5.1 ABSORBING AEROSOLS FROM AGRICULTURAL BURNING AND BIOMASS BURNING

Jeffrey S. Gaffney and N. A. Marley
University of Arkansas at Little Rock, Little Rock, AR

1. INTRODUCTION

The absorption of solar radiation by atmospheric aerosols is a major uncertainty in assessing radiative balance on regional scales. Of particular concern are carbonaceous aerosols as they are the major light absorbing species in the troposphere. Incomplete combustion of hydrocarbon fuels leads to the formation of carbon soots or "black carbon", which have been well known as a significant, if not the major, absorbing aerosol species in the troposphere. Fossil fuel combustion, particularly in diesel engines, has received significant attention as the major source of black carbon aerosols. Other sources of absorbing carbonaceous aerosols include biomass burning of agricultural fields and forest fires as well as the formation of absorbing secondary organic aerosols (SOA) from biogenic precursors.

The measurement of radioactive carbon content (^{14}C) in aerosols has been used to examine the relative strengths of carbonaceous aerosol sources from biomass as well as fossil fuels. Results have shown that biomass sources are significant and in many cases are at a level equal to or greater than fossil fuel sources. Recent measurements obtained in Mexico City clearly indicate that there are significant amounts of absorbing carbonaceous aerosols from both primary and secondary biogenic sources (Gaffney et al., 2008; Marley et al., 2008) and these data are consistent with other results reported in the literature (Hildeman et al., 1994; Klinedinst, and Currie, 1999; Lewis and Stiles, 2006; Lewis et al., 2004; Allen 2001; Szidat,.et al, 2004; Jordan, et al., 2006; Bench et al., 2007; Takahashi, et al., 2007). These biogenic carbonaceous aerosols are strong absorbers in the UV-VIS-NIR and IR spectral regions important to radiative forcing in the troposphere and in many cases are stronger absorbers than black carbon.

Data are briefly overviewed here that demonstrate the potential effects of biomass burning from agricultural burning practices, as well as forest and grass fires and these data are discussed in light of the changing climate and energy demands. Also proposed here is a future field experiment in the southwestern United States that would focus on agricultural burning (sugar cane, straw-grass, and other agricultural field wastes) and the use of C-isotopes to evaluate the impacts of these sources of absorbing carbonaceous aerosols in comparison to sources of black carbon from fossil fuel combustion.

*Corresponding author address: Jeffrey S. Gaffney, University of Arkansas at Little Rock, 2801 S. University Ave., Little Rock, AR 72204-1099; e-mail: jsgaffney@ualr.edu.

2. CARBON ISOTOPIC MEASUREMENTS

Radiocarbon measurements can distinguish between fossil fuel and non-fossil fuel carbon sources. All biogenic materials are labeled with a relatively constant initial $^{14}C/^{12}C$ ratio (Currie et al., 1982). The aerosols produced from fossil fuels contain no ^{14}C because their age is much greater than the 5730-year half-life of the ^{14}C. Therefore, the ^{14}C content in atmospheric aerosols provides a direct measure of the relative contributions of carbonaceous materials derived from fossil fuels and that derived from modern biomass sources.

The ^{14}C content of atmospheric aerosols was determined in samples collected in Mexico City in April 2003 during the MCMA2003 study and in March 2006 as part of the Megacity Aerosol Experiment, Mexico City 2006 (MAX-Mex) sponsored by the U.S. Department of Energy (DOE). The sampling methodology and experimental procedures have been reported elsewhere (Gaffney et al., 2008; Marley et al., 2008). These results, reported as the fraction of modern carbon contained in the aerosol samples, are summarized in Figure 1.

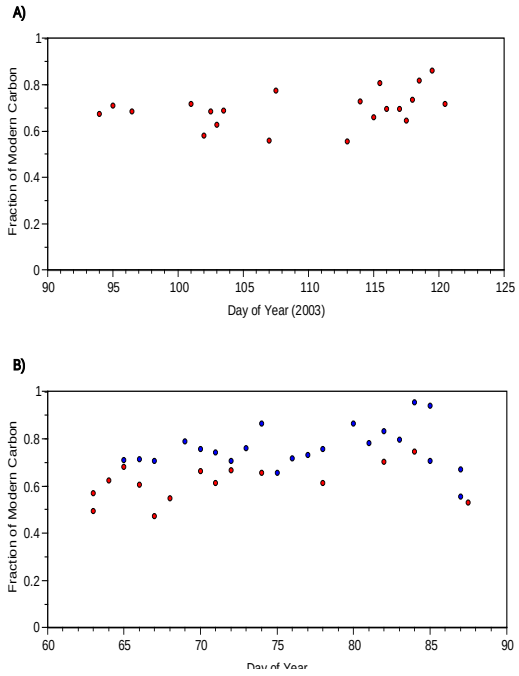

Figure 1. The fraction of modern carbon in aerosol samples collected in Mexico City (red) and 18 miles north of Mexico City (blue) in April 2003 (A) and March 2006 (B).

The fraction of modern carbon in the Mexico City aerosol samples was found to be greater than 0.5 (> 50%) suggesting a large biogenic contribution to the carbonaceous aerosols even in this large urban area. The fraction of modern carbon at a suburban site, located 18 miles north of Mexico City, was higher than observed in the city primarily due to the fact that the suburban site was impacted by grass fires during much of the study period. The very high values (0.9) reported occasionally would be expected if some of the biomass burning included older trees that would have been labeled with bomb carbon from the uptake of carbon dioxide during the period of above ground nuclear testing between 1950-1960.

The results obtained in Mexico City are consistent with results reported in other urban studies. Some of these results are summarized in Table 1. Early measurements made in Los Angeles and Denver previous to the year 2000 showed lower fractions of modern carbon reflecting a higher percentage of fossil fuel derived materials (Hildeman *et al.,* 1994; Klinedinst and Currie, 1999). More recent measurements in the U.S. have resulted in larger modern carbon fractions reflecting a lower percentage of fossil-derived absorbing carbon. This is consistent with measurement taken on arctic haze in Barrow, AK that found values in the 0.3-0.4 range (Gaffney et al, 1984). This is possibly a result of implementing tighter controls on motor vehicle emissions and the addition of biofuels throughout the U.S. (Gaffney and Marley, 2000) compounded by little controls on open burning.

Location	Year	Modern C	Reference
Los Angeles	1982	0.3-0.5	Hildemann
Denver	1996-97	0.3-0.4	Klinedinst
Nashville	1999	0.7	Lewis
Houston	2000	0.5	Allen
Tampa	2002	0.8	Lewis & Stiles
Zurich	2002	0.6	Szidat
Launceston	2003-04	0.9	Jordan
Seattle	2004-05	0.6	Bench
Tokyo	2004-05	0.4-0.5	Takahashi
Phoenix	2005-06	0.5-0.6	Bench

Table 1. The fraction of modern carbon reported for some urban areas.

The very high fraction of modern carbon observed in Launceston, Tasmania were attributed to residential wood burning in the wintertime with 1/3 of households using wood heaters or open fireplaces (Jordan, et al., 2006). The high modern fractions observed in Nashville and Tampa during the summertime were attributed to SOA formation from biogenic precursors (Lewis and Stiles, 2006; Lewis et al., 2004)

Stable carbon isotope ratios ($^{13}C/^{12}C$) are also useful for the identification of carbonaceous aerosol sources. Different plant species utilize two different photosynthetic pathways, denoted C-3 and C-4 according to the number of carbon atoms fixed by each pathway (Smith and Epstein, 1971). The C-3 plants have a more selective chemistry and fractionate the heavier ^{13}C isotope by about 12-14 parts per thousand compared to the less selective C-4 plants. The C-3 and C-4 plants will therefore be labeled with different $^{13}C/^{12}C$ ratios.

The $^{13}C/^{12}C$ ratios found in the Mexico City aerosol samples are shown in Figure 2. These results are expressed as the difference between the measured ratio and that of a standard ($\delta\ ^{13}C$). The samples from the suburban site are generally higher in $\delta\ ^{13}C$ than the samples collected in Mexico City, again indicating the influence of local grass fires in the vicinity of the suburban site.

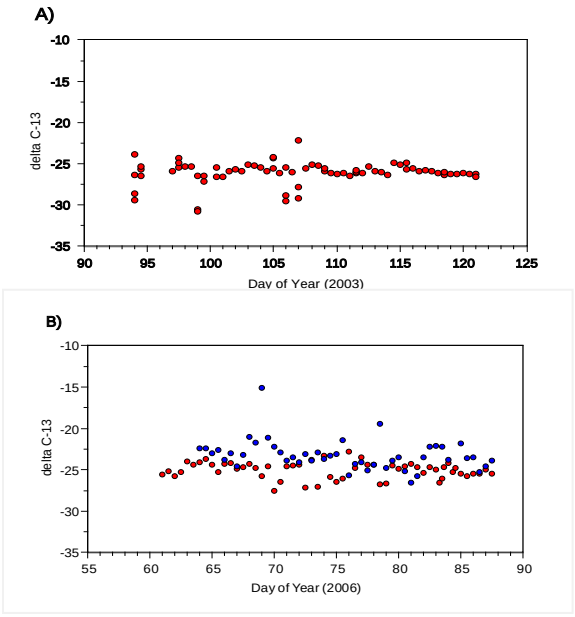

Figure 2. The $^{13}C/^{12}C$ ratios, reported as the difference from the measured ratios and a standard ($\delta\ ^{13}C$), in arerosol samples collected in Mexico City (red) and 18 miles north of Mexico City (blue) in April 2003 (A) and March 2006 (B).

3. AEROSOL ABSORPTION

The UV-visible absorption of the aerosol samples collected in Mexico City 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). Black carbon absorption is relatively constant from the ultraviolet to the infrared with an Ångstrom absorption exponent of 1 (Marley et al., 2001). The deviation of the Ångstrom absorption exponents from 1 serves as an indication of the presence of aerosol components other than black carbon.

The relationship between the fraction of modern carbon and the Ångstrom absorption exponents for the Mexico City aerosols is shown in Figure 2. The data in Figure 2 show an increase in the aerosol Ångstrom absorption

exponent with the fraction of modern carbon indicating an enhanced UV absorption due to the presence of the oxidized biomass derived aerosol species.

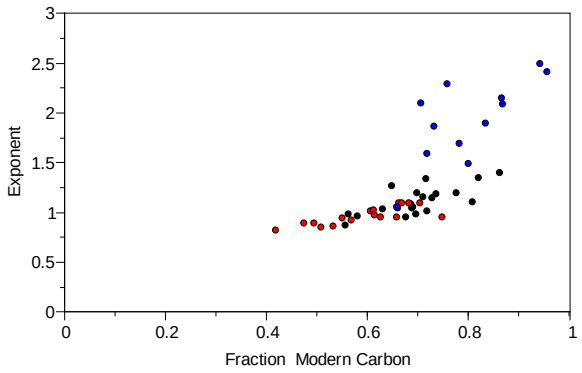

Figure 2. Ångstrom absorption exponent as a function of the fraction of modern carbon in Mexico City aerosols in April 2003 (black) and March 2006 (red) and 18 miles north of Mexico City in March 2006 (blue).

3. PROPOSED FIELD STUDY

With the currently increasing interests in alternative biofuels, such as ethanol, significant increases in atmospheric aerosols may occur from biomass burning sources. The use of isotopic signatures for certain agricultural sources may be extremely useful in evaluating the production of absorbing aerosols from agricultural burning. For example, sugar cane (C4-plant) debris, which is currently burned after the crop is harvested, is a significant source of biomass aerosol in the southern states, particularly in Louisiana. Since sugar cane is enriched in both ^{13}C and ^{14}C, aerosols produced from its combustion can be readily distinguished from those produced from the combustion of trees (C3-plant) or fossil fuels (See Figure 3).

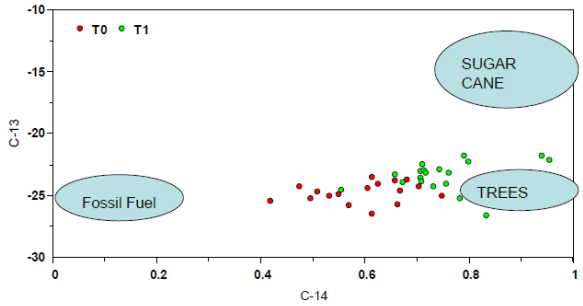

Figure 3. A carbon isotopic map showing the differentiation of sugar cane from trees and fossil fuels. The isotopic composition of aerosols collected in Mexico City (red) and 18 miles north of Mexico City (green) are also shown, demonstrating the influences from fossil fuels in Mexico City and grass fires north of the city.

We propose that a field study conducted in the southern United States, where this type of source is clearly an important contributor, would be very useful for addressing agricultural burning as a primary source of absorbing aerosols including black carbon as well as oxidized partially burned compounds such as conjugated carbonyls and acids. Other possible sites could include Hawaii and the Caribbean Islands (e.g. Puerto Rico) where significant sugar cane burning is practiced. These proposed studies would be on larger scales than smaller controlled burns and would yield more representative measurements of the production of absorbing aerosols from these sources.

4. CONCLUSIONS

A significant fraction of modern carbon derived from biogenic sources has been observed in Mexico City as well as other urban areas where the fraction of fossil carbon is expected to be high. These biomass derived aerosols have an enhanced optical absorption over that expected from black carbon aerosols. Carbon isotopic signatures from both stable and radiocarbon give significant information concerning the sources. A field study that examines biomass burning from agricultural burning of sugar cane debris would be extremely useful in addressing the potential impacts from enhanced biofuel development in terms of the associated absorbing aerosol production and its impacts on climate forcing.

5. ACKNOWLEDGEMENT

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