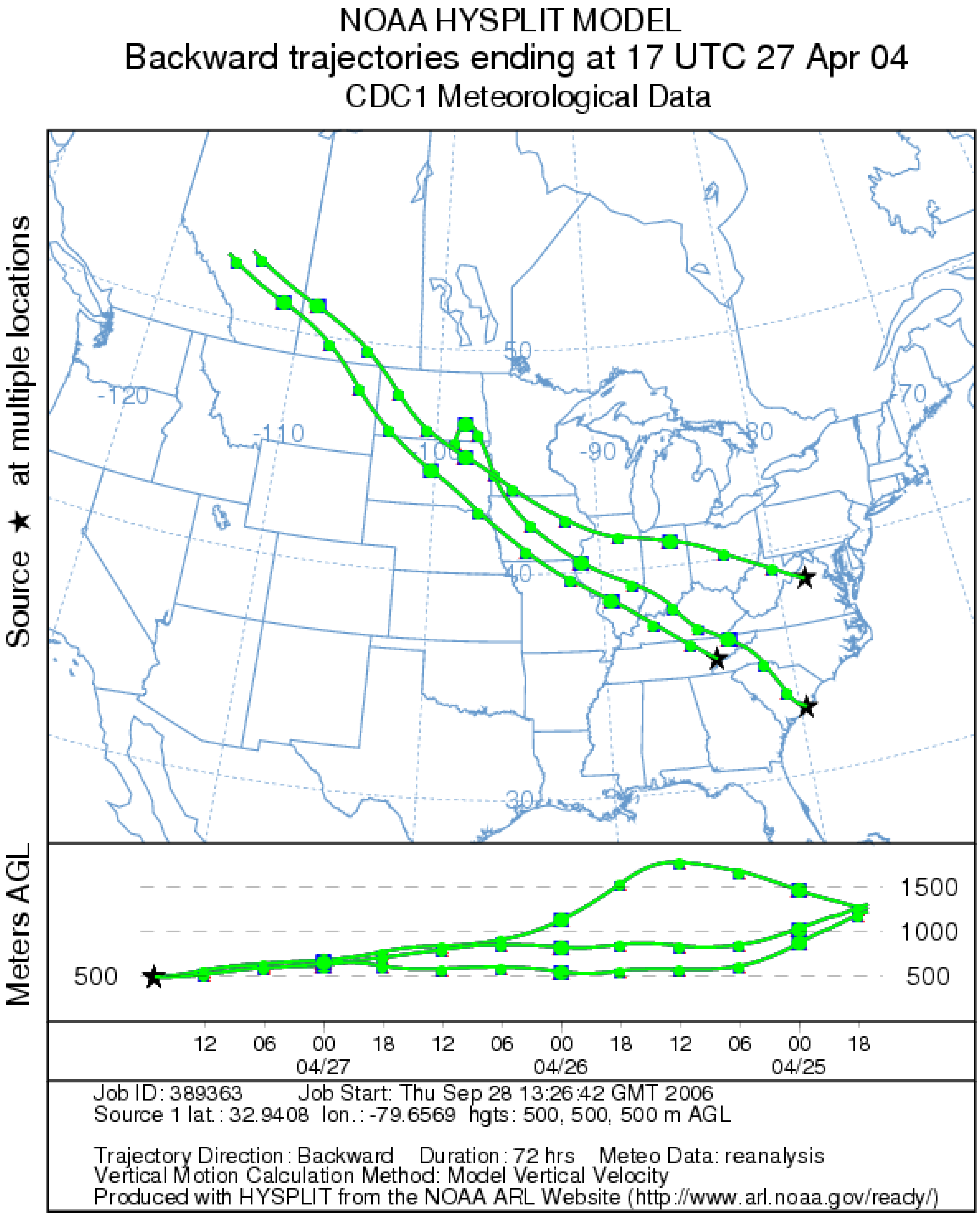


Figure 7. 72-Hr Back-trajectories for CARO, GRSM, and SHEN
Arriving Noon (EDT), April 27, 2004

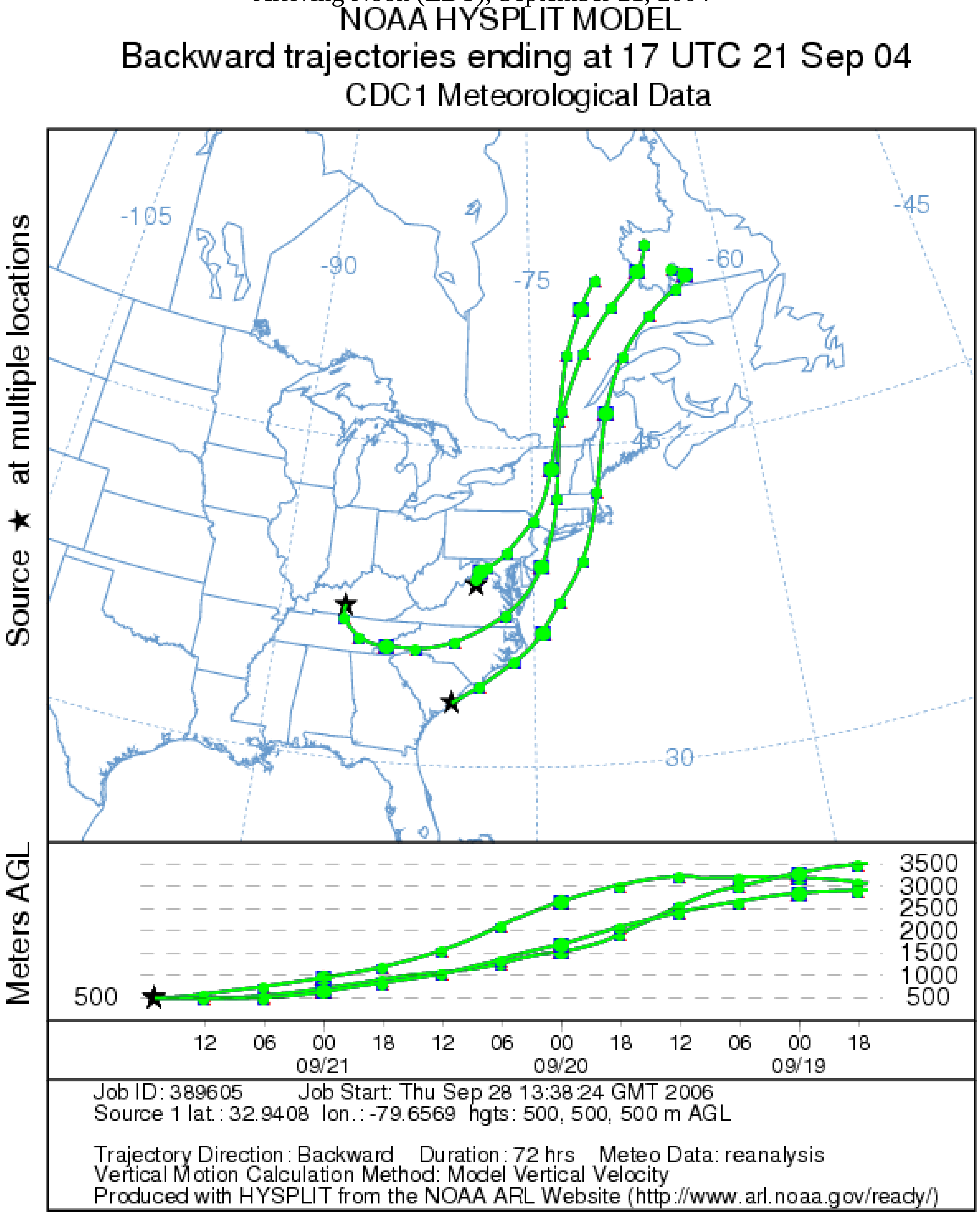


NOAA HYSPLIT MODEL
Backward trajectories ending at 17 UTC 27 Apr 04
CDC1 Meteorological Data

Job ID: 389363 Job Start: Thu Sep 28 13:26:42 GMT 2006
Source 1 lat.: 32.9408 lon.: -79.6569 hgts: 500, 500, 500 m AGL

Trajectory Direction: Backward Duration: 72 hrs Meteo Data: reanalysis
Vertical Motion Calculation Method: Model Vertical Velocity
Produced with HYSPLIT from the NOAA ARL Website (http://www.arl.noaa.gov/ready/)

Figure 8. 72-Hr Back-trajectories for CARO, MACA, and SHEN
Arriving Noon (EDT), September 21, 2004

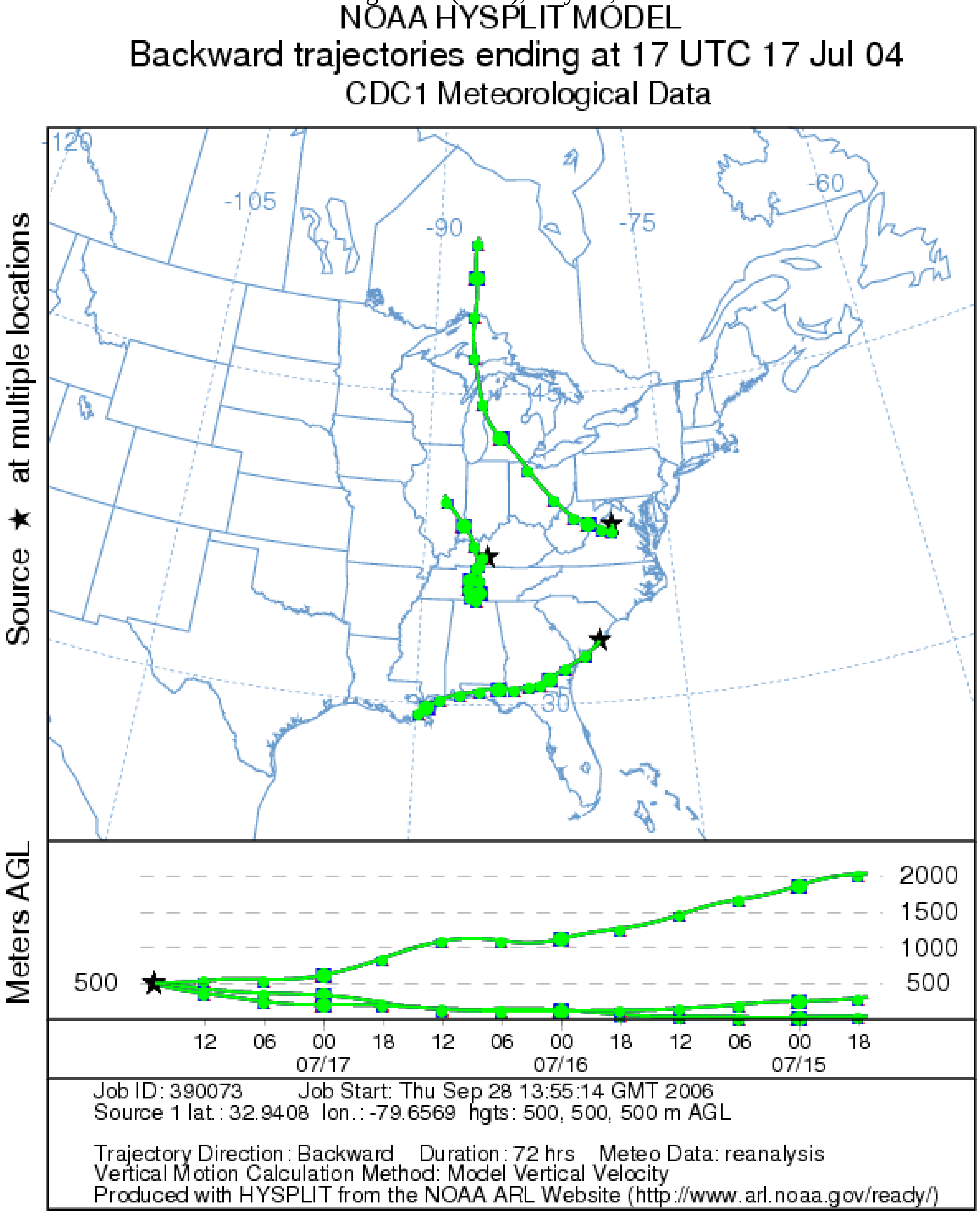


NOAA HYSPLIT MODEL
Backward trajectories ending at 17 UTC 21 Sep 04
CDC1 Meteorological Data

Job ID: 389605 Job Start: Thu Sep 28 13:38:24 GMT 2006
Source 1 lat.: 32.9408 lon.: -79.6569 hgts: 500, 500, 500 m AGL

Trajectory Direction: Backward Duration: 72 hrs Meteo Data: reanalysis
Vertical Motion Calculation Method: Model Vertical Velocity
Produced with HYSPLIT from the NOAA ARL Website (http://www.arl.noaa.gov/ready/)

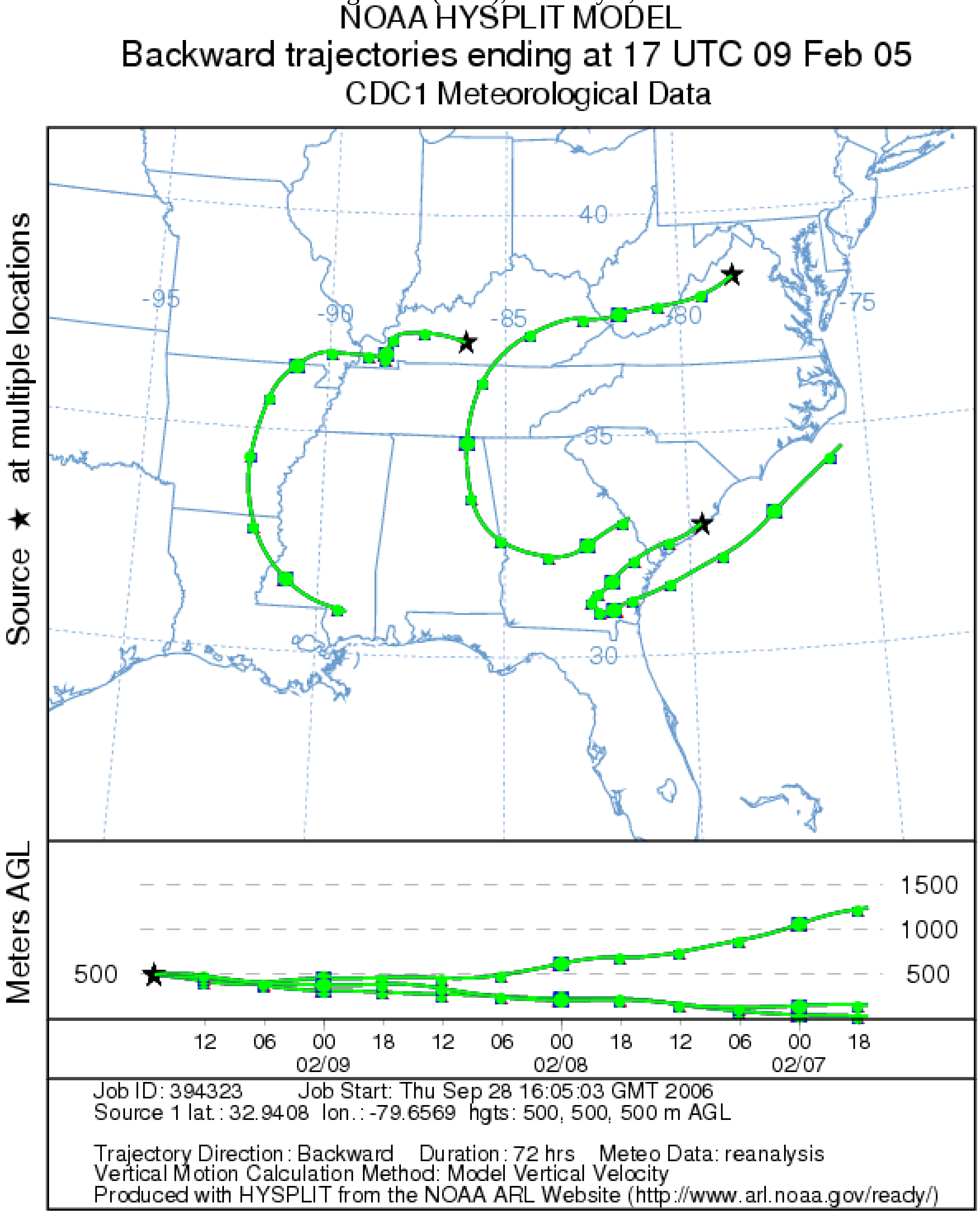
Figure 9. 72-Hr Back-trajectories for CARO, MACA, and SHEN
Arriving Noon (EDT), July 17, 2004



Job ID: 390073 Job Start: Thu Sep 28 13:55:14 GMT 2006
Source 1 lat.: 32.9408 lon.: -79.6569 hgts: 500, 500, 500 m AGL

Trajectory Direction: Backward Duration: 72 hrs Meteo Data: reanalysis
Vertical Motion Calculation Method: Model Vertical Velocity
Produced with HYSPLIT from the NOAA ARL Website (http://www.arl.noaa.gov/ready/)

Figure 10. 72-Hr Back-trajectories for CARO, MACA, and SHEN
Arriving Noon (EDT), February 9, 2005



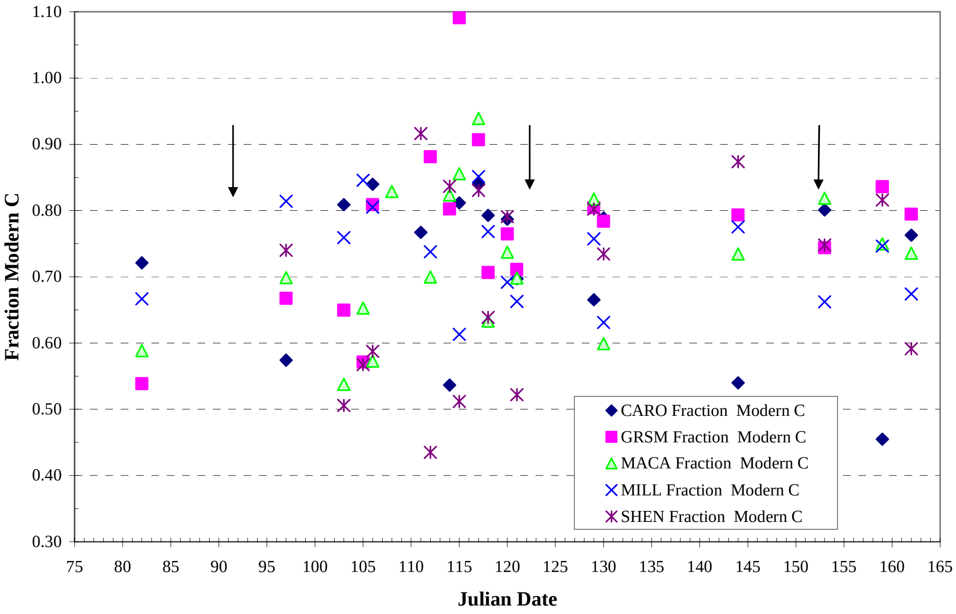
NOAA HYSPLIT MODEL
Backward trajectories ending at 17 UTC 09 Feb 05
CDC1 Meteorological Data

Job ID: 394323 Job Start: Thu Sep 28 16:05:03 GMT 2006
Source 1 lat.: 32.9408 lon.: -79.6569 hgts: 500, 500, 500 m AGL

Trajectory Direction: Backward Duration: 72 hrs Meteo Data: reanalysis
Vertical Motion Calculation Method: Model Vertical Velocity
Produced with HYSPLIT from the NOAA ARL Website (http://www.arl.noaa.gov/ready/)

Figure 11. Time Series of Fraction of Modern Carbon

VISTAS Sites, Spring 2004 and 2005 (Arrows denote 1 April, 1 May, 1 June)



Appendix A1. Data from Cape Romain

Run date	Fraction Modern C, f_m	δ13C, °%	AMS C, μg/m3	$PM_{2.5}$ Mass, μg/m3
04/21/2004	0.787	-26.0		14.2
04/24/2004	0.665	-26.5	2.03	13.0
04/27/2004	0.540	-26.9	3.64	9.7
04/30/2004	0.801	-27.0	3.50	12.0
05/09/2004	0.455	-25.7	2.70	3.9
05/24/2004	0.763	-26.0	2.18	13.6
06/02/2004	0.820	-26.6	4.17	22.0
06/08/2004	0.647	-26.9	1.48	11.0
06/11/2004	0.659	-26.2	3.35	9.1
06/20/2004	0.783	-26.1	4.19	18.7
07/08/2004	0.756	-25.6	7.08	14.4
07/17/2004	0.718	-26.6	2.79	9.7
07/20/2004	0.571	-26.2	4.21	3.6
08/04/2004	0.756	-26.3	4.07	10.9
08/07/2004	0.760	-26.8	2.97	16.6
08/13/2004	0.761	-27.0	1.99	13.1
08/16/2004	0.594	-26.9	2.70	4.0
08/19/2004	0.730	-25.9	4.41	9.1
08/22/2004	0.642	-26.8	3.76	5.4
08/28/2004	0.674	-27.1	1.34	14.8
08/31/2004	0.596	-27.1	3.21	12.4
09/21/2004	0.737	-27.1	2.02	13.6
10/06/2004	0.836	-25.8	3.60	29.6
10/12/2004	0.714	-25.2	2.93	23.7
10/21/2004	0.460	-26.6	3.23	5.0
10/27/2004	0.796	-25.7	6.70	12.9
10/30/2004	0.682	-25.5	5.16	10.5
11/02/2004	0.779	-26.3	1.53	5.9
11/17/2004	0.794	-26.8	6.81	17.1
11/20/2004	0.643	-25.9	3.39	9.7
12/02/2004	0.798	-27.1	2.84	13.4
12/05/2004	0.787	-26.8	5.96	14.2
12/08/2004	0.665	-26.7	3.00	13.0
01/31/2005	0.747	-26.2	3.17	11.2
02/09/2005	0.902	-26.7	7.15	15.9
02/21/2005	0.702	-26.0	2.12	7.9
02/24/2005	0.620	-25.4	2.24	10.3
03/20/2005	0.887	-26.2	5.86	19.6
03/23/2005	0.721	-26.5	3.17	8.6
04/07/2005	0.574	-26.7	1.97	8.4
04/13/2005	0.809	-27.0	4.29	13.7
04/16/2005	0.840	-27.2	3.95	10.4
04/25/2005	0.812		3.50	11.8
04/28/2005	0.793		2.58	10.9
05/01/2005	0.697		2.69	9.4
05/10/2005	0.789		5.93	24.8

Appendix A2. Data from Great Smoky Mountains National Park

Run date	Fraction Modern C, f_m	δ13C, °%	AMS C, μg/m3	$PM_{2.5}$ Mass, μg/m3
04/15/2004	0.571	-26.1	2.39	10.2
04/24/2004	0.802	-26.1	4.12	16.1
04/27/2004	0.907	-25.9	3.20	9.1
04/30/2004	0.765		2.51	11.8
05/09/2004	0.804	-27.0	4.59	15.1
05/24/2004	0.793	-26.4	3.25	12.1
06/02/2004	0.744	-27.5	3.13	
06/08/2004	0.836	-27.2	4.35	21.3
06/11/2004	0.795	-26.4	4.64	24.2
06/20/2004	0.641	-26.4	3.60	18.6
07/08/2004	0.717	-26.0	2.40	18.4
07/17/2004	0.816	-27.0	3.99	15.4
07/20/2004	0.723	-26.0	4.76	7.6
08/04/2004	0.781	-25.7	1.73	27.9
08/07/2004	0.686	-26.6	2.77	12.1
08/13/2004	0.587	-26.2	2.36	10.8
08/16/2004	0.710	-26.1	4.31	26.2
08/19/2004	0.856		6.26	26.0
08/22/2004	0.635	-25.7	2.78	7.5
08/28/2004		-27.1	0.42	21.9
08/31/2004	0.685	-25.7	2.79	17.8
09/21/2004	0.596	-26.5	3.40	15.9
10/06/2004	0.710	-26.5	4.12	12.9
10/12/2004	0.690	-27.0	2.23	9.1
10/21/2004	0.736	-26.0	3.26	13.3
10/27/2004	0.793	-26.7	4.88	16.8
10/30/2004	0.772	-26.1	3.47	18.1
11/02/2004	0.411	-33.6	3.22	7.1
11/17/2004	0.624	-26.2	2.85	7.4
11/20/2004	0.711	-26.8	2.45	8.5
12/02/2004	0.812	-26.7	2.02	4.6
12/05/2004	0.721	-26.4	3.26	9.0
12/08/2004	0.731	-26.6	1.99	5.5
12/29/2004	0.784	-26.5	3.50	8.8
02/09/2005	0.680	-26.9	2.44	5.7
02/24/2005	0.655	-25.8	2.32	9.9
03/20/2005	0.780	-25.5	3.00	13.3
03/23/2005	0.539	-26.8	1.85	4.7
04/07/2005	0.667	-26.8	1.97	7.4
04/13/2005	0.650	-27.0	1.56	6.8
04/16/2005	0.809	-26.5	5.17	17.4
04/22/2005	0.881	-26.8	4.97	13.9
04/25/2005	1.091	-26.6	2.62	8.2
04/28/2005	0.706	-26.5	2.19	8.0
05/01/2005	0.711	-26.2	2.75	10.5
05/10/2005	0.784	-26.3	3.06	17.1

Appendix A3. Data from Mammoth Cave National Park

Run date	Fraction Modern C, f_m	δ13C, °%	AMS C, μg/m3	$PM_{2.5}$ Mass, μg/m3
04/15/2004	0.653	-25.8	4.23	15.1
04/18/2004	0.829	-26.1	7.29	20.6
04/24/2004	0.823	-26.0	5.57	20.3
04/27/2004	0.939	-25.9	4.09	12.3
04/30/2004	0.737	-26.2	4.52	17.7
05/09/2004	0.817	-26.2	6.27	20.5
05/24/2004	0.735	-27.3	4.19	14.6
06/02/2004	0.819	-26.7	2.81	4.5
06/08/2004	0.750	-26.3	4.17	18.9
06/11/2004	0.736	-26.6	4.52	17.6
07/08/2004	1.085	-26.1	2.95	2.1
07/17/2004	0.873	-26.4	2.66	4.3
07/20/2004	0.815	-25.0	5.38	15.3
08/04/2004	0.826	-25.4	5.84	20.3
08/07/2004	0.683	-26.0	2.84	26.1
08/13/2004	0.580	-26.3	2.15	1.6
08/16/2004	0.640	-25.5	3.26	6.6
08/19/2004	0.833	-25.0	6.97	10.5
08/22/2004	0.710	-26.1	2.48	23.4
08/28/2004	0.706	-25.8	3.85	1.7
08/31/2004	0.603	-25.9	2.69	6.5
09/21/2004	0.658	-26.5	3.55	3.3
10/06/2004	0.526	-26.5	2.19	6.5
10/12/2004	0.662	-27.1	2.86	4.6
10/21/2004	0.558	-26.2	2.98	7.5
10/27/2004	0.753	-26.5	4.34	9.0
10/30/2004	0.725	-25.6	3.38	13.4
11/02/2004	0.733	-26.6	2.33	6.1
11/17/2004	0.630	-26.5	4.63	6.6
11/20/2004	0.712	-26.0	3.73	11.5
12/02/2004	0.585	-26.4	2.62	16.2
12/05/2004	0.735	-26.2	4.24	3.6
12/08/2004	0.760	-26.1	2.04	9.5
12/29/2004	0.732	-26.0	3.92	6.6
01/31/2005	0.608	-26.0	2.57	14.7
02/09/2005	0.634	-26.6	1.52	7.5
02/21/2005	0.820	-26.2	3.47	11.3
02/24/2005	0.576	-25.9	2.28	5.5
03/20/2005	1.772	-25.1	2.81	23.5
03/23/2005	0.589	-26.1	2.57	13.1
04/07/2005	0.699	-26.6	2.78	7.5
04/13/2005	0.538	-27.0	1.12	7.2
04/16/2005	0.573	-26.1	3.45	12.1
04/22/2005	0.700	-26.8	0.98	7.5
04/25/2005	0.855	-26.6	2.24	3.0
04/28/2005	0.633	-26.8	1.64	3.1
05/01/2005	0.698	-26.6	1.43	3.8
05/10/2005	0.599	-26.9	2.19	6.3

Appendix A4 Data from Millbrook, NC site

Run date	Fraction Modern C, f_m	δ13C, °%	AMS C, μg/m3	$PM_{2.5}$ Mass, μg/m3
04/15/2004	0.846	-27.1	8.34	22.8
04/27/2004	0.851		6.29	19.0
04/30/2004	0.692	-26.6	4.47	14.7
05/09/2004	0.757	-26.6	5.63	23.7
05/24/2004	0.775	-26.1	5.32	29.5
06/02/2004	0.662	-26.8	5.54	14.0
06/08/2004	0.746	-26.5	4.16	15.1
06/11/2004	0.674	-26.5	4.98	16.6
06/20/2004	0.665	-26.8	3.54	10.5
07/08/2004	0.635	-27.2	5.79	16.3
07/17/2004	0.857	-27.1	9.08	26.1
07/20/2004	0.775	-25.7	7.11	30.3
08/04/2004	0.726	-26.3	8.37	40.9
08/07/2004	0.692	-26.0	4.60	11.3
08/13/2004	0.598	-26.4	2.85	4.2
08/16/2004	0.651	-26.9	2.82	6.3
08/19/2004	0.742	-26.6	6.65	24.8
08/22/2004	0.776	-26.5	4.64	7.5
08/28/2004	0.700	-26.9	4.35	4.4
08/31/2004	0.684	-26.6	4.62	15.5
09/21/2004	0.612	-26.8	4.01	3.6
10/06/2004	0.612	-26.9	4.02	7.8
10/12/2004	0.588	-27.0	6.42	17.9
10/21/2004	0.768	-26.3	3.10	3.1
10/27/2004	0.614		11.14	25.2
10/30/2004	0.802	-29.2	7.63	33.3
11/02/2004	0.714	-26.4	6.33	14.9
11/17/2004	0.544	-27.0	0.82	16.4
11/20/2004	0.719	-26.1	8.40	21.1
12/02/2004	0.534	-26.6	5.61	8.8
12/05/2004	0.734	-26.6	9.81	15.3
12/08/2004	0.315	-26.5	6.72	5.5
12/29/2004	0.665	-33.2	7.21	18.5
01/31/2005	0.712	-26.3	4.06	10.9
02/09/2005			8.85	18.3
02/21/2005	0.790	-26.2	5.22	14.5
02/24/2005	0.539	-26.3	2.10	4.8
03/20/2005	0.864	-25.3	5.15	17.4
03/23/2005	0.667	-26.4	2.90	7.8
04/07/2005	0.814	-27.2	6.48	16.2
04/13/2005	0.759	-26.5	2.34	5.4
04/16/2005	0.805	-27.2	3.77	7.9
04/22/2005	0.738	-26.4	6.25	20.6
04/25/2005	0.613	-17.0	10.68	8.9
04/28/2005	0.768	-26.6	3.19	6.9
05/01/2005	0.663	-26.2	3.90	13.4
05/10/2005	0.631	-26.3	4.58	11.7

Appendix A5. Data from Shenandoah National Park

Run date	Fraction Modern C, f_m	δ13C, °%	AMS C, μg/m3	$PM_{2.5}$ Mass, μg/m3
04/15/2004	0.567	-26.7	1.96	6.7
04/18/2004	0.573	-26.6	1.43	6.7
04/21/2004	0.916	-26.6	9.02	28.3
04/24/2004	0.837	-25.9	5.43	18.4
04/27/2004	0.830	-25.8	4.08	14.6
04/30/2004	0.791	-26.3	3.60	11.2
05/09/2004	0.802	-25.9	4.67	19.0
05/24/2004	0.874	-25.9	5.69	20.5
06/02/2004	0.748	-26.1	2.56	6.6
06/08/2004	0.816	-26.2	5.32	29.5
06/11/2004	0.592	-26.6	1.80	9.5
06/20/2004	0.655	-26.6	2.04	3.6
07/08/2004	0.758	-26.7	2.46	10.7
07/17/2004	1.022	-24.7	8.35	27.6
07/20/2004	0.582	-31.0	6.30	21.7
08/04/2004	0.808	-25.3	3.40	-0.7
08/07/2004	0.838	-25.6	3.47	13.0
08/13/2004	0.655	-25.6	2.13	7.4
08/16/2004	0.747	-26.4	3.37	17.4
08/19/2004	0.864	-25.8	5.35	22.6
08/22/2004	0.753	-26.2	3.97	18.0
08/28/2004	0.831	-25.8	4.71	21.0
08/31/2004	0.379	-34.3	4.25	13.0
09/21/2004	0.613	-26.9	1.64	2.2
10/06/2004	0.666	-25.8	2.67	6.5
10/12/2004	0.336	-27.2	1.10	4.5
10/21/2004	0.705	-25.9	2.84	-0.3
10/27/2004	0.603	-26.2	2.52	12.0
10/30/2004	0.780	-26.1	2.50	11.5
11/02/2004	0.770	-26.4	4.07	14.7
11/17/2004	0.503	-26.6	1.52	8.7
11/20/2004	0.495	-26.4	3.23	9.9
12/02/2004	0.653	-26.5	1.34	2.1
12/05/2004		-26.0	1.85	5.1
12/08/2004	0.591	-26.5	1.28	4.5
12/29/2004	0.693	-26.0	3.54	8.5
01/31/2005	0.725	-25.6	2.25	7.0
02/09/2005	0.522	-26.8	1.47	6.2
03/20/2005	0.928	-25.0	2.53	16.4
03/23/2005	0.027	-26.8	9.22	23.9
04/07/2005	0.740	-26.1	3.47	11.4
04/13/2005	0.506	-26.1	2.10	8.3
04/16/2005	0.588	-26.2	1.73	4.4
04/22/2005	0.435	-26.4	1.52	4.3
04/25/2005	0.512	-27.0	0.98	4.7
04/28/2005	0.639	-26.2	1.47	6.7
05/01/2005	0.522	-26.3	0.66	10.1
05/10/2005	0.735	-26.2	4.11	14.2

Table 3. Sampling Days With All Sites With Valid Samples

Run date	f_m Value Rank	f_m at Sites Similar?(Y/N)	f_m Range	Comments
Spring				
04/27/2004	High	Y	0.83-0.91	*
04/30/2004	Med-High	Y	0.69-0.79	
05/09/2004	Med-High	N	0.66-0.82	CARO value << other sites
05/24/2004	Med-High	N	0.54-0.87	
06/02/2004	Med-High	N	0.66-0.81	MILL value << other sites
06/08/2004	Low-High	N	0.46-0.84	* CARO value << other sites
06/11/2004	Med-High	N	0.59-0.80	SHEN value < other sites
03/23/2005	Medium	N	0.54-0.72	SHEN value (0.027) is outlier, not included
04/07/2005	Med-High	N	0.57-0.81	
04/13/2005	Med-High	N	0.51-0.81	
04/16/2005	Med-High	N	0.57-0.84	
04/25/2005	Med-v High	N	0.51-1.09	* lrg range, SHEN<<GRSM
04/28/2005	Med-High	N	0.63-0.79	
05/01/2005	Med-High	N	0.52-0.71	*
05/10/2005	Med-High	N	0.60-0.79	
Summer				
07/08/2004	Med-v High	N	0.64-1.08	
07/17/2004	Med-v High	N	0.66-1.02	* all high xc CARO
07/20/2004	Med-High	Y	0.58-0.82	
08/04/2004	High	Y	0.73-0.83	* MILL sl < high range.
08/07/2004	Med-High	Y	0.68-0.84	
08/13/2004	Med	Y	0.57-0.66	
08/16/2004	(High) Med	N	0.64-0.76	
08/19/2004	High	Y	0.76-0.86	
08/22/2004	Med-High	Y	0.64-0.78	
08/31/2004	Low-Med	N	0.38-0.73	* SHEN value << other sites
Autumn				
09/21/2004	Med	Y	0.60-0.66	*
10/06/2004	Med	N	0.53-0.71	
10/12/2004	Low-Med	N	0.34-0.69	SHEN value << other sites
10/21/2004	(High) Med	Y	0.56-0.77	range 0.70-0.77 excl MACA
10/27/2004	Med-High	N	0.60-0.84	
10/30/2004	Med-High	Y	0.72-0.80	
11/02/2004	Low-High	N	0.41-0.77	CARO, GRSM << other 3 sites
11/17/2004	Med-High	N	0.50-0.80	* CARO value >> other sites
11/20/2004	Med	Y	0.50-0.72	range 0.68-0.72 excl SHEN
12/02/2004	Med-High	N	0.53-0.81	
12/08/2004	Low-Med	N	0.32-0.76	MILL value << other sites
Winter				
12/29/2004	Med-High	N	0.66-0.80	*
01/31/2005	Medium	N	0.61-0.75	included tho GRSM missing
02/09/2005	Med-High	N	0.52-0.90	MILL missing, CARO>>others
02/24/2005	Med	N	0.54-0.66	included tho SHEN missing
03/20/2005	High	Y/N	0.78-1.77	* range 0.78-0.93 excl MACA (outlier high)

* indicates back-trajectories obtained.