Gulf Coast Aerosol Research and Characterization Program (Houston Supersite)

PROGRESS REPORT

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Submitted by:

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Title: **Gulf Coast Aerosol Research and Characterization Study**

Investigators: **Dr. David Allen (PI) and Dr. Matthew Fraser (Co-PI)**

Institutions: **University of Texas and Rice University**

Research Category: **Air Quality/Fine Particulate Matter**

Project Period: **01/15/00-11/30/03**

Objective of Research: **Characterize fine particulate matter and fine particulate matter formation processes in Southeast Texas**

Progress Summary/Accomplishments:

**During the final quarter of 2000, the intensive sampling period for the Houston Supersite was conducted, in coordination with an air quality study focussed on gas phase chemistry (the Texas Air Quality Study). Data analysis is ongoing and selected preliminary findings are presented in this report.**
During the final quarter of 2000, the intensive sampling period for the Houston Supersite was conducted, in coordination with an air quality study focused on gas phase chemistry (the Texas Air Quality Study). Selected preliminary findings are presented in this report. Specifically, preliminary results of the radiocarbon measurements of ambient aerosol are presented.

I. Fine Particulate Matter Source Attribution for Southeast Texas using $^{14}C/^{13}C$ ratios, University of Texas, U.S. EPA and NIST

This report will describe part of the sample collection and analysis activities performed during the six week Houston “Supersite” intensive study that occurred in August and September 2000. Specifically, this report will investigate the hypothesis that geologically modern carbon, from biomass burning and/or biogenic secondary organic aerosol, is a major contributor to fine particulate matter concentrations in southeast Texas.

Two decades ago, $^{14}C$ measurements were made on seven fine particle (<4 µm aerodynamic diameter) samples collected on the University of Houston campus (Dzubay et al., 1982). The measured biogenic carbon fraction varied from 18 to 62% with a mean value of 40±15% (standard deviation). This was the first experimental indication that biogenic sources may contribute significantly to fine aerosol in Houston, and is consistent with later $^{14}C$ results from Los Angeles that also showed a surprisingly high biogenic contribution to fine aerosol. (Currie et al., 1983; Berger et al., 1986; Kaplan and Gordon, 1994; Hildemann et al., 1996).

The most likely sources of modern carbon in fine aerosol in Houston are secondary organic aerosol formed by the reactions of biogenic precursors and primary emissions due to biomass burning. According to recent emission inventories, biogenic hydrocarbons are the dominant source of hydrocarbon emissions in southeast Texas (Wiedinmyer, 1999; Wiedinmyer et al., 2000, 2001). In the urban counties of the Houston metropolitan area, approximately 50% of all volatile organic carbon (VOC) emissions are estimated to be of biogenic origin, and for the whole of eastern Texas,
biogenics may constitute as much as 80-90% of the VOC emissions. These biogenic emissions are not distributed uniformly throughout the region. As shown in Figure 1, the heavily forested areas north of Houston’s urban core have relatively high emissions of biogenic hydrocarbons. Most of the hydrocarbon mass emitted by vegetation in southeast Texas is in the form of isoprene. These isoprene emissions may contribute to ozone formation in some areas, but the contribution of isoprene to secondary aerosol formation is believed to be small (Pandis et al., 1991). Nevertheless, emissions of α-pinene and other potential secondary aerosol precursors are significant in southeast Texas, and therefore biogenic hydrocarbons may contribute to particulate matter formation.

Fires may also contribute to fine particulate matter concentrations in southeast Texas. In an inventory of emissions associated with forest, grassland and agricultural burning in Texas, Dennis (2000) reported that some counties in southeast Texas have fine particulate matter emissions associated with fires that total approximately 1 ton/day per county (approximately 0.5 tons/year/sq. mi.). The emissions in southeast Texas are attributed primarily to slash burning associated with commercial timber harvesting in the forests north and northeast of Houston. In addition, Fraser (2001) has made measurements of a molecular tracer of cellulose combustion and finds concentrations of levoglucosan that are consistent with seasonal average fine PM source contributions from fires of a few tenths of micrograms per cubic meter.

Still, a large amount of uncertainty remains concerning the extent to which fires and biogenic emissions contribute to fine particulate matter formation. One method for evaluating the contribution of these sources to air pollutant formation is to obtain accurate measurements of radiocarbon ($^{14}$C). $^{14}$C is absent in fossil fuels, since it decays with a half-life of 5730 years, yet is present in living materials at measurable levels, $^{14}$C/$^{12}$C ≈ 1.2 * $10^{-12}$ (Klouda et al., 1999). Therefore, the measured $^{14}$C/$^{13}$C ratio within a sample can provide information about the combined impact of biomass burning and biogenic VOCs on particulate matter concentrations (since the natural abundance of $^{13}$C relative to $^{12}$C is ~1%).

As noted earlier, Dzubay et al. (1982) found, in measurements made two decades ago, that modern carbon accounted for 40% ± 15% of the carbonaceous material in aerosol samples collected in urban Houston. In more recent studies, Klouda et al. (1999)
made exploratory measurements of $^{14}\text{C}/^{13}\text{C}$ in VOC samples collected in Houston. Samples were collected in 1994 at three sites: 1) a northern suburban/rural site (morning and afternoon), 2) an industrial site in the industrialized (ship channel) area (afternoon), and 3) the Sam Houston National Forest 80 kilometers north of Houston (afternoon). The ship-channel site in Houston was entirely void of $^{14}\text{C}$. In contrast, the National Forest sample showed a low, but significant modern carbon fraction, 23% ± 8%. The largest percentage of modern carbon observed, 55% ± 4%, was from the Houston suburban/rural site in the afternoon (Klouda et al., 1999). These $^{14}\text{C}$ measurements, which were confined to VOCs, indicate that biogenic hydrocarbons may play a role in either ozone or fine particulate matter formation in Houston. To investigate this hypothesis further, approximately 75 fine particulate matter samples and 30 VOC samples were collected at various sites in southeast Texas during the intensive sampling period associated with the Houston “Supersite” (August and September, 2000). Measurements of elemental carbon and organic carbon were made for all of the fine particulate matter samples, and all of the VOC samples were analyzed for hydrocarbon composition using gas chromatography/mass spectroscopy (U.S. EPA, 1989; Lonneman, 2000). These data were used to identify a group of 13 particulate matter samples that would be subjected to $^{14}\text{C}$ analysis. For some of the sampling periods for which particulate matter radiocarbon data were obtained, elemental composition data based on x-ray fluorescence were also available (U.S. EPA, 2001a). These data, and the emission inventories of Dennis (2000) and Wiedinmyer (1999), were used to deduce potential sources of the $^{14}\text{C}$ detected in the samples, and, as reported in this manuscript, the data indicate that fires and biogenic secondary organic aerosol formation may contribute significantly to fine particulate matter concentrations in some parts of southeast Texas.

METHODS

Sampling sites

Samples were collected at 5 ambient sampling sites. These sites were:

- Galveston Island, which was selected to be representative of clean background air from the Gulf of Mexico
• Houston Regional Monitoring Network Site 3 (HRM3) and LaPorte airport, which were selected to be representative of industrialized sites in the Houston Ship Channel Region,
• Aldine, which was selected to be representative of an urban receptor site, and
• Conroe, which was selected to be representative of the heavily forested areas north of the urban core.

The locations of the ambient sites are shown in Figure 1 and details of the sampling locations have been reported by Lemire (2001).

Sample collection and analysis

Particulate matter samples were collected using filters and ambient air samples for VOC analysis were collected using canisters. The specific procedures used in this work are described by Lemire (2001). The procedures for VOC sampling will not be described in detail here since the focus of this article is on a subset of the particulate matter samples selected for radiocarbon analysis.

Particulate matter samples were collected using two Model 310 Universal Air Samplers® (MSP, Inc., Minneapolis, MN). The samplers collected a fine-fraction (PM$_{2.5}$) filter sample, separated using a virtual impactor, and a coarse-fraction filter sample (particle aerodynamic diameter > 2.5 μm). Flow rates through the fine- and coarse-particle channels were 270 and 15 L min$^{-1}$, respectively. Each fine particle sample was collected within an 81.0-mm diameter area on a 90-mm diameter quartz-fiber filter through use of a special filter holder adapter. Prior to sampling, the filters were heated to 500 °C for six hours and stored in tight screw-top aluminum foil-lined amber glass jars. Sections (6.4 cm by 16.5 cm) of quartz-fiber filter material for coarse-fraction sampling were cut from untreated 20 by 25 cm filters. Nominal sampling durations were 6 or 24 hours.

In addition to the ambient air samples, a total of ten samples of vegetation were collected at four locations in the Houston area (Table 1). The samples included a variety of leaf types such as oak and plane tree. The samples were transported and stored in zip-lok freezer bags. All samples collected at a given site were composited into a single sample on which $^{14}$C measurements were performed, as described later. These samples
were intended to provide a calibration point for the $^{14}$C content of same-year living material from the same locale in which ambient PM$_{2.5}$ samples were collected.

**EC/OC/TC and Radiocarbon Analysis**

Elemental carbon (EC), organic carbon (OC) and total carbon (TC) were determined for all of the particulate matter samples using evolved gas analysis with a thermo-optical analyzer as described in NIOSH standard method 5040 (NIOSH, 1996; Chow et al., 2001). The thermo-optical analysis also had the capability to quantify carbonate carbon, but no measureable carbonate was found on any of the samples. The samples included seventy-three ambient field samples, two backup filter field samples, eight field blank samples, and a transportation blank. A group of four specified filters and six randomly selected filters were selected for replicate analyses.

Based primarily on the results of the EC/TC measurements, as well as previous radiocarbon measurements, 13 filters were selected for $^{14}$C measurements (all of the remaining filter samples will be analyzed and reported on at a later date). Preparing carbonaceous material deposited on quartz-fiber filters for $^{14}$C accelerator mass spectrometry (AMS) involved three steps: (1) the isolation of the carbon fraction of interest, (2) the combustion of sample carbon to CO$_2$, and (3) the subsequent reduction of the CO$_2$ to graphitic carbon, the form of carbon required for AMS analysis. Sample aliquots of sufficient area are taken from the samples such that greater than 100 µg C was recoverable whenever possible. Filter aliquots were placed in precleaned quartz tubes containing CuO and Ag wire. Tubes were evacuated, sealed with a H$_2$/O$_2$ torch and heated to 900 °C to combust TC to CO$_2$ and purify the CO$_2$ of any SO$_2$ or halogens present. The average recovery of TC from filters, standard reference materials (SRMs) and reference materials (RMs) was 100 ± 8% ($\mu$, n=18). Vegetation samples were treated similarly except that combustion took place in a quartz tube attached to a vacuum line and heated with a Bunsen burner in the presence of O$_2$. The CO$_2$ was cryogenically distilled, quantified by manometry in a calibrated volume, and transferred to a quartz breakseal tube for storage prior to AMS target preparation.
Accelerator mass spectrometry measurements were performed using samples prepared as described by Jull et al. (1986). The sample CO₂ was reduced over granular Zn at 400°C to CO and further reduced to graphitic carbon over Fe powder at 600°C. Accelerator mass spectrometry measurements of ¹⁴C/¹³C ratio were then made at the University of Arizona-NSF AMS Facility (Donahue et al, 1990).

¹⁴C results are reported as the percentage of modern carbon (pMC) according to the following expression

\[
\frac{^{14}C/^{13}C_{PM 2.5}}{0.95 \times ^{14}C/^{13}C_{SRM 4990b}} \times 100
\]

where the denominator is defined as modern carbon (Stuiver, 1983). To estimate biogenic contributions, some knowledge of the ¹⁴C composition of the possible biogenic source(s) is necessary. In the case of forest fires or slash burning, the age of the material burned and the atmospheric ¹⁴CO₂ record must be known to derive the average ¹⁴C content of wood burned (Klouda et al., 1991). For example, tree logs and slash 50 years old on average would have a pMC = 127. (Note that pMC can be greater than 100 because of the addition of ¹⁴C from atmospheric nuclear weapons testing during the 1950’s and early 1960’s followed by its decline by exchange with the ocean and biosphere as well as the addition of fossil fuel CO₂ (Levin and Hesshaimer, 2000).) In contrast, the pMC of biogenic emissions is similar to that of the local vegetation, i.e., average pMC = 107 for the Houston area (see Table 1). For this work, the percentage of biogenic PM₂.₅ carbon is taken to be

\[
\frac{pMC_{PM 2.5}}{107} \times 100
\]
If forest fires or slash burning were contributing, the % Bio. C\textsubscript{PM2.5} would be correspondingly smaller.

RESULTS AND DISCUSSION

Table 1 gives the pMC results for the composite vegetation sample at each of the four sites where these samples were collected. The results cluster closely, with an average pMC, standard uncertainty ($u$) of 106.8 (1.5). This is consistent with the current pMC for global atmospheric $^{14}$CO\textsubscript{2} (Levin and Hesshaimer, 2000).

Table 1. Percentage modern carbon for vegetation samples

<table>
<thead>
<tr>
<th>Site</th>
<th>pMC ($u^*$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conroe</td>
<td>1.084 (0.005)</td>
</tr>
<tr>
<td>Aldine</td>
<td>1.069 (0.004)</td>
</tr>
<tr>
<td>HRM3</td>
<td>1.047 (0.004)</td>
</tr>
<tr>
<td>LaPorte</td>
<td>1.072 (0.005)</td>
</tr>
</tbody>
</table>

* standard uncertainty

Table 2 lists pMC data for a number of standard reference materials (SRMs) that were analyzed for $^{14}$C for method validation. Results are consistent with expected pMC values. The small non-zero value of pMC for SRM 2975 Diesel Soot may indicate either fuel additives or slight contamination from the processing of this material.

Table 3 lists the subset of fine particulate matter samples collected during the field program that were selected for $^{14}$C analysis. Sampling location, sampling period, TC concentration ($\text{TC} = \text{EC} + \text{OC}$), EC/TC, pMC\textsubscript{TC} and biogenic percentage are reported in the Table. Eventually, all of the samples will be subjected to radiocarbon analysis, however, an initial group of samples was selected that would indicate whether biogenic hydrocarbons might be a significant source of secondary organic aerosol. Criteria for selecting this subset of samples included:
1) Samples collected at the Aldine and Conroe sites were selected since these sites were located in regions where biogenic aerosol precursor emissions were expected to be greatest (see Figure 1).

2) Both 24 hour and 6 hour (afternoon) samples were selected.

3) Samples with low ($\leq 0.1$), moderate ($0.1 \leq \text{EC/TC} \leq 0.2$), and high ($\geq 0.2$) EC/TC ratios were selected to provide a range of source distributions in the samples.

Table 3 shows that the TC concentrations are often a substantial fraction of the proposed NAAQS for PM$_{2.5}$ (15 $\mu$g m$^{-3}$, annual average). EC is seen to be a relatively small fraction of TC, $0.14 \pm 0.08$ and $0.08 \pm 0.05$ (mean, $\mu$) at Aldine and Conroe, respectively. The relative magnitudes seem reasonable on the basis of Conroe being the more rural site. For quality control purposes the EC/TC result for the “prototype” SRM 1649a on quartz-fiber filter (Klouda et al., 1996) was $0.254 \pm 0.031$ (mean, $\mu$, n = 4). This compares well with the value for this method reported in a recent round-robin intercomparison (Currie et al., 2001, in preparation).
Table 2. AMS $^{14}$C Results of Standard Reference Materials and Reference Materials:

<table>
<thead>
<tr>
<th>SRM/RM</th>
<th>Description</th>
<th>Carbon Mass (µg)</th>
<th>pMC (Measured)</th>
<th>$u_c$</th>
<th>pMC (Expected)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SRM 4990c</td>
<td>Oxalic Acid (1977)</td>
<td>153</td>
<td>136.1</td>
<td>1.8</td>
<td>134.07†</td>
</tr>
<tr>
<td>RM 21</td>
<td>Graphite</td>
<td>113</td>
<td>1.3</td>
<td>0.2</td>
<td>&lt; 0.1</td>
</tr>
<tr>
<td>SRM 2975</td>
<td>Diesel Soot</td>
<td>122</td>
<td>4.6</td>
<td>0.3</td>
<td>0**</td>
</tr>
<tr>
<td>SRM 1649a</td>
<td>Washington, D.C. Urban Dust (1975)</td>
<td>317</td>
<td>49.9</td>
<td>0.3</td>
<td>51.0‡</td>
</tr>
<tr>
<td>RM PM 2.5</td>
<td>Baltimore (1998-1999)</td>
<td>138</td>
<td>59.0</td>
<td>0.7</td>
<td>--**</td>
</tr>
</tbody>
</table>

* combined standard uncertainty.
† estimated standard uncertainty of the weighted average of the certified (expected) value of SRM 4990c equals 0.04 (Stuiver, 1983).
** no prior pMC result is available for this material.
‡ weighted average, standard uncertainty = 0.2, n=3 (Currie et al., 2001).
Table 3. Total Carbon Concentration, EC/TC Ratio, and AMS $^{14}$C Results of Fine Particulate Matter Samples in Houston

<table>
<thead>
<tr>
<th>Location</th>
<th>Date</th>
<th>Local Start</th>
<th>Duration</th>
<th>TC*</th>
<th>$u_c$**</th>
<th>EC/TC*</th>
<th>$u_c$**</th>
<th>pMC$_{TC}^\dagger$</th>
<th>$u_c$**</th>
<th>Bio. TC$_{PM2.5}^\ddagger$</th>
<th>$u_c$**</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(Aug. 2000)</td>
<td>Time (h)</td>
<td>(h)</td>
<td>($\mu g/m^3$)</td>
<td>($\mu g/m^3$)</td>
<td>(%)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Aldine</td>
<td>9</td>
<td>0000</td>
<td>24.0</td>
<td>3.0</td>
<td>0.2</td>
<td>0.25</td>
<td>0.03</td>
<td>35.8</td>
<td>0.2</td>
<td>33.6</td>
<td>0.2</td>
</tr>
<tr>
<td>Aldine</td>
<td>12</td>
<td>0600</td>
<td>6.0</td>
<td>5.6</td>
<td>0.5</td>
<td>0.11</td>
<td>0.03</td>
<td>58.3</td>
<td>0.3</td>
<td>54.6</td>
<td>0.3</td>
</tr>
<tr>
<td>Aldine</td>
<td>13</td>
<td>0000</td>
<td>24.0</td>
<td>5.8</td>
<td>0.3</td>
<td>0.06</td>
<td>0.01</td>
<td>72.6</td>
<td>0.2</td>
<td>68.0</td>
<td>0.2</td>
</tr>
<tr>
<td>Aldine</td>
<td>14</td>
<td>1830</td>
<td>5.5</td>
<td>2.9</td>
<td>0.3</td>
<td>0.13</td>
<td>0.05</td>
<td>53.7</td>
<td>0.5</td>
<td>50.2</td>
<td>0.5</td>
</tr>
<tr>
<td>Aldine</td>
<td>15</td>
<td>0015</td>
<td>23.8</td>
<td>2.7</td>
<td>0.2</td>
<td>0.28</td>
<td>0.03</td>
<td>26.9</td>
<td>0.1</td>
<td>25.2</td>
<td>0.1</td>
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<tr>
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<td>18</td>
<td>1215</td>
<td>6.0</td>
<td>6.4</td>
<td>0.5</td>
<td>0.09</td>
<td>0.02</td>
<td>49.0</td>
<td>0.3</td>
<td>45.9</td>
<td>0.3</td>
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<tr>
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<td>0.2</td>
<td>0.08</td>
<td>0.01</td>
<td>61.0</td>
<td>0.2</td>
<td>57.1</td>
<td>0.2</td>
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<td>24.0</td>
<td>4.0</td>
<td>0.2</td>
<td>0.11</td>
<td>0.01</td>
<td>60.5</td>
<td>0.1</td>
<td>56.6</td>
<td>0.1</td>
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<tr>
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<td>2.9</td>
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<td>0.18</td>
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<td>0.15</td>
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<tr>
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<td>6.8</td>
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<td>0.04</td>
<td>0.02</td>
<td>77.2</td>
<td>0.5</td>
<td>72.3</td>
<td>0.5</td>
</tr>
<tr>
<td>Conroe</td>
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<td>1215</td>
<td>6.0</td>
<td>5.6</td>
<td>0.5</td>
<td>0.03</td>
<td>0.02</td>
<td>65.5</td>
<td>0.4</td>
<td>61.3</td>
<td>0.4</td>
</tr>
<tr>
<td>Conroe</td>
<td>30</td>
<td>0000</td>
<td>24.0</td>
<td>2.2</td>
<td>0.2</td>
<td>0.08</td>
<td>0.02</td>
<td>60.0</td>
<td>0.3</td>
<td>56.2</td>
<td>0.2</td>
</tr>
</tbody>
</table>

* Corrected for filter blank = $0.35 \pm 0.10 \mu g TC/cm^2$.

** $u_c$, combined standard uncertainty using error propagation.

$^\dagger$ Corrected for TC composite (n=3) filter blank = $51.1 \pm 0.8$ pMC and average concentration of $0.35 \pm 0.10 \mu g TC/cm^2$ (n=3).

$^\ddagger$ $(pMC_{TC}/107) \times 100$
The data shown in Table 3 indicate relatively high percentages of the carbonaceous component of fine particulate matter at the Aldine and Conroe sites was of modern origin. As shown in Figure 2, \( \text{pMC}_{\text{TC}} \) is strongly correlated (inversely) with the sample’s EC/TC value. The linear regression is

\[
\text{pMC}_{\text{TC}} = -0.179 \times \text{EC/TC} + 77.03 \quad (r^2 = 0.855)
\]

Both primary and secondary sources may contribute to this modern carbon \(^{14}\text{C}\). The main biogenic primary sources that might be anticipated in southeast Texas are 1) forest fire activity, 2) cooking, and 3) vegetative detritus. The main biogenic secondary source is likely to be organic aerosol formed from gas phase biogenic emissions. Each of these possibilities is discussed below.

During parts of the field campaign, local fires might be expected to be a significant source of fine particulate matter. Specifically, from 28 August to 5 September, there was substantial forest fire activity reported to the east and north/northeast of Houston. These fires could have generated particulate matter in the samples collected during this period, and some of the samples from the period when the fires were active show high and fluctuating total carbon concentrations, consistent with smoke plumes passing over the sites. The samples listed in Table 3, however, were not collected during the period of the local fires. Regional fires still could have contributed to particulate matter concentrations, although elemental composition data that were available for the August 18, 19 and 25 samples collected at Aldine (U.S. EPA, 2001a) indicated relatively low concentrations of potassium, suggesting that fire events are a relatively minor source for these samples. Future analyses of molecular tracers for cellulose burning (Simoneit et al., 1999), which may be conducted on some of these samples, may provide a more accurate assessment of the source strength of fires.

An additional source of primary \(^{14}\text{C}\) is cooking. Standard profiles of the elemental composition for meat cooking suggests that magnesium, chlorine, copper, and sodium (U.S. EPA 2001b) may be good atomic tracers for cooking. These elements were not detected at levels consistent with cooking sources in the samples for which elemental analysis data are available. Again, future analyses of molecular hydrocarbon tracers, which may be conducted on some of these samples, may provide a more accurate
assessment of the source strength of cooking. For now, however, these sources appear to be relatively minor on these days. Finally, vegetative detritus may be a primary source of $^{14}$C, however, this source is expected to contribute primarily to coarse aerosol.

Secondary organic aerosol (SOA), formed as a result of the atmospheric reactions of biogenic hydrocarbons, may be a significant source of $^{14}$C found in fine particulate matter. One method for assessing the total magnitude of SOA in particulate matter samples (biogenic and non-biogenic) relies on OC/EC ratios. It is generally assumed that all EC is primary and that the primary EC will have some primary OC associated with it. The remaining OC, not associated with primary EC, is assumed to be secondary. Typical values, based on ambient measurements, for OC/EC in primary aerosol are 2.0 - 2.4 (Turpin and Huntzicker, 1991 and Strader et al., 1999) and therefore, particulate matter samples with an OC/EC ratio in excess of 2.4 (an EC/TC ratio less than 0.3) are generally assumed to contain secondary organics. Most of the OC/EC ratios measured at Aldine and Conroe are well in excess of 2.4, indicative of the presence of secondary organics.

Although pMC measurements were performed only for TC, they can be used to obtain pMC information specific to OC, which when combined with the OC/EC indicator for SOA, can lead to an estimate of the biogenic contribution to SOA. This is done as follows.

In general the measured pMC for TC can be written in terms of the pMCs for the OC and EC components as

$$pMC_{TC} = pMC_{OC}*OC/TC + pMC_{EC}*EC/TC$$

For each sample the maximum and minimum for $pMC_{OC}$ can then be found by setting $pMC_{EC}$ to its minimum and maximum values, respectively, and solving for $pMC_{OC}$. While the minimum value for $pMC_{EC}$ is zero, corresponding to a purely fossil-fuel origin, its maximum value requires some consideration. As noted above the pMC for both gaseous biogenic emissions and fresh biomass (vegetative growth occurring in 2000) is 107. In contrast, pMC for 50-year-old biomass is 127. Biomass with an age either older or younger than 50 years has a smaller pMC (Klouda et al., 1991). Since there was
generally only a small difference in the results of using either of the latter pMCs, for simplicity the intermediate value of 117 was used for the pMC	extsubscript{EC} maximum.

Figure 3 shows the pMC	extsubscript{OC} values determined by this method, plotted against (OC/EC)	extsuperscript{-1}. Each plotted point is the mean of the pMC	extsubscript{OC} upper and lower bound, which are represented by the extremes of the “error” bars. Average values for the pMC lower bounds, upper bounds, and their means are 51, 65, and 58, respectively. For the SOA model assumed here the OC of any sample with OC/EC > 2.4 (OC/EChas an SOA component, and that component is an increasing fraction of OC as OC/EC increases. Thus Figure 3 shows that SOA is a large contributor to OC for virtually all the samples, and that the SOA has a large biogenic content.

CONCLUSIONS

Radiocarbon measurements of a limited group of fine particulate matter samples collected at sites in southeast Texas, during the summer of 2000, suggest that fires and biogenic secondary organic aerosol may be significant contributors to fine particulate matter concentrations at some sites in Texas. Additional measurements, particularly measurements of molecular hydrocarbon tracer species for cellulose combustion, and measurements of biogenic SOA precursors, are required to refine the estimates of contributions from these sources. These measurements were made by other investigators in the field program and will be reported in subsequent publications.

REFERENCES


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Figure 1. Sampling locations superimposed on a mapping of biogenic hydrocarbon emissions for southeast Texas. The biogenic emissions are based on the inventory reported by Wiedinmyer (1999, 2001). Blue regions represent emission rates of 0-500 moles per hour per 2km by 2 km grid cell. Green, yellow and red represent emission rates of 500-1000, 1000-1500 and 1500-2000 moles per hour per grid cell, respectively. Urban Houston is located primarily in Harris county (county boundaries are black lines), which contains the Aldine, HRM 3 and LaPorte sites.