

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

2. Gas and particle phase formic acid

Jiumeng Liu,¹ Xiaolu Zhang,¹ Eric T. Parker,^{1,2} Patrick R. Veres,^{3,4,5} James M. Roberts,⁴ Joost A. de Gouw,^{3,4} Patrick L. Hayes,^{3,6} Jose L. Jimenez,^{3,6} Jennifer G. Murphy,⁷ Raluca A. Ellis,^{7,8} L. Greg Huey,¹ and Rodney J. Weber¹

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[1] Gas and fine particle (PM_{2.5}) phase formic acid concentrations were measured with online instrumentation during separate one-month studies in the summer of 2010 in Los Angeles (LA), CA, and Atlanta, GA. In both urban environments, median gas phase concentrations were on the order of a few ppbv (LA 1.6 ppbv, Atlanta 2.3 ppbv) and median particle phase concentrations were approximately tens of ng/m³ (LA 49 ng/m³, Atlanta 39 ng/m³). LA formic acid gas and particle concentrations had consistent temporal patterns; both peaked in the early afternoon and generally followed the trends in photochemical secondary gases. Atlanta diurnal trends were more irregular, but the mean diurnal profile had similar afternoon peaks in both gas and particle concentrations, suggesting a photochemical source in both cities. LA formic acid particle/gas (p/g) ratios ranged between 0.01 and 12%, with a median of 1.3%. No clear evidence that LA formic acid preferentially partitioned to particle water was observed, except on three overcast periods of suppressed photochemical activity. Application of Henry's Law to predict partitioning during these periods greatly under-predicted particle phase formate concentrations based on bulk aerosol liquid water content (LWC) and pH estimated from thermodynamic models. In contrast to LA, formic acid partitioning in Atlanta appeared to be more consistently associated with elevated relative humidity (i.e., aerosol LWC), although p/g ratios were somewhat lower, ranging from 0.20 to 5.8%, with a median of 0.8%. Differences in formic acid gas absorbing phase preferences between these two cities are consistent with that of bulk water-soluble organic carbon reported in a companion paper.

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1. Background

[2] Organic acids are a common component of ambient air [Chebbi and Carlier, 1996; Sullivan and Weber, 2006] and a

¹School of Earth and Atmospheric Sciences, Georgia Institute of Technology, Atlanta, Georgia, USA.

²Now at School of Chemistry and Biochemistry, Georgia Institute of Technology, Atlanta, Georgia, USA.

³Cooperative Institute for Research in Environmental Sciences, University of Colorado Boulder, Boulder, Colorado, USA.

⁴Chemical Sciences Division, Earth System Research Laboratory, NOAA, Boulder, Colorado, USA.

⁵Now at Max Planck Institute for Chemistry, Mainz, Germany.

⁶Department of Chemistry and Biochemistry, University of Colorado Boulder, Boulder, Colorado, USA.

⁷Department of Chemistry, University of Toronto, Toronto, Ontario, Canada.

⁸School of Engineering and Applied Sciences, Harvard University, Cambridge, Massachusetts, USA.

Corresponding author: R. Weber, School of Earth and Atmospheric Sciences, Georgia Institute of Technology, Atlanta, GA 30332, USA. (rodney.weber@eas.gatech.edu)

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range of acids has been detected and reported in rural, polar, marine and urban environments in the gas phase as well as in clouds and in aerosols [Khare et al., 1999; Paulot et al., 2011; Sorooshian et al., 2007]. Organic acids can comprise significant fractions of atmospheric particle ionic and water-soluble organic carbon and participate in photochemical reactions [Chebbi and Carlier, 1996; Khare et al., 1999; Sommariva et al., 2011]. Oxalate is often the most abundant aerosol organic acid identified [Kawamura et al., 2010, and references therein], whereas formic and acetic acids are among the most abundant gas phase organic acids and are ubiquitous in the aerosol phase, but generally are minor mass fractions due to their high volatility [Khare et al., 1999; Löflund et al., 2001].

[3] Formic acid has both primary and secondary sources [Chebbi and Carlier, 1996; Khare et al., 1999; Paulot et al., 2011]. The primary sources include fossil fuel combustion [Khare et al., 1999; Talbot et al., 1988], biogenic emissions [Talbot et al., 1990; Kesselmeier et al., 1998; Kesselmeier, 2001] and biomass burning emissions [Goode et al., 2000; Christian et al., 2003; Yokelson et al., 2009]. Secondary sources of formic acid involve photo-oxidation of volatile

Table 1. Summary of Instrumentation and Approximate Sampling Setups for the Various Species Reported

Analytical Technique	Inlet Height Above Ground Level (m)	Inlet Length (m)	Species Measured
<i>CalNex (LA)</i>			
NOAA-CIMS	5	1.5	Gaseous organic acids and nitric acid
GIT-CIMS	1.5	2	Gaseous organic acids
Mist chamber-TOC	7	12	WSOC _g
Sunset OC/EC	7	12	OC and EC
PILS-TOC	7	12	WSOC _p
PILS-IC	7	12	PM _{2.5} anions (including organic acids)
HR-ToF-AMS	5	7	PM ₁ non-refractory compounds
<i>Atlanta</i>			
GIT-CIMS	~30 m/1 m ^a	4	Gaseous organic acids
Mist chamber-TOC	~30 m/4 m ^a	8	WSOC _g
Sunset OC/EC	~30 m/4 m ^a	8	OC and EC
PILS-TOC	~30 m/4 m ^a	8	WSOC _p
PILS-IC	~30 m/4 m ^a	8	PM _{2.5} anions (including organic acids)

^aSampling was from a penthouse rooftop laboratory located roughly 30 m above ground level with the inlet 1 to 4 m above the roof surface.

organic compounds (VOCs), such as the oxidation of alkenes and monoterpenes by ozone or OH radicals [Madronich and Calvert, 1990; Neeb et al., 1997; Lee et al., 2006], as well as aqueous phase degradation of larger organic components from photo-oxidation of semi-volatiles [Ervens et al., 2008; Paulot et al., 2011]. Recently the aging of organic aerosols has also been proposed as a major global source of formic acid [Paulot et al., 2011].

[4] In highly polluted urban environments, typical concentrations of gaseous formic acid (HCOOH) can be up to several ppbv [Khare et al., 1999; Veres et al., 2011], while concentrations in the condensed phase, measured as the formate anion (HCOO⁻), can reach tens of ng/m³ [Chebbi and Carlier, 1996; Khare et al., 1999]. Aerosol formate is typically about two orders of magnitude lower than formic acid gas phase concentrations [Baboukas et al., 2000]. Most previous work on formic acid gas-particle partitioning was based on gas phase measurements using scrubbers (e.g., mist chambers) and particle phase measurements by integrated filter collection. These studies have found a higher fraction of formic acid in the condensed phase in winter than summer, apparently due to reduced vapor pressures at lower temperatures [Chebbi and Carlier, 1996; Khare et al., 1999]. Filter sampling, however, constrains partitioning studies by only providing highly time-integrated data (e.g., 12 to 24 h averages) and limits investigating the response of formic acid to diurnally changing meteorological parameters. In this study formic acid ambient concentrations and particle/gas (p/g) ratios are investigated using online measurement techniques in two contrasting cities, Los Angeles (LA), CA and Atlanta, GA. Los Angeles is an urban environment dominated by anthropogenic emissions, whereas Atlanta air quality is influenced by a mix of anthropogenic and biogenic emissions.

2. Experimental Methods

2.1. Sampling Sites

[5] Ground-based measurements were made in Pasadena, CA on the California Institute of Technology campus as part of the 2010 CalNex (Research at the Nexus of Air Quality and Climate Change) experiment from 15 May to 15 June

2010. Located within the Los Angeles Basin (here-after referred to as LA) approximately 16 km downwind of central LA, the site (34.140582 N, 118.122455 W) was regularly impacted by emissions transported from the source-rich downtown LA area [Hersey et al., 2011; Veres et al., 2011]. Following CalNex, a subset of the instruments was moved to Atlanta for continuous sampling between 3 August and 10 September 2010. Identical measurements between the two studies included gas and particulate formic acid and water-soluble organic carbon (WSOC), PM_{2.5} inorganic anions, and PM_{2.5} organic and elemental carbon (OC and EC, respectively). The Atlanta measurements were conducted from the roof of the Environmental Science and Technology Building (33.778427 N, 84.396181 W) on the Georgia Institute of Technology (GIT) campus (~30–40 m above ground level). A summary of instruments/sampling setups for both the LA and Atlanta studies is given in Table 1.

2.2. Instrumentation

2.2.1. Gases

[6] A suite of organic and inorganic acids was measured by negative ion-proton transfer-chemical ionization mass spectrometry (NI-PT-CIMS) through proton transfer with acetate ions and detection of the conjugate anion with a quadrupole mass spectrometer [Veres et al., 2008]. Two NI-PT-CIMS were deployed in LA while only the Georgia Institute of Technology (GIT) CIMS was deployed in Atlanta. In LA, Formic acid was measured by both GIT and the National Oceanic and Atmospheric Association (NOAA) CIMS, which were in reasonable agreement with a slope of 0.95 and r² of 0.80 (auxiliary material Figure S1).¹ NOAA CIMS measured nitric acid only in LA; no nitric acid data is available for the Atlanta study. Details of the sampling configurations are given in Table 1. The limit of detection (LOD) and measurement uncertainty is estimated at 0.02 ppbv and 25% for formic acid, respectively, and 0.08 ppbv and 37% for nitric acid by NOAA CIMS during CalNex-LA campaign, while the LOD of GIT CIMS was

¹Auxiliary materials are available in the HTML. doi:10.1029/2012JD017912.

0.02 ppbv in LA and 0.12 ppbv in ATL with an uncertainty of 30%.

[7] Gas-phase water-soluble organic carbon (WSOC_g) was measured with a mist chamber [Hennigan *et al.*, 2008]. Air was sampled at roughly 21 ± 1 L/min and was first passed through a Teflon filter for particle removal and then scrubbed of soluble gases (gases with a Henry's Law constant greater than 10^3 M/atm) [Spaulding *et al.*, 2002] in a glass mist chamber [Cofer and Edahl, 1986] initially filled with 10 mL of ultra-pure deionized water (>18.0 M Ω -cm). WSOC_g was then quantified with a Sievers Total Organic Carbon (TOC) analyzer (Model 800, GE Analytical Instruments; Boulder, CO) that was shared between the gas and particle WSOC instruments. Data were corrected by blank measurements performed prior to every mist chamber sampling cycle by loading the chamber with pure water, without sample airflow. The LOD and measurement uncertainty is estimated at $0.83 \mu\text{gC}/\text{m}^3$ and 8%.

[8] Along with the measurements of WSOC and formic acid, the mixing ratios for a variety of Volatile Organic Compounds (VOCs) were determined with a NOAA Gas Chromatography Mass Spectrometry (GC-MS) [Gilman *et al.*, 2009] during the CalNex-LA campaign. In both studies, meteorological data were provided by weather stations located on the respective campuses.

2.2.2. Aerosols

[9] PM_{2.5} soluble nitrate (NO₃⁻) and formate (HCOO⁻) concentrations, along with a range of other soluble anions, were determined using a Particle-Into-Liquid-Sampler coupled to an Ion Chromatograph (PILS-IC), similar to that described by Orsini *et al.* [2003]. Sample air was aspirated at 16.7 ± 0.7 L/min through a URG PM_{2.5} cyclone, a parallel plate carbon denuder [Eatough *et al.*, 1993] and honeycomb acid (citric acid) and base (sodium carbonate) coated denuders, then mixed with water vapor near 100°C generated from deionized water. The resulting droplets were collected by impaction and produced a liquid sample that was analyzed online by a Dionex Ion Chromatograph (UTAC-ULP1 concentrator column, AG11guard column and AS11 anion column) using a gradient NaOH eluent procedure lasting 20 min. Systematic blank measurements were made throughout the study period by diverting sample flow through a HEPA filter downstream of the denuder and upstream of the PILS. A linear interpolation of blank data was performed and subtracted from the ambient data. During the last several days of the study (12 June–15 June, 2010), the inlet cyclone was alternated between cyclones of PM₁ and PM_{2.5} cut sizes (URG) during daytime periods to investigate size-dependent concentration differences. (This was done for anions, OC, EC, and particle WSOC). Sample heating due to the PILS particle condensation growth collection method may cause potential collection losses of semi-volatile components [Sorooshian *et al.*, 2006]. Of the measured compounds, the most susceptible is thought to be formate (HCOO⁻) because it was the most volatile of the anions measured in this study. Sample heating may also promote some particulate organic constituents (e.g., glyoxylic acid) and oligomers to decompose and form small organic compounds prior to IC analysis, which might cause an overestimation in formate [Ervens *et al.*, 2008]. Post study comparisons involving simultaneous ambient air sampling with a manually operated Mist Chamber, which does not heat the

sample (in this case the Mist Chamber inlet filter was replaced with gas denuders) and PILS indicated that PILS formate concentrations can be systematically underestimated by up to 30%. Data were not corrected for the potential systematic error. Random measurement uncertainty based on a quadrature sum of squares that included the precision of standards, variability in sample airflow rate, liquid flow rate, and blanks (all one standard deviation), was estimated at 13% for nitrate and 15% for formate. LODs are $0.03 \mu\text{g}/\text{m}^3$ for nitrate and $0.02 \mu\text{g}/\text{m}^3$ for formate, respectively.

[10] A second PILS coupled to a TOC analyzer provided online measurements of PM_{2.5} water-soluble organic carbon (WSOC_p) following methods implemented in previous studies [Sullivan *et al.*, 2004]. PILS-TOC included a URG PM_{2.5} cyclone inlet and parallel plate carbon denuder upstream. An automated valve that directed sample flow through a Teflon filter located immediately upstream of the PILS and downstream of the denuders performed dynamic blanks twice daily. A linear interpolation between successive blanks was used to blank correct the online measurements. Instrument LOD and measurement uncertainty are estimated at $0.20 \mu\text{gC}/\text{m}^3$ and 7%, respectively. More details on this measurement and discussion of WSOC partitioning results can be found in Zhang *et al.* [2012a].

[11] A high-resolution time-of-flight aerosol mass spectrometer (HR-ToF-AMS, Aerodyne Research Inc., hereinafter "AMS" for short) was deployed in LA and provided measurements of non-refractory inorganic and organic aerosol components (P. L. Hayes *et al.*, Aerosol composition in Los Angeles during the 2010 CalNex Campaign studied by high resolution aerosol mass spectrometry, submitted to *Journal of Geophysical Research*, 2012). Ambient air was dried prior to sampling by the HR-ToF-AMS. The AMS measures submicron non-refractory species [Canagaratna *et al.*, 2007]. Differences in AMS and PILS upper size measurement limits and measurement of non-refractory versus soluble aerosol components likely account for the significant difference in nitrate concentrations measured by these two instruments while sampling during CalNex, a site influenced by marine air masses. The linear regression (ODR fit) of AMS to PILS nitrate slope was 0.66 ($r^2 = 0.86$). In the following analysis we interpret AMS measurements to be dominated by volatile nitrate (i.e., ammonium nitrate), which is most important in the submicron mode, and the PILS both volatile and nonvolatile nitrate (e.g., ammonium nitrate plus sodium nitrate), the latter being more important in the 1–2.5 μm PM range (Hayes *et al.*, submitted manuscript, 2012). AMS measurement uncertainty is estimated at 30% [Middlebrook *et al.*, 2012]. AMS/PILS sulfate were in good agreement, with regression slope of 1.01, and r^2 of 0.84.

[12] PM_{2.5} organic carbon and elemental carbon (OC and EC) were measured semi-continuously with a Sunset Labs OC/EC analyzer (Model 3F, Forest Grove, OR) following the National Institute for Occupational Safety and Health (NIOSH) [1996] method. Optical EC is used in this analysis since it was less noisy than thermal EC. A parallel plate carbon denuder [Eatough *et al.*, 1993] upstream of the instrument was installed to reduce positive sampling artifacts. Measurements were blank corrected based on systematic blank measurements made throughout the study period by installing a Teflon filter (47 mm dia., 2.0 μm pore size, Pall Life Sciences) on the cyclone inlet. A linear change

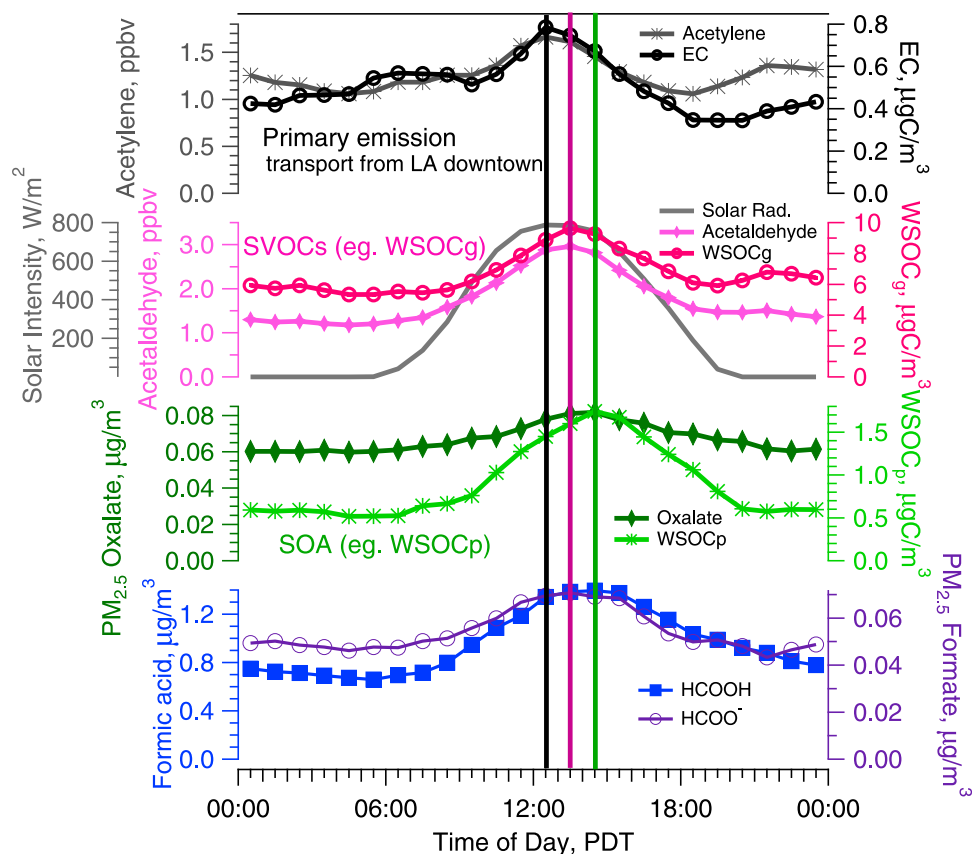


Figure 1. Los Angeles diurnal profiles of selected primary, secondary gases and particles, and gas and particle formic acid measured during CalNex. Means of hourly binned data are plotted.

in blank concentrations was assumed between consecutive blank measurements and was subtracted from the ambient data. OC blanks ranged from 1.3 to 2.6 $\mu\text{gC}/\text{m}^3$ and EC blanks varied from below LOD to 0.03 $\mu\text{gC}/\text{m}^3$. Uncertainty due to random measurement errors is estimated to be 28%. Systematic errors due to particle volatility are possible [Grover *et al.*, 2009]. Significant discrepancies were observed between the AMS OA (organic aerosol mass, i.e., OM) and Sunset Labs OC, with a study average OM/OC slope of 3.28 and $r^2 = 0.76$, where a slope closer to 2 is more realistic [Turpin and Lim, 2001; Hayes *et al.*, submitted manuscript, 2012]. Possible causes include loss of semi-volatile compounds from the collection filter media within the OC/EC analyzer, or due to the presence of the denuder [Grover *et al.*, 2009]. Other unidentified systematic errors associated with the measurements cannot be ruled out.

3. Results

3.1. Los Angeles Diurnal Variation in Air Pollutant Concentrations

[13] As a coastal city with clean upwind sector (Pacific Ocean) and a basin-shaped topography, LA has been observed to have a regular and distinct diurnal pattern in air pollutants. Emissions from the western regions of the LA Basin were transported across the basin in a northeastward direction by land-sea breezes on a daily basis [Veres *et al.*, 2011]. The CalNex-LA sampling site at Pasadena, CA, located ~ 16 km NE of downtown LA, is a receptor of

gaseous and particulate pollutants transported from downtown LA. The arrival of transported emissions is readily observed in the diurnal profiles of primary emissions (Figure 1). Acetylene and $\text{PM}_{2.5}$ EC reached daily maximum concentrations in Pasadena between 12:00 and 13:00 PDT after being transported from downtown LA over the course of a few hours. Only minor enhancements were observed between 6:00 and 9:00 PDT from local morning rush-hour traffic.

[14] Secondary gas and aerosol components followed behind the arrival of primary species, coupled to both transport and photochemical processes. Diurnal maximum concentrations of gaseous photochemical products, such as acetaldehyde, formic acid, and WSOC_g , occurred at 13:30 PDT, which is near the peak for solar insolation and after primary emissions reached their peak (Figure 1). Secondary organic aerosol components, including oxalate and WSOC_p , then followed the secondary gases, with daily maximum concentrations approximately 1 h later than the gases, indicating a gas-to-particle conversion process (Figure 1).

[15] The complete study time series shows that gas and particle phase formic acid had consistent and clear diurnal trends (Figure 2). Both gas and particle phase formic acid followed other photochemical gas/particle products with peak concentrations in the early afternoon (Figure 1). However, the diurnal trends in both gas and particle phase formic acid were generally broader than other secondary gas and particle species (e.g., WSOC), and particle formic acid had a

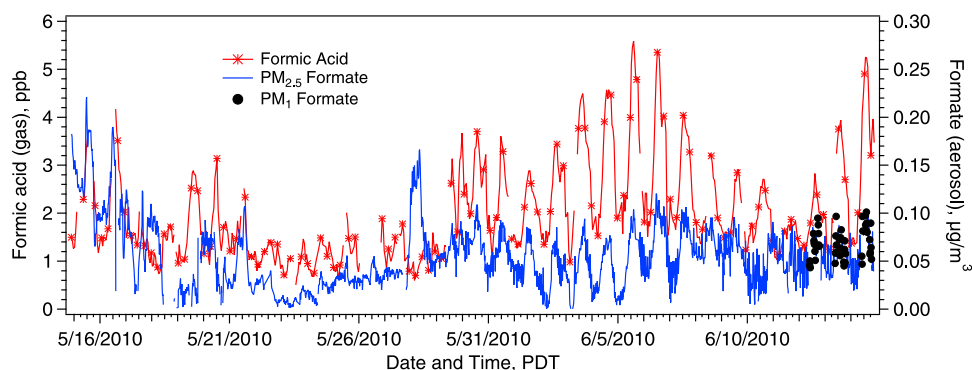


Figure 2. Los Angeles time series of gaseous (HCOOH) and particulate (HCOO^-) formic acid measured during CalNex (15 May 2010 to 15 June 2010) on the campus of the California Institute of Technology. At the end of the study (12 June–15 June 2010), the formate sample inlet was alternated between a PM_{10} and $\text{PM}_{2.5}$ cyclone during daylight sampling periods.

daily concentration peak that was closer in time to the peak of the gas phase components (13:30 PDT), compared to other SOA components (WSOC_p , oxalate) that peaked at $\sim 14:30$ PDT (Figure 1).

[16] For the entire CalNex-LA study, gaseous formic acid was in the range of 0.37 ppbv to 5.86 ppbv and had an average concentration of 1.89 ± 0.59 ppbv (mean $\pm 1\sigma$, $n = 731$) (see Table 2 for a summary). The data are consistent with previous studies in urban environments [Kawamura and Kaplan, 1985; Grosjean, 1988]. For the aerosol phase, the range of $\text{PM}_{2.5}$ formate concentrations observed during the entire campaign was from the LOD ($0.02 \mu\text{g}/\text{m}^3$) to $0.21 \mu\text{g}/\text{m}^3$ and the mean formate concentration was $0.054 \mu\text{g}/\text{m}^3$. Most formate was associated with particles below $1 \mu\text{m}$ since little difference was observed between PM_{10} and $\text{PM}_{2.5}$ concentrations ($\text{PM}_{10}/\text{PM}_{2.5}$ mean $\sim 104\% \pm 17\%$, $n = 18$), when PM_{10} and $\text{PM}_{2.5}$ cyclones were interchanged during daylight periods of the final week of sampling (Figure 2).

Table 2. Summary of Gas and Particulate Phase Formic Acid Concentrations and Partitioning Ratio (p/g, Given in %), for Los Angeles (LA) and Atlanta (ATL)

	Mean	Median	Min	Max	Stdev
<i>Concentrations</i>					
Formic acid (HCOOH), LA (ppbv)	1.89	1.61	0.37	5.86	0.59
Formic acid (HCOOH), ATL (ppbv)	2.79	2.29	0.12	7.93	1.01
Formate (HCOO^-), LA (ng/m^3)	54	49	LOD ^a	210	34
Formate (HCOO^-), ATL (ng/m^3)	43	39	LOD ^a	130	21
<i>Formic Acid p/g in Percentage in LA</i>					
p/g for whole campaign (%)	1.64	1.31	0.01	11.9	1.35
p/g during night (8 pm–8 am next day ^b) (%)	1.84	1.43	0.01	11.9	1.61
p/g during day (8 am–8 pm) (%)	1.38	1.24	0.05	8.63	0.87
p/g during overcast periods (%)	3.67	2.88	0.43	11.9	2.64
<i>Formic Acid p/g in Percentage in ATL</i>					
p/g for whole campaign (%)	1.08	0.83	0.20	5.83	0.74
p/g during night (8 pm–8 am next day ^c) (%)	1.33	1.10	0.35	5.83	0.85
p/g during day (8 am–8 pm) (%)	0.82	0.69	0.20	3.53	0.49

^aLOD = $0.02 \mu\text{g}/\text{m}^3$.

^bSampling times are in PDT (Pacific Daylight Time).

^cSampling times are in EDT (Eastern Daylight Time).

[17] Formic acid was predominately found in the gas phase with particle-to-gas (p/g) ratios typically between 1 to 2% throughout the study (Table 2). Ratios from previous studies generally range from 0.8 to 10% [Chebbi and Carlier, 1996; Baboukas et al., 2000; Löflund et al., 2001]. The high volatility and resulting minor partitioning to the particle phase may partially explain why the average diurnal trend of particle formic acid tended to track the gas phase species, instead of other SOA components that probably undergo further partitioning processes or are formed within the particle (or aqueous) phase, such as oxalate and WSOC_p (WSOC_p p/g ratios are closer to 10 to 20% [Zhang et al., 2012a]).

[18] The LA study mean \pm standard deviation formic acid p/g ratio was $1.6\% \pm 1.3\%$, but at times the ratio reached up to 10%. Highest partitioning to the particle phase observed in LA occurred during a few unique periods when partitioning to liquid water was most apparently observed. Factors that may contribute to this variability are investigated.

3.2. Los Angeles Formic Acid Partitioning

[19] Gas-phase formic acid could partition to the particle phase through absorption to the preexisting organic phase, or undergo dissolution into aerosol water, or some combination of both. A schematic of possible partitioning routes for formic acid is shown in Figure 3. Due to its high solubility (Henry's law constant at 20°C is $\sim 4 \times 10^5 \text{ M}/\text{atm}$

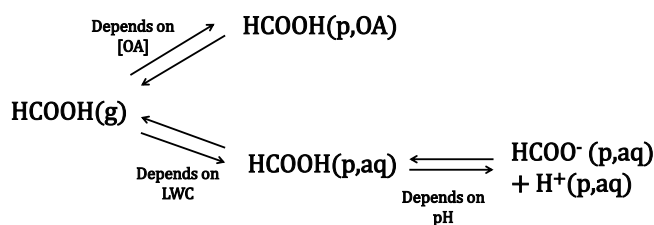


Figure 3. Schematic representation of possible partitioning routes for formic acid. OA stands for the total organic aerosol mass, or some sub-fraction that formic acid could partition to, while (p, aq) represents another route where formic acid undergoes dissolution into aerosol water and then resides in the condensed phase.

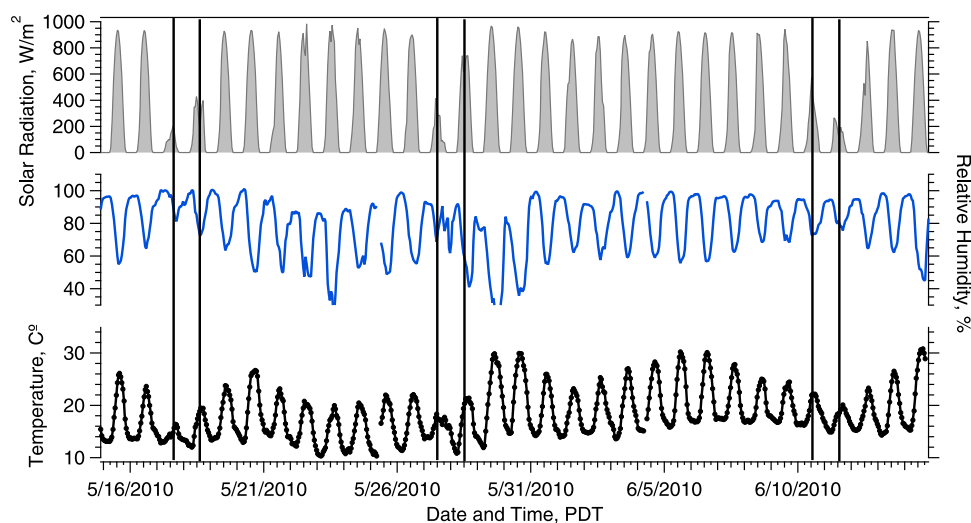


Figure 4. Los Angeles time series of solar radiation, temperature and relative humidity during the CalNex-LA campaign (15 May 2010 to 15 June 2010), with three overcast periods (14:30 May 17 to 9:30 May 18, 22:30 May 27 to 15:30 May 28, and 12:30 June 10 to 12:30 June 11, 2010, PDT) identified by times between vertical lines.

[Chameides, 1984; Lelieveld and Crutzen, 1991]), partitioning to the aqueous fraction of aerosols may be expected if particle water is present. Chang *et al.* [2010] performed a model simulation of overall SOA formation in the Los Angeles basin and found that SOA partitioning to both organic and aqueous phases are important and that the aqueous phase becomes more important during periods of low SOA concentrations. Similar behavior was observed for formic acid in this study.

[20] The regular diurnal temperature and relative humidity (RH) trends during the LA study are shown in Figure 4. During CalNex, RH often reached over 90% by midnight and remained at or near saturation levels until sunrise. RH rarely fell below 60% at its lowest point in mid-afternoon (Figure 4). Despite the expected higher nighttime particle water concentrations and formic acid's relatively high solubility, observed formic acid p/g ratios generally did not have a strong dependence on time of day (Figure 5a), or RH (Figure 6a), although p/g ratios were slightly more variable at night when RH was highest (Figure 5a). Part of this variability in the average diurnal profile occurred during unique isolated periods of overcast conditions when formic acid p/g ratios did not follow RH trends. The median p/g value ranged from 1.33 to 1.77% at night (20:00–08:00 PDT) and 1.15–1.43% during day (08:00–20:00 PDT). However, during the three overcast periods shown in Figure 4 (14:30 May 17 to 9:30 May 18, 22:30 May 27 to 15:30 May 28, and 12:30 June 10 to 12:30 June 11, 2010, PDT), the p/g ratio was substantially higher than the study mean values (Figures 5b and 6b). Apart from these unique episodes, the formic acid p/g ratio seemed largely independent of RH (e.g., particle water) suggesting partitioning to some other phase, possibly the organic aerosol phase.

[21] In the following analysis, formic acid partitioning is investigated for the two types of periods discussed: (1) when

formic acid appeared to be related to RH (partitioning to liquid water) and (2) when the dependence on liquid water was not as evident.

3.2.1. Los Angeles Formic Acid Partitioning to Particle Water

[22] The overcast periods, when formic acid tracked RH, were associated with much lower daytime concentrations of photo-chemically generated species. For example, during the same time of day (11:30–17:30 PDT), HNO₃ concentrations were one-fifth, WSOC_g approximately one-half and gaseous formic acid less than one-third of the respective study average concentrations. Daytime temperatures were slightly lower than non-overcast conditions (Figure 4), which could further favor partitioning to the particle phase. HYSPLIT (R. R. Draxler and G. D. Rolph, HYSPLIT (Hybrid Single - Particle Lagrangian Integrated Tracker) Model, 2012, <http://ready.arl.noaa.gov/HYSPLIT.php>; G. D. Rolph, Real-time Environmental Applications and Display sYstem (READY) Website, 2012, <http://ready.arl.noaa.gov>) back-trajectory calculations do not indicate a common air mass source region during these three overcast periods (auxiliary material Figure S2).

[23] Uptake of gas phase formic acid by aerosol water can be investigated most simply by assuming the gas and particle are in equilibrium and comparing measured p/g ratios to those predicted by Henry's law, assuming ideal solution behavior. Under these assumptions the expected formic acid p/g ratio is:

$$\frac{[\text{HCOO}^-]_p}{[\text{HCOOH}]_g} = K_H * \text{LWC} * \frac{K_a}{[\text{H}^+]} \quad (1)$$

where LWC is the particle liquid water concentration, K_H the Henry's law constant for formic acid, K_a the formic acid dissociation constant, and [H⁺] the hydrogen ion concentration

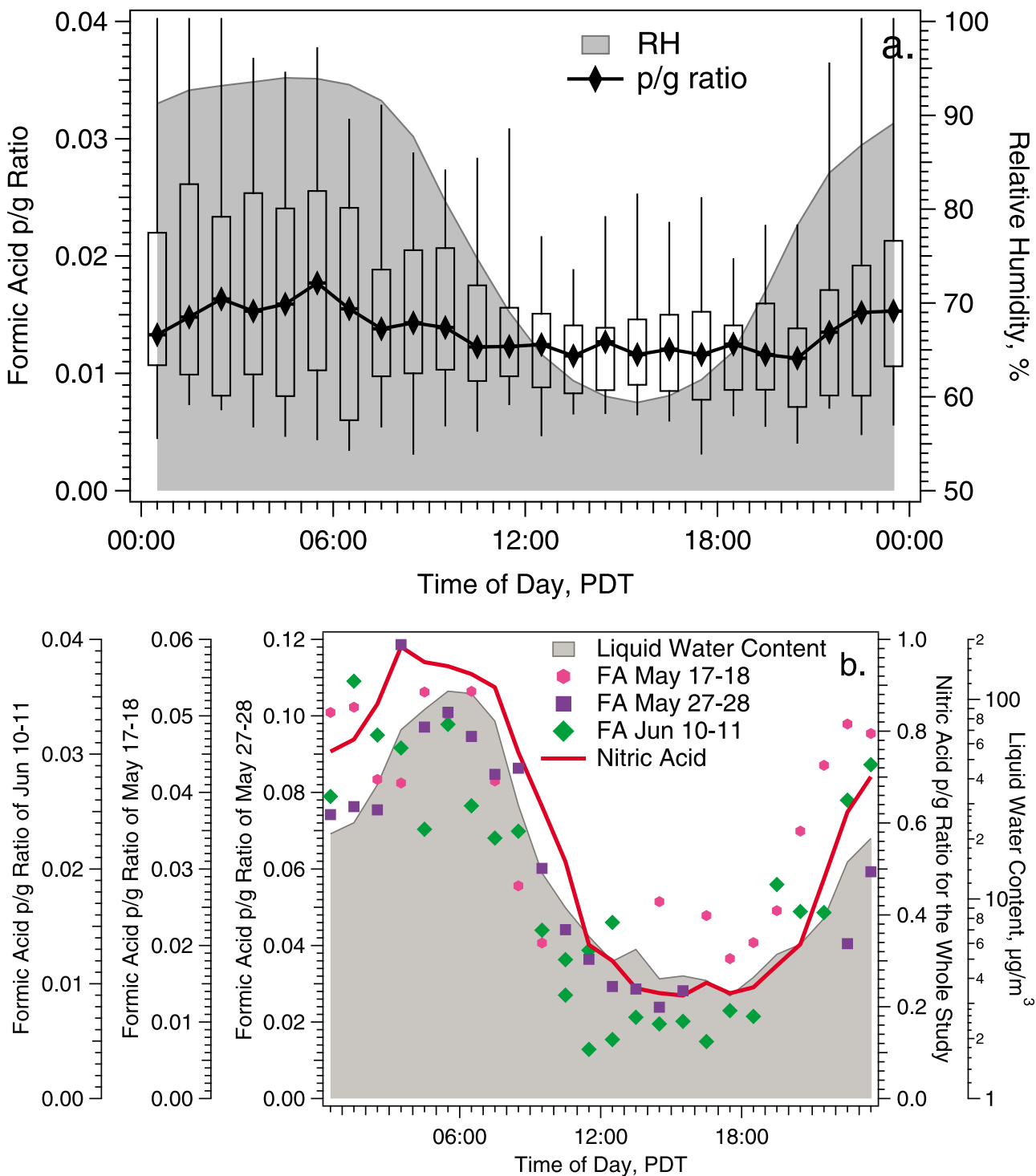


Figure 5. Los Angeles (a) diurnal profile of formic acid p/g ratios and RH, and (b) hourly averaged data for the three overcast periods as well as the diurnal profiles of nitric acid p/g ratio and LWC. In Figure 5a, median values (data point within box), 25th and 75th percentiles (lower and upper box bounds), and 10th and 90th percentiles (lower and upper whiskers) of hourly binned data are plotted. Note the p/g scale differences in Figures 5a and 5b.

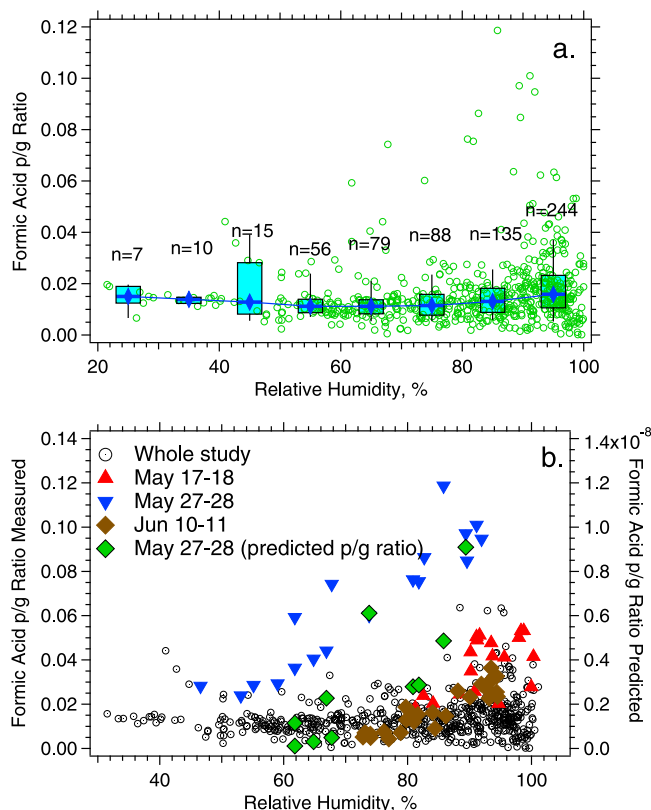


Figure 6. CalNex-LA formic acid p/g ratios as a function of RH with (a) p/g statistical results for data binned by 10% RH intervals and number of data points in each bin, and (b) all data and specific overcast periods identified in Figure 4, as well as formic acid p/g ratio predicted by Henry's law during overcast period May 27–28. Box plot description is given in Figure 5.

(mol/L). Both K_H and K_a depend on temperature, and were calculated using ambient temperatures by:

$$K_H(T) = K_H^0 * \exp\left(d(\ln(k_H))/d(1/T) * \left(\frac{1}{T} - \frac{1}{298.15 \text{ K}}\right)\right) \quad (1')$$

$$K_a(T) = K_a^0 * \exp\left(151 * \left(\frac{1}{T} - \frac{1}{298.15 \text{ K}}\right)\right) \quad (1'')$$

where, $K_H^0 = 3.7 \times 10^3 \text{ mol/kg}\cdot\text{bar}$, $d(\ln(k_H))/d(1/T) = 5700 \text{ K}$, $K_a^0 = 1.8 \times 10^{-4} \text{ M}$ [Chameides, 1984; Lelieveld and Crutzen, 1991]. The application of Henry's law assumes the aerosols have deliquesced.

[24] In the following analysis we apply pH predicted by R. A. Ellis et al. (Gas-particle partitioning of ammonia at the CalNex-LA ground site and the influence of aerosol pH, manuscript in preparation, 2012) determined from the Extended-Aerosol Inorganic Model (www.aim.env.uea.ac.uk/aim/aim.php) [Wexler and Seinfeld, 1991; Wexler and Clegg, 2002] into equation (1). Although predicting aerosol pH can be highly uncertain [Yao et al., 2006], Ellis et al. (manuscript in preparation, 2012) show that pH is better constrained through measurements of both aerosol ions and gas phase ammonia, as was done during CalNex. Aerosol water (LWC) was predicted by thermodynamic models (ISORROPIA-II or E-AIM, results were similar).

Measurements and thermodynamic models show that aerosol water concentrations are largely determined by inorganic salt concentrations, with studies showing a deviation smaller than $\sim 15\%$ among inorganic models [Fountoukis et al., 2009, and references therein]. Other studies suggest not including organic species can produce errors in predicted LWC of up to $\sim 20\%$ [Speer et al., 2003; Aggarwal et al., 2007]. (Note, including measured concentrations of organic acids in the E-AIM calculations had little effect on predicted LWC; $<3\%$ in this study).

3.2.1.1. Measured Formic Acid Partitioning Compared to Henry's Law

[25] The three periods showing the clearest formic acid p/g dependence on RH were all associated with a clear diurnal trend in RH, weak photochemistry due to low solar radiation, and significant variation in formic p/g ratios. RH was mostly above 70% during the three periods, prompting the assumption that particles were often deliquesced and thus Henry's law is applicable.

[26] The formic acid p/g ratio predicted by equation (1) has a RH dependence similar to the observed ratio (Figure 6b), but is roughly 7 orders of magnitude lower, suggesting essentially no partitioning to the particle phase. For these periods the predicted LWC values ranged from 5 to $40 \mu\text{g}/\text{m}^3$ and particle pH 3.24–4.57 (mean \pm std pH = 3.88 ± 0.34). In contrast, based on the predicted LWC and observed formic acid p/g ratio, a pH of 9.31 ± 0.60 is predicted for formic acid to conform to Henry's law, which is not reasonable since

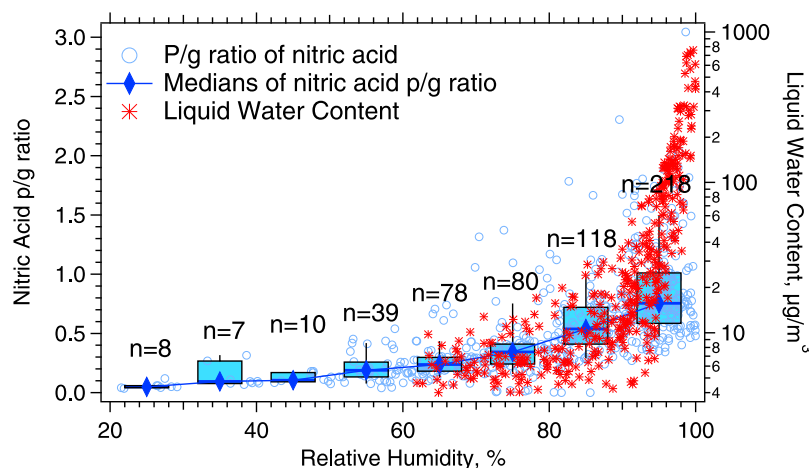


Figure 7. Los Angeles p/g ratios of nitric acid as a function of ambient RH. AMS non-refractory PM₁ nitrate is used to determine the ratio. Box plot description is given in Figure 5. Also included is the ISORROPIA-II predicted liquid water content (LWC) using PM₁ ammonium, sulfate and nitrate data by AMS. LWC is plotted on a log scale since at RH greater than roughly 95% it is predicted to increase dramatically.

most previous studies showed acidified aerosol particles in urban environments impacted by marine aerosols [Keene *et al.*, 2004; Yao *et al.*, 2006].

[27] Under-prediction of PM_{2.5} formate concentrations by Henry's law may be due to several reasons. Formic acid p/g ratios are highly sensitive to pH, and uncertainty in pH of the particle fractions that the gas phase is partitioning to, is potentially a large source of error. Past studies have noted that pH can also vary with aerosol size [Keene *et al.*, 2004]. There are uncertainties related to the LWC prediction due to the role of organics, but as noted above these are likely small. Other uncertainties associated with using bulk measurements and unknown particle mixing state are possible, including variability in particle water between different particles and other components that may interact with formic acid but are not included in the models (e.g., amines, carbonates). The assumption that formic acid partitions to an ideal solution is also likely not true at all times during the overcast periods, given that many inorganic ions are present. However, considering non-ideal solution behavior does not significantly change the large discrepancy; E-AIM estimated formic acid activity coefficients could increase the predicted formic acid p/g ratio by at most roughly a factor of 10 under the lowest RH of the overcast periods. Finally, production of formate in the aerosol phase through heterogeneous processes followed by a process that inhibits evaporation, such as the formation of oligomers, could also account for the higher than expected formate p/g ratios.

[28] Similar formic acid discrepancies from an aqueous equilibrium state have also been reported [Keene *et al.*, 2004; Healy *et al.*, 2008] based on filter sampling methods. Keene *et al.* [2004] found that formic acid was expected to partition almost exclusively to the gas phase. Significant particle concentrations were, however, detected. They argued that this discrepancy might have been due to positive artifacts related to filter sampling. Our online measurements, which may be less susceptible to artifacts, are consistent with these filter-based studies. A similar enhanced partitioning has been observed for other soluble atmospheric components,

including hydrogen peroxide [Arellanes *et al.*, 2006], carbonyls [Matsunaga *et al.*, 2005], dicarbonyls [Healy *et al.*, 2008; Volkamer *et al.*, 2009], and bulk water-soluble organic carbon (WSOC) [Hennigan *et al.*, 2008].

3.2.2. Los Angeles Formic Acid Partitioning During Periods of No Observed RH Dependence

[29] Highest formic acid concentrations for both gas and particulate phases occurred during daytime hours, peaking in the early afternoon when other photo-chemically derived compounds (including nitric acid, several organic acids and WSOC_g) were also at their highest concentrations [Veres *et al.*, 2011], indicating that photochemistry contributed to formation of both gas and particle phases. Further evidence for photochemical sources for formic acid is indicated by a significant weekend enhancement in both, relative to weekdays. Gas phase formic acid mixing ratios were 1.2 times higher on the 5 weekends (10 days) during the study relative to weekdays, and similarly PM_{2.5} formate levels were 1.3 times higher. The difference is thought to be due to higher weekend oxidant concentrations (e.g., O₃ was 1.4 times higher on weekends) resulting from a significant reduction in NO_x emissions on weekends relative to weekdays [Bahreini *et al.*, 2012; Pollack *et al.*, 2012].

[30] Although concentrations of gas and particle formic acid were highest during the early afternoon peak in photochemical production (Figure 1), p/g ratios were lower (1.38% mean) and less variable (0.87% stdev, see Table 2) at these times compared to nighttime or overcast periods. During these afternoon photochemical periods, RH was typically at the daytime minimum of 60–70% (mean ± stdev = 62 ± 3%), and particle liquid water concentrations are generally expected to be the lowest (8.3 ± 2.8 µg/m³), in contrast to the high LWC values of greater than 40 µg/m³ when RH exceeded 95% (e.g., see Figure 7).

[31] If formic acid has multiple routes for partitioning (i.e., water or OA), it is likely that during overcast periods when OA is low (average OA concentration = 3.68 µg/m³, 54.0% of study average) the particle water route may be relatively more important; in contrast, during the photo-chemically

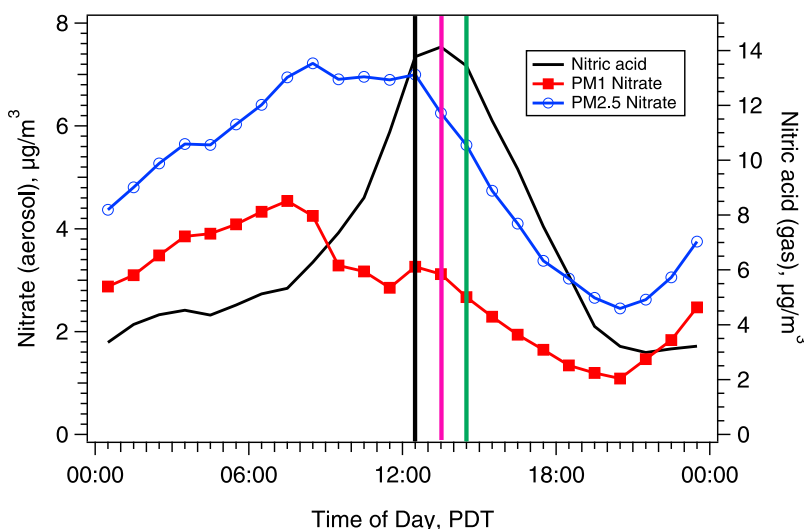


Figure 8. Los Angeles diurnal profiles of gas phase nitric acid, AMS non-refractory PM₁ nitrate, and PILS water soluble PM_{2.5} nitrate. Means of hourly binned data are plotted. The three bars represent the peak concentration timing of primary emission, secondary gases and SOA indicated in Figure 1.

active afternoon periods the opposite conditions occur: OA concentrations are at a maximum and RH (LWC) at a minimum, conditions most conducive for partitioning to OA. A rough estimation based on measured OA concentration and formic acid p/g ratio gives a partitioning coefficient (K_p) ranging from 0.00003 to 0.024 (average \pm stdev = 0.0036 ± 0.0038) $\text{m}^3/\mu\text{g}$, which are roughly three orders of magnitude higher than the theoretical value ($2.04 \times 10^{-6} \text{ m}^3/\mu\text{g}$). However, the specific component of the aerosol the formic acid partitioned to is not completely clear; no correlation was found between formic acid p/g ratio and any other aerosol components, including OA, or AMS PMF factors such as oxygenated organic aerosol (OOA), semi-volatile oxygenated organic aerosol (SV-OOA), low volatility oxygenated organic aerosol (LV-OOA) factors), or hydrocarbon-like organic aerosol (HOA) (auxiliary material Figure S3).

3.2.3. LA Nitric Acid Partitioning and RH as a Contrast to Formic Acid

[32] Like formate, aerosol nitrate is also semi-volatile (excluding nonvolatile forms, such as NaNO_3), but nitric acid forms salts and has a much higher effective K_H upon dissociation. As noted above, both gas phase formic and nitric acids had similar diurnal profiles, peaking at mid-day along with other photo-chemically generated gaseous species (Figure 1 versus Figure 8). However, while particle phase formate tended to peak in the afternoon, both AMS and PILS nitrate were usually highest in early morning (Figure 8). Note that AMS PM₁ non-refractory nitrate (e.g., dominated by semi-volatile ammonium nitrate (Hayes et al., submitted manuscript, 2012)) concentrations dropped off relative to PM_{2.5} soluble nitrate (e.g., $\text{NH}_4\text{NO}_3 + \text{NaNO}_3$) as the morning progressed, consistent with the more volatile NH_4NO_3 responding to increasing daytime temperatures.

[33] The contrasts in the particle phase formate and nitrate diurnal profiles are consistent with differences in formic and nitric p/g ratios relative to RH (particle water). Whereas the formic acid p/g ratio generally did not track RH, nitric acid p/g ratios did follow RH (Figures 5b and 7). This contrast between the relationship of formic acid and nitric acid p/g

ratio with RH further supports the idea that the partitioning of formic acid is not dominated by partitioning to aerosol water; other absorption media possibly exist, such as the organic aerosol fraction. Although there was no evidence showing the partitioning of formic acid was correlated to OA, WSOC was observed to correlate with both RH (e.g., particle LWC) and OA [Zhang et al., 2012a].

3.3. Atlanta Formic Acid Concentrations and Partitioning

[34] Observed gas and particle phase formic acid concentrations in Atlanta are shown in Table 2. Gas phase formic acid mixing ratios were higher in Atlanta (LA median of 1.61 ppbv, Atlanta median of 2.29 ppbv) and particle phase formate levels were slightly lower in Atlanta (LA median of 49 ng/m^3 versus Atlanta median of 39 ng/m^3). The time series of both gas and particle phase formic acid were not nearly as regular in Atlanta as LA (Figure 9), which is expected due to the significantly different meteorological and topographical differences between these two sites: LA is bordered by the Pacific Ocean to the West and San Gabriel Mountains to the Northeast, whereas Atlanta is a continental setting lacking nearby major geological features. In general average diurnal profiles show peak gas and particle formic acid concentrations later in the afternoon (15:30 Eastern Daylight Time (EDT)), suggesting a link to photochemical sources, but roughly three hours later than the peak in solar insolation (12:30 EDT) (Figure 10). Curiously, this is the same time that oxalate concentrations reached a maximum (although a small peak relative to a large background) and both may be at least partially due to transport from aloft [Zhang et al., 2012a]. These organic acid peaks are not well synchronized with the overall WSOC_g or WSOC_p , except that the gaseous phase formic acid and WSOC_g began to increase together in the early morning (07:30 EDT), while formate and WSOC_p increased together later in the morning (09:30 EDT). Like WSOC_g , gas phase formic acid maintained fairly high concentrations until evening (18:00 EDT) and then dropped off more rapidly in the morning, whereas

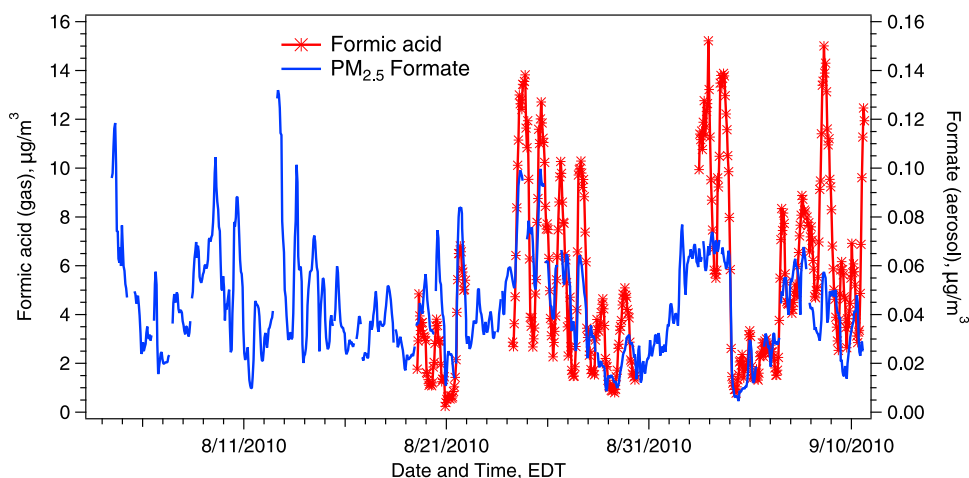


Figure 9. Atlanta time series of gaseous and particulate formic acid measured on the campus of the Georgia Institute of Technology from 3 August 2010 to 10 September 2010.

formate concentrations dropped off in the afternoon and maintained fairly consistent levels until the morning increase. The result is that the formic acid p/g ratio tended to be higher in the early morning hours (02:00–08:00), a period of high RH. The same was observed for WSOC, but the extent of WSOC partitioning to the particle phase in the early morning was even stronger [Zhang *et al.*, 2012a].

[35] The study average formic acid p/g ratio in Atlanta was on the order of 1% (Table 2), slightly lower than LA, but with a more pronounced diurnal variation and more of the extremes biased to higher p/g ratios (Figure 11). Gas phase formic acid concentrations were on average higher in Atlanta (Atlanta mean \pm stdev = 2.79 ± 1.01 ppbv, LA = 1.89 ± 0.59 ppbv) while particle phase concentrations were slightly lower (Table 2). In contrast to LA, Atlanta formic acid partitioning generally had a more consistent relationship to RH

(although not as clear following sunset), and hence apparently to particle water. This can be seen in both the average diurnal profile (Figure 11) and the binned p/g ratio versus ambient RH (Figure 12), although less data at high RH in Atlanta makes this comparison less robust.

3.4. Formic Acid Partitioning Absorbing Phases: LA Versus Atlanta

[36] A difference in RH-partitioning dependence between LA and Atlanta was also observed for the bulk WSOC measured during these studies [Zhang *et al.*, 2012a]. In LA, WSOC partitioning appeared to be linked to an absorbing phase correlated with OC as opposed to RH, whereas in Atlanta, WSOC partitioning was linked to RH, but not OC, when RH was greater than $\sim 70\%$ (i.e., when LWC is sensitive to RH). When the particles were drier (i.e., RH less than

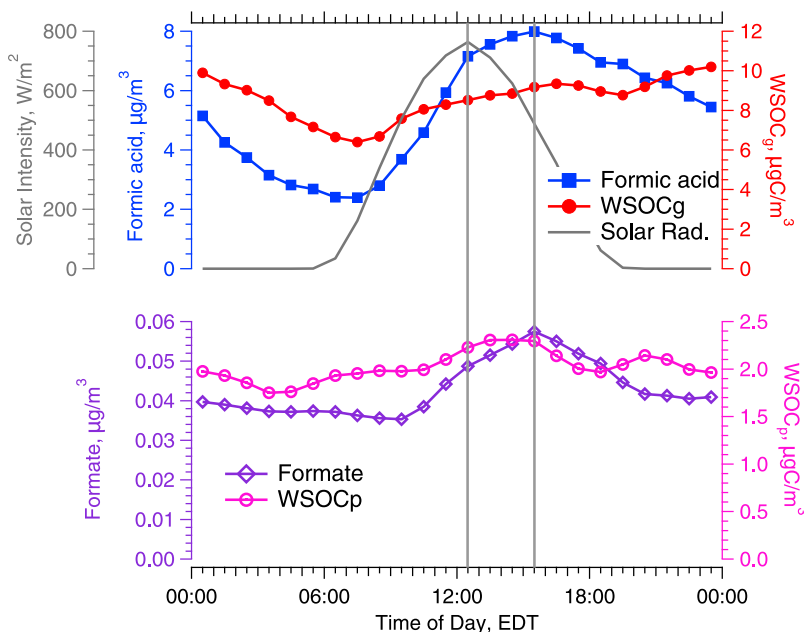


Figure 10. Atlanta diurnal profiles of WSOC_g and gas phase formic acid, and PM_{2.5} WSOC_p and formate, as well as solar radiation. Means of hourly binned data are plotted.

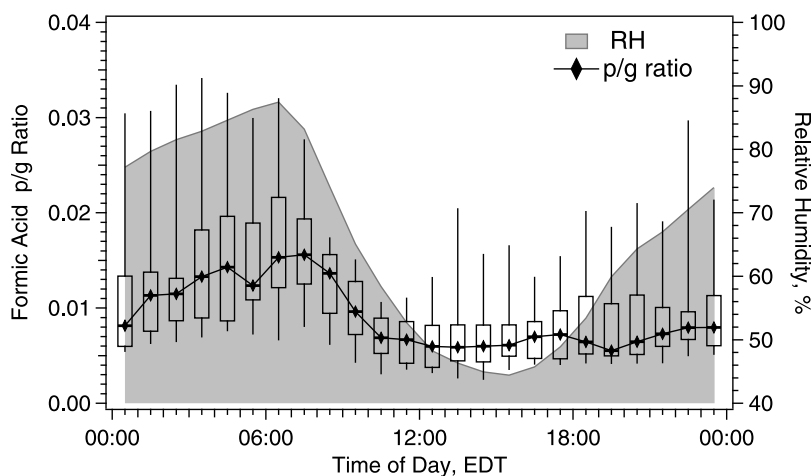


Figure 11. Atlanta diurnal profile of formic acid p/g ratios and RH based on averages of hourly binned data. Box plot description is given in Figure 5.

~70%), there was evidence that WSOC partitioning correlated with OC in Atlanta. Thus, in a general sense, WSOC and formic acid may partition to similar absorbing phases in both locations: more likely the organic components in LA (or some fraction within), but in Atlanta partitioning to particle water seems more prevalent.

[37] Causes for the differences in formic acid absorbing phases between these two cities may be due to a number of factors.

[38] 1. *Differences in aerosol liquid water content.* The extent of absorption to particle water or organic mass is sensitive to the mass of the absorbing phase available. The LA experiment was in May/June, whereas the Atlanta experiment was in August/September with generally higher temperatures and lower RH's compared with LA (Figure 13). Zhang *et al.* [2012a] used the inorganic species concentrations and found that ISORROPIA-II predicted similar LWC levels at two sites for $RH < 70\%$, but higher LWC in LA at $RH > 70\%$. By this calculation, there was typically more

liquid water available in LA, while observation suggests a greater preference of Atlanta WSOC and formic acid to partitioning to particle water, relative to LA.

[39] 2. *Differences in OA concentrations.* The theory of equilibrium absorptive partitioning to the organic phase predicts that the particle-to-gas ratio will depend on the concentration of the absorbing phase, in this case possibly OA [Pankow, 1994], or some component of the OA (e.g., polar organic compounds). In LA, during overcast periods when formic acid partitioned to water, OA was significantly lower than other periods of the study ($3.68 \mu\text{g}/\text{m}^3$ versus study average of $6.81 \mu\text{g}/\text{m}^3$) making the aqueous phase a more favorable route for partitioning. However, the OA concentration differences between LA and Atlanta are not significant; during these two studies LA AMS OA was on average $6.81 \mu\text{g}/\text{m}^3$, while ATL OA was at $\sim 5.09 \mu\text{g}/\text{m}^3$ (estimated by $OC \times 1.6$ for urban aerosols [Turpin and Lim, 2001]). Differences in polar organic concentrations, which may be a more likely absorbing phase for formic acid, or the

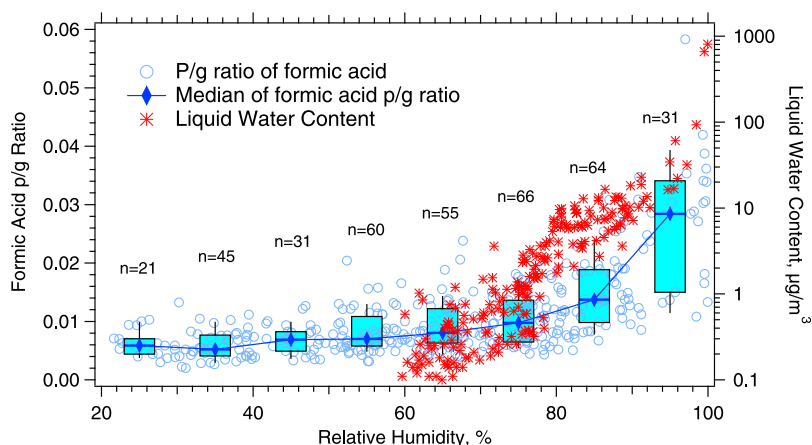


Figure 12. Atlanta p/g ratios of formic acid as a function of ambient RH. Box plot description is given in Figure 5. ISORROPIA-II predicted liquid water content (LWC) was based on $\text{PM}_{2.5}$ sulfate and nitrate measurements and ammonium assumed to be in ion balance with the anions. LWC is plotted on a log scale since at RH greater than roughly 95% it is predicted to increase dramatically.

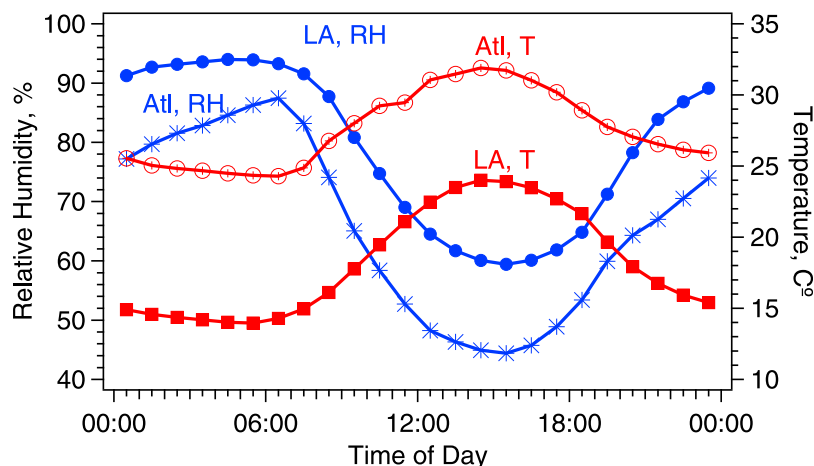


Figure 13. Meteorological conditions in Los Angeles and Atlanta during study periods. Means of hourly binned data are plotted.

relative polarity of organic aerosols between these two cities, may be a more likely explanation for partitioning preferences of formic acid.

[40] 3. *Differences in liquid water pH.* As a weak acid, formic acid partitioning is greatly influenced by the solution pH (equation (1)). One characteristic of LA ambient air is the high levels of nitric acid that could serve as a strong acid reservoir readily available to partition to water as particle LWC responds to changing RH. During the overcast periods of low photochemistry in LA, nitric acid levels were one-fifth the study average and so a droplet pH closer to neutral is expected and would favor formic acid absorption to liquid water at that time. However, the calculated pH for the overcast periods was not significantly closer to neutral compared to other times, but predicted pHs are uncertain so the possible role of nitric acid is not clear. High concentrations of nitric acid in LA could generally suppress formic acid dissolution and account for little variability in diurnal trends in formic acid p/g ratio. Significantly lower levels of nitric acid in Atlanta may account for a greater partitioning preference to water. Based on measured values, average nitric acid was ~ 2.5 ppbv during CalNex and ~ 1.5 ppbv in Atlanta during the 1999 supersite. Whether this is a viable explanation for differences in formic acid partition is not clear, but the effect of pH would only influence a fraction of the WSOC. Given that roughly half the $WSOC_p$ is acidic [Sullivan and Weber, 2006], it is doubtful that pH alone explains differences in partitioning preferences of WSOC in these two cities.

[41] 4. *Differences in organic aerosol composition.* Aerosol composition can influence partitioning by affecting the physical properties of the absorbing organic phase, and to a lesser extent the particle LWC. Aerosol composition is linked to differences in emissions, dispersion and transport, and length of time for atmospheric aging processes. Differences in all these categories exist between LA and Atlanta. In terms of organic components, LA emissions are largely anthropogenic, whereas Atlanta is a mix of biogenic and anthropogenic. LA has a clean upwind sector (Pacific Ocean), a regular land-sea breeze and limited dispersion due to local topology. Atlanta is situated in a mid-continental region with significant biogenic emissions and prevailing winds. Thus, LA has a substantial buildup of fresh anthropogenic SOA

(with $\Delta WSOC = 1.23 \mu\text{gC}/\text{m}^3$, where $\Delta WSOC$ is a proxy for fresh SOA and Δ implies day minus night), whereas in Atlanta greater dispersion and a large regional background results in only a minor increase in fresh SOA ($\Delta WSOC = 0.56 \mu\text{gC}/\text{m}^3$) that rides on the large regional signal [Zhang *et al.*, 2012b] of aged organics mainly from biogenic emissions [Weber *et al.*, 2007]. This is also evident in the WSOC/OC ratios, where in LA (with OC based on AMS data) the WSOC/OC ratio was 37%, in contrast to the Atlanta ratio of 62%. Thus it is expected that the Atlanta accumulation mode aerosol would be more oxygenated [Simon *et al.*, 2011]. Differences in concentrations of inorganic components may also have some influence. LA is dominated by NH_4^+ , NO_3^- and SO_4^{2-} , whereas Atlanta is dominated by NH_4^+ and SO_4^{2-} . Complex interactions between inorganic/organic (polar/non-polar) particle components as a function of O/C ratios have been shown to impact particle interactions with water, resulting in phase separations and transitions between various phases as a function of RH [Bertram *et al.*, 2011]. These processes could play some role in explaining the differences in formic acid partitioning between LA and Atlanta.

4. Conclusions

[42] Gas and particle concentrations of formic acid, and factors affecting formic acid particle/gas ratios, are presented based on summer measurements made during separate one-month studies in Los Angeles, CA, and Atlanta, GA, USA. In both studies gas phase formic acid was measured via NI-PT-CIMS and particle formate with a PILS-IC setup to provide continuous data at a 20-min duty cycle or faster.

[43] Gas phase formic acid concentrations were moderately higher in Atlanta (LA median 1.61 ppbv; Atlanta median 2.29 ppbv), whereas particle phase concentrations were higher in LA (LA median 49 ng/m^3 , Atlanta median 39 ng/m^3). Similar diurnal patterns of higher daytime and lower nighttime gas and particle concentrations were observed in both cities, but in LA the gaseous and particle phase formic acid daily trends closely followed most other secondary gas species, whereas in Atlanta they were not as synchronized with other secondary compounds. In LA, photochemistry is clearly a major contributor to formic acid formation; in

Atlanta transport (e.g., variation in air mass origin) may play a larger role in the diurnal trends, along with photochemistry.

[44] Formic acid p/g ratios were on the order of a few percent (1–2%) in both cities. In LA, for the most part, no specific component of the aerosol was correlated with p/g ratios, so the exact nature of the absorbing phase remains unclear; although based on overall WSOC partitioning behavior [Zhang et al., 2012a], partitioning to OA, or some component of the OA, may be possible route. Formic acid p/g ratios in LA depended little on RH, except on three brief occasions that were all characterized by overcast conditions with little daytime photochemical production. Henry's Law predicts very little partitioning to water, based on particle LWC and pH inferred from thermodynamic models. Including non-ideal solution behavior still significantly underpredicts the particle phase concentrations. In contrast to formic acid, nitric acid partitioning is linked to ambient RH throughout the CalNex-LA study.

[45] In contrast to practically no RH-dependence in LA, formic acid had a clearer trend of partitioning to liquid water in Atlanta based on correlations with ambient RH, despite lower RHs and lower calculated liquid water in Atlanta. This contrast is similar to differences in bulk WSOC partitioning also measured in these two cities during these studies [Zhang et al., 2012a]; WSOC preferentially partitioned to OA in LA, whereas in Atlanta when particles were expected to have deliquesced (RH > 70%), WSOC partitioning was related to RH. Causes for the observed differences in partitioning preferences for formic acid and WSOC between LA and Atlanta are not known, but one of the biggest differences between these two cities is likely the composition of the secondary organic aerosol resulting from differences in VOC emissions.

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