# J1.1 BIOGENIC CARBON DOMINANCE BASED ON 13C/12C AND 14C MEASUREMENTS OF TOTAL CARBON AT T-0 AND T-1 SITES DURING MILAGRO

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## 1. INTRODUCTION

Megacities, large urban and suburban centers whose populations exceed ten million inhabitants, are steadily increasing worldwide with the most rapid growth in the tropical areas of South America and Asia. These megacities suffer from increased particulate pollution due to the high traffic densities and increased energy usage. In addition, many developing megacities have high levels of biomass combustion from land clearing, trash burning and both domestic and industrial use of wood fuels.

The Mexico City metropolitan area (MCMA) is the largest urban center in North America and the second largest megacity worldwide. It occupies ~3540 km$^2$ with a population of ~19 M (CAM, PROAIRE 2002-22010). The presence of highly absorbing aerosols in Mexico City leads to a reduction in solar flux of 17.6 % locally (Raga et al., 2001). The mass of these absorbing aerosols exported from this megacity into the surrounding region is estimated to be 6,000 metric tons per day or 2 mega-tons per year (Gaffney et al., 1999). Since freshly formed combustion aerosols are hydrophobic, they are expected to be more resistant to washout and have longer lifetimes than more hygroscopic aerosols such as sulfate and nitrate (Gaffney and Marley 2005; Dua et al., 1999). In addition, since these aerosols are introduced into the atmosphere at altitudes that would be considered to be in the free troposphere 300 km away they are assumed to have longer lifetimes than aerosols released at lower altitudes (Raga_et al., 2001). The MCMA is therefore a major source of carbonaceous aerosols to the surrounding regions and the release of these highly absorbing aerosols will have an impact on the radiative balance and climate on a regional scale.

In order to better understand the sources, evolution, and transport of pollutant aerosols and gasses from the Mexico City basin and their resulting impacts on regional climate, a multiagency field campaign was undertaken called the Megacities Initiative: Local and Global Research Observations (MILAGRO). The MILAGRO study was composed of five collaborative field experiments. The Megacity Aerosol Experiment, Mexico City 2006 (MAX-Mex) was sponsored by the U.S. Department of Energy (DOE) to investigate the direct radiative effect of aerosols in the Mexico City plume as a function of time, location and processing conditions. As part of the MAX-Mex component of the MILAGRO study, aerosol samples were collected at a site located at the Instituto Mexicano del Petroleo (IMP), in the northwestern part of the Mexico City center. This site, known as T0, was chosen to represent the fresh emissions in the MCMA. Aerosol samples were also collected at the Technological University of Tecamac, located 18 miles northwest of T0. This site, known as T1, was expected to represent a mixture of fresh and aged pollutants as they exit the basin.

Aerosol samples collected on quartz fiber filters have been analyzed for carbon isotopic analyses ($^{13}$C/$^{12}$C and $^{14}$C). The contributions of biomass burning as well as trash burning to the total aerosol loadings in Mexico City and the surrounding areas can be evaluated using these stable and radioactive isotopes of carbon. Radiocarbon ($^{14}$C), resulting from a nuclear reaction in the upper atmosphere, is subsequently incorporated into $CO_2$ molecules, which in turn are taken up by all living photosynthetic plants. After death, the plants cease to take up additional $CO_2$. The remaining $^{14}$C then decays at a constant rate. The radiocarbon ages and fraction of modern carbon can be calculated from the measured activity. These values are used here to represent the relative “age” of the carbon sources responsible for carbonaceous aerosols in the 0.1 to 1.0 μm range. Since fossil fuels are million of years old, all of their original $^{14}$C has decayed and they have zero $^{14}$C content. However, biogenic materials such as grasses, woody plants, trees, and carbon paper products in trash burning, as well as charcoal or wood burning for fuel are enriched in $^{14}$C. So a measure of the $^{14}$C content can give a solid indication of the relative amounts of biomass versus fossil derived aerosol carbon.

Stable carbon isotopes are also useful in that the various grasses and plants that have either C-4 or C-3 biochemical pathways can be distinguished. The difference in atomic masses of the three carbon isotopes, $^{12}$C, $^{13}$C, and $^{14}$C, affects the chemical reactivity and the physical processes sufficiently to

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cause selective uptake of $^{12}CO_2$ over both $^{13}CO_2$ and $^{14}CO_2$ during photosynthesis. The C-3 plants utilize the Calvin-Benson photosynthetic cycle, which has a more selective chemistry and fractionates the heavier carbon by about 12 parts per thousand as compared to the less selective C-4 or Hatch-Slack pathway. The $^{13}C/^{12}C$ ratio (R) is used to characterize the stable carbon isotopic composition. This ratio is expressed as a del $^{13}C$ value, which represents the per-mille difference between the measured carbon isotopic ratio (R) and that of a carbon standard ($CO_2$ prepared from Peedee belemnite, PDB).

The results of carbon isotope measurements in aerosol samples collected at the T-0 and T-1 sites are presented here. These measurements are used as an indication of the impact of biomass burning to atmospheric aerosols in the MCMA region.

## 2. METHODOLOGY

Samples of fine (<1 micron) aerosols were collected from March 1 to March 28, 2006 at the IMP laboratories. This site, known as T0, is located in the north central part of Mexico City at latitude 19° 29' N, longitude 99° 09' W, and at an altitude of 2240 m above sea level. The aerosol samplers were located on the rooftop of Building No. 32 (Héctor Lara Sosa Building) 15 m above ground level. Aerosol samples were also collected from March 4 to March 27, 2006 at the Technological University of Tecamac, 30 km (18 mi) north of Mexico City. This site, known as T1, is at latitude 19° 43' N and longitude 98° 58' W at an altitude of 2340 m above sea level.

The aerosol samples were collected on quartz fiber filters by using high volume samplers (Hi-Q Environmental Products, Model HVP-3800AFC) equipped with cascade impactors (Thermo Anderson). The air samplers are equipped with brushless, three stage centrifugal fan blowers controlled by an electronic mass flow sensor that detects changes in the operators pre-set flow rate caused by changes in temperature, barometric pressure, and pressure drop due to dust loading on filter media. It compensates for these changes by adjusting the motor speed to maintain the pre-set flow rate at 40 standard cubic feet per minute (SCFM). Three separate LCD's, display elapsed time, total volume of air sampled, and instantaneous flow rate. The quartz filter samples were taken at 12-hour intervals from 5 am to 5 pm (day) and from 5 pm to 5 am (night). The volume of air sampled during the 12-hour time period averaged 740 $m^3$ with an average aerosol loading of 13 mg total carbon content. The aerosol samples were analyzed for carbon-13 and total carbon content. A selected number of samples were analyzed for carbon-14. In addition, selected samples were separated into OC and EC fractions for isotopic characterization of each fraction. In order to evaluate the sources of secondary organic and primary black carbon to fine aerosol loadings.

The quartz filters were placed inside quartz tubes and combusted with copper oxide in vacuum to produce a sufficient amount of $CO_2$ for graphitization at the Center for Accelerator Mass Spectrometry at Lawrence Livermore National Lab. For the organic carbon (OC) and elemental carbon (EC) determinations samples were rapidly heated to 400 C and combusted to $CO_2$ using helium carrier gas and CuO catalyst for OC, then followed by sample heating to 700 C in an oxygen/helium carrier with CuO to convert EC to carbon dioxide (Tanner, Gaffney, Phillips 1982). Once at LLNL, the $CO_2$-filled tubes were then placed in a graphite rig with vacuum conditions and subjected to a double reduction process using Fe-powder as a catalyst. The resulting graphitic carbon was then pounded into an Al target and tested for $^{14}C$ activity on a Tandem Van de Graff accelerator mass spectrometer. Samples of $CO_2$ were also isolated for the purpose of del $^{13}C$ determination by stable isotope mass spectrometry at the University of Illinois at Chicago.

## 2. RESULTS

The fraction of modern carbon in fine aerosol samples collected at site T0 and T1 is shown in Figure 1. The modern carbon fraction is > 0.5 (> 50%) for both day- and nighttime samples, suggesting biomass burning as a major source of carbonaceous aerosols at both sites. The fraction modern was lower at site T0, indicating a larger contribution from "older" carbon, closer to what would be expected from fossil fuels. Site T1 was impacted by grass fires during much of the study period resulting in a higher fraction of modern carbon. The very high values (0.9) would be expected if some of the biomass burning included older trees (carbon dioxide uptake during 1950-1960) that would have been labeled with bomb carbon.

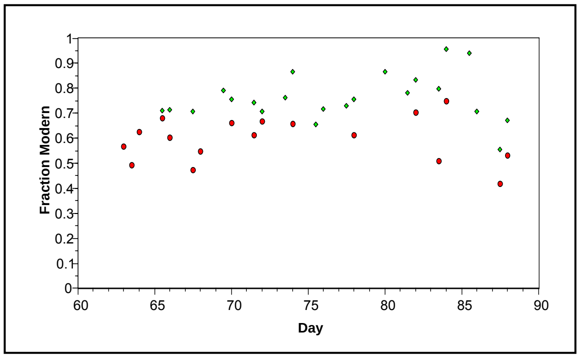

**Figure 1. Fraction of modern carbon in 12-hour aerosol samples collected at site T0 (red) and T1 (green) during MILAGRO.**

The evolution of absorbing aerosols downwind of Mexico City has been described previously in a comparison of measurements obtained at site T1 with those obtained at site T2 (Rancho La Bisnaga), located 35 km (22 mi) north-northeast of T1 (Doran et al., 2007a, 2007b; Doran, 2007). This study focused on the changes in elemental carbon (EC) and organic carbon (OC) content of the aerosols and the resulting effects on the aerosol mass specific absorption coefficients. It was concluded from this work that emission sources outside the MCMA, including biomass-burning sources, are important contributors to the regional aerosol burden. The radiocarbon measurements presented here confirm that biomass burning is a major source of regional aerosols in the Mexico City basin.

The del $^{13}$C values determined in fine aerosol samples collected at site T0 and T1 is shown in Figure 2. Site T0, provides more negative del $^{13}$C values consistent with the combustion of C-3 plants, wood, and charcoal. Site T1, however, provides del $^{13}$C values that are generally less negative (i.e. enriched in $^{13}$C relative to $^{12}$C). This most likely reflects contributions of biomass combustion sources into the submicron, such as local burning of C-4 grasses.

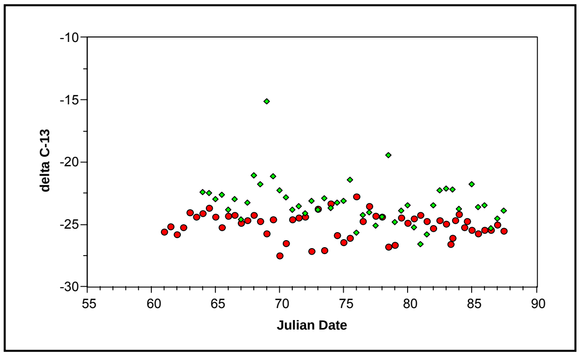

**Figure 2. Delta $^{13}$C in 12-hour aerosol samples collected at site T0 (red) and T1 (green) during MILAGRO.**

Significant rain events occurred toward the end of the study period. The precipitation extinguished grass and field fires, reducing inputs from biomass burning and resulting in a decrease in the fraction of modern carbon in aerosol samples. Additionally, the del $^{13}$C values after the rain events appear to become more negative at Site T1, which could reflect the extinguishing of C-4 source, such as local grassfires, and are consistent with combustion of C-3 plants, wood, and fossil fuel sources that are all expected to be approximately -25 $^{o}$/oo (Gaffney, et al, 1978).

Figure 3. shows a plot of the total carbonaceous aerosol $^{13}$C versus $^{14}$C content in samples taken at sites T0 and T1. Clearly, there is a significant clustering of the results obtained at the two sites. The samples from the urban site T0, shown in red, have lower $^{13}$C and $^{14}$C content than the samples from the more rural site T1, shown in green. Again this is consistent with the influence of C-4 grass biomass burning being more prevalent a source at the more rural T1 site.

The results on OC and EC fractions in the aerosol samples from sites T0 and T1 are given in Figure 4. These all show a consistently higher $^{14}$C content in the OC fractions relative to the EC fractions with the total $^{14}$C values generally falling in a mid range for both sites. Again, the data are consistent with significant biomass derived material contributing to both the refractory carbon as well as more volatile OC fractions. The lower $^{14}$C values for the EC versus OC fractions are expected due to the expectation of EC being significantly sourced from diesel fuel combustion.

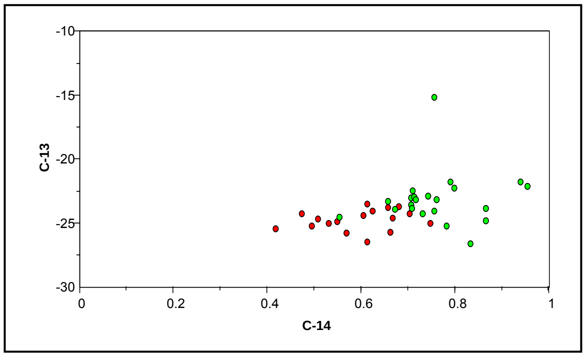

**Figure 3. Carbon-13 as a function of carbon-14 content in 12-hour aerosol samples collected at site T0 (red) and T1 (green) during MILAGRO.**

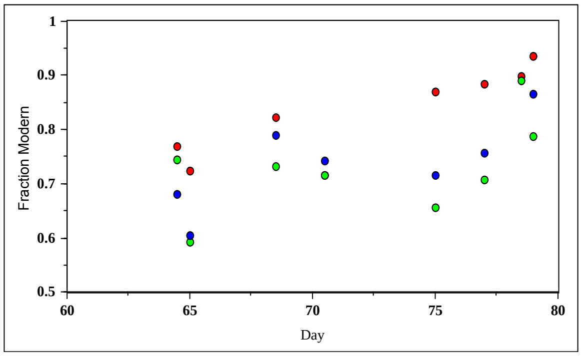

**Figure 4. Fraction of modern carbon in organic carbon (red), elemental carbon (green), and total carbon (blue) fractions of 12-hour aerosol samples collected at site T0 and T1 during MILAGRO.**

The variation in the $^{14}$C as a function of day (5 am to 5 pm, AM) or night (5 pm to 5 am, PM) is shown in Figure 5. In many cases the PM samples were found to have higher $^{14}$C content than the AM samples at both T0 and T1 sites. This can be attributed to the emissions from local biomass burning, as well as trash burning, which would be concentrated in the nocturnal boundary layer as well as the reduced emissions from motor vehicles during the evening period. This effect would be expected to be more evident at the T0 site, where this difference in PM vs AM is most pronounced.

At the T1 site the difference in $^{14}$C content of AM and PM samples is less pronounced, consistent with a lower volume of local fossil fuel sources at the T1 site during the daytime periods. It should also again be noted that the values are lower at the end of the sampling period at both sites consistent with heavy rain events during this time period, which marked the end of local fire contributions to the aerosols. This would include trash burning in the city as well as the local fires in the valley of Mexico that were contributing to the enhanced $^{14}$C observed during the earlier part of the study.

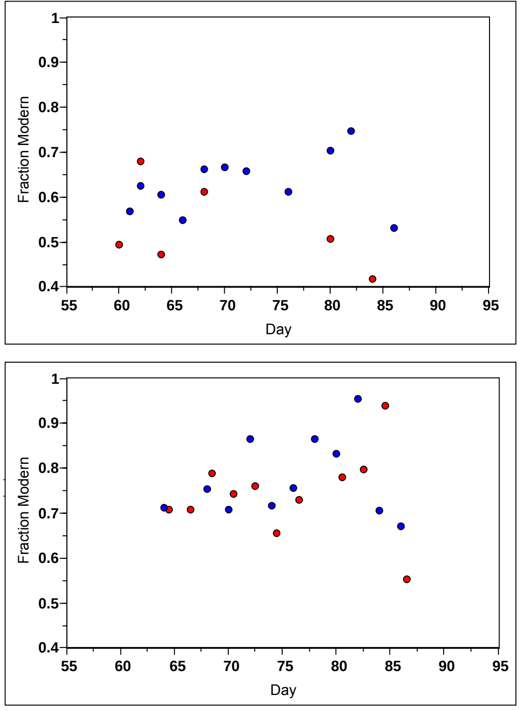

**Figure 5. Fraction of modern carbon in 12-hour Day (red) and night (blue) aerosol samples collected at site T0 (top) and T1 (bottom) during MILAGRO.**

The UV-visible absorption of the aerosol samples has been obtained using integrating sphere spectroscopy (Marley et al, 2001)and the absorption profiles have been used to determine the aerosol Ångstrom absorption exponents ($\lambda^{-\alpha}$) by linear regression (Marley and Gaffney, 2007; Marley et al., 2007). Since, as a broadband absorber, EC absorption is relatively constant from the ultraviolet to the infrared with an Ångstrom absorption exponent of -1 (Marley et al., 2001), a comparison of the Ångstrom exponents serves as an indication of the presence of aerosol components with an absorption different from that expected from EC content alone. The Ångstrom exponents determined from aerosol absorption measurements made in the field at site T0 varied from – 0.7 to – 1.3 during the study and were generally lower in the afternoon than the morning hours, indicating an increase in secondary aerosol formation and photochemically generated UV absorbing species in the afternoon (Marley et al., 2007).

The relationship between the fraction of modern carbon and the wavelength dependence of aerosol absorption at sites T0 and T1 is shown in Figure 6. Also included in Figure 6 are samples collected in Mexico City during the MCMA 2003 study at another T0 site. This site was located at the National Center for Environmental Research and Training (Centro Nacional de Investigación y Capacitación Ambiental, or CENICA), on the Iztapalapa campus of the Universidad Autónoma Metropolitana (UAM). This site is approximately 16.1 km south-southwest of the 2006 T0 site. The data in Figure 6 show a linear correlation between fraction of modern carbon and aerosol Ångstrom absorption coefficient, indicating an enhanced uv absorption for the biomass derived fractions. Indeed, the two outliers circled in Figure 6 are for samples taken from a period where Yucatan fires had impacted the T0 site in 2003 (Massie et al, 2006). Those samples have an even more enhanced uv absorption that would be anticipated by a significant wood source for the biomass burning relative to grass fire sources in the 2006 and rest of the 2003 study.

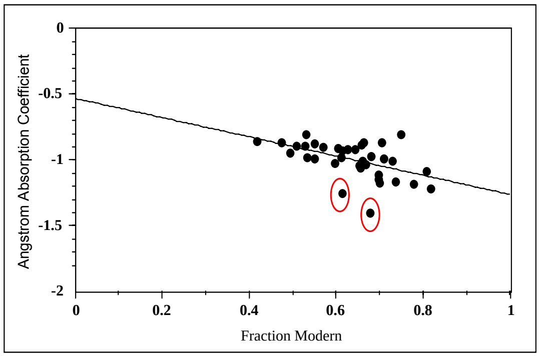

**Figure 6. Ångstrom Absorption Coefficient versus fraction modern carbon in fine aerosols at sites T0 (2003 and 2006) and T1 (2006). Day = red, night = blue. Circled values were for two samples collected during a major biomass event in 2003 where Yucatan fires impacted Mexico City (Massie, et al, 2006).**

It should also be noted that the enhanced uv absorption would also be produced by secondary organic aerosols (SOA) that would have similar chemical and physical properties to the primary organic biomass burning aerosols. They both are expected to contain significant carbonyl and conjugated carbonyl content as well as oxidized PAH compounds that will strongly absorb solar radiation in the long uv and short visible regions.

## 4. CONCLUSIONS

Significant contributions to the organic and elemental fractions of the carbonaceous aerosols arise from biomass burning sources in Mexico City and the surrounding region. The contributions likely include trash burning, grass fires, and wood burning activities as well as agricultural burning practices. Both stable and radiocarbon data indicate that the T1 site was more impacted than the T0 site by grassfires that were occurring in the region during the MILAGRO study. The biomass derived aerosol has significant optical absorption that should be included in normal “black carbon” aerosol modeling for megacity regions as well as the tropical areas where high biomass burning is known to frequently occur. Adding other tracers to the isotopic markers would allow for the various sources to be better evaluated, and this is currently being pursued. Both stable and radiocarbon measurements are clearly useful in the evaluation of the sources of carbonaceous aerosols and their impacts on regional climate and air quality.

## 5. ACKNOWLEDGEMENT

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