

On the gas-particle partitioning of soluble organic aerosol in two urban atmospheres with contrasting emissions:

1. Bulk water-soluble organic carbon

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[1] The partitioning of semi-volatile compounds between the gas and particle phase influences the mass, size and chemical composition of the secondary organic aerosols (SOA) formed. Here we investigate the partitioning of water-soluble organic carbon (WSOC) and the formation of SOA in Los Angeles (LA), California and Atlanta, Georgia; urban regions where anthropogenic volatile organic compound (VOC) emissions are dominated by vehicles, but are contrasted by an additional large source of biogenic VOCs exclusive to Atlanta. In Atlanta, evidence for WSOC partitioning to aerosol water is observed throughout the day, but is most prevalent in the morning. During drier periods (RH < 70%), the WSOC partitioning coefficient (F_p) was in proportion to the organic mass, suggesting that both particle water and organic aerosol (OA) can serve as an absorbing phase. In contrast, despite the higher average RH, in LA the aerosol water was not an important absorbing phase, instead, F_p was correlated with OA mass. Particle water concentrations from thermodynamic predictions based on measured inorganic aerosol components do not indicate significant differences in aerosol hygroscopicity. The observed different WSOC partitioning behaviors may be attributed to the contrasting VOC mixture between the two cities. In addition, different OA composition may also play a role, as Atlanta OA is expected to have a substantially more aged regional character. These results are consistent with our companion studies that find similar partitioning differences for formic acid and additional contrasts in SOA optical properties. The findings provide direct evidence for SOA formation through an equilibrium partitioning process.

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1. Introduction

[2] Organic aerosols (OA) are important components of tropospheric fine particles throughout the U.S., and can have

a large influence on climate, visibility, and human health [Hand *et al.*, 2012]. Secondary organic aerosols (SOA) often comprise a large fraction of the total OA [Zhang *et al.*, 2007], and are major contributor to poor air quality in urban environments [Docherty *et al.*, 2008; de Gouw and Jimenez, 2009], especially during summer when more intensive photochemical processes lead to highly oxidizing conditions. Despite the prevalence of SOA, its sources and formation pathways remain poorly understood. SOA formation is generally thought to occur through gas-particle partitioning of semi-volatile organic compounds (SVOCs) formed by the gas-phase oxidation of volatile organic compounds (VOCs) [Seinfeld and Pankow, 2003]. Results from chamber experiments suggest that the partitioning of SVOCs is highly dependent on the quantity of pre-existing OA mass [e.g., Odum *et al.*, 1996], and the observed SOA mass in chambers has been well described by an equilibrium absorptive partitioning model [Pankow, 1994], although the system may not be in equilibrium and thus may be kinetically controlled under certain conditions [Perraud *et al.*, 2012]. It has been

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challenging to extend this model to the complex ambient atmosphere given the wide spectrum of SVOCs of unclear identity and physiochemical properties [Hallquist *et al.*, 2009]. Model simulations that incorporate SOA formation from traditional VOC precursors (e.g., terpenes, isoprene, and aromatics) represented by absorptive partitioning to OA tend to significantly underestimate ambient SOA mass by up to an order of magnitude in polluted regions [de Gouw *et al.*, 2005; Heald *et al.*, 2005; Volkamer *et al.*, 2006]. Newer models including primary SVOC and intermediate volatility organic compounds (IVOC) result in much improved predictions, but it is unclear whether this is for the right reasons [Hodzic *et al.*, 2010; Dzepina *et al.*, 2011]. The presence of the high-molecular-weight compounds (i.e., oligomers, humic-like substances) in ambient particles [Surratt *et al.*, 2007; Stone *et al.*, 2009] and the higher oxygen-to-carbon (O:C) ratio observed in the ambient air relative to chamber experiments [Aiken *et al.*, 2008; Ng *et al.*, 2010] may be explained by an aqueous phase oxidation process [Ervens *et al.*, 2011]. Furthermore, there is evidence that absorptive partitioning to particle water can lead to SOA formation [Blando and Turpin, 2000; Volkamer *et al.*, 2009]. Gas-phase water-soluble organic species (e.g., glyoxal and methylglyoxal) have been shown to undergo heterogeneous oxidation in the aqueous phase leading to reduced vapor pressures and SOA [Volkamer *et al.*, 2007; Ervens and Volkamer, 2010; Lim *et al.*, 2010]. Recent studies suggest that the mass of SOA formed through this mechanism may be substantial [Hennigan *et al.*, 2008a; Chang *et al.*, 2010; Parikh *et al.*, 2011].

[3] Despite its fundamental importance to SOA formation, few studies have reported gas-particle partitioning in the ambient atmosphere. Previous studies of SVOC partitioning have been limited to a few alkanes and alkanolic acids [Williams *et al.*, 2010a], carbonyls [Matsunaga *et al.*, 2005], carboxylic acids [Fisseha *et al.*, 2006; Liu *et al.*, 2012], and PAHs [Terzi and Samara, 2004]. Instead of investigating single compounds, an alternative approach for studying partitioning is to measure a group of compounds with similar properties, such as water-soluble organic carbon in both gas (WSOC_g) and particle phase (WSOC_p) [Hennigan *et al.*, 2008a, 2009]. This approach allows for the examination of integrated gas-particle partitioning behaviors of a large class of SVOCs and a substantial fraction of SOA mass. An analysis by Hennigan *et al.* [2008a] found that in Atlanta WSOC partitioning was related to ambient relative humidity (RH), and presumably aerosol water content, highlighting the importance of uptake of soluble VOCs by dissolution as a source of SOA mass and the potential for some of those compounds to remain in the aerosol phase through multi-phase reactions that produce lower volatility products. The reversibility of the observed WSOC partitioning, especially when RH decreases, may be significant, but cannot be obtained from this data set. Previous study in Mexico City found that roughly 25% the WSOC may re-partition when RH was reduced [Hennigan *et al.*, 2008b].

[4] SOA formation in urban atmospheres has received extensive attention in the past years and has been investigated through multiple field studies conducted in major urban areas around the world [e.g., de Gouw *et al.*, 2008; Aiken *et al.*, 2009; Williams *et al.*, 2010b; Stone *et al.*, 2010; Hersey *et al.*, 2011]. The CalNex 2010 (Research at the

Nexus of Air Quality and Climate Change) field campaign was undertaken in the California South Coast Air Basin and Central Valley during May to July 2010, with one goal being to better understand the sources and processes contributing to regional SOA loading. The metropolitan Los Angeles (LA) is one of the largest urban centers in the U.S., spanning a land area of approximately 12,600 km² that includes a population of over 17 million people (2010 United States Census). SOA is a major source of LA fine particle mass and is formed mainly from anthropogenic emissions in this area [Docherty *et al.*, 2008; Hersey *et al.*, 2011; Zhang *et al.*, 2011; Bahreini *et al.*, 2012]. Compared to LA, the Atlanta metropolitan region has a significantly lower population density, with 5.3 million people (2010 United States Census) spread across an area of 21,700 km². Urban Atlanta also has substantial summertime SOA production [Lim and Turpin, 2002], but with important contributions from both biogenic and anthropogenic emissions [Weber *et al.*, 2007; Goldstein *et al.*, 2009]. In this study, we contrast the partitioning of WSOC in LA and Atlanta based on data obtained from a suite of instruments deployed during the spring/summer of 2010. We find that gas-particle partitioning of WSOC differs between Atlanta and LA, providing important insight on SOA formation pathways in these two urban environments. The findings are consistent with additional contrasts in the partitioning behaviors of formic acid [Liu *et al.*, 2012], concentrations and trends of specific aerosol components (oxalate), as well as some physical properties of SOA (WSOC light absorption, detailed in Zhang *et al.* [2011]) between the two cities.

2. Experimental Methods

2.1. Field Sites

[5] Ambient gas and particle measurements were carried out in Pasadena, CA and Atlanta, GA in the spring and summer of 2010, respectively; each study was one month in duration. Measurements at the Pasadena ground site were conducted on the campus of the California Institute of Technology from May 15 to June 15, 2010 as a part of the CalNex-LA field campaign. The site (34.140582 N, 118.122455 W) was located ~16 km downwind of downtown LA, and was regularly impacted by urban plumes advected from LA [Veres *et al.*, 2011]. General details of the sampling location and spring/summer climatology were provided by Hersey *et al.* [2011] and Washenfelder *et al.* [2011]. Atlanta measurements were made from August 6 to September 7, 2010 in the rooftop laboratory of the Ford Environmental Science and Technology building on the Georgia Institute of Technology (GIT) campus (33.778427 N, 84.396181 W) located in central Atlanta. The measurement platform was 30–40 m above the ground, situated ~400 m from a heavily traveled interstate highway. A number of studies have reported ambient data collected from this site [Hennigan *et al.*, 2008a, 2009; Hecobian *et al.*, 2010; Zhang *et al.*, 2011].

2.2. Instrumentation

2.2.1. Gas and Particle Phase WSOC Measurements

[6] Gaseous and particulate WSOC (i.e., WSOC_g, WSOC_p) concentrations were determined using a Mist Chamber/Particle-Into-Liquid Sampler coupled with a Total Organic Carbon Analyzer (MC/PILS-TOC) [Hennigan

et al., 2009]. During CalNex, the instruments were situated inside a trailer where the temperature was kept at $\sim 25^{\circ}\text{C}$. The sample inlet was ~ 7 m above the ground level and 8.8 m long, and was insulated to minimize the temperature and RH changes of the sampled air before entering the instruments. Gas-phase samples were collected in a five-minute batch using a glass MC fitted with a Teflon filter (47 mm dia., $2.0\ \mu\text{m}$ pore size, Pall Life Sciences) upstream to remove particles in the sampled air. Aerosol samples were collected continuously via a PILS with a $\text{PM}_{2.5}$ cut size cyclone and a parallel plate carbon denuder [Eatough *et al.*, 1993]. Both gaseous and particulate samples in the aqueous stream were transferred through a $0.45\ \mu\text{m}$ pore PTFE syringe filter (Fisher Scientific) alternatively to a single TOC analyzer (GE Analytical) to quantify the carbon content in the solution. For the PILS channel, light absorption spectra of the soluble $\text{PM}_{2.5}$ components were measured using a UV-Vis spectrophotometer with 1-m liquid-waveguide capillary absorption cell (World Precision Instruments) placed upstream of the TOC analyzer [Zhang *et al.*, 2011].

2.2.2. Other Co-located Aerosol Measurements

[7] $\text{PM}_{2.5}$ organic carbon (OC) and elemental carbon (EC) were quantified semi-continuously with a Sunset Labs OCEC Analyzer (Sunset Laboratory Inc., Tigard, OR). The measurements consisted of a 45-min sampling period followed by 15-min of analysis. A parallel plate carbon denuder was placed inline to remove volatile gases [Eatough *et al.*, 1993]. Periodic blank measurements were made throughout the study by placing a Teflon filter (47 mm dia., $2.0\ \mu\text{m}$ pore size, Pall Life Sciences) on the $\text{PM}_{2.5}$ inlet. Blank-corrected optical EC and OC data are reported in this paper. $\text{PM}_{2.5}$ soluble organic acids (e.g., formate and oxalate) and inorganic anions (e.g., NO_3^-) were measured with a PILS coupled to a Dionex Ion Chromatograph with conductivity detection (PILS-IC) [Liu *et al.*, 2012].

[8] Exclusive to the CalNex study, non-refractory PM_1 (NR- PM_1) components were measured with a high-resolution time-of-flight aerosol mass spectrometer (AMS, Aerodyne Research Inc.) [DeCarlo *et al.*, 2006; Hayes *et al.*, 2012]. Further separation of AMS OA spectra was achieved using Positive Matrix Factorization (PMF) [Ulbrich *et al.*, 2009]. In the following analysis of the CalNex data, AMS NR- PM_1 NO_3^- is reported since PILS-IC soluble $\text{PM}_{2.5}$ NO_3^- is shown to be significantly higher due to contributions from NaNO_3 [Liu *et al.*, 2012; Hayes *et al.*, 2012]. In Atlanta where NaCl is negligible [Zhang *et al.*, 2010], PILS-IC $\text{PM}_{2.5}$ NO_3^- is reported. AMS OA mass (OM) and Sunset Labs OC were highly correlated (for complete study $r^2 = 0.76$), but OM/OC ratios were significantly higher than expected (regression slope of 3.3 compared to 1.4–2.3 expected for typical urban environments [Turpin and Lim, 2001]) [Hayes *et al.*, 2012]. This difference was likely attributed to the loss of semi-volatile compounds from the inline carbon denuder or the collection filter media within the OCEC analyzer [Grover *et al.*, 2009]. Recent measurements (unpublished) in Atlanta for two weeks in the fall of 2011 comparing an Aerosol Chemical Speciation Monitor (ACSM, Aerodyne Research Inc. [Ng *et al.*, 2011]) with the same Sunset Labs OCEC instrument, operated identically to the CalNex study, showed excellent agreement (OM/OC regression slope of 1.7, $r^2 = 0.92$) between the two instruments, which is consistent with substantially lower contributions of semi-volatile SOA in Atlanta [Peltier *et al.*,

2007]. In the following analysis, we focused on the qualitative relationship between WSOC gas-particle partitioning and OC mass since only OC data were available in both LA and Atlanta. LA data are reported in PDT and Atlanta data in EST. All data are reported at ambient temperature and pressure.

3. Results

3.1. General Diurnal Trends of Gaseous and Particulate Pollutants

[9] *LA diurnal profiles.* Regular and distinct diurnal trends in primary and secondary gas and particle phase species were observed at the LA site throughout the measurement period (Figure 1a). Primary emissions from local sources were identified by the morning rush hour peak of EC and other primary VOCs (not plotted) between 5:00 and 8:00, which were then followed by a substantially larger enhancement of EC (ΔEC of $0.48\ \mu\text{gC m}^{-3}$) at 12:00 as air masses were transported from downtown LA to the site after 3–5 h advection time [Veres *et al.*, 2011]. Both WSOC_g and WSOC_p reached their daily maximum concentrations following EC peak abundance in the early afternoon when solar radiation was most intense, indicating photochemical production as a major source. On a diurnal basis, WSOC_g steadily increased from a morning minimum of $5.2\ \mu\text{gC m}^{-3}$ at 5:00 to a daily maximum of $9.6\ \mu\text{gC m}^{-3}$ at 13:00. The variation of WSOC_p concentration closely tracked that of AMS OOA (oxygenated organic aerosol) component, showing substantial enhancement from a background of $0.6\ \mu\text{gC m}^{-3}$ in the late evening and early morning to a peak value of $1.7\ \mu\text{gC m}^{-3}$ at 14:00. The correlations of WSOC_p with OOA and SV-OOA (semi-volatile OOA) were both reasonably good ($r^2 = 0.74$ and 0.67 , respectively), suggesting that the WSOC mass formed in the afternoon was mainly less aged, semi-volatile oxygenated organic species.

[10] *Atlanta diurnal profiles.* Diurnal trends of EC, WSOC_g and WSOC_p observed in central Atlanta were distinctly different from those in LA (Figure 1b). Unlike the CalNex measurement site, the Atlanta site was located in the urban center and therefore was immediately impacted by local emissions, identified from the diurnal variation of EC. EC exhibited a clear morning rush hour enhancement of $0.19\ \mu\text{gC m}^{-3}$ (from $0.34\ \mu\text{gC m}^{-3}$ to $0.53\ \mu\text{gC m}^{-3}$) between 4:00 and 7:00 from primary vehicle emissions, and decreased sharply afterwards to a daily minimum of $0.21\ \mu\text{gC m}^{-3}$ in the afternoon as the boundary layer expanded. The average EC concentration in Atlanta ($0.33 \pm 0.26\ \mu\text{gC m}^{-3}$) was $\sim 65\%$ of that in LA ($0.51 \pm 0.30\ \mu\text{gC m}^{-3}$) during the sampling periods, in good agreement with anthropogenic VOC emissions in Atlanta being $\sim 60\%$ of those in LA based on emission inventories (Table 1). However, while WSOC_g concentrations tended to be in the same range at the two sites, the mean WSOC_p concentration was significantly higher in Atlanta (Table 1). Unlike LA where WSOC_g and WSOC_p exhibited regular and similar diurnal patterns, in Atlanta both had only moderate enhancements relative to a high background and reached their maximum concentrations at different times of the day. As shown in Figure 1b, photochemical production led to an increase in WSOC_p concentration between 9:00 and 16:00, whereas WSOC_g , representative of the overall water-soluble SVOC trend, continued to build up throughout the day and

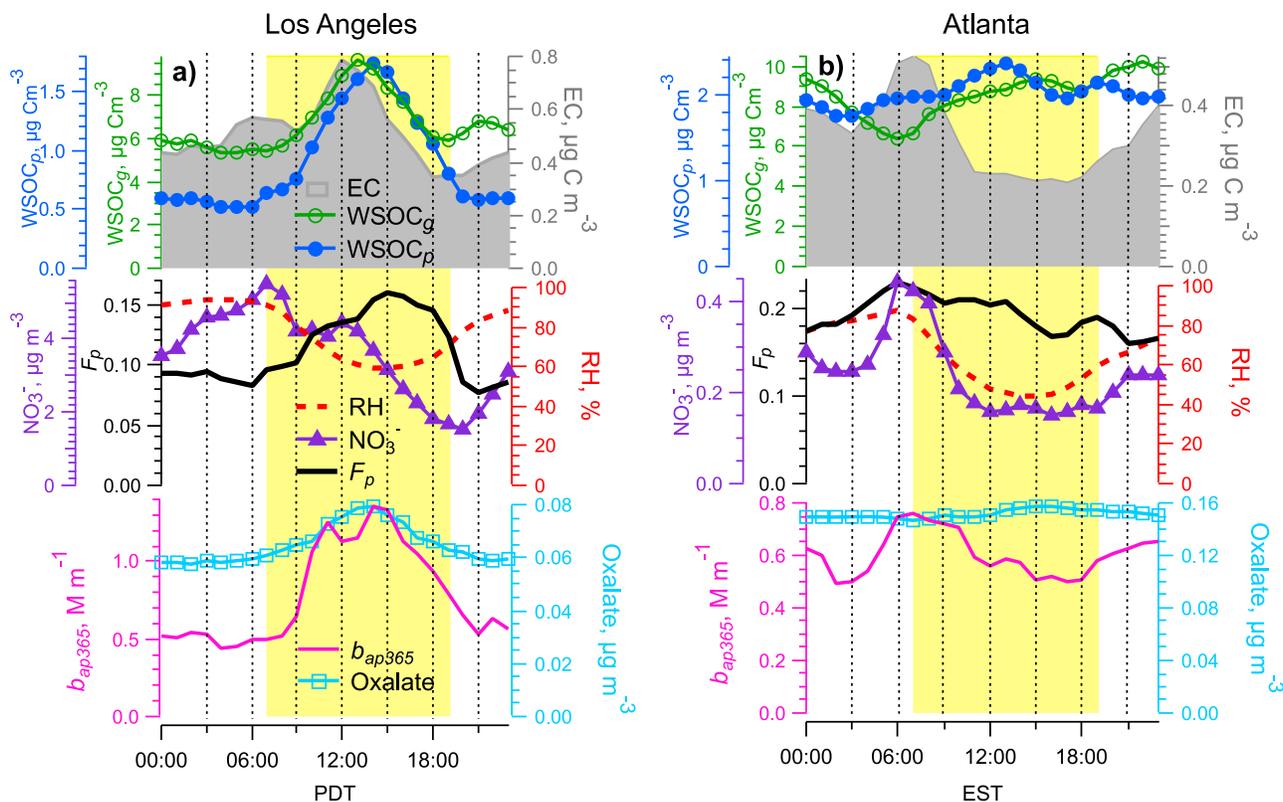


Figure 1. (top) Average diurnal variations of WSOC_g, WSOC_p and EC, (middle) WSOC partitioning coefficient (F_p), NO_3^- (PM_{10} in LA and $\text{PM}_{2.5}$ in Atlanta) and RH, and (bottom) oxalate and soluble brown carbon (indicated by b_{ap365}) in (a) LA and (b) Atlanta. The yellow shadings in both plots indicate daytime periods when solar radiation is above zero. Note that the y axis scales for Figures 1a and 1b are set to be different to investigate relatively small changes in the diurnal trends.

reached a daily maximum of $10.0 \mu\text{g C m}^{-3}$ at 23:00. This nighttime enhancement in WSOC_g has been observed in Atlanta during previous summer studies and is thought to be associated with O_3 and NO_3 radical oxidation of biogenic VOCs that persist late into the evening [Hennigan *et al.*, 2009]. WSOC_p concentrations at night returned to a regional background level of $\sim 2.0 \mu\text{g C m}^{-3}$, suggesting SVOC formed through dark reaction mechanisms did not contribute significantly to the SOA mass relative to daytime

production, as has been reported in other studies [Hennigan *et al.*, 2009].

3.2. WSOC Gas-Particle Partitioning

3.2.1. RH and Particle Liquid Water Content (LWC)

[11] Particle liquid water content (LWC) was predicted with the ISORROPIA-II thermodynamic equilibrium model [Fountoukis and Nenes, 2007] for the $\text{NH}_4^+ \text{-SO}_4^{2-} \text{-NO}_3^-$ system, using AMS NR- PM_{10} data during CalNex (which

Table 1. Summary of Statistics of VOC Emissions and Measured Species in Pasadena (LA) and Atlanta During the Sampling Periods^a

Sampling Period		Pasadena, CA May 15–Jun 15, 2010	Atlanta, GA Aug 6–Sep 7, 2010
VOC emission ($\text{molecule Carbon cm}^{-2} \text{ s}^{-1}$)	Anthropogenic	3.27×10^{13}	1.94×10^{13}
	Isoprene	8.06×10^{11}	3.85×10^{12}
WSOC _g ($\mu\text{g C m}^{-3}$)	Mean \pm std.	6.69 ± 3.10	8.64 ± 3.34
	Max	18.52	25.27
	Min	1.10	2.96
WSOC _p ($\mu\text{g C m}^{-3}$)	Mean \pm std.	0.90 ± 0.66	2.04 ± 1.00
	Max	3.68	5.04
	Min	0.01	0.16
F_p	Mean \pm std.	0.11 ± 0.05	0.19 ± 0.07
	Max	0.23	0.40
	Min	0.002	0.018
Oxalate ($\mu\text{g m}^{-3}$)	Mean \pm std.	0.065 ± 0.023	0.152 ± 0.019
	Max	0.148	0.217
	Min	0.015	0.127

^aAnthropogenic VOC emission data were from EPA 2005 National Emissions Inventory (NEI). Isoprene emission data were obtained from the Web site: <http://tropo.aeronomie.be/models/isoprene.htm>, and were calculated based on MEGAN (Version 2.0)-ECMWF [Guenther *et al.*, 2006; Müller *et al.*, 2008].

Table 2. Mean Particle Liquid Water Content (LWC) Predicted by ISORROPIA-II and the Average Measured F_p Values for Each RH Bin in LA and Atlanta

RH Bin (%)	Los Angeles		Atlanta	
	LWC ($\mu\text{g m}^{-3}$)	F_p	LWC ($\mu\text{g m}^{-3}$)	F_p
20–30	0.30 \pm 0.12	0.102 \pm 0.021	0.29 \pm 0.21	0.159 \pm 0.053
30–40	0.59 \pm 0.41	0.094 \pm 0.041	0.86 \pm 0.57	0.175 \pm 0.063
40–50	1.11 \pm 0.61	0.127 \pm 0.040	1.34 \pm 0.72	0.168 \pm 0.066
50–60	3.31 \pm 2.59	0.149 \pm 0.042	1.77 \pm 0.98	0.175 \pm 0.064
60–70	5.80 \pm 3.03	0.145 \pm 0.045	2.51 \pm 1.46	0.188 \pm 0.061
70–80	7.35 \pm 4.53	0.123 \pm 0.052	3.41 \pm 1.94	0.204 \pm 0.064
80–90	11.80 \pm 9.12	0.096 \pm 0.040	5.61 \pm 3.00	0.225 \pm 0.062
90–100	151.26 \pm 208.56	0.095 \pm 0.035	56.37 \pm 96.90	0.264 \pm 0.050

ignores the influence of supermicron particles that tend to contain most of the sea-salt related species such as NaCl and NaNO_3 [Murphy *et al.*, 2006] and PILS-IC $\text{PM}_{2.5}$ data in Atlanta (where salts are not prevalent [Zhang *et al.*, 2010]). Local meteorological data (i.e., RH and temperature) were used for both cities. The model results are summarized in Table 2. As expected, in both cities LWC exhibited a positive relationship with ambient RH, and LWC increased rapidly at RH levels above 80%, indicating substantial water uptake by the inorganic components when ambient RH reached the deliquescence point of the particles in the modeled system. Due to the limitations with model-predicted LWC and the fact that the predicted LWC was highly sensitive to RH (especially for RH above 90%), for simplicity in the following analyses, ambient RH was used as a proxy of LWC and hence the aerosol hygroscopicity.

3.2.2. Diurnal Variation of WSOC Partitioning Coefficient (F_p)

[12] Partitioning behavior of WSOC in Atlanta has been investigated by exploring the dependence of F_p on possible absorbing aerosol components, where F_p is defined as the fraction of total WSOC ($\text{WSOC}_g + \text{WSOC}_p$) in the particle phase (WSOC_p) [Hennigan *et al.*, 2008a, 2009]. Figures 1a (middle) and 1b (middle) show the diurnal variations of F_p in LA and Atlanta, together with the diurnal profiles of nitrate aerosol concentrations and ambient RH. NO_3^- is formed by partitioning of HNO_3 to the particle phase and is enhanced by high LWC, low temperature, and the presence of NH_3 due to sensitivity to particle pH. During CalNex, non-refractory NO_3^- was the dominant inorganic anion in the fine aerosol mode, mainly in the form of NH_4NO_3 [Hayes *et al.*, 2012]. Liu *et al.* [2012] examined CalNex nitrate partitioning and found a strong dependence of $\text{NO}_3^-/\text{HNO}_3$ ratio on ambient RH. Since the diurnal variability of NO_3^- during CalNex resembled that of the $\text{NO}_3^-/\text{HNO}_3$ ratio [Liu *et al.*, 2012] and no HNO_3 measurement was made in Atlanta, only the NO_3^- trend was plotted in Figure 1 to represent the partitioning behavior of nitrate aerosol. As expected, in both LA and Atlanta, NO_3^- exhibited a daily maximum concentration in early morning, coinciding with higher RH and lower T, similar to previous observations in Mexico City by Hennigan *et al.* [2008b] where they have shown that comparisons of NO_3^- and WSOC_p can provide unique insights on secondary aerosol formation processes.

[13] F_p of WSOC had different diurnal patterns and correlations with aerosol water in LA and Atlanta. In Atlanta, peak F_p coincided with NO_3^- at 6:00 when RH was also the highest of the day. Shortly after sunrise, NO_3^- concentration

started to decrease as the particles began to dry out, and F_p did not follow the sharp decrease of NO_3^- , but instead remained at ~ 0.20 until the late afternoon, then decreased as WSOC_p was approaching background levels. In contrast, during CalNex, F_p largely tracked photochemically produced WSOC_p and thus followed an opposite diurnal trend to NO_3^- and RH. These different diurnal F_p patterns are apparently related to the different gas-particle partitioning behaviors of WSOC in these two contrasting cities, which will be discussed next.

3.2.3. Partitioning Preference of WSOC in LA and Atlanta

[14] The partitioning of a species between the gas and particle phase in environmental chamber experiments can be predicted by the gas-particle absorptive partitioning theory by introducing the temperature-dependent partitioning coefficient (K_p). At a given temperature, the partitioning of SVOCs is highly dependent upon the mass loading of the absorptive organic aerosols [Pankow, 1994; Odum *et al.*, 1996]. However, recent laboratory studies have revealed the importance of an additional SOA formation route, involving dissolution of water-soluble VOCs and SVOCs (e.g., small carbonyls) into particle water followed by hydration and possibly further oxidation to lower volatility products [Ervens *et al.*, 2011 and references therein]. Absorption to water has been indirectly observed in the ambient atmosphere through the relationship of F_p with RH (and presumably particle liquid water content) in Atlanta [Hennigan *et al.* 2008a, 2009] and the positive relationship between RH and the fraction of organic acids in the total organic aerosols during airborne studies off the Pacific coast and over the continental U. S. [Sorooshian *et al.*, 2010].

[15] *The F_p -RH relationship.* Figure 2 shows the contrasting WSOC partitioning behaviors relative to ambient RH in LA and Atlanta. As expected from the diurnal trends, there is no well-defined relationship between F_p and RH ($r = -0.36$) in LA. The highest median F_p values occur at RHs between 50 and 70%, generally in the middle of the day when most SOA was photochemically produced. However, despite on average a 13% lower RH in Atlanta than in LA during the sampling periods (Figures 1a (middle) and 1b (middle)), the F_p observed in Atlanta exhibited a strong dependence on RH, consistent with findings by Hennigan *et al.* [2008a] in the summer (May through September) of 2007. Atlanta F_p showed little variation with an average median value of 0.17 ± 0.01 between 20 and 70% RH, and increased sharply with RH when RH was greater than 70%. F_p reached a maximum median value of 0.26 at RH greater

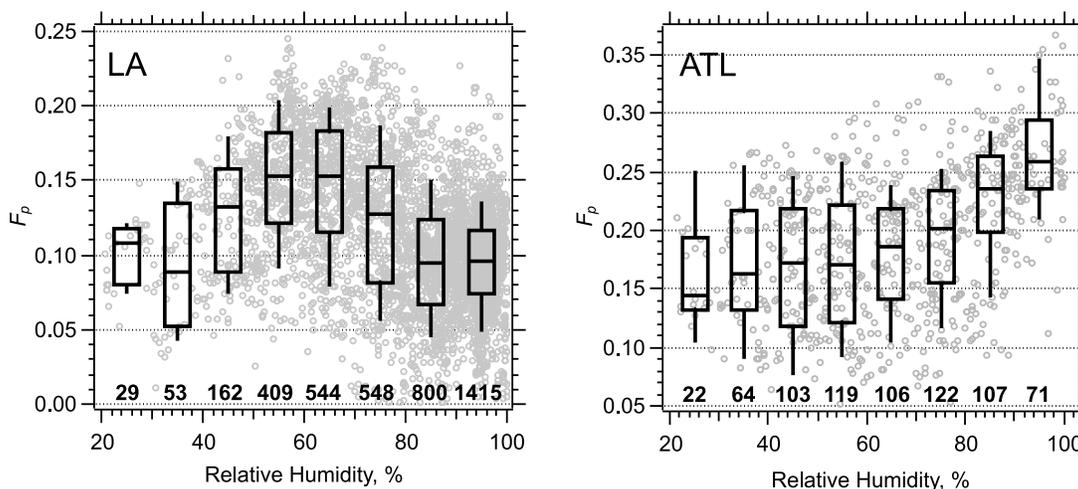


Figure 2. Box plots of F_p versus RH in (left) LA and (right) Atlanta. Data points shown as gray open circles are binned by RH. Median values (horizontal bars), 25th and 75th percentiles (lower and upper box bounds, respectively), and 10th and 90th percentiles (lower and upper whiskers, respectively) are shown in the plots. Numbers under each box indicate the number of data points in each RH bin. Note that the y axis scales for LA and ATL plots are different.

than 90%, translating to a mass increase of $WSOC_p$ due to uptake by water of $\sim 0.51 \mu\text{gC m}^{-3}$.

[16] *The F_p -OC relationship.* The dependence of F_p on OC mass also differed between the two cities (Figure 3). For LA aerosols there was an overall correlation between F_p and OC ($r^2 = 0.35$) (for correlation between F_p and AMS OM, $r^2 = 0.28$), and the median F_p from the binned data is strongly correlated with binned OC ($r^2 = 0.99$) (for correlation between binned F_p and AMS OM, $r^2 = 0.96$), suggesting that the water-soluble SVOC partitioning was dependent on the mass concentration of the organic phase (OA). Although the characteristics of the absorbing organic phase are somewhat ambiguous [Song *et al.*, 2007; Hallquist *et al.*, 2009], in LA the absorbing medium is probably SOA since the dependence of F_p on AMS OOA mass was much stronger ($r^2 = 0.97$ for binned data) than on HOA (hydrocarbon-like organic aerosol) mass ($r^2 = 0.63$ for binned data). The correlation between F_p and OA was also consistent with the diurnal trends, where the daily peak of F_p coincided with the peaks of major SOA components such as $WSOC_p$ (Figure 1a) and SV-OOA. We note that the correlation between F_p and OC in LA might be partly due to the strong correlation between $WSOC_p$ and OC ($r^2 = 0.73$) since the sampled air masses were advected from downtown LA, which tended to merge primary emissions and secondary formation processes and resulted in highly correlated air masses. However, the F_p dependence on OC is not likely to be solely driven by the correlated air masses since a tighter correlation between $WSOC_p$ and OC was found in Atlanta ($r^2 = 0.79$), where a similar dependence of F_p on OC mass was not observed. In Atlanta the F_p -OC relationship appeared to be more scattered and complex. There was only a weak dependence of F_p on OC at lower OC concentrations. At higher OC concentrations, F_p leveled off at a median value of ~ 0.21 .

[17] To better understand if some of the scatter in the F_p -OC relationship in both cities can be attributed to a RH effect on WSOC partitioning, the data were segregated into

two sub data sets by high (above 70%) and low (below 70%) RH levels. Figure 3b shows that for the LA data, similar trends in the F_p -OC relationship for the two sub data sets, which followed the trend for all the data, were observed. The F_p values for the high RH (>70%) group were consistently lower, possibly due to less WSOC partitioning in the particle phase at night when RH was generally higher. Hennigan *et al.* [2008a] also observed lower F_p values during nighttime relative to daytime, and attributed this difference in part to the diurnal variability of ambient oxidant or NO_x levels. In Atlanta, however, the F_p -OC trends for the two sub data sets were distinctly different (Figure 3b). For data with higher RH, there was no well-defined F_p -OC relationship, indicating the dominant role of liquid water in WSOC partitioning when ambient RH was sufficiently high. For data with lower RH, when no F_p -RH relationship was observed, there was nearly a linear dependence of F_p on OC ($r^2 = 0.94$ for binned data), which was very similar to the trend observed in LA, suggesting that the absorbing phase for WSOC partitioning in Atlanta could shift from particle water, when sufficient LWC was present, to organic aerosols when the particles were generally drier. In the atmosphere, these two types of partitioning processes may occur simultaneously and shift in importance as the ambient RH changes dramatically throughout a diurnal cycle at the ground, or as particles experience increasing humidity as they are mixed toward the top of the boundary layer. For example, between 8:00 and 9:00 for 22 out of 36 days during the Atlanta sampling period, the hourly RH was above 70%, compared to zero days with an RH above 70% between the times of 14:00 and 15:00. However, despite lower RH during these afternoon periods (between 12:00 to 18:00), a similar dependence of F_p on RH as that seen for the whole data set was still observed (not plotted). In the previous study by Hennigan *et al.* [2009] that was conducted over 5 months (May to September 2007) in Atlanta, a clear F_p -RH relationship was also found at any time during the day. In

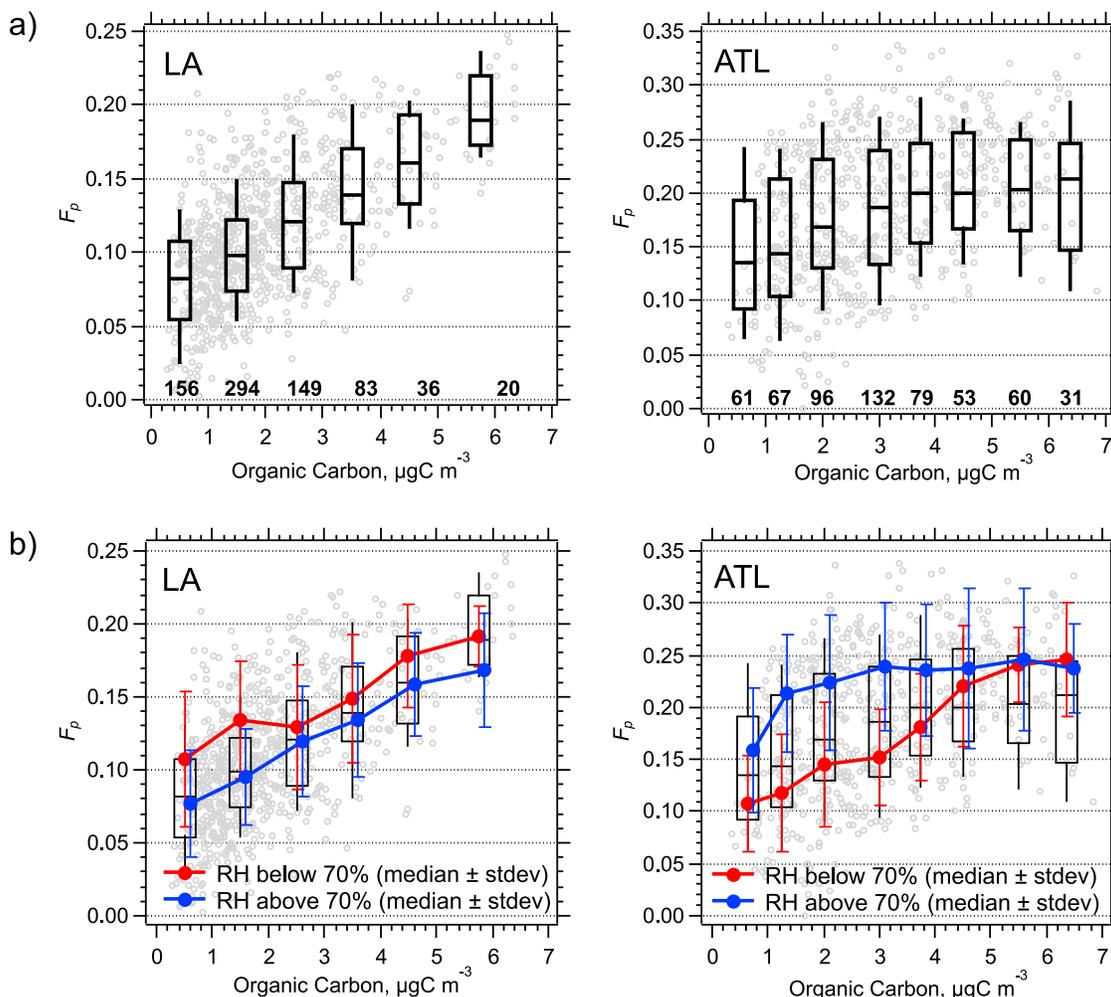


Figure 3. F_p versus organic carbon (OC) mass in (left) LA and (right) Atlanta (a) for the whole data sets as those presented in Figure 2, and (b) for the two sub data sets where data are segregated for high and low RH levels (blue and red markers and lines, respectively). Note that the y axis scales for LA and ATL plots are different.

summary, our August data set suggests that during afternoon lower RH periods, partitioning to liquid water could still occur, but not likely as important an absorbing phase as OA.

3.2.4. Partitioning and WSOC Production: Optimal Conditions for Partitioning to Water

[18] The comparison between LA and Atlanta F_p not only showed a difference in their diurnal trends and relationships with RH and OC, but also a significant difference in F_p magnitude. In Atlanta where the absorbing phase included particle water, the F_p levels were always measurably larger than those in LA (Table 2). On average, F_p in Atlanta (0.19 ± 0.07) was roughly twice that of LA (0.11 ± 0.05) (Table 1). The highest F_p correlates with highest RH, suggesting greater uptake of water-soluble SVOCs by dissolution to water compared to absorption by OA.

[19] For absorptive partitioning to particle water of the freshly formed SVOCs (WSOC_g) to be an effective pathway to form SOA, both wet particles and sufficient oxidants are required. Although RH is the highest at night, all our analyses have shown that most WSOC_p production in Atlanta is during daytime and hence driven by photochemical oxidation processes [Hennigan et al., 2009; Zhang et al., 2012].

The optimal period for multiphase SOA formation is then before noon when aerosols are drying from the high RH period before sunrise, but could still remain wet due to their low efflorescence RH [Bertram et al., 2011]. As discussed in Section 3.2.2, there is evidence for this mechanism from the NO_3^- diurnal trend in LA (Figure 1) and the NO_3^- formation in the morning hours in Mexico City during a wet period (3/27 to 3/30/2006) [Hennigan et al., 2008b]. In Mexico City, NO_3^- and WSOC_p were strongly correlated between 8:00 and 12:45, suggesting very similar atmospheric processes affecting the formation and loss of both species. Thus, it appears possible that some of the Mexico City morning WSOC_p formation was related to partitioning to liquid water. However, as noted above, in Atlanta F_p remained high for a period extending into the early afternoon, when aerosols were most likely dry, allowing partitioning to shift to absorption by organic components. The data suggest that for the month of August, the increase in WSOC_p within Atlanta likely involves a combination of partitioning to water and absorption to OA, with the former being most prevalent in the morning hours and the latter in the afternoon when WSOC_p concentrations were highest. Recent laboratory studies,

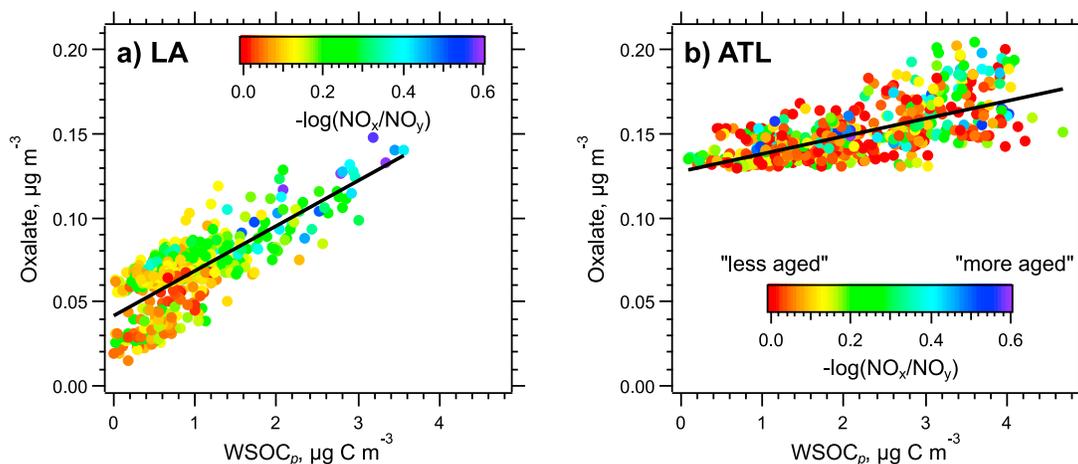


Figure 4. Oxalate versus $WSOC_p$ as a function of photochemical age (indicated by $-\log(NO_x/NO_y)$) in (a) LA and (b) Atlanta.

generally performed at low RH ($\sim 30\%$), have suggested the possibility of “glassy” SOA formation, a kinetic uptake process that does not follow the equilibrium partitioning theory due to the slow diffusivity within the formed particles [Virtanen *et al.*, 2010; Cappa and Wilson, 2011; Perraud *et al.*, 2012]. One piece of evidence for ambient “glassy” SOA formation would be that the SOA ($WSOC_p$) mass did not change with temperature or pre-existing OA mass. However, our ambient observations in this study do not show evidence for this process, but instead appear to confirm the importance of absorptive partitioning to OA as a source of $WSOC_p$ production in both LA and Atlanta.

[20] Contrasts between F_p -RH and F_p -OC relationships in LA and Atlanta are consistent with differences observed for other SOA components and properties, including partitioning of formic acid, oxalate formation pathways, and $WSOC_p$ light absorption properties (i.e., brown carbon). These additional contrasts discussed below support the differences in observed partitioning of bulk WSOC.

3.3. Additional Differences Between LA and Atlanta

3.3.1. Formic Acid Partitioning

[21] In a companion paper, Liu *et al.* [2012] presented a detailed analysis of formic acid partitioning in LA and Atlanta based on the same studies discussed in this work. As a low molecular weight carboxylic acid, formic acid is volatile and is expected to be predominately in the gas phase. Formic acid particle/gas (p/g) ratios in both LA and Atlanta were typically only a few percent (~ 1 – 2%), yet the relationship of formic acid with RH differed. In LA, formic acid p/g ratios generally showed limited correlation with RH, with the exception of a few episodes of overcast periods when photochemistry was suppressed. During these three brief 1 to 2 day periods formic acid p/g ratios on average followed increasing RH, providing evidence for gas-phase formic acid partitioning to liquid water, and the p/g ratios were the largest at these times (up to 10% when RH > 90%). In contrast to LA, Atlanta formic acid p/g ratios behaved in a similar way as $WSOC_p$, with higher p/g ratios at higher RH. Overall, the contrasts in formic acid partitioning between LA and Atlanta are similar to those in bulk WSOC.

3.3.2. Contrasts in $PM_{2.5}$ Oxalate Formation Pathways

[22] Oxalate is one of the most ubiquitous carboxylic acids in tropospheric aerosols, contributing to a few percent of the total organic mass in the continental atmosphere [Kawamura and Ikushima, 1993; Huang *et al.*, 2006; Sorooshian *et al.*, 2007], and up to 21% in the coastal Pacific atmosphere [Sorooshian *et al.*, 2010]. In this study, oxalate ranged from 0.015 to 0.148 $\mu\text{g m}^{-3}$ in LA and between 0.127 and 0.217 $\mu\text{g m}^{-3}$ in Atlanta, comprising on average 2.0% and 2.7% of the total $WSOC_p$ on a carbon mass basis in LA and Atlanta, respectively (Table 1).

[23] Oxalate is mostly a product of secondary production processes with minor contributions from primary emissions such as biomass burning and fossil fuel combustion [Huang and Yu, 2007; Schmidl *et al.*, 2008; Zhang *et al.*, 2010; Myriokefalitakis *et al.*, 2011], and is often detected in the accumulation mode internally mixed with sulfate [Huang *et al.*, 2006; Sorooshian *et al.*, 2006], suggesting significant contribution from multiphase reactions. Laboratory studies have shown that oxalate can be formed from small aldehydes reacting with OH radical in the aqueous phase [Lim *et al.*, 2010; Tan *et al.*, 2010]. Gas-phase oxidation of parent organic species leading to oxalate is not well established [Warneck, 2003], but has been speculated based on ambient observations [Chebbi and Carlier, 1996; Sorooshian *et al.*, 2006; Sullivan and Prather, 2007]. Since oxalate can be formed by condensation of gas-phase oxalic acid, as well as from multiphase reactions in the aqueous phase, differences in oxalate sources and formation mechanisms in LA and Atlanta provide insight on SOA formation pathways between these two urban environments.

[24] In LA and Atlanta we observed different oxalate diurnal trends and their association with $WSOC_p$ (Figures 1a (bottom) and 1b (bottom)). In LA, the diurnal profile of oxalate was nearly identical to that of $WSOC_p$, showing maximum concentration in the early afternoon tracking most SOA components. Oxalate was well correlated with $WSOC_p$ and OOA ($r^2 = 0.68$ and 0.73 , respectively). Furthermore, as shown in Figure 4a, oxalate and $WSOC_p$ evolved together with increasing photochemical age, indicated by $-\log(NO_x/NO_y)$ [Kleinman *et al.*, 2008], suggesting their common sources and formation mechanisms. Two branches (γ -

intercepts) are evident in Figure 4a and are attributed to different air mass histories. During CalNex sampling between May 29 and June 6, a general stagnation event in the LA basin led to a substantial increase in background levels for several species, including oxalate and LV-OOA (low-volatility OOA). The average nighttime concentration of oxalate increased substantially from $0.28 \mu\text{g m}^{-3}$ prior to the stagnation event (before May 29) to $0.63 \mu\text{g m}^{-3}$ during the event (after May 29), resulting in the two branches of Figure 4a. However, similar oxalate/WSOC_p ratios (0.020 and $0.026 \mu\text{g}/\mu\text{gC}$) were obtained for these two periods. Veres *et al.* [2011] measured several gas-phase organic acids during CalNex, such as formic, pyruvic/butyric and propionic acids, and concluded they were formed through rapid photochemical production within the urban plume. Oxalic acid appeared to be produced in a similar fashion as other measured organic acids; in the gas phase and partitioning to the condensed phase to form aerosol oxalate (note, no gas-phase oxalic acid data were available during CalNex).

[25] Higher average oxalate concentrations, as well as a larger fraction of oxalate in the total WSOC_p, were found in Atlanta than in LA (Table 1). The larger y-intercept value of oxalate versus WSOC_p (Figure 4b) corresponds to a substantially higher background level of oxalate in Atlanta and is indicative of significant regional contribution, as has been observed for WSOC_p [Zhang *et al.*, 2012] and other WSOC_p components (soluble brown carbon) [Zhang *et al.*, 2011]. Despite the much higher background level, the daytime enhancement of oxalate was only ~5% relative to the average nighttime concentration, roughly 1/6 of that observed in LA. Unlike LA where the diurnal trend of oxalate tracked WSOC_p, in Atlanta oxalate peaked 2–3 h later than WSOC_p (Figure 1b), suggesting rapid formation through gas phase oxidation of parent VOCs followed by condensation was not an important source for Atlanta oxalate. The correlation between oxalate and WSOC_p in Atlanta was weaker ($r^2 = 0.45$) than in LA and was not related to photochemical age (Figure 4b), which further suggested that daytime WSOC_p and oxalate were not formed by similar mechanisms. Instead, unlike LA where oxalate appeared to form in the gas phase and partition to the particle phase, in Atlanta oxalate trends appeared to be driven more by a regional contribution and possibly slower production through a multiphase reaction pathway.

3.3.3. Contrasts in PM_{2.5} Soluble Brown Carbon

[26] Soluble light-absorbing organic aerosol (brown carbon) concentrations and their associations with WSOC_p were substantially different between LA and Atlanta (Figures 1a (bottom) and 1b (bottom)). Zhang *et al.* [2011] showed that in LA soluble brown carbon was correlated with WSOC_p, and a detailed chemical analysis identified nitro-aromatics as one source for the colored organics. These two findings are consistent, as many chromophores associated with SOA are expected to contain aromatic moieties, and much of the SOA formed in the LA basin is linked to these similar anthropogenic precursors (i.e., aromatics) [Hersey *et al.*, 2011; Zhang *et al.*, 2011; Bahreini *et al.*, 2012]. Focusing on the WSOC_p that was freshly formed within each urban environment, the mass absorption efficiency at the wavelength of 365 nm (bulk absorption at 365 nm per WSOC_p mass) was found to be 4–6 times higher in LA, indicating that much of the soluble

organic aerosols formed within Atlanta were chemically different from those in LA.

4. Discussion

[27] Differences in WSOC and formic acid partitioning preferences, oxalate formation pathways, and the extent to which brown carbon was present in the freshly formed SOA between LA and Atlanta, all point to differences in SOA compositions and formation mechanisms within these two urban environments. Particle composition can affect what acts as the main absorbing phase. Our results suggest that absorption to aerosol water plays an important role in SOA formation within Atlanta, but not in LA. This difference could be caused by: (1) contrasting particle hygroscopicity, which determines the amount of water uptake by particles, affecting gas-particle partitioning and the extent of any subsequent condensed phase reactions; (2) different types of SVOCs that partition to the particle phase; and (3) other properties of the particle water, such as pH, which could influence the uptake of weak organic acids, a significant fraction (~40%) of the summer WSOC_p in Atlanta [Sullivan and Weber, 2006]. A detailed discussion regarding the influence of particle pH on organic acid partitioning is reported by Liu *et al.* [2012] with respect to formic acid partitioning. The first two hypotheses are explored next.

[28] *Particle hygroscopicity.* Despite higher RHs in LA, differences in the actual amount of particle water could be a hypothesis to explain the greater propensity of Atlanta WSOC_g to partition to particle water. However, the results from ISORROPIA-II model, summarized in Table 2, show that for RH ranging between 20 and 50%, the modeled LWC were comparable in LA and Atlanta, and for RH higher than 50%, LWC was predicted to be 2–3 times higher in LA than in Atlanta. The model does not consider the effect of organic components on particle hygroscopicity, which has generally been thought to be minor given the much lower hygroscopicity of the organics relative to the inorganic components, such as (NH₄)₂SO₄ [Jimenez *et al.*, 2009]. Previous field studies conducted in similar locations and time periods as the present study have derived the hygroscopicity parameter κ . κ values ranged between 0.15 and 0.51, with an average of 0.31 in LA (Pasadena) during spring-summer of 2009 [Hersey *et al.*, 2011], and ranged between 0.05 and 0.52, with an average of 0.21 at an urban Atlanta site 2 km from the GIT campus in the summer of 2008 during the AMIGAS study [Padró *et al.*, 2011]. The average RH levels during these two past studies and those in the current study were within $\pm 5\%$.

[29] Both thermodynamic calculations and field measurements suggest that the overall aerosol water contents were similar in the two urban environments during the study periods discussed here (LA: May–June, Atlanta: August) and may not have a major impact on the different SOA partitioning pathways. However, since the actual concentrations of the particle water that the SVOCs partitioned to were not explicitly measured in these studies, some uncertainty remains. For example, one could expect that the organic fraction of fine particles in the southeast to be more hygroscopic since it was composed of a significant fraction of regional, aged aerosols, relative to the large fraction of freshly formed SOA that were more hydrophobic in LA

[Zhang *et al.*, 2011; Zhang *et al.*, 2012]. This hypothesis is also supported by, as discussed in section 3.3.2, the much higher fraction of oxalate aerosol in the total WSOC_p in Atlanta than LA. Although the organic fraction may not greatly affect the amount of particle water present in these regions, it could have an important impact on the actual uptake of various gaseous species by affecting phase separations within the particle and the formation of hydrophobic or hydrophilic surface layers [Bertram *et al.*, 2011; You *et al.*, 2012]. You *et al.* [2012] have shown clear evidence that Atlanta ambient particles could undergo liquid-liquid phase separation below 70% RH with an inner phase of ammonium sulfate and an outer phase of secondary organic material, which may explain the dependence of F_p on OC mass in Atlanta when RH was low. Zuend and Seinfeld [2012] also suggest that WSOC does not necessarily partition to the aqueous phase but rather to the hydrophilic organic phase due to liquid-liquid phase separation and salting-out effects at lower RH range. More information on the behavior of aerosol liquid phases as a function of RH in both Atlanta and LA is needed to better understand the role that phase separation plays in WSOC uptake by particles.

[30] *VOC emissions.* Although the exact role that the organic aerosol composition plays in WSOC partitioning is not clear, the type of SVOCs that partition may partially determine what the dominant absorbing phase is. LA and Atlanta have large difference in the mix of VOCs that could lead to SOA. Anthropogenic VOCs and isoprene emission fluxes from the emission inventories are summarized in Table 1. In LA, anthropogenic hydrocarbons are the dominant VOCs emitted and the likely SOA precursors [Hersey *et al.*, 2011; Williams *et al.*, 2010b], which have been confirmed by radiocarbon analysis on CalNex PM₁ filters [Zhang *et al.*, 2011]. In Atlanta, the emissions of anthropogenic VOCs are significantly less, approximately half of that in LA, consistent with a lower urban population density. In contrast, the emission of isoprene is predicted to be 5 times higher in Atlanta due largely to the greater presence of isoprene-emitting vegetation. Other biogenic VOC emissions, such as monoterpenes emission, are also substantially higher in the southeast [Guenther, 1997]. Radiocarbon analysis has shown that the secondary WSOC_p in Atlanta in the summer is largely modern (~70 to 80%) [Weber *et al.*, 2007]. Based on the brown carbon data, Zhang *et al.* [2011] concluded that the daily freshly formed WSOC_p within the city of Atlanta was most likely biogenic SOA. A number of other ambient studies have also shown preferential formation of biogenic SOA in polluted environments [Goldstein *et al.*, 2009; Spracklen *et al.*, 2011; Worton *et al.*, 2011; Setyan *et al.*, 2012].

[31] The effect of biogenic VOCs may be that it not only influences the absorbing phase, but also results in oxidized VOCs and SVOCs that are more likely to partition to water. Laboratory studies have shown that isoprene is highly reactive with OH radical and in the presence of high NO_x concentrations, the isoprene oxidation produces low molecular weight products (e.g., glyoxal and methylglyoxal) that could undergo reactive uptake by wet aerosols, and given sufficient time, transform to stable products [Liggio *et al.*, 2005a, 2005b; Lim *et al.*, 2010]. Satellite observations of glyoxal columns indicate significantly higher amounts of glyoxal in the southeastern U.S. than along the west coast [Myriokefalitakis *et al.*, 2008], likely due to a greater

abundance of vegetation that emits the glyoxal precursor. Contrasting VOC emissions are consistent with differences in observed WSOC characteristics (color) and trends in specific aerosol components (oxalate).

5. Conclusions

[32] Ambient measurements of gas and particle phase water-soluble organic aerosols were conducted in Pasadena, CA (as part of the CalNex-LA campaign) and Atlanta, GA in the spring-summer of 2010. WSOC gas-particle partitioning, analyzed through the fraction of total WSOC in the particle phase, F_p , exhibited differing relationships with ambient RH and OC mass in the two urban environments. Consistent with previous studies, in Atlanta F_p was correlated with RH and inferred particle water content from a thermodynamic model. The correlation was observed throughout the day and was especially prevalent in the morning, when RH was higher. During the drier period (RH below 70%), F_p was found to have a dependence on OC mass, suggesting that in Atlanta during August, both particle water and organic components could serve as the partitioning absorbing phase, depending on ambient conditions. In contrast, in LA the diurnal variation of F_p did not track RH. As a result, no correlation was found between F_p and RH, despite a much higher average RH and predicted particle water content in LA relative to Atlanta. Instead, F_p scaled well with OC mass, consistent with SVOCs partitioning to the organic phase, as observed in environmental chamber studies. These ambient observations do not show evidence for possible “glassy” SOA formation that has been observed in recent laboratory studies.

[33] Besides the contrast in WSOC partitioning behavior between LA and Atlanta, a number of other differences, including oxalate formation pathways (discussed in this paper), WSOC light-absorbing properties [Zhang *et al.*, 2011], and partitioning of formic acid [Liu *et al.*, 2012], were observed between these two urban environments. Many of the differences may be attributed to different SOA precursors within the two urban environments, resulting in different types of SOA, and possibly SOA formation mechanisms. Both cities have abundant anthropogenic VOC emissions from fossil fuel combustion, with Atlanta having an additional large source of biogenic VOCs in the summer. These ambient observations show direct evidence for different gas-particle partitioning behaviors and provide insights on SOA formation mechanisms that vary with location.

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