No evidence for acid-catalyzed secondary organic aerosol formation in power plant plumes over metropolitan Atlanta, Georgia


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Aircraft-based measurements of the water-soluble fraction of fine PM organic carbon (WSOC) and inorganic salt composition in the Atlanta, GA region were conducted in the summer of 2004. Five notable plumes of SO$_2$, apparently from coal-fired power plants, were intercepted, and had NH$_4$/SO$_4^-$ molar ratios ranging from approximately 0.8 to 1.4 compared to molar ratios near 2 outside of the plumes. Sulfate aerosol concentrations increased from a regional background of 5–8 $\mu$g m$^{-3}$ to as high as 19.5 $\mu$g m$^{-3}$ within these plumes. No increase in WSOC concentrations was observed in plumes compared to out-of-plumes within a WSOC measurement uncertainty of 8%. These measurements suggest that secondary organic aerosol formation via heterogeneous acid-catalyzed reactions within power plant plumes are not likely a significant contributor to the ambient aerosol mass loading in Atlanta and the surrounding region. Because this region is rich in both biogenic and anthropogenic volatile organic carbon (VOC), the results may be widely applicable. Citation: Peltier, R. E., A. P. Sullivan, R. J. Weber, A. G. Wollny, J. S. Holloway, C. A. Brock, J. A. de Gouw, and E. L. Atlas (2007), No evidence for acid-catalyzed secondary organic aerosol formation in power plant plumes over metropolitan Atlanta, Georgia, Geophys. Res. Lett., 34, L06801, doi:10.1029/2006GL028780.

1. Introduction

Compounds containing organic carbon (OC) are a large fraction of ambient fine particles in the southeastern United States (U.S.), and during the summer when air quality generally worsens, secondary organic aerosol (SOA) is a large component of this particulate OC. Many laboratory studies with both biogenic and anthropogenic volatile organic compounds (VOCs) have suggested that heterogeneous reactions involving acid aerosols can catalyze the formation of secondary organic aerosol through polymerization reactions [Gao et al., 2004; Inumia et al., 2004; Jang and Kamens, 2001; Kalberer et al., 2004; Limbeck et al., 2003; Tolocka et al., 2004]. However, little ambient data exists to test these experiments, and from the few observations, the results tend to be mixed. Ambient measurements in Houston, TX by Broc et al. [2003] show that measured particle volumes increased at much higher rates than what could be explained by SO$_2$ oxidation and condensation in plumes that contained both high levels of VOCs and SO$_2$, whereas plumes mainly of VOCs did not exhibit this increase. In contrast, Gao et al. [2006] found no evidence for oligomer formation and no correlation between particle-inferred acidity and a large number of organic acids measured in the southeastern United States. Zhang et al. [2004] found no significant enhancement of organic carbon concentration during the Pittsburgh Supersite experiment during acidic aerosol events, suggesting that acid-catalyzed formation of secondary organic aerosol is not a significant contributor during these conditions. The findings of this paper adds to these ambient results by presenting recent airborne measurements conducted over metropolitan Atlanta to investigate evidence for acid-catalyzed reactions that may lead to organic aerosol formation. In this paper, measurements and discussion of WSOC concentrations in acidic aerosol conditions caused by power plant plumes are compared with WSOC concentrations under apparently more neutralized aerosol conditions occurring immediately surrounding each plume. This is a more direct measurement compared to other studies that rely on correlations between apparent aerosol acidity and organic aerosol concentration from ground-based data. Elucidating the sources of fine PM is important since, for example, the Atlanta metropolitan region often fails to meet National Ambient Air Quality Standards for particulate matter. If acid-catalyzed aerosol formation is an important process as some smog chamber studies suggest, it is likely to occur in the Atlanta metropolitan region since it is rich in both biogenic and anthropogenic VOCs and is surrounded by large coal-fired power plants that generate acidic sulfur-containing aerosols.

In support of the New England Air Quality Study in the summer of 2004, US National Oceanic and Atmospheric Administration’s WP-3D research aircraft was deployed for airborne sampling of atmospheric components. The payload included measurements of CO, SO$_2$, ozone, VOCs, particle size and number distribution, and fine particle bulk composition. For the majority of the mission, the aircraft was stationed at Portsmouth, NH (43.08N, –70.82W). Most of the research flights concentrated on the northeastern US, eastern Canada, and Ohio River Valley with particular emphasis on urban and power generation facility outflow. Near the end of the study, while the aircraft was transiting to its home base in Florida, US, a large region of northern Georgia was sampled for approximately 105 minutes. SOA is thought to be formed through oxidation of VOCs, which increases polarity and decreases its vapor.
pressure [Seinfeld and Pankow, 2003]. Thus, a large fraction of the compounds comprising SOA are likely oxygenated and soluble or partially soluble in water. Recent studies in Tokyo confirm this; WSOC was highly correlated with oxygenated organic aerosol (OOA), determined by multivariate analysis of organic spectrum by Aerosol Mass Spectrometry (Aerodyne Research, Inc, Billerica, MA), and comprised roughly 75% of the oxygenated aerosol mass [Kondo et al., 2007]. Comparisons between Tokyo WSOC and SOA mass estimated via the EC tracer method found similar results [Miyazaki et al., 2006]. Furthermore, these studies and others (R. J. Weber et al., preprint, 2007) have also found little or no evidence for significant concentrations of primarily emitted WSOC, in the absence of biomass burning emissions. Because biomass burning trace gases were at background concentrations in the region sampled (e.g., mean acetonitrile = 130 pptv ± 11 pptv), in this analysis we use WSOC as a reasonable (though not necessarily complete) measure of secondary organic aerosol mass fraction.

2. Methods

Fine particle (PM1.0) bulk chemical composition was measured onboard the WP-3D by two, automated Particle-Into-Liquid Samplers (PILS). One PILS was coupled to ion chromatographs (instrument package is referred to as PILS-IC), and another PILS was coupled to a Total Organic Carbon analyzer (referred to as PILS-TOC). PILS-IC has been described in previous research [Ma et al., 2003; Orsini et al., 2003; Weber et al., 2001]. The PILS-TOC instrument is described in detail by Sullivan et al. [2006]. PILS-IC measures aerosol inorganic ion concentrations (sulfate, nitrate, chloride, sodium, ammonium, calcium, potassium, and magnesium ions) at a rate of a 90-second integrated sample every 2.45 minutes. The ion chromatographs were calibrated using dilutions of NIST-traceable stock solutions in concentrations that bracketed expected sampled PILS effluent flow. PILS-TOC measures the water-soluble fraction of organic carbon (WSOC) every three seconds. The TOC instrument is factory-calibrated, though this was verified by calibration standards both before and after the completion of the field campaign. Both instruments, including specific operating parameters, are described in greater detail by R. E. Peltier et al. (preprint, 2007) and Sullivan et al. [2006]. The PILS-IC instrument has a reported uncertainty of 10%, while the PILS-TOC instrument has an uncertainty of approximately 8%.

Aerosol was sampled from a single Low-Turbulence Inlet [Wilson et al., 2004] at a volumetric flow rate of 15 liters per minute for each instrument (total flow = 30 liters per minute). Upstream of the instruments, particle size was restricted to PM1.0 by a non-rotating micro-orifice impactor [Marple et al., 1991]. Both instruments utilized denuders to minimize potential interferences from gases; in the case of PILS-IC, sampled aerosol passed through a monolithic carbon denuder and a set of etched-glass honeycomb denuders. One denuder was coated with a solution of citric acid and another with sodium carbonate. PILS-TOC sample was denuded by a parallel plate denuder consisting of activated carbon paper [Eatough et al., 1993]. In order to minimize volatile losses from particles due to re-equilibrium,
denuders were located as close as possible to the PILS entrance (residence time ~ 0.15 s). Aerosol flow from each instrument was periodically diverted through a filter to remove sampled particles. This allowed for an assessment of gas phase interferences that penetrated the denuders, as well as an assessment of background interferences present within the reagents (e.g., eluents, purified water) used in each instrument.

Additional supporting measurements were used throughout the analysis and include 1 s sulfur dioxide (SO2) and carbon monoxide (CO) [Holloway et al., 2000]. PM1.0 volume was measured at 1 s resolution using a combination of three instruments: a condensation particle counter (CPC), a modified Lasair 1001 optical particle counter (OPC), and a white light optical particle counter (WLOPC) [Brock et al., 2000]. Particle volume reported here includes size ranges from 150 nm to 1.0 µm at a relative humidity of ~40%. Volatile organic compounds, such as toluene, isoprene, methacrolein, and methyl vinyl ketone, were measured by 10 s integration whole air sampling canister, and then analyzed offline by Gas Chromotography – Mass Spectroscopy (GC-MS).

3. Results

[A low altitude (~1000 m) flight segment lasting for 105 minutes was performed over the Atlanta metropolitan region. Wind speed and direction measured on the WP-3D were typically less than 5 m s⁻¹ and variable throughout the sampled region suggesting stagnant ambient conditions. The flight path is depicted in Figure 1. Measurements of high PM1.0 particle volume concentrations show a polluted air mass within the planetary boundary layer (PBL) amplified in several locations by local power plant plumes that can be readily identified by SO2 spikes (see Figure 2). These plumes are identified by letters A through E in Figures 1 and 2.

The time series for PM1.0 volume, sulfate, and WSOC, and gases SO2, various VOCs, and CO in Figure 2 show that all these components rapidly increased in concentration as the aircraft descended into the PBL, which was delineated by a weak temperature inversion (ΔT = 1°C) at ~2500 m. Concentrations remained elevated throughout the entire region sampled for altitudes below ~2500 m. Ambient relative humidity (not plotted) ranged from 60–78% throughout the sampling period.

Measurements of liquid water indicate the aircraft penetrated a cloud in the region identified by X in Figures 1 and 2, and were not included in the analysis since the aerosol inlets were not equipped to handle in-cloud sampling. While some cumulus clouds were present at altitudes above the aircraft, all data that are discussed were from cloud-free samples. In-cloud heterogeneous reactions have been shown to enhance oxalate aerosol formation [Sorooshian et al., 2006a] which would lead to increased WSOC concentration. This route for gas-to-particle conversion is not investigated.

There appears to be a regional sulfate concentration of 5–8 µg m⁻³ that is present throughout most of the flight within the PBL. Superimposed on this regional sulfate, there are several spikes in sulfate concentration that are correlated with clear SO2 spikes from local power plants. These plumes were typically 12–40 km in width, based on the higher time resolution SO2 measurements. Despite the nearby power plants, identifying specific sources for each intercepted plume is not straightforward as the winds tended

Table 1. Median Plume Concentrations/Ratio of Various Compounds Within the Plume and out of the Plume

<table>
<thead>
<tr>
<th></th>
<th>CO, ppbv</th>
<th>SO2, ppbv</th>
<th>NH4/SO4²⁻</th>
<th>Biogenic VOCs, ppbv</th>
<th>Toluene, pptv</th>
<th>SO2²⁻, µg/m³</th>
<th>NH4⁺, µg/m³</th>
<th>WSOC, µgC/m³</th>
</tr>
</thead>
<tbody>
<tr>
<td>Within plume</td>
<td>140.4 ± 26.3</td>
<td>3.3 ± 5.4</td>
<td>1.1 ± 0.5</td>
<td>1.10 ± 0.49</td>
<td>71.2 ± 52.8</td>
<td>8.8 ± 4.54</td>
<td>2.0 ± 0.3</td>
<td>2.5 ± 0.2</td>
</tr>
<tr>
<td>Out of plume</td>
<td>157.6 ± 15.1</td>
<td>0.4 ± 0.5</td>
<td>2.0 ± 1.1</td>
<td>0.94 ± 0.63</td>
<td>62.9 ± 40.7</td>
<td>5.0 ± 2.34</td>
<td>1.8 ± 0.8</td>
<td>2.4 ± 0.2</td>
</tr>
</tbody>
</table>

*Standard deviation is also included. Biogenic VOCs are defined as isoprene + methyl vinyl ketone + methacrolein.*
to be light and variable during the measurement period. Sulfate aerosol and fine particle volume are sharply elevated within these plumes. Thus, overall sulfate from local power plants accounts for much of the spatial variability in the fine particle volumes recorded within Atlanta and the surrounding region PBL. These increases in sulfate are significant. For example, in the SO2 spike labeled A, the sulfate increased from about 5 to 19.5 µg m⁻³ and the fine particle volume increased from about 20 to over 45 µm² cm⁻³. In this experiment the PILS-IC samples were integrated over 90 seconds and cannot accurately identify very narrow plumes (under typical flight speeds, plumes less than 16 km wide). These power plant plumes thus likely have sulfate concentrations on smaller scales that are significantly larger than the more averaged values recorded by the PILS-IC.

[12] Air masses were characterized as either in-plume or out-of-plume as determined by 1 second SO2 measurements for all PBL data. Summarized in Table 1, on average across all five plumes, sulfate concentration was a factor of 2 higher inside the plume, and SO2 mixing ratio was larger by nearly a factor of 8 (though with a large standard deviation), when compared to outside of plume conditions. Median molar ratio of ammonium to sulfate ion was 2.0 outside of the plumes compared to 1.1 inside of the plumes. It should be noted that NH₄⁺/SO₄²⁻ molar ratios may be slightly higher due to loss of NH₃ in the PALS [Sorooshian et al., 2006b]. Because NH₄⁺ and SO₄²⁻ were the dominant fine particle cations and anions observed, the much larger imbalance is most likely due to unmeasured H⁺, suggesting that, as expected, aerosol H⁺ concentration (e.g., aerosol acidity) was higher in power plant plumes.

[13] The water-soluble fraction of organic aerosol was somewhat spatially uniform; small-scale plumes characterized by sharp increases in WSOC were generally not observed within the PBL suggesting that much of the WSOC in Atlanta was regional in nature. The overall large-scale trend of CO was matched well by WSOC. WSOC and CO were highly spatially correlated in Atlanta and surrounding region (inside the PBL) with r² = 0.80 and a slope of 32 µg C m⁻³/ppmv for all data plotted in Figure 2. There are a few notable exceptions to this correlation. For example, in Figure 2 during the period of 19:01 to 19:08 UTC (local eastern daylight time is UTC - 4 hours), and corresponding to the SO2 spike labeled C, the aircraft was sampling almost directly over Atlanta, and CO concentrations were significantly higher than the surrounding area. The tolune mixing ratio, a measure of anthropogenic VOC emissions, also spiked, and ozone (not plotted) showed a similar trend to CO in this region. In contrast, WSOC remained essentially unchanged in these regions of more fresh emissions suggesting that WSOC is largely not composed of primary vehicle emissions, but possibly indirectly linked to them via SOA formation given the overall high correlation between WSOC and CO on larger regional spatial scales (R. J. Weber et al., preprint, 2007).

[14] In-plume versus out-of-plume percent changes in WSOC concentrations ranged from −3.4% to +7.2%. On average across all five plumes, the net change in WSOC concentration was just +0.1 µg C m⁻³, corresponding to a 4.2% increase, which is less than the uncertainty of the WSOC measurement. Focusing on individual plumes as shown in Table 2, the net WSOC change in plume A was lower in the plume by 3.4%, or 0.1 µg C m⁻³, despite a low NH₄⁺/SO₄²⁻ molar ratio (~0.9). Plumes B and C had slight increases of 1.6% and 4.2%, respectively, (below instrument LOD, and 0.1 µg C m⁻³, respectively). Plumes D and E had net WSOC increases of 7.2% and 5.9% (or 0.2 and 0.1 µg C m⁻³, respectively). Plume C is noteworthy in that it was located directly over urban Atlanta where CO and toluene (mobile source emissions) are significantly higher than surrounding regions, yet little enhancement in WSOC within the plume is observed. Plumes A and E had the lowest NH₄⁺/SO₄²⁻ molar ratios observed and hence likely highest aerosol H⁺ concentrations, yet increases in WSOC were not significant. In contrast, plume D had the largest increase in WSOC (+0.2 µg C m⁻³), yet this increase is not greater than the 8% uncertainty of the instrument (see auxiliary material). Therefore, these plumes do not provide evidence for measurable SOA under conditions of a more acidic aerosol.

[15] As summarized in Table 1, biogenic and anthropogenic VOCs were spatially variable (i.e., large standard deviation for each VOC). Median concentration of toluene, a representative of anthropogenic VOCs that has the potential for SOA formation, was 71 pptv within plumes and 62 pptv outside of plumes. Median biogenic VOCs (isoprene + methacrolein + methyl vinyl ketone) were ~1.1 ppbv within the plumes and 0.94 ppbv outside of

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**Table 2. For All Plumes Sampled, Percent Change in Concentration/Ratio of Various Compounds Between In-Plume and Out-Of-Plume**

<table>
<thead>
<tr>
<th>Approximate time</th>
<th>Plume A</th>
<th>Plume B</th>
<th>Plume C</th>
<th>Plume D</th>
<th>Plume E</th>
</tr>
</thead>
<tbody>
<tr>
<td>ΔCO₂, %</td>
<td>-5.1</td>
<td>1.5</td>
<td>7.1</td>
<td>-2.5</td>
<td>3.4</td>
</tr>
<tr>
<td>ΔSO₂, %</td>
<td>651.6</td>
<td>277.3</td>
<td>351.1</td>
<td>345.2</td>
<td>360.8</td>
</tr>
<tr>
<td>MR, NH₄/SO₄²⁻</td>
<td>0.9</td>
<td>1.1</td>
<td>1.3</td>
<td>1.3</td>
<td>0.9</td>
</tr>
<tr>
<td>ΔBiogenic VOC, %</td>
<td>81.9</td>
<td>n/a</td>
<td>-6.4</td>
<td>77.7</td>
<td>-63.8</td>
</tr>
<tr>
<td>Δ Toluene, %</td>
<td>-6.2</td>
<td>n/a</td>
<td>154.8</td>
<td>-18.2</td>
<td>-60.6</td>
</tr>
<tr>
<td>ΔSO₄²⁻, %</td>
<td>99.1</td>
<td>11.1</td>
<td>24.6</td>
<td>34.3</td>
<td>91.3</td>
</tr>
<tr>
<td>ΔNH₄⁺, %</td>
<td>23.8</td>
<td>2.6</td>
<td>5.6</td>
<td>9.5</td>
<td>42.9</td>
</tr>
<tr>
<td>ΔWSOC, %</td>
<td>-3.4</td>
<td>1.6</td>
<td>4.2</td>
<td>7.2</td>
<td>5.9</td>
</tr>
</tbody>
</table>

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aCO, SO₂, and WSOC compare in-plume concentrations with the mean concentration of 90 seconds of data immediately before and after the plume interception (as determined by 1 s SO₂ concentration). Sulfate and ammonium ion compares in-plume conditions with the mean ratio/concentration of one data point just before and after plume interception. In the case of biogenic VOCs and toluene, percent change compares in-plume measurements with average out-of-plume concentrations for entire low-level flyby of Atlanta (Table 1) due to insufficient number of data points just outside of individual plumes. With the exception of plumes A and C, plume interception time was less than the time integral of the ion measurement which adds some uncertainty to this measurement.
the plumes. VOCs, both in and outside the plume, are of sufficient concentration that there should be secondary semi-volatile organic carbon (SVOC) available for SOA formation. However, lack of WSOC enhancement inside the plumes relative to outside the plumes indicates that acid-catalyzed formation of secondary organic aerosol is insignificant.

[16] In summary, these limited measurements show that more acidic conditions in freshly emitted power plant plumes with PM1.0 NH₄²⁺/SO₄²⁻ molar ratios in the range of ~0.9–1.4 do not lead to substantial increases in the water-soluble organic component (i.e., SOA) of ambient particles in metropolitan Atlanta, Georgia and the surrounding region. Despite adequate concentrations of biogenic and anthropogenic VOCs that can lead to SOA formation, preferential heterogeneous acid-catalyzed reactions in many of the coal-fired power plant plumes are likely not a major contributor to the secondary organic aerosol formed in the Atlanta metropolitan area and surrounding region. In regions where less NH₃ is available to neutralize sulfate formed from strong point sources (e.g., leading to NH₄²⁺/SO₄²⁻ molar ratios less than ~1.0), acid-catalyzed reactions may be important. It is also possible that acid-catalyzed SOA formation may occur on timescales that are longer than those observed within the relatively fresh power-plant plumes sampled here, but before the particles are neutralized by ammonia. The results of this study also do not preclude that other regions with a substantially different mix of VOCs may significantly involve acid-catalyzed SOA production. However, the regions sampled in this study contain both anthropogenic and biogenic VOCs suggesting that these results may be applicable to many regions.

References


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