A Study of Secondary Organic Aerosol Formation in the Anthropogenic -Influenced
Southeastern USA

Rodney J. Weber¹, Amy P. Sullivan¹,², Richard E. Peltier¹, Armistead (Ted). Russell³, Bo. Yan¹, Yingjun Chen¹ Mei. Zheng¹, Joost de Gouw⁴,⁵, Carsten Warneke⁴,⁵ Charles. Brock⁴,⁵, John S. Holloway⁴,⁵, Elliot L. Atlas⁶, and Eric Edgerton⁷

¹ School of Earth and Atmospheric Sciences, Georgia Institute of Technology, Atlanta, GA 30332, USA.
² Department of Atmospheric Science, Colorado State University, Fort Collins, CO 80523
³ School of Civil and Environment Engineering, Georgia Institute of Technology, Atlanta, GA 30332, USA.
⁴ Cooperative Institute for Research in Environmental Sciences, University of Colorado, Boulder, CO 80309, USA.
⁵ Chemical Sciences Division, Earth System Research Laboratory, NOAA, Boulder, CO 80305, USA.
⁶ Marine and Atmospheric Chemistry, RSMAS, University of Miami, Miami, FL 33149, USA.
⁷ Atmospheric Research & Analysis, Inc. Cary, NC USA.

Running Title: SOA formation in the polluted southeast

ABSTRACT

The formation of secondary organic aerosol (SOA) in an anthropogenic - influenced region in the southeastern United States is investigated by a comparison with urban plumes in the northeast. The analysis is based on measurements of fine particle organic compounds soluble in water (WSOC) as a measure of secondary organic aerosol. Aircraft measurements over a large area of northern Georgia, including the Atlanta metropolitan region, and in plumes from New York City and surrounding urban regions in the northeast show that fine particle WSOC are spatially correlated with vehicle emission tracers (e.g., CO), yet the measurements indicate that vehicles do not directly emit significant particulate WSOC. In addition to being correlated, WSOC concentrations were in similar proportions to anthropogenic tracers in both regions, despite biogenic volatile organic compounds (VOCs) that were on average 10 to 100 times higher over northern Georgia. In contrast, radiocarbon analysis on WSOC extracted from integrated filters deployed in Atlanta suggests that roughly 70 to 80% of the carbon in summertime WSOC is modern. If both findings are valid, the combined
results indicate that in north Georgia fine particle WSOC was secondary and formed
through a process that involves mainly modern biogenic volatile organic compounds, but
which is strongly linked to an anthropogenic component that may largely control the
mass of SOA formed. Independent of the radiocarbon results, a strong association
between SOA and anthropogenic sources has implications for control strategies in urban
regions with large biogenic VOC emissions.

1.0 BACKGROUND

The Atlanta Georgia metropolitan region and other locations in the south and
southeastern U.S.A. often exceed fine particle (PM2.5) National Ambient Air Quality
Standards. Fine particles in these regions are mainly sulfate, sulfate-associated
ammonium, and organic carbon (OC). Although sources for OC are not well known,
based on elemental carbon (EC) as a tracer for primary emissions, analysis of Atlanta OC
and EC during summer suggests that the OC is approximately half primary and half
secondary, with substantially higher fractions of secondary OC on short time scales [Lim
and Turpin, 2002]. In rural areas OC is mostly secondary due to lower concentrations of
primary OC (see Table 1 below). The formation of secondary organic aerosol (SOA) can
involve anthropogenic and biogenic volatile organic compounds (VOCs). Of the
anthropogenic VOCs, chamber experiments indicate that aromatic compounds from
vehicle emissions produce the majority of anthropogenic SOA [Odum et al., 1997].
However, a number of recent studies clearly show that anthropogenic VOCs lead to much
more SOA than expected [de Gouw et al., 2005; Volkamer et al., 2006] suggesting other
unknown production pathways. Chamber studies also indicate that biogenic VOCs, such
as mono-terpenes [Hoffmann et al., 1997], and possibly isoprene [Kroll et al., 2005;
Limbeck et al., 2003], have high aerosol formation yields and so are also thought to be an
important source of SOA. Because many urban regions in the south and southeast are
densely forested, and most anthropogenic VOCs are thought to have low yields, the
current view is that SOA in these regions is largely from biogenic precursors. This is also
supported by radiocarbon analysis (\(^{14}C\)) on the total carbonaceous fraction of fine
particles collected at surface-based sites ([Lewis and Stiles, 2006] and references therein).
In this study, we use measurements of various trace gases and the water-soluble organic carbon (WSOC) component in fine particles to comprehensively investigate sources of SOA. The analysis involves comparing polluted air masses over northern Georgia, including metropolitan Atlanta, with New York City plumes that contain significantly less biogenic VOCs.

2.0 METHOD

Fine particle WSOC is used in the following analysis as an estimate of SOA mass. In the absence of biomass burning emissions, this appears to be a reasonable assumption. In Tokyo, Japan, WSOC was highly correlated (r^2 > 0.78) with the oxygenated fraction of organic aerosols determined through Aerosol Mass Spectrometry (Aerodyne AMS) [Kondo et al., 2006], and with SOA predicted by the EC tracer method [Miyazaki et al., 2006]. In these studies WSOC was roughly 75% of the measured total oxygenated aerosol organic carbon or predicted secondary carbon. Measurements also show that significant WSOC mass is not emitted directly by mobile sources (discussed below).

A brief description is provided of the online (mainly airborne) and offline (ground-based) instrumentation used to generate the data discussed in the following analysis. The radiocarbon analysis is described in more detail since this is the first time we have applied it to WSOC extracted from integrated filter samples.

2.1 Online WSOC, CO, and VOCs: Airborne data in this study include PM1 WSOC measured on-line with a Particle-Into-Liquid Sampler coupled to a Total Organic Carbon (PILS-TOC) analyzer for a continuous 3-second integrated measurement. Due to inevitable heating in airborne sampling systems, the WSOC reported here likely not does include semi-volatile SOA. Carbon monoxide (CO) was measured at 1 Hz by vacuum ultraviolet fluorescence [Holloway et al., 2000], and a host of biogenic and anthropogenic VOCs were measured on-line by proton-transfer-reaction mass spectrometry (PTRMS), and off-line on whole air samples (WAS) via gas-chromatography with a variety of detection methods. See Sullivan et al., [2006] and de Gouw et al., [2005] for more details on these methods. WSOC and CO were also measured from the Georgia Institute of Technology (GIT) Environmental Science and Technology roof top laboratory located in
central Atlanta approximately 15 m above ground level. At this site, PM2.5 WSOC was measured with a PILS-TOC identical to the airborne system, and CO with a Model 300E CO analyzer (Teledyne Instruments, San Diego, CA).

2.2 Offline OC, EC, and WSOC: Fine particle (PM2.5) OC, EC, and WSOC were determined at two ground-based sites in Atlanta and one rural site from 12 or 24-h integrated filter samples collected with a Hi-Volume sampler (Thermo Anderson, undenuded, flow rate 1.13 m$^3$/min). Using pre-baked quartz filters, OC and EC were quantified from filter punches using a Sunset Labs ECOC analyzer (Forest Grove, Oregon) [Birch and Carey, 1996] following NIOSH Method 5040 [Eller and (Eds.), 1996]. WSOC was determined by extracting a portion of the filters in water followed by analyses with the same TOC analyzer used in the online technique. In other studies in Atlanta, filter-extracted WSOC has been found to agree to within 10% of the on-line WSOC [Sullivan and Weber, 2006a]. Aerosol concentrations measured from the aircraft are reported at standard conditions (20°C, 1 atmosphere), whereas the aerosols measured at the surface are reported at ambient temperature and pressure.

2.3 Radiocarbon on WSOC: PM2.5 WSOC extracted from High Volume filters was also analyzed for carbon isotopes to determine the fraction of modern and fossil carbon associated with the fine-particle WSOC. Measurements of modern and fossil carbon fractions in aerosol samples have been used in a number of other studies to investigate aerosol sources [Lemire et al., 2002; Lewis and Stiles, 2006; Lewis et al., 2004; Mei et al., 2006; Szidat et al., 2004]. The analysis for $^{14}$C employed here follows these earlier studies. The method is based on comparing concentrations of the unstable $^{14}$C isotope (half life ~5730 years) to stable $^{13}$C or $^{12}$C. Recently formed biological material, such as plants and their emitted VOCs, have $^{14}$C/$^{12}$C ratios that are similar to that found for atmospheric CO$_2$, since $^{14}$C is continually formed in the atmosphere and exchanged with living plants. Fossilized carbonaceous material is, however, isolated from the atmosphere and has no source for $^{14}$C. Radioactive decay over the long time spans for the formation of fossilized carbon leads to $^{14}$C/$^{12}$C ratios below detection limits. The fraction of aerosol particle carbon in the sample that is modern ($F_M$) is corrected for isotopic fractionation
[Tanner et al., 2004] and determined from the sample $^{14}\text{C}/^{12}\text{C}$ ratio and comparison to a modern carbon standard reference material (SRM: either NBS Oxalic Acids I, NIST-SRM-4990, or Oxalic Acid II, NIST-SRM-4990C) by,

$$F_M = \frac{{(^{14}\text{C}/^{12}\text{C})_{\text{sample}}}}{(0.95 \times (^{14}\text{C}/^{12}\text{C})_{\text{SRM}})}.$$  (1)

For radiocarbon dating, the denominator is defined as “modern” carbon [Olsson, 1970] and is the isotopic ratio for 1890 wood [Lewis et al., 2004; Stuiver, 1983]. Inferring the fraction of biogenic compounds in the analyzed aerosol particle sample from $F_M$ is complicated by variability in past atmospheric $^{14}\text{C}$ concentrations due to nuclear bomb testing in the 1950 and 1960s. Plants formed after this period will have higher $^{14}\text{C}$ concentrations than those formed prior. The biogenic carbon fraction, defined here as $F_B$, (also called contemporary carbon [Mei et al., 2006] and the true modern fraction [Tanner et al., 2004] in other studies) has been estimated from $F_M$ by dividing by a constant factor. Tanner et al. [2004] used 1.1, Lewis et al. [2004] suggests a factor in the range of 1.08 to 1.25. In the following analysis we use 1.1 since this is near the middle of the range given by Lewis et al. This range leads to an uncertainty in $F_B$ of at most ~10%.

The fraction of fossil carbon in the sample ($F_F$) is calculated as one minus $F_B$, or

$$F_F = 1 - F_B = 1 - F_M / 1.1.$$  

In the following analysis it is also assumed that all modern carbon in the fine aerosol WSOC is associated with SOA from biogenic VOCs, and that vehicle fuels contain no biogenic carbon. Additives such as corn-based ethanol and biodiesel from vegetable oils may contribute to fine particulate modern carbon, possibly leading to an over estimation of the contribution of biogenic VOCs to SOA, however, they were not in wide spread use during the measurement period of this study.

Analysis for carbon isotopes was performed at the National Ocean Sciences Accelerator Mass Spectrometry Facility (NOSAMS) at the Woods Hole Oceanographic Institution, MA. Typically, greater than 200 µg of carbon were needed for routine $^{14}\text{C}$ analysis (although smaller samples can also be analyzed at greater expense). To prepare the WSOC for radiocarbon analysis, the carbon concentration in the extract was determined with the TOC analyzer. The remaining liquid sample volume was determined
gravimetrically and then concentrated in a rotary evaporator to approximately 5 ml. This volume was pipetted onto a 47 mm pre-baked quartz filter by adding a small aliquot to the filter, which was then dried by blowing nitrogen over the surface. This filter plating procedure was repeated until all of the ~5 ml concentrated sample was transferred to the filter. The procedure was performed under a laminar flow hood with activated carbon scrubbers. The loaded filters were then placed in plastic Petri dishes and shipped to NOSAMS at Woods Hole Oceanographic Institute for radiocarbon analysis. (A simplified method involving $^{14}$C analysis of liquid samples is being developed).

The NOSAMS method for measuring carbon isotopes from samples on quartz filters is discussed elsewhere [Tanner et al., 2004]. Briefly, the quartz filter is placed in a pre-fired quartz tube containing powdered CuO and Ag. The pressure in the tube is reduced to below 3 mTorr and the tube sealed with a torch. The contents in the tube is then combusted for 5 hours at 850°C. Evolved CO$_2$ is analyzed for concentrations of $^{14}$C, $^{13}$C, and $^{12}$C. Comparison of the carbon concentration in samples measured at NISCOM to WSOC extracted from the filter indicate that about 2/3 of the sample was recovered in the process of sample concentrating, plating, and analysis. Replicating the complete High Volume quartz filter extraction, liquid sample concentration, and replating procedure also created a sample blank. The carbon concentration evolved and analyzed for $^{14}$C by NOSAMS on the blanks was on average 6% (± 2%, 1 standard deviation) of the four samples analyzed and discussed below, with F$_B$ = 28% (F$_F$ = 72%). Thus, contamination will lead to a small (less than 1%) under-estimate of the biogenic fraction and an approximately 6% (on average) over estimation of the fossil fraction.

Uncertainties associated with the radiocarbon dating method to determine F$_B$, as reported by NOSAMS, are less than 1%. Possible overestimation of F$_B$ due to $^{14}$C contamination, either in the sampling or extraction process, is a concern but not considered in this analysis.

3.0 RESULTS

3.1 Fine Particle WSOC and Direct Emissions from Mobile Sources

Ground-based measurements in central urban Atlanta at the Georgia Institute of Technology (GIT) over a number of summers have shown that fine particle WSOC is a large fraction of the carbonaceous aerosol. In the summers of 2004 and 2005 at GIT,
WSOC was typically on the order of 55% to 65% of the organic carbon (OC) by mass, but often exceeded 75% during periods of poor air quality [Sullivan and Weber, 2006b]. These results are in general agreement with the predicted SOA mass of Lim and Turpin, [Lim and Turpin, 2002].

To investigate if vehicle emissions are a significant direct source for WSOC in Atlanta, two sets of simultaneous (paired) measurements were made in the summer of 2005 at various distances from vehicle traffic sources using two identical High-Volume samplers. In the first experiment, a sampler was situated within a meter of a major expressway (Interstate-75/85 with 7 traffic lanes each direction) and the other at GIT approximately 400 m away. This section of the freeway has limited diesel traffic due to regulations. In the second experiment, the High-Volume sampler was moved from the highway to Yorkville, a rural site ~ 80 km west of Atlanta (see Figure 3). Table 1 summarizes comparisons between carbonaceous aerosols measured at the expressway to GIT, and GIT to Yorkville.

Particulate EC is a known primary component of vehicle emissions, and, as expected, highest concentrations are observed along the expressway and lowest at the rural Yorkville site (Table 1). EC was a factor of about 10 larger at the expressway than at GIT, and a factor of 6 higher at GIT than Yorkville. Organic carbon is composed of both primary and secondary compounds and so exhibits less difference between the various sites. OC was a factor of 1.4 times higher at the expressway compared to GIT, and GIT was 1.2 times higher than Yorkville. WSOC showed little variability. Expressway WSOC was 1.1 times higher than GIT, and GIT was 1.07 times higher than Yorkville. (Integrated filter measured WSOC precision was ~5% based on side-by-side tests of samplers and methods). A paired t-test on the hypothesis that the WSOC is equal at both sites has an observed significant level (p-value) of 0.039 and 0.017 for the expressway/GIT and Yorkville/GIT experiments, respectively. These results show that much of the WSOC has a regional characteristic. For the most part it is not directly emitted by vehicles and is likely secondary in nature. Aircraft data presented below also show no evidence for a strong primary source of WSOC. Furthermore, a recent study in Tokyo found no significant concentrations of primary WSOC [Miyazaki et al., 2006], and a number of studies show little evidence for primary WSOC in vehicle emissions.
Some studies have identified specific components of OC that are directly emitted by vehicles and are soluble in water ([Fisseha et al., 2006] and references therein). Our results suggest that these types of primary emissions were a minor fraction of the total WSOC measured during these experiments, possibly due to the much higher concentrations of SOA.

3.2 Airborne Measurements of CO, VOCs, and Fine Particle WSOC

Fine particle (PM1) WSOC, CO, and various VOCs were measured over a large region of the northeastern U.S.A. during July and August of 2004 as part of the National Oceanic and Atmospheric Administration’s (NOAA) Intercontinental Transport and Chemical Transformation study - 2004 (ITCT-2K4). At the conclusion of the experiment, on August 15, 2004, a number of sampling passes were made over northern Georgia, including metropolitan Atlanta, as the aircraft returned to its operational base in Tampa, FL. The data provide a unique opportunity to compare evidence of SOA formation in two very different regions impacted by anthropogenic emissions.

Results from investigating plumes advecting from the northeastern urban centers are discussed in more detail elsewhere [Brock et al., 2006; Sullivan et al., 2006]. Some results are presented here to aid in the comparison with measurements over northern Georgia.

3.2.1 Plumes from New York City

During ITCT-2K4 plumes from urban centers could be readily identified in air masses with high CO concentrations and back trajectories that intercepted specific urban regions. In all cases, WSOC was highly spatially correlated with CO and no clear or strong linkage could be found between biogenic VOCs and WSOC [Sullivan et al., 2006]. As an example, Figure 1 shows the aircraft flight path and altitude over the northeastern US and Canada on July 22, 2004, and the measured concentrations of WSOC, CO, and the sum of the biogenic VOCs; monoterpenes, isoprene, and isoprene photochemical products, methyl-vinyl ketone (MVK) and methacrolein (MACR). Biomass burning influence was negligible during this sampling period since the mean concentration of the biomass burning tracer acetonitrile for the period plotted was at background levels, 178 ± 34 pptv (± 1 standard deviation) [de Gouw et al., 2006]. The measurements clearly show
a high spatial correlation between WSOC and CO, in this case mostly due to changes in
measurement altitude. This type of WSOC - CO spatial correlation was seen throughout
the mission, in both urban plumes and more regionally polluted air mass [Sullivan et al.,
2006]. Back trajectory analysis indicated that the CO was from various regions along the
Washington-to-Boston urban corridor transported to the measurement region over a
period of a few days. Analysis of plumes transported from these urban regions
(discussed below) suggest that most WSOC is formed within 24 hours after emission,
thus at the time of the measurements, WSOC formation had likely slowed and the WSOC
in Figure 1 was somewhat aged.

High concentrations of biogenic VOCs were also observed during this flight when
the aircraft flew over forested regions and where emissions had mixed with air masses
advecting from urban regions from the southwest. These biogenic VOCs are apparently
fairly fresh since they are highly reactive and are expected to have short life spans. No
correlation between WSOC and the biogenic VOCs measured in these biogenic VOC-
rich regions may, in part, be due to insufficient time for aerosol production. However,
the measurements show that the region sampled during this flight contained substantial
biogenic VOC sources, yet in no place was there any indication that they had a significant
influence on WSOC mass. Thus, the aircraft results of Figure 1 suggest a strong linkage
between WSOC mass and anthropogenic emissions and little evidence for a strong purely
biogenic source. These results are similar to other studies in the region. Ship-based
measurements in the Gulf of Maine during this study also found that oxidized (e.g.,
secondary) organic aerosol was linked to anthropogenic and not biogenic emissions
[Quinn et al., 2006]. Anthropogenic emissions were also identified as the source of
particulate organic matter in the same region measured during the 2002 New England Air
Quality Study [de Gouw et al., 2005].

To quantitatively investigate the formation of organic aerosol within
anthropogenic plumes as they aged, the changes in WSOC mass can be compared to CO,
a relatively unreactive co-emitted tracer (i.e., CO is correlated with WSOC). Sullivan et
al., [2006] and Brock et al., [2006] following two different approaches and using
somewhat different data sets (some portions overlap) have performed a detailed
investigation into WSOC formation in the northeastern US urban plumes measured
during ITCT-2K4. Sullivan et al., [2006] focused on well-defined plumes that could be clearly traced by air mass back trajectories to specific urban centers. To calculate the increase in concentrations within plumes relative to a regional background of WSOC and CO, a constant background for WSOC (0.75 mgC/m³) and CO (CO 121 ppbv) was assumed. Seven plumes transported from NYC were intercepted on four different research flights at various distances from the metropolitan region. Brock et al., [2006] focused on portions of six specific flights that included three flights not considered by Sullivan et al, and performed a more detailed analysis to estimate background concentrations. They used a WSOC background of 0.3 µgC/m³ and CO background of 25 ppbv. Both results are included in the following comparisons with the Atlanta/north Georgia data to provide a sense of the range in results depending on the type of analysis.

The results of Sullivan et al. [2006] are summarized in Table 2. Similar to what was observed in Figure 1, in all NYC plumes encountered during the mission, the WSOC was highly correlated with CO (r² between 0.78 and 0.92) suggesting a link between WSOC and vehicle emissions, though it is recognized that reaction of biogenic sources can also contribute to CO formation, but would be very diffuse. Table 2 also shows that WSOC/CO tended to increase with increasing plume transport time from NYC.

The view that photochemical processes produce WSOC is supported by measured changes in concentrations due to increased photochemical processing of anthropogenic VOCs with increasing plume age. Along with CO, toluene and benzene are also emitted directly by vehicles. Both react with the hydroxyl radical (OH), but at different rates; the OH-toluene rate constant (k_{toluene}) is $5.63 \times 10^{-12}$ cm³ molecules⁻¹ s⁻¹ and OH-benzene rate constant (k_{benzene}) is $1.22 \times 10^{-12}$ cm³ molecules⁻¹ s⁻¹ [Atkinson and Arey, 2003]. Thus, more photochemically aged plumes should have smaller toluene/benzene ratios, and as shown in Table 2, toluene to benzene decrease with increasing plume transport age.

Using estimates of the emission ratio of benzene and toluene and an estimated OH concentration, the photochemical age of the air mass can be estimated [de Gouw et al., 2005] by:

$$D_t = \left[ \frac{\ln(t / b)}{\ln(t / \bar{b})} \right] \frac{\ln(t / \bar{b})}{\ln(t / b)},$$

(2)
where $t/b$ is the ratio of toluene to benzene. An emission ratio $(t/b)_0$ of 3.7 is used [de Gouw et al., 2005] based on measurements within plumes from urban regions that had undergone little oxidation. This value is consistent with emissions estimated from tunnel studies [Kirchstetter et al., 1991] and nighttime measurements in urban Atlanta (discussed below). As in de Gouw et al. [2005], a 24-hr average OH concentration of $3 \times 10^6$ molecules cm$^{-3}$ is used. For the Sullivan et al., [2006] data, and the analysis of North Georgia data to follow, when calculating $t/b$, background toluene concentrations are assumed to be zero and background benzene at 18 pptv, based on measurements in pristine air. Brock et al. [2006] uses zero background toluene and 18.75 pptv for background benzene that decreases with increasing plume age.

Table 2 shows that the calculated photochemical ages have the same trends and are in reasonable agreement with estimates of air mass transport times from NYC. Systematic decreases in the NO$_x$/NO$_y$ ratio with plume transport age are also consistent with these photochemical age calculations [Brock et al., 2006].

Combining the analysis of $\frac{\text{WSOC}}{\text{CO}}$ and photochemical ages, Figure 2 shows the results of Sullivan et al. [2006] (summarized in Table 1), and Brock et al., [2006]. In both analysis $\frac{\text{WSOC}}{\text{CO}}$ is lowest in fresh plumes close to NYC, and increases with plume photochemical age. For the Sullivan et al. analysis $\frac{\text{WSOC}}{\text{CO}}$ reaches a fairly constant value of $\sim 32 \pm 4$ µgC/m$^3$/ppmv in plumes that had advection times greater than about 30 hours. Based on an exponential fit to the Brock et al. results, a similar leveling off of $\frac{\text{WSOC}}{\text{CO}}$ at $\sim 35$ µgC/m$^3$/ppmv is observed after approximately 20 to 30 hours. The increases in $\frac{\text{WSOC}}{\text{CO}}$ are concurrent with decreases in toluene, indicating photochemical processing in these plumes. The leveling out of $\frac{\text{WSOC}}{\text{CO}}$ after about 20 hrs or so could be due to depletion of precursors, or passivation of surfaces reducing gas-to-particle conversion, or it could be from other non-SOA formation factors, such as preferential aerosol scavenging, or dilution with a non-zero background CO [McKeen et al., 1996]. During the measurement period there was no indication of wet scavenging, and the decrease in toluene relative to benzene produces photochemical ages in reasonable agreement with transport times, so dilution effects seem unlikely. Furthermore, similar rapid increases in organic aerosol concentration
normalized to a conservative species that then levels off after a number of hours following emission have been reported in other studies under conditions likely containing differing regional backgrounds [de Gouw et al., 2005; Takegawa et al., 2006]. The results from measurements over northern Georgia are now compared to these northeastern U.S.A. urban plumes.

3.2.2 The North Georgia Polluted Boundary Layer

On the return to Tampa FL following the ITCT-2K4 experiment, the NOAA WB-P3 made a number of passes over northern Georgia, including the Atlanta metropolitan region. During the time of the boundary layer over-flight surface-measured PM$_{2.5}$ mass concentrations in metro Atlanta were ~17 µg/m$^3$, typical for the relatively clean summer of 2004. A map of the flight track colored by CO concentrations is plotted in Figure 3. From the aircraft soundings, the boundary layer was stable and capped by a weak temperature inversion (DT = 1°C) at ~2.5 km altitude (note, the altitude of Atlanta is ~310 m). Relative humidity dropped from an average (± standard deviation) boundary layer value of 76 ± 8% to less than 20% above the inversion. Figures 3 and 4 combined show that boundary layer concentrations of WSOC and CO were enhanced over an extensive region of northern Georgia extending well beyond the metropolitan region due to stagnant conditions that had existed for a few days prior to the measurements. Superimposed on the regional (aged-urban) CO are smaller areas of significantly higher CO concentrations. The most obvious example is identified as point C in Figures 3 and 4 recorded when the aircraft sampled just west of central Atlanta and associated with enhanced emissions over the more densely populated center of the metropolitan region. WSOC does not track CO in these fresh emissions, consistent with most WSOC being secondary.

For all the boundary layer data recorded over north Georgia WSOC-CO $r^2$ is 0.80 (Figure 5). Considering only data during the low-level legs (18:27 to 19:44 UTC, i.e., no sounding data) the WSOC-CO $r^2$ is 0.71, indicating that the correlation is not mainly driven by the transitions from the clean free troposphere to polluted boundary layer air masses, but is instead due to regional variability. The consistency of the WSOC – CO correlation over the range in the data is demonstrated in Figure 5 by the high correlation.
Vehicle emissions appear to be the main source of the CO measured in this region. For all boundary layer air over northern Georgia, acetylene, a vehicle emission tracer ([Harley et al., 1992]), is correlated with CO ($r^2 = 0.91$), and WSOC ($r^2 = 0.60$). Biomass burning was not a significant contributor to the observed CO and WSOC since the biomass-burning tracer acetonitrile was at background levels with an average concentration of 127 pptv [de Gouw et al., 2006].

**3.2.3 Comparison of North Georgia/Metro Atlanta with New York City Plumes**

The airborne data collected over northern Georgia can be compared to the measurements in plumes advecting from New York City (NYC) recorded earlier in the experiment. These comparisons are of interest because higher biogenic VOC emissions in the southeastern U.S.A. may be expected to lead to significantly higher concentrations of biogenic SOA (e.g., higher WSOC relative to anthropogenic CO). This comparison is clearly limited by the short duration of the measurements over northern Georgia and is not meant to represent typical climatology, it is, however, an insightful case study.

Table 3 compares the median concentrations of biogenic and anthropogenic compounds measured in the northeastern urban plumes identified by Sullivan et al., [2006] to those measured in the boundary layer over northern Georgia for the period shown in Figure 4 (ignoring in-cloud data). On average, the mainly biogenic-derived VOCs $\Delta$-pinene, $\beta$-pinene, isoprene, methyl-vinyl ketone (MVK) and methacrolein (MACR) had concentrations that were 10 to 100 times higher over Atlanta and north Georgia. Based on differences in vegetation type and density, higher biogenic VOC concentrations are expected in the southeast, and models predict significantly more biogenic SOA over the southeast than the northeast [Tsigaridis and Kanakidou, 2003].

In contrast to the biogenic compounds, the directly emitted anthropogenic species CO and acetylene, and the secondary anthropogenic compound isopropyl nitrate [de Gouw et al., 2005] were on average approximately factors of 1.5 to 2 times higher in the NYC plumes. Surprisingly, fine particle WSOC was on average ~ 1.8 times higher in the NYC plumes. A similar ratio of anthropogenic emissions and PM1 WSOC between northern Georgia and NYC plumes, despite large differences in biogenic VOC concentrations, is unexpected. A more detail comparison between NYC plumes and the
north Georgia measurements is made by first comparing WSOC to isopropyl nitrate. We then focus on relative increases in WSOC to CO as a function of photochemical age. Both airborne measurements and surface measurements made in metropolitan Atlanta during the flyover are included in the comparison.

3.2.4 WSOC and Isopropyl Nitrate: Isopropyl nitrate is a useful tracer for anthropogenic VOC oxidation products [de Gouw et al., 2005] since it has no direct source, is produced mainly from propane oxidation, and propane is mainly from anthropogenic sources (motor vehicles, natural gas use, etc.). Figure 6 shows WSOC versus WAS measurements of isopropyl nitrate concentrations for all data over north Georgia (except in-cloud sampling). Also plotted are data collected in NYC plumes that were over ~1 day old. The latter are plumes labeled as 0721A, 0721B, and 0722A in Table 2. The comparison is restricted to these NYC plumes to contrast Atlanta to NYC plumes that are not still chemically evolving. Table 2 and Figure 2 suggest that it takes approximately one day for WSOC formation in the NYC plumes to be mostly completed. Under these assumptions, WSOC in northern Georgia is correlated with isopropyl nitrate and WSOC is in similar proportions to isopropyl nitrate in the polluted northern Georgia boundary layer and chemically processed NYC plumes.

3.2.5 Photochemical Age and \( \frac{[\text{WSOC}]}{[\text{CO}]} \) Measured in Northern Georgia: Following the method for analyzing the NYC plumes, the photochemical age of air masses measured at the surface and from the aircraft above northern Georgia are calculated based on ratios of toluene to benzene (Equation 2). A daily average OH concentration of \( 3 \times 10^6 \) cm\(^{-3}\) and toluene to benzene emission ratio of 3.7 are assumed; the same values for the photochemical age calculations in the NYC plumes. The toluene/benzene emission ratio of 3.7 is reasonable based on measured nighttime concentrations in urban Atlanta. For the night before the over-flight (8/15/06 0:00 to 8:00 Eastern Daylight Time) hourly data from the EPA PAMS (Photochemical Assessment Monitoring Stations) South DeKalb site located in Atlanta near a junction of two freeways and approximately 20 km southeast of GIT, report a mean (± one standard deviation) toluene to benzene ratio of 3.7
± 0.2. In contrast to these nighttime values, PAMS surface measurements during the period of the over-flight (15:00 to 16:00 Eastern Daylight Time) report an average toluene/benzene ratio of 2.25 pptv/pptv, corresponding to a photochemical age of 10.5 hours by equation 2. This photochemical age calculation is reasonable since the time from sunrise to the time of the measurement was roughly 8 hours, and there will be lingering partially reacted benzene and toluene from the prior day fumigated down from the boundary layer.

The photochemical age of the air masses measured from the aircraft at an altitude of 0.73 km while directly over Atlanta (14:30 to 15:30 Eastern Daylight Time, 18:30 to 19:30 UTC) was higher than the surface measurement, suggesting more chemically processed air at higher altitudes in the boundary layer. Toluene/benzene ratios based on WAS data, and the corresponding photochemical ages were 1.2 ± 0.4 pptv/pptv and 25 ± 10 hours, respectively, compared to the surface photochemical age of 10.5 hours. For all the airborne data while sampling in the north Georgia boundary layer, highest toluene/benzene ratios (1.6 ± 0.1 pptv/pptv) and correspondingly shortest photochemical ages (18 ± 2 hours) were recorded directly over Atlanta. Greater photochemical ages were recorder away from the downtown region.

Irregardless of the 24-hr average OH concentration used to calculate the photochemical ages, these aircraft measured toluene/benzene ratios are significantly less than the surface nighttime values and surface values measured during the over flight indicating the compounds measured at 0.6 to 1.1 km altitude had undergone significant photochemical processing since emission. It is reasonable then to believe that photochemical processes leading to SOA formation may have also occurred since the NYC results show that the process is fairly rapid.

To calculate the change in WSOC mass relative to CO as a function of air mass photochemical age over northern Georgia, WSOC and CO are merged to the WAS sampling periods (toluene and benzene measurements). [WSOC/CO is calculated for each of these WAS measurement intervals by assuming constant background concentrations based on the results from the linear regression curve shown in Figure 5. This is done since no measurements were made “upwind” of more pristine air masses. Results from the linear regression, slope, intercept and r², are largely insensitive to what
boundary layer data are used, if the fresh CO peak over metropolitan Atlanta is excluded. For example, similar linear regression results are obtained when only considering the level legs during the boundary layer sampling interval. In the following analysis a background WSOC concentration of zero and background CO of 91 ppbv determined from the x-intercept from the WSOC – CO linear regression is used. (Note, if the CO peak over Atlanta is included, the intercept (background CO) is smaller and WSOC/CO is also smaller than the values plotted in Figure 2, hence less SOA formation is predicted).

For comparison WSOC/CO as a function of photochemical age measured over northern Georgia are also included with the NYC data in Figure 2. The Atlanta/northern Georgia results are fairly consistent with the NYC plumes. Furthermore, the slope of the WSOC – CO linear regression (Figure 5) for measurements over northern Georgia, which represents the average WSOC/CO, is 38 µgC/m³/ppmv for data not considering fresh CO, and 32 µgC/m³/ppmv for all boundary layer data. These values are comparable to that measured in the NYC plumes that had photochemically aged approximately 1 day, calculated by both Sullivan et al., [2006] and Brock et al., [2006]. Furthermore, the results are also similar to that reported by de Gouw et al., [2005] from ship-based measurements off the New England coast down wind of Boston MA during the summer of 2002 in which a different technique was used to measure the organic aerosol and VOCs.

A measurement made at the surface at GIT is also included in Figure 2 and demonstrates that there was a difference between WSOC/CO measured at 0.6 to 1 km altitude to that measured at the surface, (as was also seen in the photochemical age calculations above). From WSOC and CO measured at GIT during the over-flight the WSOC/CO was ~10 µgC/m³/ppmv (assuming a WSOC background of 0 µgC/m³ and CO background of 91 ppbv). Thus, the NYC data show that lower WSOC/CO ratios are observed closer to the point of anthropogenic emissions (e.g., closer to the urban center), and in the north Georgia data, substantially lower ratios are observed at the surface in the metropolitan area, in closer proximity to vehicle emissions, compared to measurements 0.6 to 1 km above the metropolitan region.
Measurements of carbonaceous aerosol and CO have also been made at the surface in Atlanta during other studies. Lim and Turpin [2002] made measurements of OC and CO during August 1999 at the Atlanta Supersite located at Jefferson Street approximately 3 km from GIT. Based on regression slopes, $\Delta$OC/$\Delta$CO ranged from approximately 4 to 6 $\mu$gC/m$^3$/ppmv. (Note, $\Delta$OC/$\Delta$CO and $\Delta$WSOC/$\Delta$CO ratios should be similar if the increase in OC and WSOC is due mainly to SOA, i.e., WSOC=OC-$\text{OC}_{\text{pri}}$, and primary OC is fairly constant). As expected, these surface ratios are close to emission ratios recorded from light duty vehicles (e.g., $\Delta$OC/$\Delta$CO \sim 1 $\mu$gC/m$^3$/ppmv) [Kirchstetter et al., 1991].

Based on the comparisons of Figure 2, the Atlanta/north Georgia results are in reasonable agreement with those of the NYC plumes. It is possible, however, that the Atlanta and surrounding region fine particle WSOC was still evolving and that more chemically aged air would have substantially higher WSOC concentrations relative to CO. There is a fundamental difference between the Atlanta/north Georgia and NYC plumes. NYC plumes were analyzed based on Lagrangian-type experiments, whereas stagnant conditions with accompanying low wind speeds over Atlanta/north Georgia make any evidence for plume evolution less distinct. However, $\Delta$WSOC/$\Delta$CO magnitudes were similar over the whole range of photochemical ages. This covers a large geographical region in northern Georgia, including measurements over Atlanta and more rural surrounding regions where air masses are more chemically aged.

In summary, the high correlations between WSOC and anthropogenic components isopropyl nitrate and CO, and the similar proportions between WSOC and these anthropogenic compounds in Atlanta/north Georgia and NYC suggest similar mechanisms for SOA formation in these two regions, despite the fact that Atlanta/north Georgia has much higher concentrations of biogenic VOCs. To investigate biogenic contributions to SOA, radiocarbon measurements of WSOC were also performed.

3.3 Radiocarbon Analysis of WSOC Collected at the Surface in Atlanta

Radiocarbon analysis on the total aerosol carbon from samples collected in Houston TX, Nashville, TN, and Tampa FL suggest that a significant fraction of the SOA in the south and southeastern U.S.A. is from biogenic VOCs [Lemire et al., 2002; Lewis...
and Stiles, 2006; Lewis et al., 2004]. Because these studies measured carbon isotopes on all carbonaceous aerosol particles collected on the filter (and volatilized at typically 850°C), the biogenic fraction of SOA could not be determined directly, but instead was inferred using methods such as chemical mass balance models [Mei et al., 2006] or the EC tracer method [Lemire et al., 2002]. To provide a possibly more direct measurement of the biogenic VOC fraction of SOA, radiocarbon analysis was performed directly on fine particle (PM2.5) WSOC collected in Atlanta.

Concentrations of carbon isotopes were determined from portions of four archived filters collected and analyzed for other carbonaceous chemical compounds as part of another study [Mei et al., 2006]. The same High Volume samplers discussed earlier were used to collect 24-hour integrated samples at Jefferson Street, a SEARCH network site near the GIT campus. The four filter samples analyzed were collected in June 2004 and were selected based on low concentrations of the unique biomass burning marker levoglucosan [Simoneit et al., 1999] (concentrations given in Table 4) to minimize contributions from biomass burning-generated WSOC that would contribute to the biogenic fraction. For the radiocarbon analysis, one quarter of the filter was extracted in 125 ml of water to obtain the WSOC fraction (see Sullivan and Weber [2006a] for details) and the sample concentrated and plated onto the pre-baked 45 mm quartz filter for subsequent radiocarbon analysis, as discussed above.

Table 4 summarizes the results and indicates that 67 to 81% of the WSOC in urban Atlanta was biogenic, suggesting that biogenic VOCs were involved in most of the SOA formed. In fact these samples tend to be on the low side for the summer of 2004. Radiocarbon analysis on WSOC from 21-pooled High Volume samples collected between June 11, 2004 to September 2, 2004 at GIT [Sullivan and Weber, 2006a] had a biogenic fraction of 82%. Although these filters were not collected at the same time as the aircraft fly over on 8/15/04 they are likely a good representation of typical summer values in urban Atlanta. These results are also in general agreement with other radiocarbon studies from the southeast [Lewis and Stiles, 2006; Lewis et al., 2004]. No filter samples were collected in aged NYC plumes and so a comparison cannot be made with the Atlanta results.
Because a significant mass of aerosol particle carbon is needed for the radiocarbon analysis, High Volume un-denuded samplers operated over extended periods (24 hours) were used to collect particles for the analysis. This leads to possible interferences from positive or negative artifacts that may influence the WSOC radiocarbon analysis. However, for the 21-pooled samples, during a previous study the WSOC extracted from the 24 hour integrated High Volume filters was found to agree well with on-line denuded measurements of WSOC ($r^2 = 0.83$, zero intercept slope = 1.10) [Sullivan and Weber, 2006a]. Furthermore, two of the four High Volume samples collected at Jefferson Street used for WSOC radiocarbon analysis coincided with online WSOC measurements at GIT. The ratio of the Jefferson Street High Volume WSOC to GIT online WSOC was 1.16 for the 6/17/04 sample and 1.19 gC/gC for the 6/23/04 sample (Table 4). Thus, these comparisons suggest that positive artifacts were not extreme. Negative artifacts have not been quantified but are generally found to be less significant than positive artifacts when sampling with integrated filters [Turpin et al., 2000].

4.0 DISCUSSION

The high correlation and similar proportions between WSOC and anthropogenic tracers observed in the northeastern urban outflow and over Atlanta/north Georgia suggest a strong linkage between anthropogenic emissions and SOA formation. These results are difficult to dismiss since despite being based on a limited data set, the correlations are strong and consistent; WSOC and CO are correlated throughout the northeastern U.S.A. and in the Atlanta/north Georgia region, and WSOC scales in a similar manner with both CO and isopropyl nitrate. Moreover, similar findings have been reported in other studies conducted in these regions. In the northeast, two other studies [de Gouw et al., 2005; Quinn et al., 2006] report that the organic aerosol formed is closely linked to anthropogenic emissions, and based on extensive filter sampling in Atlanta during the summer of 2004, Sullivan and Weber [2006a] found that the majority of the chemical compounds comprising WSOC were correlated with anthropogenic VOCs.
In contrast, the radiocarbon data show that the majority (~70 to 80%) of the Atlanta WSOC is biogenic, suggesting that biogenic VOCs were a major precursor. Similar findings reported by other radiocarbon studies on aerosol collected in the southeastern U.S.A. [Lewis and Stiles, 2006; Lewis et al., 2004] indicate that biogenic carbon is a predominant component of the organic aerosol in these regions.

There are a number of ways to reconcile these apparently opposing results. First, it may be that SOA formation in the NYC plumes and north Georgia/Atlanta is predominately from anthropogenic VOCs, and that contribution from biogenic VOCs, inferred from the radiocarbon data, is too large. In regions where anthropogenic emissions dominate, such as Mexico City, recent measurements show that the SOA mass is much larger than expected [Volkamer et al., 2006] making anthropogenic SOA formation a viable mechanism for producing WSOC in both NYC plumes and the polluted north Georgia/Atlanta region.

Secondly, biogenic VOC contributions to WSOC in north Georgia/Atlanta could be significantly smaller than what is inferred from the radiocarbon measurements of Table 4 due to a combination of a number of factors, such as contributions from biomass burning emissions, uncertainty in the factor used to convert the modern (F_M) to biogenic fraction (F_B), artifacts associated with the integrated filter sampling, biogenic fuel additives, and ^14C contamination. Biomass burning contributions are expected to be minor since levoglucosan concentrations were low (less than 0.056 µgC/m^3). However, some biomass burning influence cannot be ruled out, and it may be higher than what we think. Based on a PM2.5 source apportionment study that included measurements at the Jefferson Street SEARCH site, a chemical mass balance suggested that of the organic carbon, biomass burning accounted for roughly 12±20% (g/g) in July 1999 and 20±20% in August 1999. Inferring biomass-burning contributions to WSOC from this data is not straightforward since many biomass-burning organic carbon emissions are not water-soluble. When converting F_M to F_B, based on the ranges of factors suggested in the literature [Lewis et al., 2004], this adds an uncertainty to F_B of about 10%. Positive artifacts due to absorption of biogenic VOCs onto the High Volume quartz fiber filter cannot be ruled out but appear to be relatively small (less than 20%). Accounting for any contributions from biogenic fuel additives to WSOC (if any) would mean that
biogenic VOCs contributed less to WSOC formation than the radiocarbon biogenic
fractions of Table 4. However, it has been shown that the $^{14}$C concentrations in fine
particles (PM2.5) generated from small two-stroke engines burning gasoline with
biogenic-ethanol is much lower than the fuel $^{14}$C concentrations, and as expected, the
ethanol fuel fraction was not efficiently converted to particulate matter [Lewis et al.,
2006]. Finally, contamination of samples with $^{14}$C cannot be ruled out, however, this
would be expected to produce highly variable results, which was not observed.
Combined, these other factors make it possible that the contribution of biogenic VOCs to
WSOC through SOA formation is significantly smaller than 70 to 80% obtained directly
from the $^{14}$C analysis.

Accepting the biogenic fractions calculated from the radiocarbon as a true
measure of the biogenic VOCs that formed SOA, along with the correlation and limiting
role of an anthropogenic species, leads to the conclusion that much of the SOA formed
was by condensation of mainly biogenic VOCs through a process that was strongly
linked to an anthropogenic precursor(s). Partitioning theory, based on smog chamber
experiments, predicts such a relationship; the mass partitioned to the condensed phase
depends on preexisting organic aerosol mass, especially when organic mass
concentrations are low. Oxidants closely linked to anthropogenic emissions may also play
a role in the observed correlations and similar scaling. For the Atlanta/north Georgia
over flight, O$_3$ was also correlated with WSOC ($r = 0.604$), but not as well correlated as
WSOC - CO ($r = 0.894$). The interplay between biogenic VOCs and anthropogenic
emissions has been noted in a modeling study that suggests that partitioning to
anthropogenic organic aerosols and anthropogenic oxidants may have significantly
enhanced global biogenic SOA production compared to pre-industrial times [Kanakidou
et al., 2000]. Although partitioning onto organic aerosol and oxidants from anthropogenic
emissions may explain the correlation, it is not clear that it can account for similar scaling
between the two regions.

Interestingly, other ambient studies in the same region have also found that
anthropogenic species play a role in SOA formation from biogenic VOCs [Gao et al.,
2006]. Speciated organic acids from samples collected in the southeastern U.S.A.
appeared to have formed from terpene oxidation with the possible involvement of NO$_x$
and SO₂. The Gao et al. [2006] analysis includes samples collected at Jefferson Street in
June 2004 and in the same summer as the measurements discussed above. However, Gao
et al. quantified less than 6% of the Jefferson Street organic aerosol mass. The WSOC
results discussed in this paper are chemically non-specific but a more comprehensive
measure of SOA, and thus suggest that the majority of the SOA formed from biogenic
VOCs is linked in some manner to anthropogenic precursors.

5.0 CONCLUSIONS

This study and others show that water-soluble organic compounds (WSOC) in
fine ambient particles appear to be mainly SOA. Using WSOC as a measure of SOA, a
comparison is made between SOA formation in chemically aging plumes advected from
New York City and aged urban air mass over north Georgia, including measurements
over metropolitan Atlanta. Measurements of biogenic VOCs showed that the
Atlanta/north Georgia region contained on average 10 to 100 times higher concentrations.
However, in both regions, SOA was highly correlated with anthropogenic emissions
(CO) and secondary organic VOCs (isopropyl nitrate), and the mass of SOA produced
relative to CO was also similar. In contrast, radiocarbon measurements (¹⁴C) made at the
surface in Atlanta during the summer in which the airborne experiment was conducted
indicates that roughly 70 to 80% of the carbon in WSOC is of biogenic (modern),
indicating a large role played by biogenic VOCs in the formation of SOA. The combined
results suggest that an anthropogenic component (or components) plays a role in the
formation of SOA, and may influence the amount of SOA mass formed, possibly
somewhat independent of the origin of the condensing VOCs. These results seem
somewhat analogous to NOx limitations on ozone formation in VOC-rich environments.
However, environmental (smog) chamber studies tend to predict that NOx inhibits SOA
formation by leading to oxygenated VOCs of higher vapor pressures [Presto et al., 2005].

Finally, it is noted that this study focuses on SOA formation in regions in the
southeast (Atlanta/north Georgia) that are heavily impacted by anthropogenic and
biogenic emissions. SOA formation in more pristine remote regions is not investigated
and the process may readily occur without an anthropogenic influence. The results
discussed here, however, may provide new insight on how SOA is formed in regions that
contain a mix of both anthropogenic and biogenic emissions. If anthropogenic emissions significantly influence the mass of SOA formed in regions having widely different biogenic VOC concentrations, then these findings imply that control strategies aimed at anthropogenic emissions may have impacts even in regions that are also rich in biogenic VOCs.

ACKNOWLEDGEMENTS

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10.1029/2005JD006485.


Table 1. Mean ± standard deviation from two separate paired experiments. In the first experiment the comparison was between four separate daytime (10:00 to 22:00 EDT, 15 to 18 June 2005) integrated filter measurements next to a major expressway versus the GIT campus in midtown Atlanta ~ 400m from away. In the second experiment, four 24-hour integrated measurements were made at Yorkville, ~80 km west of GIT (see Figure 3) starting on 23 July 2005 at 10:00 and ending 27 July 2005 at 10:00 EDT. All concentrations are in µgC/m$^3$ and the ratio is by carbon mass.

<table>
<thead>
<tr>
<th></th>
<th>EC</th>
<th>OC</th>
<th>WSOC</th>
<th>WSOC/OC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Expressway</td>
<td>3.61 ± 1.06</td>
<td>10.82 ± 1.63</td>
<td>4.73 ± 0.69</td>
<td>0.44 ± 0.02</td>
</tr>
<tr>
<td>GIT</td>
<td>0.48 ± 0.10</td>
<td>7.83 ± 1.03</td>
<td>4.33 ± 0.79</td>
<td>0.55 ± 0.04</td>
</tr>
<tr>
<td>GIT</td>
<td>0.90 ± 0.24</td>
<td>10.50 ± 1.75</td>
<td>6.72 ± 1.41</td>
<td>0.64 ± 0.05</td>
</tr>
<tr>
<td>Yorkville</td>
<td>0.15 ± 0.01</td>
<td>8.51 ± 1.72</td>
<td>6.26 ± 1.29</td>
<td>0.74 ± 0.04</td>
</tr>
</tbody>
</table>
Table 2. Evolution of WSOC in urban plumes transported from New York City. Tabulated values are means within each plume and standard deviations are included when sufficient data. Transport times were calculated from the HYSPLIT Trajectory Model. VOC data are from WAS measurements. ND = no data

<table>
<thead>
<tr>
<th>Plume ID</th>
<th>WSOC-CO $r^2$</th>
<th>Transport Time (hours)</th>
<th>$\Delta$WSOC/$\Delta$CO ($\mu$g C/m$^3$/ppmv)</th>
<th>$\Delta$Toluene/$\Delta$Benzene (pptv/pptv)</th>
<th>Photochemical Age, (hours)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0720A</td>
<td>0.92</td>
<td>1 ± 0</td>
<td>11.3 ± 4.1</td>
<td>2.5</td>
<td>ND</td>
</tr>
<tr>
<td>0720B</td>
<td>0.81</td>
<td>3 ± 1</td>
<td>8.5 ± 1.2</td>
<td>2.9</td>
<td>5</td>
</tr>
<tr>
<td>0814A</td>
<td>0.83</td>
<td>13 ± 1</td>
<td>3.1 ± 1.1</td>
<td>2.1</td>
<td>12</td>
</tr>
<tr>
<td>0814B</td>
<td>0.86</td>
<td>20 ± 0</td>
<td>21.8 ± 2.7</td>
<td>1.1</td>
<td>26</td>
</tr>
<tr>
<td>0721A</td>
<td>ND</td>
<td>26 ± 1</td>
<td>28.8 ± 6.8</td>
<td>0.73</td>
<td>34</td>
</tr>
<tr>
<td>0721B</td>
<td>0.89</td>
<td>33 ± 3</td>
<td>31.8 ± 4.1</td>
<td>0.64</td>
<td>37</td>
</tr>
<tr>
<td>0722A</td>
<td>0.78</td>
<td>55 ± 1</td>
<td>32.0 ± 4.1</td>
<td>0.13</td>
<td>72</td>
</tr>
</tbody>
</table>

Table 3. Median (± 1 standard deviation) concentrations of biogenic and anthropogenic trace gases measured over north Georgia and the seven NYC plumes. The ratio of the medians is also given, values in parenthesis ( ) are the inverse of Georgia/NYC ratio. All VOC are WAS measurements.

<table>
<thead>
<tr>
<th></th>
<th>Georgia</th>
<th>NYC</th>
<th>Georgia/NYC</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha$-pinene, pptv</td>
<td>3.9 ± 8.2</td>
<td>0.2 ± 5.2</td>
<td>20</td>
</tr>
<tr>
<td>$\beta$-pinene, pptv</td>
<td>2.9 ± 4.9</td>
<td>0.5 ± 4.4</td>
<td>6</td>
</tr>
<tr>
<td>isoprene, pptv</td>
<td>274 ± 229</td>
<td>2.1 ± 162</td>
<td>131</td>
</tr>
<tr>
<td>MACR, pptv</td>
<td>209 ± 93</td>
<td>15 ± 38</td>
<td>14</td>
</tr>
<tr>
<td>MVK, pptv</td>
<td>667 ± 3257</td>
<td>40 ± 127</td>
<td>17</td>
</tr>
<tr>
<td>CO, ppbv</td>
<td>153 ± 17</td>
<td>231 ± 43</td>
<td>0.66 (1.5)</td>
</tr>
<tr>
<td>acetylene, pptv</td>
<td>241 ± 22</td>
<td>255 ± 125</td>
<td>0.95 (1.1)</td>
</tr>
<tr>
<td>isopropyl nitrate, pptv</td>
<td>9.7 ± 1.6</td>
<td>14.7 ± 3.1</td>
<td>0.66 (1.5)</td>
</tr>
<tr>
<td>WSOC, $\mu$g m$^{-3}$</td>
<td>2.21 ± 0.62</td>
<td>3.58 ± 1.21</td>
<td>0.62 (1.6)</td>
</tr>
</tbody>
</table>

MVK: methyl-vinyl ketone; MACR: methacrolein
Table 4 Concentrations of PM2.5 components collected at Jefferson Street in Atlanta, Georgia U.S.A. All concentrations shown for a single date were made from fractions of the same filter. Biogenic and Fossil Fractions of WSOC are in units of g/g.

<table>
<thead>
<tr>
<th>Sample Date</th>
<th>Levoglucosan $\mu$gC m$^{-3}$</th>
<th>EC $\mu$gC m$^{-3}$</th>
<th>OC $\mu$gC m$^{-3}$</th>
<th>WSOC $\mu$gC m$^{-3}$</th>
<th>Biogenic Fraction</th>
<th>Fossil Fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>6/14/04</td>
<td>0.036</td>
<td>0.49</td>
<td>3.84</td>
<td>2.59</td>
<td>0.81</td>
<td>0.19</td>
</tr>
<tr>
<td>6/17/04</td>
<td>0.053</td>
<td>0.95</td>
<td>4.18</td>
<td>2.16</td>
<td>0.70</td>
<td>0.30</td>
</tr>
<tr>
<td>6/23/04</td>
<td>0.030</td>
<td>0.30</td>
<td>2.59</td>
<td>1.77</td>
<td>0.76</td>
<td>0.24</td>
</tr>
<tr>
<td>6/29/04</td>
<td>0.056</td>
<td>0.70</td>
<td>4.86</td>
<td>2.57</td>
<td>0.67</td>
<td>0.33</td>
</tr>
</tbody>
</table>

For reference, the NOSAMS accession number for the four samples in the same order as the table are: OS-54054, OS-45052, OS-53999, and OS-54053.
Figure 1: a) NOAA WP-3B aircraft flight path on July 22, 2004 during ITCT-2K4.  
b) Aircraft altitude above sea level and measured fine particle (PM1) WSOC, CO, and 
biogenic VOCs. Biogenic VOCs are the sum of monoterpenes, isoprene, methyl-vinyl 
ketone, and methacrolein measured by PTRMS. Locations of enhanced biogenic VOCs, 
identified by 1, 2, 3, and 4, are shown in a)
Figure 2: \( \frac{[\text{WSOC}]}{[\text{CO}]} \) measured from aircraft over North Georgia USA, including the Atlanta metropolitan region, compared to surface measurements in Atlanta, and New York City (NYC) plumes analyzed by Sullivan et al., [2006] and Brock et al., [2006]. The solid line is an exponential fit of the form \( (A_0 + A_1 \exp(-A_2 x)) \) to the Brock et al. data. The fit coefficients are \( (A_0 = 34.7, A_1 = -26.5, \text{and } A_2 = 0.0466) \). Negative photochemical ages in the Brock et al. analysis are likely due to uncertainties in the analysis method for determining background benzene concentrations used to determine photochemical age. The color-coding of the Brock et al. analysis shows that toluene concentrations decreased with photochemical age, indicating greater photo-oxidation with age. For all data, WSOC was highly correlated with CO (see Figure 5).
Figure 3: Aircraft flight path, wind vectors, and measured CO concentrations over northern Georgia, including the metropolitan Atlanta region. Average ± standard deviation of wind speed in the boundary layer was 3.1 ± 1.5 m/s. Distances are approximate. Letters A through E are shown in the time series of Figure 4.
Figure 4: Fine particle WSOC, CO, and acetylene recorded over northern Georgia, including the Atlanta metropolitan region. Letters A, B, C, D, and E correspond to measurement locations shown in Figure 3. Data during in-cloud sampling are excluded (region A). Local time is EDT = UTC – 4. The WSOC data gap at ~19:30 UTC is due to a preprogrammed automatic background measurement.
Figure 5: Linear regression of WSOC and CO measured in the boundary layer over northern Georgia, excluding periods of in-cloud sampling. Slope uncertainty is at a 95% confidence level.
Figure 6: WSOC and isopropyl nitrate measured over Atlanta and in plumes from New York City (NYC) that were over 1 day old. Regression fit at 95% confidence is for combined Atlanta and NYC data.

Slope = 0.20 ± 0.04 µgC/m³/pptv
Intercept = 0.29 ± 0.41 µgC/m³
$r^2 = 0.74$