Transport-driven aerosol differences above and below the canopy of a mixed deciduous forest

Alexander A.T. Bui[1], Henry W. Wallace[1, a], Sarah Kavassalis[2], Hariprasad D. Alwe[3], James H. Flynn[4], Matt H. Erickson[4, b], Sergio Alvarez[4], Dylan B. Millet[3], Allison L. Steiner[5], Robert J. Griffin[1, 6]

[1] Department of Civil and Environmental Engineering, Rice University, Houston, TX, 77005, USA
[2] Department of Chemistry, University of Toronto, Toronto, ON, M5S 3H6, Canada
[3] Department of Soil, Water, and Climate, University of Minnesota, St. Paul, MN 55108, USA
[4] Department of Earth and Atmospheric Sciences, University of Houston, Houston, TX, 77204, USA
[5] Department of Climate and Space Sciences and Engineering, University of Michigan, Ann Arbor, MI, 48109, USA
[6] Department of Chemical and Biomolecular Engineering, Rice University, Houston, TX, 77005, USA
[a] now at: Washington State Department of Ecology, Lacey, WA, 98503, USA
[b] now at: TerraGraphics Environmental Engineering, Pasco, WA, 99301, USA

Correspondence to: Robert J. Griffin (rob.griffin@rice.edu)

Abstract. Exchanges of energy and mass between the surrounding air and plant surfaces occur below, within, and above a forest's vegetative canopy. The canopy also can lead to vertical gradients in light, trace gases, oxidant availability, turbulent mixing, and properties and concentrations of organic aerosols (OA). In this study, a high-resolution time-of-flight aerosol mass spectrometer is used to measure non-refractory submicron aerosol composition and concentration above (30m) and below (6m) a forest canopy in a mixed deciduous forest at the Program for Research on Oxidants: Photochemistry, Emissions, and Transport tower in northern Michigan during the summer of 2016. Three OA factors are resolved using positive matrix factorization: more-oxidized oxygenated organic aerosol (MO-OOA), isoprene-epoxydiol-derived organic aerosol (IEPOX-OA), and 91Fac (a factor characterized with a distinct fragment ion at *m/z* 91) from both the above- and below-canopy inlets. MO-OOA was most strongly associated with long-range transport from more polluted regions to the south, while IEPOX-OA and 91Fac were associated with shorter-range transport and local oxidation chemistry. Overall vertical similarity in aerosol composition, degrees of oxidation, and diurnal profiles between the two inlets was observed throughout the campaign, which implies that rapid in-canopy transport of aerosols is efficient enough to cause relatively consistent vertical distributions of aerosols at this scale. However, four distinct vertical gradient episodes are identified for OA, with vertical concentration differences (above-canopy minus below-canopy concentrations) in total OA of up to 0.8 $\mu g/m^3$, a value that is 42% of the campaign average OA concentration of 1.9 $\mu g/m^3$. The magnitude of these differences correlated with concurrent vertical differences in either sulfate aerosol or ozone. These differences are likely driven by a combination of long-range transport mechanisms, canopy-scale mixing and local chemistry. These results emphasize the importance of including vertical and horizontal transport mechanisms when interpreting trace gas and aerosol data in forested environments.

Deleted: .

Deleted:

1 Introduction

Aerosols play a key role in the energy balance of the Earth's climate system by scattering and absorbing incoming solar radiation and by impacting cloud lifetime and reflectivity (IPCC, 2007). These climatic effects depend strongly on the chemical speciation of the aerosol particles. Approximately 20-90% of submicron aerosol mass worldwide on average has been predicted to be organic material (Kanakidou et al., 2005), and this is supported by field studies in a variety of urban, urban downwind, and rural locations across the Northern Hemisphere (Jimenez et al., 2009; Zhang et al., 2007). The bulk of this organic material is thought to be secondary organic aerosol (SOA), which is formed in the atmosphere by the reaction of volatile organic compounds (VOCs) with oxidants such as hydroxyl radical (OH), ozone (O_3), nitrate radical, and chlorine atom, with the resulting products then partitioning to the particle phase.

Precursor VOCs that contribute to SOA formation are emitted from both anthropogenic and biogenic sources. Biogenic VOCs (BVOCs) primarily are emitted into the atmosphere from terrestrial vegetation, and on a global scale, emissions of BVOCs exceed those of anthropogenic VOCs (Fehsenfeld et al., 1992; Guenther et al., 2000, 1995). Major SOA precursor BVOCs include isoprene (C_5H_8) and terpenes. To date, more than 5000 terpene compounds have been identified, including monoterpenes (C_{10}), sesquiterpenes (C_{15}), and diterpenes (C_{20}) (Geron et al., 2000). However, factors such as the addition of functional groups (aldehydes, alcohols, carboxylic acids, alkyl nitrate, etc.) and the wide variety of possible reaction pathways rapidly increase the number of relevant atmospheric VOCs beyond what is initially emitted (Goldstein and Galbally, 2007).

If other loss processes, including deposition, were not considered, the final atmospheric fate of the carbon associated with BVOCs would be oxidation to carbon dioxide. However, partitioning of oxidation products to the aerosol phase as SOA interrupts this oxidation sequence. Partitioning of VOC oxidation products between the gas and aerosol phases depends on multiple factors such as the phase and concentration of pre-existing primary OA (POA) or SOA, particulate-phase SOA reactions, and the presence of aerosol liquid water (ALW) (Seinfeld and Pandis, 2006). As a result of the large number of precursor VOCs, the highly non-linear oxidation chemistry, and the presence of multiple aerosol phases in the atmosphere, SOA formation is complex and relatively poorly understood (Goldstein and Galbally, 2007).

The physical environment strongly impacts these chemical SOA formation processes. For example, in forested areas in which BVOC emissions are prevalent, the exchanges of energy and mass between the forest and the atmosphere are influenced by the forest's vegetation canopy. Absorption of light by a canopy can diminish the amount of radiation that is received below the canopy, influencing photolysis rates of photolabile species (Baldocchi et al., 1995; Brown et al., 2005; Fuentes et al., 2007; Makar et al., 2017; Schulze et al., 2017) and oxidant availability (Fuentes et al., 2007). Loss of BVOC oxidation products to deposition within the canopy also has been found to be an important factor in determining the oxidative capacity of a forested environment (Pugh et al., 2009).

Vertical transport, also influenced by the canopy, likewise impacts the concentrations of BVOC and SOA in forested environments. Roughness elements created by the leaves, branches, and stems in a dense vegetative canopy combined with above-canopy wind shear leads to coherent structures (Finnigan, 2000). These turbulent flow structures contribute to the fluxes of heat, energy, and matter in forest canopies (Thomas and Foken, 2007). The physical motion of coherent structures occurs via two main mechanisms: upward "bursts," in which air is ejected upward from the canopy into the atmosphere, and downward "sweeps," in which air is directed downward from the atmosphere into the canopy. Vertically resolved sonic anemometer measurements, which provide temperature and three-dimensional wind velocity components at each vertical measurement location, can be used to derive in-canopy mixing metrics.

The relative magnitudes of timescales for turbulent transport and chemical processing govern how trace compounds are distributed within the canopy (Baldocchi et al., 1995; Fuentes et al., 2007; Steiner et al., 2011). A modeling study by Gao et al. (1993) found that in-canopy chemical processing of isoprene occurs on a much longer timescale than turbulent transport, making in-canopy reactions less important compared to the turbulent transport and emission of isoprene in determining its

79 in-canopy concentrations. On the other hand, for compounds with an estimated chemical loss timescale that is roughly
80 equivalent to the timescales of turbulent transport (e.g., O_3-initiated oxidation of the sesquiterpene β-caryophyllene), rapid
81 in-canopy chemical loss could dominate (Stroud et al., 2005). Furthermore, partitioning to the aerosol-phase was inferred as
82 a potential reason for observations of decreased mixing ratios of oxidation products of very reactive BVOCs in a ponderosa
83 pine forest canopy (Holzinger et al., 2005).
84   Several studies have attempted to model vertical profiles of trace gases and aerosols in a forest canopy considering both
85 chemistry and turbulent transport. Bryan et al. (2012) found that forest canopy-atmosphere interactions were highly
86 sensitive to turbulent mixing parameterizations during a field campaign in northern Michigan. Differences in highly reactive
87 BVOCs and BVOC oxidation products have been estimated above and below the canopy in modeling and measurement
88 efforts (Alwe et al., 2019; Ashworth et al., 2015; Holzinger et al., 2005; Schulze et al., 2017; Stroud et al., 2005; Wolfe and
89 Thornton, 2011). Schulze et al. (2017) found that rapid through-canopy transport (minimum in-canopy residence time of 10
90 min) leads to relatively consistent simulated above- and below-canopy SOA composition and concentration.
91   Because in-canopy mixing plays a role in the vertical distribution of trace gases and aerosols in a forest canopy, vertical
92 differences in OA components and other inorganic aerosol species such as sulfate (SO_4) could be caused by the degree of
93 mixing between the above- and below-canopy environments. During the PROPHET-CABINEX 2009 campaign, the degree
94 of atmosphere-canopy coupling between the above-canopy atmosphere and the forest was analyzed by Steiner et al. (2011).
95 In this study, the degree of coupling was calculated using the ratio of the kinematic heat flux above the canopy to the
96 kinematic heat flux in the upper canopy. Opposing kinematic heat flux directions (negative ratios) imply that the below-
97 canopy environment is uncoupled from the atmosphere. In 2009, coupling conditions ranged between strong coupling
98 (greater than zero but less than the threshold value defined by the slope of a regression between the two heat fluxes), weak
99 coupling (greater than the defined threshold value), and uncoupled (negative). Uncoupled conditions occurred most
100 commonly in the early morning hours between 4AM and 8AM local time. This set of hours represents approximately 30%
101 of every day over the whole 2009 study period. This suggests that early morning hours may contribute to more instances of
102 uncoupled canopy-atmosphere conditions but that coupling between the forest canopy and the atmosphere occurs a majority
103 of the time (Steiner et al., 2011).
104   Past field studies, such as those above a tropical forest in Brazil and a temperate forest in California, found that in-
105 canopy SOA formation, deposition, and thermal gradient effects on gas-particle partitioning all influence net OA fluxes
106 (Farmer et al., 2013). In the same study, the authors found that oxygenated OA tended to deposit in the canopy, whereas the
107 forest canopy released less oxygenated OA. The source of OA fluxes between forests and the atmosphere has been
108 associated with vertical turbulent transport between the forest atmosphere and the surface layer directly above the canopy;
109 however, there have been few studies that have provided high temporal resolution measurements of both OA composition
110 throughout a forest canopy and canopy mixing strength. In a mixed forest in Ontario, Canada, Gordon et al. (2011) found
111 that the frequent occurrence of net upward aerosol flux was associated with decoupled canopy conditions where entrainment
112 of particle-free air from above the canopy created a positive flux above the forest. On the other hand, Whitehead et al.
113 (2010) found that the particle number concentration and submicron particle composition in the trunk space (i.e., below-
114 canopy) and above-canopy environments showed minimal variation with height during daytime due to stronger turbulence
115 and mixing conditions. In light of these limited studies, there is a need for additional measurements and data to inform the
116 exchange of aerosols between the forest and the atmosphere.
117   Recent work from the Program for Research on Oxidants and PHotochemistry, Emissions and Transport (PROPHET)
118 during the Atmospheric Measurements of Oxidants in Summer (AMOS) campaign in 2016 has indicated that flux of
119 isoprene and monoterpenes at the canopy-atmosphere boundary represents over half of the net carbon flux, while oxygenated
120 VOCs (OVOCs) constitute a majority of the species with detectable VOC fluxes (192 of the 236 species with identified
121 molecular formulas). The authors report that the observed and modelled net carbon flux during the campaign was upward
122 (canopy emission) during the campaign in 2016 (Millet et al., 2018). Vertical gradients of BVOCs in this mixed forest
123 environment vary greatly depending on canopy vegetation height, primary emission versus secondary production, and
124 diurnal variability (Alwe et al., 2019). Correlation analysis of VOC vertical gradients suggests that formic acid (HCOOH)

Formatted: Font: (Default) Times New Roman

Deleted: In 2009, coupling conditions ranged between strong coupling, weak coupling, and uncoupled. Uncoupled conditions

127 originates from a secondary photochemical production. During the same campaign, distinct sample-to-sample variability in
128 the molecular-level aerosol composition (73 +/- 8%) was observed despite less variability in elemental composition of the
129 bulk OA, indicating the chemical complexity of functionalized OA at the site (Ditto et al., 2018).
130   Here, measurements using an Aerodyne high-resolution time-of-flight aerosol mass spectrometer (HR-ToF-AMS) are
131 used to characterize ambient aerosol above and below the canopy in a mixed, deciduous forest during the PROPHET-AMOS
132 campaign in 2016, with the aim of evaluating quantitatively potential chemical and physical phenomena leading to observed
133 differences between particulate matter above and below the forest canopy. These measurements provide data for validation
134 of forest canopy-atmosphere exchange models and allow an assessment of turbulent transport in the forest canopy and the
135 resulting impacts on above- and below-canopy SOA composition and concentration. These data also could assist in the
136 determination of whether or not SOA is forming within the forest canopy.

137 **2 Methods**

138 **2.1 Site description**

139   Measurements were made during the PROPHET-AMOS 2016 campaign from 1 July – 31 July 2016. The PROPHET
140 site (45.55° N, 84.78° W) is situated in a temperate, mixed deciduous forest in the northern portion of Michigan's Lower
141 Peninsula at the University of Michigan Biological Station (UMBS). The surrounding forest consists of aspens (60.9%),
142 northern hardwoods (16.6%; maple, beech, birch, ash, and hemlocks), upland conifers (13.3%; white and red pines), non-
143 forest cover types (7.6%; bracken ferns/grass/developed/road), and northern red oak (1.6%) (Cooper et al., 2001; Bergen and
144 Dronova, 2007). The forests in this region are currently undergoing succession, where the dominant aspens have matured
145 and are now being replaced by northern hardwoods and pines (Bergen and Dronova, 2007). It is expected that this new
146 forest composition will shift BVOC emissions from an isoprene-dominated environment to one that is more influenced by
147 monoterpenes (Toma and Bertman, 2012). The height of the forest canopy varies, but the mean canopy height is
148 approximately 22.5 meters (VanReken et al., 2015). The site's physical layout and site meteorology have been described
149 elsewhere (Carroll et al., 2001; Cooper et al., 2001). The PROPHET site features a 31-m scaffolding tower, allowing
150 measurements to be made at variable heights within and above the vegetation canopy.
151   Due to the sparse surrounding population, the PROPHET site at UMBS has minimal local anthropogenic influences.
152 The closest major urban centers include Detroit, Michigan (350 km to the southeast, population: 672,795), Milwaukee,
153 Wisconsin (350 km to the southwest, population: 595,047), and Chicago, Illinois (450 km to the southwest, population:
154 2,704,958) (Carroll et al., 2001). The closest nearby towns include Pellston, Michigan (5 km to the west, population: 828),
155 Petoskey, Michigan (30 km to the southwest, population: 5,749), and Cheboygan, Michigan (30 km to the northeast,
156 population: 4,726). Population totals are based on 2016 population estimates for cities and towns in the United States (US)
157 from the US Census Bureau (US Census Bureau, 2018).
158   The mean temperature during the campaign was 20.6 +/- 4.6 °C (mean +/- one standard deviation), which is 3-4°C
159 warmer than the mean temperature during the 2009 PROPHET-CABINEX campaign (16.9 °C) (VanReken et al., 2015).
160 Temperature conditions during this study are consistent with mean summertime temperatures from studies in 2008 and 2010
161 (Toma and Bertman, 2012) and with historical mean temperature data for the month of July from the Pellston Regional
162 Airport (Figure S1 in the Supplemental Information (SI)). The mean relative humidity (RH) during the campaign was 73.8
163 +/- 17.5% , which is similar to conditions during the CABINEX campaign (74.5 +/- 17.5%) (VanReken et al., 2015). Winds
164 recorded at the top of the PROPHET tower originated mostly from the west, southwest, and northwest (as shown in Figure
165 S2 in the SI). The historical average precipitation according to the National Atmospheric Deposition Program (NADP)
166 National Trends Network for the month of July from 1979-2015 for UMBS is 69.0 +/- 37.8 mm. During the PROPHET-
167 AMOS 2016 campaign, the total accumulated precipitation was 79.0 mm, indicating that precipitation at the site during the
168 campaign was within one standard deviation of the historical July average (NADP, 2016).

2.2 Instrumentation and sampling

A summary of the trace-gas measurements, instrumentation, and meteorological parameters on board the University of Houston/Rice University Mobile Air Quality Laboratory (MAQL) are summarized in Table S1 of the SI. Details and operation of the MAQL have been described previously in the literature (Leong et al., 2017; Wallace at al., 2018). The MAQL was situated approximately 10 meters to the east of the PROPHET tower. A photograph of the MAQL in stationary sampling mode is shown in Figure S3 in the SI. Table S2 in the SI lists the measurements, measurement methods, and sampling heights of other participating institutions at PROPHET-AMOS 2016 during the campaign. Measurements are reported in local time (LT, Eastern Daylight Time (EDT)) during the campaign.

2.2.1 Trace gases

Below-canopy trace gases including nitric oxide (NO), nitrogen dioxide (NO_2), total reactive nitrogen (NO_y), O_3, carbon monoxide (CO), and sulfur dioxide (SO_2) were measured from a common inlet on the sampling arm of the MAQL. Reported values of nitrogen oxides (NO_x) represent the sum of NO and NO_2, while reported values of NO_y include NO_x and its reservoir species. These measurements were taken at a height of 6 m above ground level.

2.2.2 HR-ToF-AMS

The HR-ToF-AMS (Aerodyne Research Inc., USA) was used to measure non-refractory submicron particulate matter ($NR-PM_1$) from the MAQL; measured composition includes OA, SO_4, nitrate (NO_3), ammonium (NH_4), and chloride (Chl). Detailed descriptions of the operation and principles of the HR-ToF-AMS have been provided elsewhere (DeCarlo et al., 2007). In brief, particles are sampled through a 100-micron critical orifice and are focused into a particle beam using an aerodynamic lens. After traversing a vacuum chamber, the particles in the beam impact onto a tungsten vaporizer heated to 600°C. The vapors formed are ionized by electron impact ionization at 70 eV. The resulting ions are detected using a high-resolution time-of-flight mass spectrometer. The HR-ToF-AMS was operated in a high mass sensitivity mode, referred to as V-mode. Ionization efficiency (IE) calibrations were performed at the beginning and end of the campaign using monodisperse 300 nanometer NH_4NO_3 particles. Gas-phase interferences were subtracted from the data based on the observed signal when ambient air was sampled through a filter. Filter zeros were run each day at varying times of day.

Sampling was performed from the raised 6-m inlet on the common sampling arm of the MAQL (below canopy) and from a 30-m inlet on the PROPHET tower (above canopy). Copper tubing was used for the sampling inlets, and each inlet was fitted with cyclones to remove particles larger than 2.5 microns in diameter. Prior to the HR-ToF-AMS critical orifice, air was sampled through a nafion dryer to dry the sample flow. A three-way valve was used to alternate HR-ToF-AMS sampling between the above- and below-canopy inlets at 10-minute intervals.

2.2.3 PTR-QiToF

Above-canopy mixing ratios and fluxes, along with in-canopy vertical gradients, were measured for a wide array of VOCs during PROPHET-AMOS 2016 by Proton Transfer Reaction-Quadrupole interface Time-Of-Flight mass spectrometry (PTR-QiToF). A detailed description of the sampling configuration, calibration and zeroing procedures, humidity corrections, and instrumental performance during the campaign is provided by Alwe et al. (2019) and Millet et al. (2018). Briefly, six identical 45-m inlet lines (0.5" OD/0.375" ID PFA, each heated to 50°C) were installed on the PROPHET tower to sample from 34 m, 21 m, 17 m, 13 m, 9 m, and 5 m above ground level. Sample flow was maintained at ~40 standard L/min (SLM) for the 34 m inlet line and at >5-10 SLM for the others. Each hour, 30 min was spent sampling from the 34 m inlet to quantify above-canopy VOC mixing ratios and fluxes. The remainder of each hour was spent characterizing in-canopy vertical gradients by sequentially sampling from the other inlets (for 5 min apiece) followed by a 5-min instrumental blank.

2.3 HR-ToF-AMS data and positive matrix factorization analysis

Data analysis for HR-ToF-AMS data was performed in Igor Pro v6.37 using the SQUIRREL v1.57 (SeQUential Igor data RetRiEvaL) and PIKA v1.16 (Peak Integration by Key Analysis) analysis toolkits. High-resolution mass spectral fitting was performed on HR-ToF-AMS V-mode data. Ratios such as the oxygen-to-carbon elemental ratio (O:C) and hydrogen-to-carbon elemental ratio (H:C) were determined according to the "improved-ambient" (IA) method (Canagaratna et al., 2015). The IA method uses specific ion fragments to correct for compositional biases, and this method has been shown to calculate accurately the elemental ratios of organic laboratory standards that are more representative of oxidized, ambient OA species (Canagaratna et al., 2015). The default values for relative IE were used for each of the following species: OA (1.4), SO_4 (1.2), NH_4 (4), NO_3 (1.1), and Chl (1.3), where values in parentheses refer to the ratio of the IE of the given species with respect to the value of IE of NO_3 obtained during routine IE calibrations using NH_4NO_3.

To account for the effects of aerosol composition on the transmission efficiency of aerosols to the detection region of the HR-ToF-AMS, a chemical composition-dependent (and therefore time-dependent) collection efficiency (CDCE) was applied to the HR-ToF-AMS data (Middlebrook et al., 2012), which led to an campaign average CDCE of 0.77 +/- 0.18. During the campaign, the HR-ToF-AMS time resolution was 40 seconds from 2 July 02:00 to 19 July 10:00 LT, after which the HR-ToF-AMS time resolution was changed to 30 seconds between 22 July 11:00 and 31 July 15:00 LT (due to instrumental changes after an HR-ToF-AMS power supply failure). Calculated detection limits of NR-PM$_1$ species are included in Table S3.

Positive matrix factorization (PMF) is a mathematical model in which measured data are decomposed into a combination of factors that have varying contributions throughout a time series. Here, the PMF model has been applied to HR-ToF-AMS data to retrieve OA factors that contain information regarding OA sources, chemical properties, and/or atmospheric processing (Jimenez et al., 2009; Ulbrich et al., 2009; Zhang et al., 2011). Subtypes of OA extracted from OA mass spectra using PMF often include (but are not limited to): more-oxidized oxygenated OA (MO-OOA), less-oxidized oxygenated OA (LO-OOA), hydrocarbon-like OA (HOA), biomass burning organic aerosol (BBOA), and cooking organic aerosol (COA) (Cubison et al., 2011; Jimenez et al., 2009; Mohr et al., 2012; Zhang et al., 2007, 2005). The OOA-related factors are generally considered to be associated with SOA, while subtypes such as HOA, BBOA, and COA are presumed to correspond to POA. Factors associated with isoprene-derived epoxydiol OA (IEPOX-OA) have also been identified using PMF using enhanced signals at m/z 82 in their OA mass spectra (Hu et al., 2015). A detailed description of the PMF model (Paatero and Tapper, 1994; Paatero, 1997; Ulbrich et al., 2009; Xu et al., 2015) is included in the SI.

The results of the separate PMF analyses on above- and below-canopy OA are included in the SI. For the above-canopy OA data, a summary of the PMF factor selection (Table S4), factor time series correlations with external data (Table S5), factor mass spectra correlations with reference mass spectra (Table S6), time series of PMF model residuals (Figure S4), and mass spectra and time series for possible two- to five-factor PMF solutions (Figure S5 - Figure S8) are shown in the SI. VOCs measured above-canopy via PTR-QiToF at the top of the PROPHET tower are defined in Table S7, and factor time series correlations with the time series of these VOCs are shown in Table S8. PMF diagnostics, such as the mass spectra and time series correlation amongst factors (Figure S9), FPEAK and SEED diagnostic plots (Figure S10), results of the FPEAK analysis (Table S9), model residual diagnostic plots (Figure S11), and results from bootstrapping analysis (Figure S12) are shown in the SI. Finally, Figure S13 displays the time series and high-resolution mass spectra of the optimal solution for the above-canopy OA dataset.

For the below-canopy OA data, a summary of the PMF factor selection (Table S10), factor time series correlations with external data (Table S11), factor mass spectra correlations with reference mass spectra (Table S12), mass spectra and time series of possible two- to five-factor PMF solutions (Figure S14 - Figure S17), factor time series correlations with VOCs measured via PTR-QiToF at the 34-m inlet on the PROPHET tower (Table S13), mass spectra and time series correlations amongst factors (Figure S18), FPEAK and SEED diagnostic plots (Figure S19), results from FPEAK analysis (Table S14 and Table S15), model residual diagnostic plots (Figure S20), and results from bootstrapping analysis (Figure S21) are

385 shown in the SI. Finally, the time series and high-resolution mass spectra of the optimal three-factor solution for below-
386 canopy OA are shown in Figure S22.

387 **2.4 HYSPLIT backward trajectory analysis**

388 **2.4.1 Trajectory cluster analysis**

389   Backward-trajectories are used in this study to determine the origin of air masses arriving at the field site using the
390 Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) model (Draxler and Hess, 1998; Stein et al., 2015).
391 Meteorological data from the US Eta data assimilation system archive at 40-km spatial resolution (EDAS40) are used for
392 HYSPLIT trajectory calculations. The EDAS40 data output is constructed using forecasted data from the Eta model, which
393 utilizes observations from surface, aircraft, and satellite data to predict meteorological parameters such as pressure, wind
394 speed, and wind direction (Cooper et al., 2001).
395   In order to assess the influence of air mass histories on aerosols at each site, a cluster analysis was performed on
396 backward trajectories using MeteoInfo v1.4.9R2 and the TrajStat v1.4.4R8 package (Wang, 2014; Wang et al., 2009). The
397 angle distance clustering type is used in this study and calculates the angular distance between two backward trajectories as
398 seen from the site, using methods outlined in Sirois and Bottenheim (1995). The number of suitable clusters is chosen based
399 on the slope of the percentage change in total spatial variation versus number of clusters and a visual inspection of the mean
400 trajectories of the cluster numbers.

401 **2.4.2 Weighted potential source contribution function (WPSCF) analysis**

402   In addition to a backward-trajectory cluster analysis performed for bulk aerosol properties and gas-phase species, two-
403 day HYSPLIT backward-trajectories initiated from the PROPHET site at 500 m above ground level are used in a weighted
404 potential source contribution function (WPSCF) analysis for OA factors. WPSCF analysis is performed in MeteoInfo
405 v1.4.9R2 using the TrajStat v1.4.4R8 package and results are plotted using ESRI's ArcMap v10.1 (Wang, 2014; Wang et al.,
406 2009). Similar PSCF analyses using backward-trajectories have been performed previously using aerosol properties (Bondy
407 et al., 2017; Chang et al., 2017; Polissar, 1999; Schulze et al., 2018).
408   The number of backward-trajectory endpoints falling within a given grid cell with coordinates (i,j) is defined as n_{ij}.
409 The number of instances in which backward-trajectories ending at a given grid cell have a value (i.e., OA factor mass
410 concentration) higher than an arbitrarily set criterion value is defined as m_{ij}. The PSCF value for a cell at location (i,j) is
411 then defined as follows:

412 $$PSCF_{ij} = \frac{m_{ij}}{n_{ij}} \tag{1}$$

413 When calculating values of PSCF, some grid cells will contain only a small number of backward-trajectory endpoints. In
414 order to reduce the high uncertainties related to a limited number of endpoints falling within a grid cell in PSCF analysis, a
415 weighting function is applied to the trajectory numbers following the methods of Polissar et al. (2001):

416 $$W_{ij} = \begin{cases} 1.00 & 80 < n_{ij} \\ 0.70 & 20 < n_{ij} \leq 80 \\ 0.42 & 10 < n_{ij} \leq 20 \\ 0.05 & n_{ij} \leq 10 \end{cases} \tag{2}$$

417 In this study, the domain of analysis is set to the geographical extents of the two-day HYSPLIT backward trajectories
418 initiated from the PROPHET site. A grid cell size of 0.5° by 0.5° is used. Median values of the OA factors are used as the
419 arbitrary criterion values. Overall, the WPSCF analysis allows for an identification of potential source areas, where higher
420 WPSCF values within a region indicate a higher likelihood that this region results in observed values higher than the
421 criterion values.

Deleted: 3

Deleted: 4

2.5 Sonic anemometer data-processing

Turbulence measurements during the campaign were obtained from five sonic anemometers installed on the PROPHET tower at the following measurement heights: 34m (CSAT 3B, Campbell Scientific Inc.), 29m (81000, RM Young), 21m (CSAT 3, Campbell Scientific Inc.), 13m (CSAT 3, Campbell Scientific Inc.), and 5m (CSAT 3, Campbell Scientific Inc.). The sonic anemometer at 34 m was operated continuously during the campaign while data are only available from the lower heights from 9 July – 29 July, 2016. High-frequency data are de-spiked (data points outside of 3.5-standard deviations are removed) and then separated into 30-minute windows to apply a tilt correction such that the x-axis is rotated into the direction of the mean wind velocity (Foken, 2008). Reynolds decomposition is then applied to the three-dimensional wind components (u, v, w), so each variable (e.g., u) is separated into its mean ($\bar{u}$) and fluctuating component (u'). The friction velocity, u*, is defined then as

$$u *^2 = -\overline{u'w'} \tag{3}$$

Any 30-minute periods that experienced rain (as measured by the rain-gauge at the UMBS AmeriFlux tower), weak winds (winds less than 0.5 m s^{-1} at the top sonic anemometer), or wind directed through the tower were excluded due to potential interference.

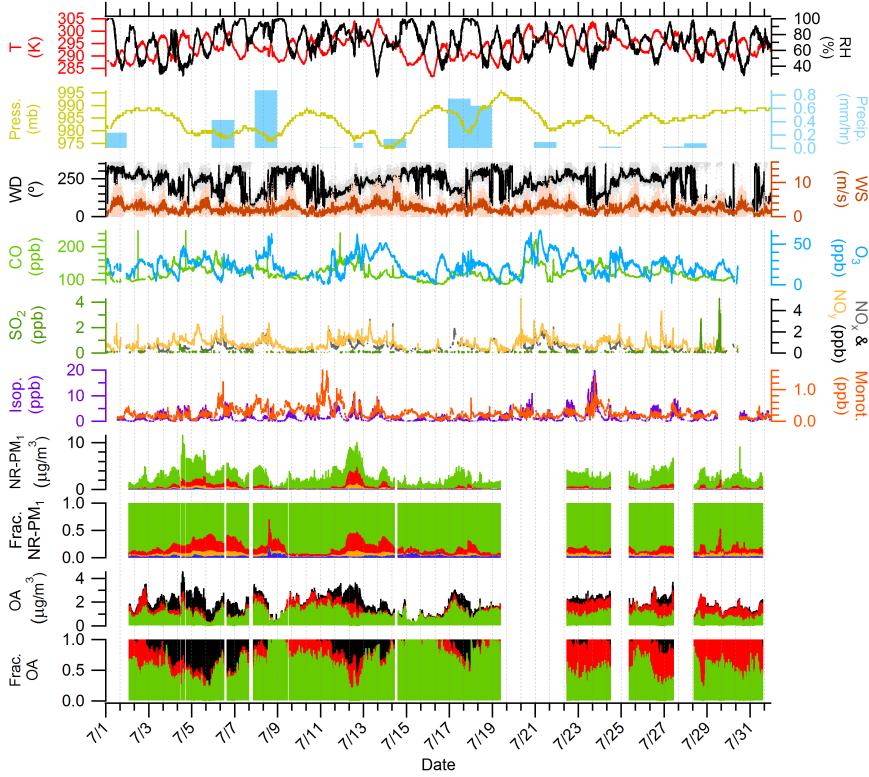
3 Results and discussion

3.1 Backward-trajectory cluster analysis

Two-day backward trajectories are initiated from the PROPHET site and calculated at one-hour intervals from the beginning to the end of the campaign (1 July 00:00 – 31 July 21:00 LT) at 500 meters above ground level, an elevation selected to be within the boundary layer during the day and to avoid trajectory interaction with the surface. A total of 742 two-day backward-trajectories are calculated over the course of the campaign. Cluster analysis resulted in three directional clusters: southerly (299 of 742), northeasterly (192 of 742), and northwesterly (251 of 742) (as shown in Figure S23 in the SI as Cluster 1, 2, and 3 respectively). Further description of cluster number selection is discussed in Figure S24 in the SI. Similar to the air mass history analyses at the PROPHET site in Cooper et al. (2001) and VanReken et al. (2015), eight-hour transitional periods between backward-trajectory classifications were removed from analysis because it is likely that the chemical species from these different air masses are mixed. In total, transitional periods composed 22% of the total number of backward-trajectories (165 of 742 total), and the remaining 577 are used for further analysis. Mean values of anthropogenically-influenced species such as SO$_4$ and benzene were not statistically significantly different ($p < 0.01$) between trajectories from northeasterly and northwesterly clusters, so trajectories from these two clusters are grouped to represent a "northerly" air mass type. During the PROPHET-AMOS study, northerly transport occurred during 60% of the study period (341 of 577), while southerly transport occurred 40% of the time (236 of 577). This type of air-mass classification is consistent with previous summertime studies at the PROPHET site where northerly transport occurred 44% (1998), 60% (2009), and 57% (2014) of the time and southerly transport occurred 24% (1998), 29% (2009), and 43% (2014) of the time (Cooper et al., 2001; Gunsch et al., 2017; VanReken et al., 2015).

3.2 Non-refractory submicron time series and bulk chemical composition

Figure 1 shows the time series of the mass concentrations of OA, SO$_4$, NH$_4$, NO$_3$, and Chl as measured by the HR-ToF-AMS. Mass concentrations plotted in Figure 1 represent time series data from both the above- and below-canopy sampling inlets. The average total NR-PM$_1$ (sum of mass concentrations of OA, SO$_4$, NH$_4$, NO$_3$, and Chl) is 2.3 +/- 1.5 µg m^{-3}. High NR-PM$_1$ concentration episodes (7/3-7/7 and 7/11-7/14) are strongly influenced by southerly air masses advecting

---

466
467 **Figure 1: Overview of time series of the following from top to bottom: temperature (T) and RH; pressure (Press.)**
468 **and precipitation (Precip.); wind direction (WD) and wind speed (WS); CO and O₃; SO₂, NOₓ, and NOᵧ; isoprene**
469 **(Isop.) and total monoterpenes (Monot.); particulate OA (green), NO₃ (blue), SO₄ (red), NH₄ (orange), and Chl**
470 **(purple); fraction of species to total NR-PM₁, OA factors derived from PMF, and fractional contribution of OA**
471 **factors to total OA. OA factors are colored as follows: MO-OOA (black), IEPOX-OA (red), and 91Fac (green).**
472 **Precipitation data are provided from the NADP site in Cheboygan County, MI. Trace gas data (CO, O₃, SO₂, NOₓ,**
473 **and NOᵧ) are measured from the 6-m inlet on the MAQL. Meteorological data (T, RH, Press., WD, and WS) and**
474 **VOC data (Isop. and Monot.) are measured from the 34-m inlet on the PROPHET tower. The OA time series include**
475 **data from both heights (6 m and 30 m), with the sampling switched at 10-minute intervals.**
476
477 to the site, as confirmed by the HYSPLIT backward-trajectory clusters shown in Figure S23 in the SI. Northerly backward-
478 trajectories originated over clean, remote areas in Canada, while southerly backward-trajectories originated over more
479 anthropogenically influenced areas. OA is the dominant NR-PM₁ component over the entire campaign, representing

480 approximately 84.2% of the NR-PM$_1$ mass. SO$_4$ contributes the second highest average mass fraction to NR-PM$_1$ (10.7%)
481 followed by NH$_4$ (3.1%), NO$_3$ (1.6%), and Chl (0.4%). During periods of northerly flow, OA represents 89.5% of the
482 average NR-PM$_1$ mass, while SO$_4$, NH$_4$, NO$_3$ and Chl represent 6.9%, 1.9%, 1.3%, and 0.4%, respectively. Periods of
483 southerly flow decrease the relative contribution of OA to 75.5% and Chl to 0.3% while increasing the relative contribution
484 of SO$_4$ to 16.8%, NH$_4$ to 5.6%, and NO$_3$ to 1.3%. The increased fractional contribution of OA during periods of northerly-
485 originating air is consistent with results from VanReken et al. (2015), who found that water-soluble organics dominated
486 aerosol mass during periods of "clean" northerly flow at the PROPHET site. Sheesley et al. (2004) also found the aerosol
487 organic carbon composition at a remote site in the upper peninsula of Michigan (approximately 100 miles from the
488 PROPHET site) was greatly influenced by the source region of the air parcel. This study found that both stagnant and
489 northerly air parcels contained higher concentrations of pinonic acid and limited amounts of primary emission tracer
490 compounds, while anthropogenically influenced air parcels from the south and northwest contained higher concentrations of
491 aromatic and aliphatic dicarboxylic acids.

492 Diurnal plots for OA, SO$_4$, NH$_4$, NO$_3$, O:C, and H:C are shown in Figure S25 in the SI. The diurnal profiles of OA,
493 SO$_4$, and NH$_4$ are all relatively flat and do not have a clear diurnal trend. The lack of clear diurnal variations for SO$_4$ is
494 consistent with regional transport as the source of SO$_4$ during this campaign. The diurnal variations of NO$_3$ show increases
495 in the morning, with a maximum around approximately 10:00 local time, and lower concentrations in the afternoon.

496 Using the backward-trajectory clustering results described in Section 3.1, mean values of NR-PM$_1$, NR-PM$_1$ species, OA
497 elemental ratios, meteorological parameters, and trace gases for the entire campaign, northerly, and southerly backward-
498 trajectory clusters are shown in Table 1. Overall, relative to northerly air masses, southerly air masses were found to be
499 warmer (~2 °C), more humid (~5%), and associated with higher concentrations of NO$_x$, NO$_y$, O$_3$, and benzene. Furthermore,
500 on average, southerly air masses had higher concentrations of NR-PM$_1$, OA, SO$_4$, NH$_4$, and NO$_3$. Higher levels of OA
501 oxidation (8% difference) based on O:C are also observed during periods of southerly flow (O:C = 0.69 versus 0.75 for
502 northerly versus southerly flow, respectively). An additional metric of oxidation, the oxidation state of carbon (OSc),
503 indicates that the degree of oxidation is higher during periods of southerly flow (OSc = -0.12 versus 0.06 for northerly versus
504 southerly flow, respectively, where OSc = 2 * O:C – H:C) (Kroll et al., 2011). The factor of 5 differences between northerly
505 and southerly SO$_4$ is consistent with the increased influence of SO$_2$ point sources from electric-generating units south of the
506 site in Ohio, Indiana, and Illinois. Overall, these observations demonstrate that anthropogenic influence from southerly flow
507 directly affects NR-PM$_1$ mass concentrations, NR-PM$_1$ composition, the degree of OA oxidation, and trace gas mixing ratios
508 at this site. Results are in agreement with VanReken et al. (2015), where southerly air masses or those "anthropogenically
509 impacted" were found to contain higher aerosol loadings (in terms of aerosol volume, particle number, and median particle
510 diameter) and hygroscopicity, along with increased trace gases abundances, as compared to northerly air masses or "clean"
511 regimes.

512 Oxygen-containing ion families (C$_x$H$_y$O$_{\geq 1}^+$) represent over 50% of the campaign-averaged OA high-resolution mass
513 spectrum, and this high degree of oxygenation is reflected in an average O:C ratio of 0.71 +/- 0.08 and an average H:C ratio
514 of 1.49 +/- 0.06. A distinct peak at m/z 44 in the average mass spectrum accounts for 14.1% of the total OA. The peak at
515 m/z 44 is mainly composed of the CO$_2^+$ ion (96.0% of m/z 44). The ratio of m/z 44 to the total signal in the organic mass
516 spectrum (f$_{44}$), a surrogate for O:C and an indicator for photochemical aging, in this study is 0.14. Together with the average
517 O:C ratio (0.71) observed in this study, these values are consistent with OOA observed across AMS datasets (Jimenez et al.,
518 2009; Ng et al., 2010). Other prominent ions in the campaign-averaged high-resolution mass spectrum include m/z 55, 82,
519 and 91. Fragments at m/z 55 represent 2.4% of the total OA, and are representative of both oxygenated and hydrocarbon
520 fragments, such as C$_3$H$_3$O$^+$ (50.2% of m/z 55) and C$_4$H$_7^+$ (42.9% of m/z 55). The possible OA sources leading to increased
521 signal at m/z 82 (0.46% of total OA) and 91 (0.62% of total OA) will be discussed in the following section. Figure S25 in
522 the SI shows the diurnal variations of O:C and H:C, indicating relatively stable diurnal cycles. Increases in H:C are observed
523 starting at 9:00 before reaching a maximum at midday (13:00) followed by a slow decrease between the hours of 13:00 and
524 20:00, while an opposite pattern is observed for mean values of O:C.
525

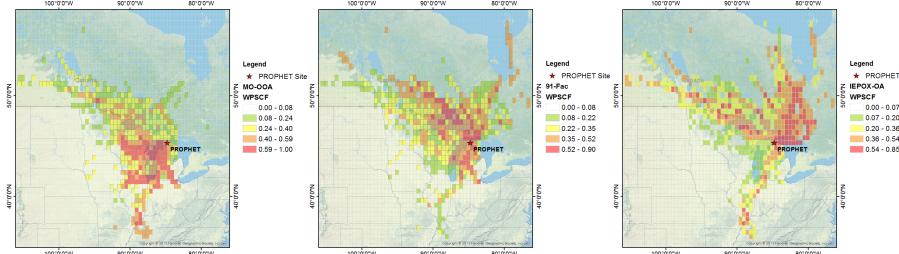
526 **Table 1: Campaign-averaged values (+/- one standard deviation from the mean) of mass concentrations of NR-PM$_1$, VOC and**
527 **trace gas mixing ratios, and meteorological parameters, as well as hourly-averaged values associated with northerly and southerly**
528 **backward-trajectory clusters. Northerly and southerly air masses are defined in Section 3.1 using a cluster analysis of HYSPLIT**
529 **two-day backward trajectories.**

Parameter	Campaign	Northerly	Southerly
NR-PM$_1$ (μg m^{-3})	2.3 ± 1.5	1.8 ± 0.7	3.6 ± 2.0
OA (μg m^{-3})	1.9 ± 1.0	1.6 ± 0.6	2.6 ± 1.3
SO$_4$ (μg m^{-3})	0.3 ± 0.4	0.1 ± 0.1	0.7 ± 0.6
NH$_4$ (μg m^{-3})	0.1 ± 0.1	0.04 ± 0.04	0.2 ± 0.2
NO$_3$ (μg m^{-3})	0.04 ± 0.03	0.02 ± 0.01	0.06 ± 0.05
Chl (μg m^{-3})	0.01 ± 0.00	0.01 ± 0.00	0.01 ± 0.00
O:C	0.7 ± 0.1	0.7 ± 0.1	0.8 ± 0.1
H:C	1.5 ± 0.1	1.5 ± 0.0	1.4 ± 0.00
OSc	-0.1 ± 0.2	-0.1 ± 0.1	0.1 ± 0.2
Isoprene (ppb)[a, b]	1.6 ± 1.9	1.5 ± 1.5	1.8 ± 1.5
Monoterpenes (ppb)[a, b]	0.3 ± 0.2	0.2 ± 0.1	0.2 ± 0.2
Benzene (ppb)[a]	0.04 ± 0.02	0.03 ± 0.01	0.05 ± 0.02
NO (ppt)[c]	24.1 ± 36.4	21.5 ± 16.2	29.7 ± 29.5
NO$_2$ (ppt)[c]	593.0 ± 445.8	369.4 ± 257.7	872.0 ± 478.6
NO$_y$ (ppt)[c]	934.5 ± 490.0	610.5 ± 271.8	1283.9 ± 412.6
O$_3$ (ppb)[c]	24.1 ± 11.9	20.1 ± 8.3	30.5 ± 13.2
CO (ppt)[c]	120.6 ± 21.5	109.6 ± 12.6	134.7 ± 21.7
SO$_2$ (ppb)[b, c]	31.3 ± 174.2	45.0 ± 212.0	23.1 ± 64.2
Temperature (°C)[c]	20.6 ± 4.6	20.3 ± 4.5	22.4 ± 4.5
Relative Humidity (%)[c]	73.8 ± 17.3	68.6 ± 17.0	73.5 ± 17.6

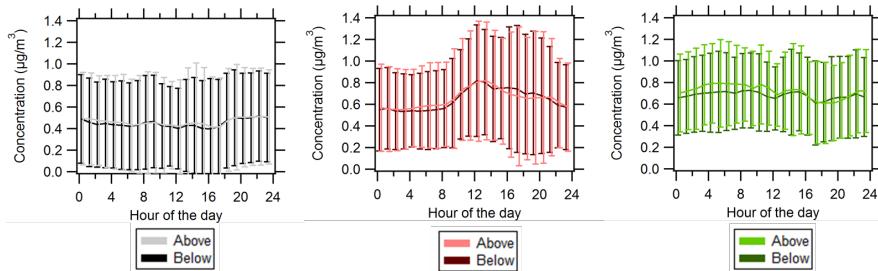
530 [a] VOC measurements using University of Minnesota's PTR-QiToF from the 34-m inlet on the PROPHET tower.
531 [b] Table entries where the differences between the northerly and southerly backward-trajectories mean values are not
532 statistically significant (p < 0.01) using a two-sample t-test.
533 [c] Trace gas and meteorological parameters measured from onboard the MAQL.
534

535 **3.3 Organic aerosol source apportionment**

536   A three-factor solution is obtained for both the above-canopy inlet at 30 meters above the UMBS forest floor (A-MO-
537 OOA, A-IEPOX-OA, A-91Fac) and the below-canopy inlet at 6 meters within the UMBS canopy (B-MO-OOA, B-IEPOX-
538 OA, and B-91Fac). The 91Fac factor represents OA with enhanced signal at m/z 91 in the mass spectrum. The addition of
539 more factors to the PMF solution beyond three factors resulted in less physically meaningful and interpretable factors. Thus,
540 the three-factor solution is considered the optimal solution for the above- and below-canopy OA datasets. In this study, seed
541 = 0 was chosen for both PMF solutions as there was minimal variation in Q/Q$_{exp}$ across the 50 seeds. Solutions at FPEAK =
542 0 were chosen because solutions at other FPEAK values did not present improved correlations between factors and reference
543 mass spectra.
544   Time series of mass concentrations and time series of fractional contributions to total OA are shown in Figure 1. The
545 O:C ratio of each of the OA factors are as follows: 0.65 (IEPOX-OA), 0.71 (91Fac), and 0.89-0.90 (MO-OOA), all of which
546 indicate the high degree of oxygenation in each of the factors. For the above-canopy PMF solution, 91Fac makes the largest

547 contribution to the total OA (43.8%), followed by IEPOX-OA (32.8%) and MO-OOA (23.4%). For the below-canopy PMF
548 solution, 91Fac also makes the largest contribution to the total OA (42.5%), followed by IEPOX-OA (34.0%) and MO-OOA
549 (23.5%). Details on the chemical composition, mass spectral characteristics and diurnal profiles of each factor are discussed
550 further in the SI.
551   Hourly averages of the above-canopy OA factors are paired with hourly two-day backward-trajectories for WPSCF
552 analysis. Results from WPSCF analysis using above-canopy OA data (Figure 2) indicate that A-MO-OOA predominantly
553 originates from southerly air masses, as supported by external measurements data such as benzene, OVOCs, carbonyls, and
554 SO₄. Air masses that originate from the south pass over the large urban centers of Chicago, Milwaukee, and Detroit. This
555 further supports the aged, transported nature and anthropogenic influences of the observed A-MO-OOA at this site. In
556 contrast, no strong indication of a distinct source region is observed for 91Fac. This could suggest a more localized source
557 of 91Fac in relation to the site. Combining these WPSCF results with correlations of 91Fac with VOC masses corresponding
558 to monoterpene oxidation suggests that 91Fac is sourced from local biogenic, monoterpene-oxidation related chemistry (Xu
559 et al., 2018). Finally, WPSCF results for A-IEPOX-OA indicate that this OA factor coincides with more northerly airflow
560 with some contributions from northwesterly flow. These northerly source regions driving A-IEPOX-OA correspond to more
561 rural, less anthropogenically influenced locations in Canada. Interestingly, an instance of high WPSCF values for A-
562 IEPOX-OA and A-MO-OOA can be traced back to areas near the southeastern tip of Missouri and western Tennessee,
563 implying long-range transport of these OA factors. Backward-trajectories associated with this instance of high WPSCF
564 values for IEPOX-OA pass over areas in the high isoprene-emitting region in the Ozarks of southern Missouri, which is
565 commonly referred to as the "isoprene volcano" (Carlton and Baker, 2011; Wiedinmyer et al., 2005). The median mass
566 concentrations of above-canopy OA factors used as the criterion values for the WPSCF method were A-MO-OOA: 0.31 μg
567 m⁻³, A-91Fac: 0.68 μg m⁻³, and A-IEPOX-OA: 0.58 μg m⁻³. Overall, WPSCF analysis indicates that transport from southerly
568 flow (A-MO-OOA), local sources (A-91Fac), and transport from northerly flow (A-IEPOX-OA) are related to the OA
569 factors observed at this site.
570

571
572 **Figure 2: WPSCF backward-trajectory analysis maps for the following hourly-averaged OA factors from left to right: above-**
573 **canopy MO-OOA, above-canopy 91Fac and above-canopy IEPOX-OA. The geographical location of the PROPHET site is**
574 **represented by a red star. WPSCF analysis is performed using HYSPLIT two-day backward trajectories, a grid cell size of 0.5° by**
575 **0.5°, and the geographical domain of the extents of the two-day backward trajectories. Median mass concentrations of above-**
576 **canopy OA factors (A-MO-OOA: 0.31 μg m⁻³, A-91Fac: 0.68 μg m⁻³, and A-IEPOX-OA: 0.58 μg m⁻³) are used as the criterion**
577 **WPSCF values. Color scales correspond to probability of source regions for each respective OA factor, and it should be noted that**
578 **the range and gradation of the color scale changes between each plot.**

579
580   Overall, PMF analysis for both sampling inlets at the site indicates that the OA is a combination of MO-OOA, 91Fac,
581 and IEPOX-OA. The dominant OA factor is 91Fac, and during periods of southerly flow MO-OOA contributes relatively
582 more (time series of the fractional contributions to total OA shown from both inlets is shown in Figure 1 and is also shown

583 separately for each inlet in Figure S13 and Figure S22 in the SI). On average, source apportionment results indicate that the
584 OA at both inlets generally had similar average fractional OA contributions and degrees of oxidation. Diurnal profiles for
585 above- and below-canopy OA are shown in Figure 3 and indicate that diurnal profiles and variations are similar between the
586 two inlets for each OA factor. It is worth noting the diurnal pattern of the IEPOX-OA factor, likely indicating a relatively
587 small influence of local isoprene emissions.
588

589
590 **Figure 3: Diurnal profiles of (left) MO-OOA, (middle) IEPOX-OA, and (right) 91Fac where solid lines represent average values**
591 **and whiskers represent one standard deviation from the mean. Darker colors represent below-canopy OA (B-MO-OOA, B-**
592 **IEPOX-OA, B-91Fac) while lighter colors represent above-canopy OA (A-MO-OOA, A-IEPOX-OA, A-91Fac). Data for below-**
593 **canopy OA factors have been offset by 15 minutes simply to aid plot interpretation.**

594

595 3.4 Vertical characterization of above- and below-canopy NR-PM$_1$ and OA factors

596 3.4.1 Similarity between above- and below-canopy environments

597 Mean values of NR-PM$_1$, NR-PM$_1$ species, OA elemental ratios, meteorological parameters, VOCs, and trace gases from
598 the above- and below-canopy inlets are summarized in Table 2. Each of the mean values for the parameters listed in Table 2
599 are within one standard deviation of each other for the below- and above-canopy sampling heights. However, results from
600 Wilcoxon rank-sum tests indicate that the medians for a majority of the above- and below-canopy parameters are
601 significantly different (p = 0.05). To provide a comparison of the two inlets on the same time scale, scatter plots of 30-
602 minute averaged values are shown in Figure 4 for OA factors, total OA, SO$_4$, and O:C. For reference, a 1:1 line is shown on
603 each scatter plot. Values falling within one standard deviation are similar between above and below canopy, while values
604 deviating farther from the 1:1 line indicate values in which the above- or below-canopy environment had differing
605 concentrations. Figure 4 illustrates that mass concentrations of OA factors, total OA, and SO$_4$ were similar over a majority
606 of the campaign and suggests that the above- and below-canopy environments were generally coupled from a PM
607 perspective. It also appears that total OA, MO-OOA, IEPOX-OA, and 91Fac show increases above canopy relative to below
608 canopy at the highest end of the range of the measurements.
609 Results from a recent study from the PROPHET-AMOS 2016 campaign by Millet et al. (2018) indicate that flux of
610 isoprene and monoterpenes at the canopy-atmosphere boundary represents over half of the net carbon flux, while OVOCs
611 constitute a majority of the species with detectable VOC fluxes. Overall, the authors report that the observed and modeled
612 net carbon flux during the campaign was upward (canopy emission) during the campaign in 2016. Additionally, in-canopy
613 gradients of directly emitted BVOCs, such as isoprene and monoterpenes, indicate patterns that are consistent with their
614 respective temperature, light, and physical emission dependencies (higher concentrations in-canopy for isoprene and higher

615 in the lower canopy for monoterpenes). On the other hand, in-canopy gradients of secondary products from BVOC
616 oxidation, such as acetic acid and glycoaldehyde, indicate patterns consistent with net nighttime uptake and a weak peak
617
618 **Table 2: Campaign-averaged values (+/- one standard deviation) of mass concentrations of NR-PM$_1$, VOC and trace gas mixing**
619 **ratios, and meteorological parameters above and below the canopy.**

Parameter [a, b]	Above	Below
NR-PM$_1$ ($\mu g\ m^{-3}$)	2.4 ± 1.6	2.3 ± 1.5
OA ($\mu g\ m^{-3}$)	1.9 ± 1.0	1.8 ± 1.0
SO$_4$ ($\mu g\ m^{-3}$)	0.3 ± 0.5	0.3 ± 0.4
NH$_4$ ($\mu g\ m^{-3}$)	0.1 ± 0.2	0.1 ± 0.2
NO$_3$ ($\mu g\ m^{-3}$)	0.04 ± 0.04	0.04 ± 0.03
Chl ($\mu g\ m^{-3}$)	0.01 ± 0.00	0.01 ± 0.00
O:C	0.7 ± 0.1	0.7 ± 0.1
H:C [c]	1.5 ± 0.1	1.5 ± 0.1
OSc	0.0 ± 0.2	-0.1 ± 0.2
Isoprene (ppb)	1.6 ± 1.9	1.8 ± 2.2
Monoterpenes (ppb)	0.3 ± 0.2	0.3 ± 0.3
Benzene (ppb)	0.04 ± 0.02	0.04 ± 0.02
NO (ppt)	36.0 ± 56.9	24.1 ± 36.4
NO$_2$ (ppt)	564.8 ± 393.2	593.0 ± 448.8
O$_3$ (ppb)	32.2 ± 12.2	24.1 ± 11.9
Temperature (°C) [c]	20.7 ± 4.1	20.6 ± 4.6
Relative Humidity (%)	71.5 ± 17.3	73.8 ± 17.3

620 [a] Summary statistics for NR-PM$_1$ measurements were calculated using 5-minute averaged data, VOC measurements using 1-
621 minute averaged data (University of Minnesota's PTR-QiToF 5-m inlet and 34-m inlet), NO$_x$ above-canopy measurements
622 using 5-minute averaged data (University of Toronto), NO$_x$ and O$_3$ below-canopy measurements using 5-minute averaged
623 data (MAQL), and O$_3$ 1-minute averaged data (CU-Boulder's 27-m inlet on the AmeriFlux Tower).
624 [b] Percent of data below detection limit for NR-PM$_1$: NH$_4$ (4% / 4%) and Chl (59% / 63%), VOCs: isoprene (30% / 30%),
625 monoterpenes (56% / 36%), benzene (100% / 100%), and NO (37% / 22%), where percentages are shown for above- and
626 below-canopy data, respectively. Unless otherwise stated, the percentage below detection limit for all other parameters is
627 0%.
628 [c] Table entries where the null hypothesis ("equal medians") between the above- and below-canopy data cannot be rejected
629 and was not statistically significant ($p > 0.05$) using a two-sided, non-parametric Wilcoxon rank-sum test. All other table
630 entries indicate that the null hypothesis ("equal medians") can be rejected at the statistical significance level ($p < 0.05$).
631
632 concentration near the mid-canopy. Correlation analysis of these secondary oxidation products and HCOOH indicates that
633 HCOOH likely originates from a secondary source in this environment (Alwe et al., 2019). In the present study, the overall
634 homogeneity in OA factors implies that, despite vertical gradients in trace gases and BVOCs from primary emission and
635 secondary production, turbulent mixing of aerosols between the forest canopy and the atmosphere is efficient.
636 Furthermore, this similarity between the above- and below-canopy environments suggests that the chemical timescales
637 of SOA formation processes likely are long relative to residence times due to turbulent mixing (Foken et al., 2012), assuming
638 relatively constant background levels. Ultimately, the observed similarity agrees with previous modeling work that predicts
639 similar SOA mass loadings at these two heights (Ashworth et al., 2015; Schulze et al., 2017). The results shown in the
640 present work also are in agreement with measurements at the site in 2009, showing that aerosol gradients on the PROPHET

641 tower "existed at times between the above-canopy (31.4m) and understory environments (5 m)," but that the understory
642 conditions were generally similar to that of the above-canopy conditions (VanReken et al., 2015). The vertical similarity in
643

644

645

646

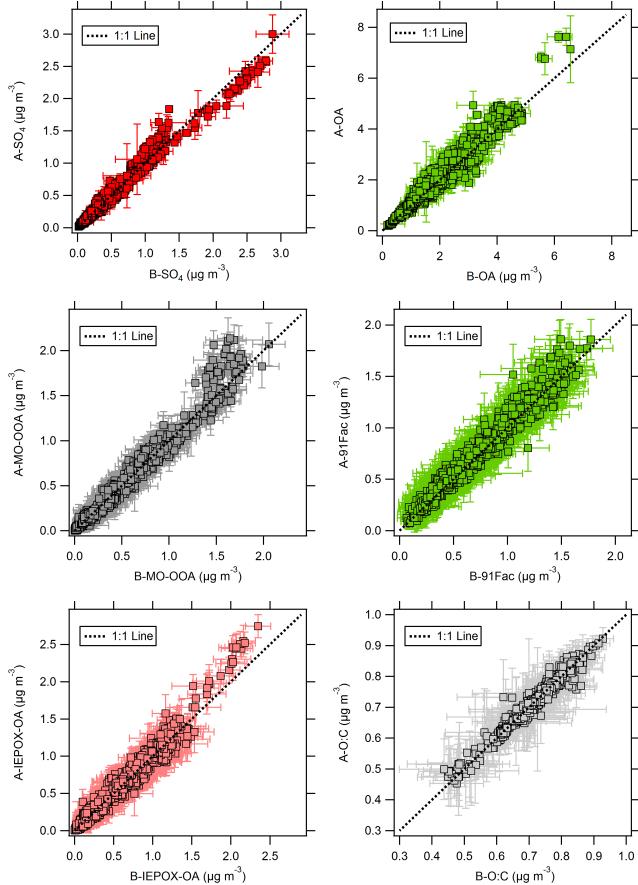



Figure 4: Scatter plots of above- (A) and below- (B) canopy hourly-averaged values for: (top from left to right) SO$_4$ and total OA, (middle from left to right) MO-OOA and 91Fac, and (bottom) IEPOX-OA and campaign O:C. The three-way valve switched between the two inlets at 10-minute intervals, so 30-minute averaged mass concentrations allows for a comparison of both inlets on the same time basis. Above-canopy values are plotted on the y-axis of each plot and below-canopy values are plotted on the x-axis of each plot. Averages are shown with squares; whiskers

represent one standard deviation from the mean. For reference, a 1:1 line is shown with each plot. Outliers on the O:C plot corresponding to periods of precipitation were removed.

NR-PM$_1$ is also in agreement with findings in the Amazon forest, where a balance between upward and downward fine particle fluxes was found (Rizzo et al., 2010) and in a southeast Asian rainforest, where PM$_1$ did not show significant variations with height during the daytime (Whitehead et al., 2010).

3.4.2 Episodes of vertical differences in NR-PM$_1$

Episodes of vertical differences in NR-PM$_1$ between the two inlets were observed, and four such episodes are described here: Episode #1 (Period: 7/3/2016 19:30 to 7/5/2016 15:00 LT), Episode #2 (11 July 15:00 to 12 July 23:00 LT), Episode #3 (7/16/2016 21:30 to 7/19/2016 08:30 LT), and Episode #4 (7/26/2016 08:30 to 7/31/2016 13:30 LT). Episodes were defined as sustained periods in which a vertical difference in OA or SO$_4$ was greater than or equal to concentrations representing ≥ 25% of the campaign averaged OA or SO$_4$. The "vertical difference," symbolized as Δ in Figure 5, is defined as the difference between above- and below-canopy values, where the positive convention indicates larger concentrations above the canopy. Episodes #1, #3, and #4 indicate increased above-canopy OA concentrations, while Episode #2 indicates increased below-canopy SO$_4$ concentrations. Episodes with higher above-canopy NR-PM$_1$ ranged up to ~1.0 µg m^{-3} higher in OA and ~0.5 µg m^{-3} higher in SO$_4$ relative to equivalent above/below mass (Δ = 0). Figure 5 shows time series of vertical differences in OA factors and SO$_4$ and estimates of friction velocity (u*) at five different heights (not equal to those for the VOC measurements) on the PROPHET tower over the campaign. Calculated from three-dimensional wind velocity data, u* is a function of the shear stress at the surface and is used in this study as a metric of in-canopy mixing (Equation 5).

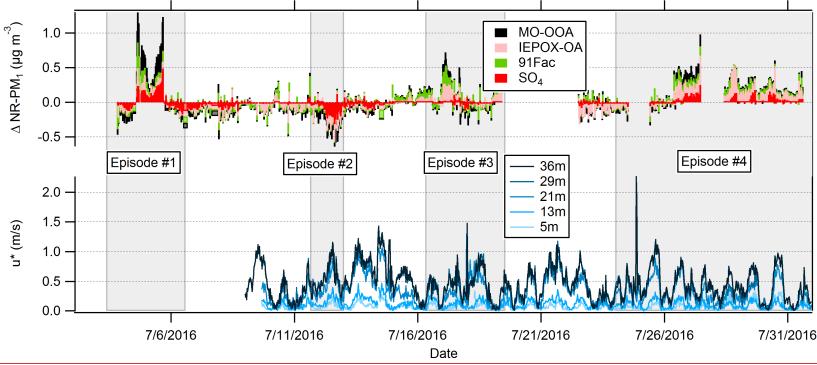
The sum of the delta values for each OA factor (∑ΔOA Factors) for the episodes are shown in Figure 6, with corresponding observations of u* and vertical differences in SO$_4$ and O$_3$. Figure 6 shows that vertical differences in OA correlate with vertical differences in SO$_4$ for Episodes #1 and #4, while ∑ΔOA Factors during Episode #3 coincides with higher above-canopy O$_3$ concentrations. Correlations between chemical species for Episode #2 are weaker. Correlation coefficients (r) for each episode are 0.69 (Episode #1 ∑ΔOA Factors-Sulfate), -0.44 (Episode #2 Sulfate-u*), 0.34 (Episode #3 ∑ΔOA Factors-Ozone), and 0.59 (Episode #4 ∑ΔOA Factors-Sulfate). These episodes have different OA factor composition: MO-OOA contributing a larger percentage during Episode #1 and #2, 91Fac contributing roughly half in Episode #3, and IEPOX-OA contributing more than half of the total OA vertical difference in Episode #4.

3.5 The role of mixing and particulate SO$_4$ in vertical differences in OA

The diurnal profile of vertical difference episodes for total OA, SO$_4$, and OA factors in 2016 indicate there is no clear diurnal pattern observed for any of these species (Figure S26 in the SI). Maximum vertical differences for SO$_4$, total OA, and MO-OOA are observed around 3PM. For total OA, a gradual increase occurs at 9AM before reaching a maximum vertical difference at 3PM, suggesting that the episodes of higher above-canopy NR-PM$_1$ begin shortly after the most common observed hours of canopy uncoupling from the site in 2009. The initiation of these events may also be attributed to venting of the nocturnal boundary layer as it breaks up in the morning hours, as observed for events of upward particle number fluxes by Whitehead et al. (2010).

To assess the agreement between the occurrence of episodes and micrometeorological measurements of in-canopy mixing, episode-specific data for Episodes #2-4 are shown in Figure 6. During Episode #1, u* data are available only at 36m, so no friction velocity data are shown, preventing a full analysis similar to those performed for the other three episodes. However, based on similarity in sulfate enhancements, it can be assumed that Episode #1 is somewhat similar to Episode #4.

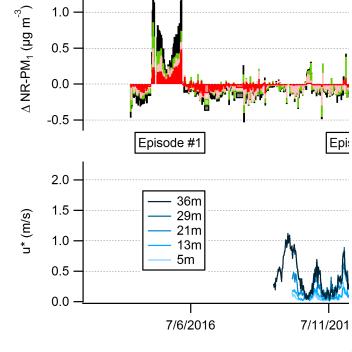
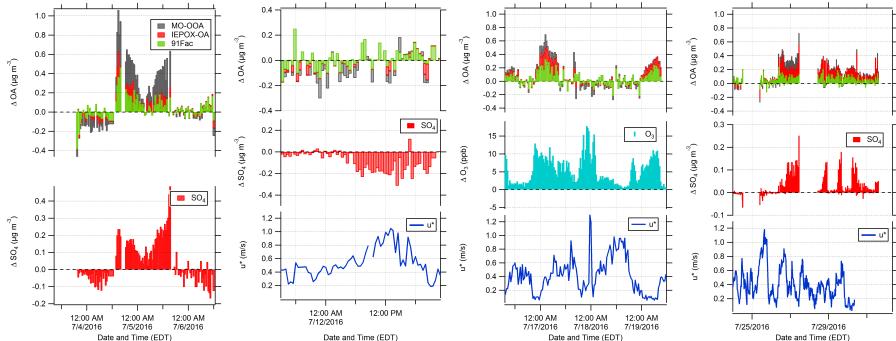
During Episode #2, based on the backward trajectory cluster analysis shown in Table 1 and the WPSCF results, regional transport is the likely source of the PM, including the enhancements below canopy. Prior to this episode, SO$_4$ and MO-OOA are uniform from below-to-above canopy. The below-canopy enhancement then reaches up to 0.3 µg m^{-3} of SO$_4$.

708 Downmixing of clean air from aloft could lead to lower concentrations above canopy, meaning that the observed difference
709 would be caused by decreasing above-canopy concentrations, not increasing below-canopy concentrations. However,
710 below-canopy concentrations are observed to increase while above-canopy concentrations decrease. Without a local, below-
711 canopy source, this indicates that pollutants from above canopy are mixed into the below-canopy region at a rate faster than
712 they are lost to deposition. Regional pollutants, advected to the site above the boundary layer, can be mixed down to the
713 surface with daytime boundary layer growth, as has been found in previous aircraft campaigns (Berkowitz et al., 1998;
714 Thornberry et al., 2001). Downward transport of air masses from the surrounding region has also been hypothesized to
715 contribute to higher ratios of organic nitrogen to organic carbon ratios in water-soluble aerosols within a forest canopy
716 relative to its forest floor (Miyazaki et al., 2014).

717

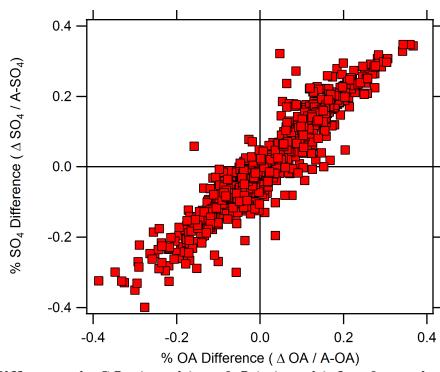
718 **Figure 5: Time series of (top) observed NR-PM$_1$ vertical differences between above- and below-canopy inlets and**
719 **(bottom) friction velocity (u*) in m/s at five different heights on the PROPHET tower. Vertical differences are**
720 **defined as Δ Species, where Δ refers to the Above-Canopy minus the Below-Canopy mass concentration. Note that**
721 **the elevations for u* are slightly different than those for trace gas sampling.**

722

723 During Episodes #3 and #4, periods of above-canopy enhancement in OA factors coincide with relatively lower u* (u* <
724 0.2 m/s during Episode #3 and u* < 0.6 m/s during Episode #4, with the average u* considering all heights over the duration
725 of the episode), with lower friction velocities and greater above-canopy enhancement in Episode 3. In the case of Episode
726 #3, lower in-canopy mixing, mostly occurring during nighttime, agrees well with periods of higher above-canopy OA factor
727 and O$_3$ concentrations. In this case, both IEPOX-OA and 91Fac contribute to the OA enhancement, likely due to strong
728 photochemistry both locally and during transport (as indicated by increased O$_3$). Episode #4 is the longest duration episode;
729 however, the agreement between low-mixing and above-canopy PM enhancements is more variable during this case. Similar
730 to Episode #3, the lowest values of friction velocity occur during the nighttime or early morning. Despite the temporal
731 misalignment of ΔOA and low u*, it should be noted that friction velocities lower than the campaign average (~0.4 m/s) are
732 observed during the latter periods of Episode #4 (7/28-7/30), which is consistent with the low mixing hypothesis presented
733 for Episode #3. Therefore, it appears that stagnant conditions above the canopy created an environment where canopy
734 exchange became limited and air masses did not fully penetrate into the canopy; aerosol deposition below canopy potentially
735 enhanced the positive delta values. This scenario could also promote in-canopy OA accumulation, but this does not appear
736 to have occurred, implying that other factors contributed to these vertical differences. Instead, it appears that increased
737 sulfate loading was associated with this transport and that this increased sulfate above the canopy led to enhancements above

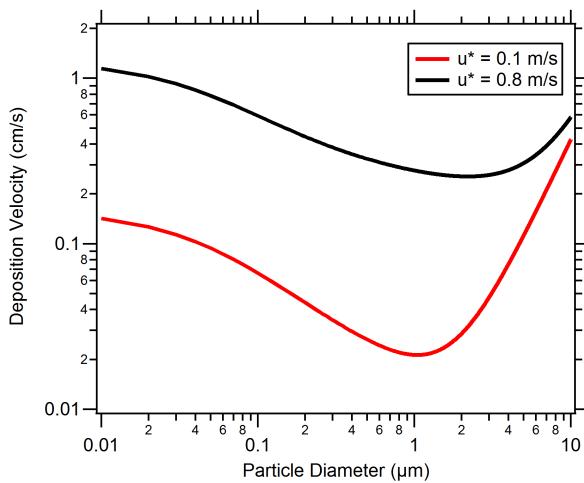
Deleted:

739 canopy, particularly of IEPOX-OA relative to 91Fac, as shown in Figure 6. This also could be related to associated changes
740 in aerosol liquid water.
741

743 **Figure 6: Time series of observed NR-PM₁ vertical difference episodes: (from left to right) Episode #1, Episode #2,**
744 **Episode #3, and Episode #4. Data shown for Episode #1, Episode #2, and Episode #4 include vertical differences in**
745 **30-minute averaged above- and below-canopy SO₄, while data shown for Episode #3 show vertical differences in 30-**
746 **minute averaged above- and below-canopy O₃. The O₃ data were measured from the AmeriFlux Tower at 6 meters**
747 **and 27 meters and were provided courtesy of CU-Boulder. Friction velocity measurements at 29m on the PROPHET**
748 **tower are also provided for Episodes #2-4.**
749

750   The probability distributions of ΔSO_4 and ΔO_3 between episodes and the average for the entire PROPHET campaign are
751 compared in Figure S27 of the SI. The cumulative distribution function (CDF) for ΔSO_4 indicates that Episodes #1 and #4
752 had higher probabilities of positive ΔSO_4 (denoting higher above-canopy concentrations), while Episode #2 had higher
753 probabilities of negative ΔSO_4 (denoting higher below-canopy concentrations). The episode-specific CDFs for #1 and #2 are
754 also different from the total campaign CDF, implying that the vertical differences observed were distinct events. The
755 average O₃ difference between the 6- and 27-m inlets on the AmeriFlux tower throughout the campaign indicated that O₃
756 was on average 5 ppb greater at the 27-m inlet, with the difference reaching as high as 34 ppb on 6 July and 20 July. The
757 probability distribution of vertical O₃ differences observed during Episode #3 is markedly different than those observed
758 during Episode #1, Episode #4, and the remainder of the campaign. This indicates that O₃ had a larger probability of being
759 between 0-10 ppb higher above the canopy during this episode compared to the rest of the campaign.
760   Based on Episode #1 and Episode #4, one of several potential driving factors of vertical differences for OA is a vertical
761 difference in particulate SO₄. Figure 7 indicates the vertical differences in OA and SO₄ relative to their respective above-
762 canopy concentrations. This metric is defined as "% PM Difference," where PM is the given PM constituent and is equal to
763 the ΔPM constituent divided by the above-canopy PM concentration. Data that fall in the upper right and bottom left
764 quadrants correspond to higher above- and higher below-canopy concentrations, respectively. The vertical difference above
765 or below the canopy can be up to approximately 35% of the total available SO₄ or OA at the site. Figure 7 indicates that
766 there is a strong linear relationship between the %SO₄ Difference and %OA Difference during the campaign, even outside of
767 the Episodes defined here.
768   The concurrent features of vertical differences in OA factors and SO₄ observed in Episodes #1, #2, and #4 and OA
769 factors and O₃ in Episode #3 suggest that long-range regional transport (enhanced MO-OOA, SO₄, and/or O₃) is a key first
770 step in causing these differences. Local through-canopy mixing then determines whether the enhancement is above

774 (Episodes #1, #3, and #4) or below (Episode #2) the canopy. The transported material can then impact local chemistry.
775 Increased SO₄ likely increases aerosol hygroscopicity resulting in increased ALW, which could result in increased
776 partitioning of semi-volatile organics to the condensed phase (i.e., IEPOX-OA) (Budisulistiorini et al., 2017; El-Sayed et al.,
777 2018; Marais et al., 2016). Pre-existing OA (i.e., MO-OOA) transported with SO₄ aerosol could also play a role in the
778 partitioning of OA above the canopy during these episodes. Vertical gradients in O₃ coinciding with Episode #3 (higher O₃
779 above) could initiate relatively local formation of extremely low volatility compounds, which are first-generation oxidation
780 products of α-pinene and O₃ (Jokinen et al., 2015). Based on the WPSCF and backward trajectory clustering results, cooler,
781 northerly air masses associated with IEPOX-OA also could promote partitioning of semi-volatile organics to the particle
782 phase. It is important to note that it is difficult to conclude the exact chemical mechanisms that are influencing these events
783 due to their low mass loadings and episodic nature and the consistently higher above-canopy O₃ concentrations during the
784 campaign.
785

786
787 **Figure 7: Scatter plot of % difference in SO₄ (y-axis) and OA (x-axis) for the entire campaign. The % difference is**
788 **calculated as Δ Species / Above-Canopy Species concentration, and is representative of the normalized Δ Species**
789 **concentration.**
790
791 Understanding these events is important because uncoupled forest-canopy conditions have been observed in a number of
792 locations (Foken et al., 2012; Whitehead et al., 2010) and could indicate differences between above-canopy and surface level
793 PM. One-dimensional modeling has revealed that the timescales of turbulent transport inside a forest canopy can be much
794 shorter (minutes) than the timescale of aerosol dynamics and deposition (hours) (Rannik et al., 2016), but this evaluation
795 suggests that advective episodes can cause vertical gradients that are not locally driven. Above-canopy OA and particle
796 fluxes have been observed in other studies (Farmer et al., 2013; Pryor et al., 2007), suggesting the need for careful evaluation
797 of whether differences are driven by local chemistry, long-range transport, or a combination thereof.
798

799 **3.6 Particle dry deposition model**

800 To investigate broadly the effects of canopy mixing on particle deposition in a forest canopy, a particle dry deposition
801 model is used. Note that we are not applying this through the canopy but to illustrate the relationship between deposition
802 and u*. The resistance model for particle dry deposition assumes that the deposition process is controlled by three
803 resistances in series: aerodynamic, quasi-laminar, and canopy resistance (Seinfeld and Pandis, 2006). Details on the particle

804 dry deposition model are included in the SI. Conditions and parameters representative of the land use category, season, and
805 forest canopy present at the PROPHET site are used as model inputs.
806   Figure 8 displays model results for deposition velocity as a function of particle diameter under stable atmospheric
807 conditions. For illustration, test cases are shown for u^* values for low in-canopy mixing ($u^* = 0.1$ m/s) and high in-canopy
808 mixing ($u^* = 0.8$ m/s). Values of u^* were chosen based on the range of u^* values observed during the campaign at 29m on
809 the PROPHET tower. For the submicron particle diameter range (0.1 to 1 micron), a characteristic minimum in deposition
810 velocity is observed for both test cases at 1 micron diameter. Deposition modeling indicates that higher deposition velocities
811 are achieved in the high in-canopy mixing test case, implying that there is less canopy transport resistance to the surface and
812 more deposition in the canopy. This corresponds to Episode #2.
813

814
815 **Figure 8: Particle dry deposition velocity resistance model results plotted by particle diameter and friction velocity.**
816 **Two test cases of low and high friction velocity, representative of data collected at the PROPHET site, are plotted in**
817 **red and black solid lines, respectively. Land-use conditions and seasonal parameters similar to the PROPHET**
818 **campaign were used as inputs to the particle dry deposition model. Additional model parameters are provided in the**
819 **SI.**
820
821   Deposition modeling also indicates relatively lower deposition velocities for the low mixing condition test case, which
822 suggests that particles aloft are transported less efficiently into the forest (similar to the conditions present for Episodes #3
823 and #4). A comparison of the deposition resistances (shown in Figure 9) indicates that aerodynamic and quasi-laminar
824 resistances in the low-mixing test case are an order of magnitude greater than the high-mixing case. The settling removal
825 resistance is the same between both test cases because it is merely a function of diameter. A greater aerodynamic resistance
826 limits turbulent transport from the above-canopy layer to the surface layer and greater quasi-laminar layer resistance limits
827 transport to just above the surface by lowering particle impaction. In total, this result emphasizes the importance of in-
828 canopy transport and mixing in governing particle concentrations in forests.
829

830

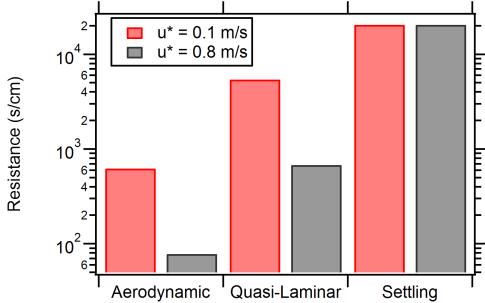



Figure 8: Deposition and particle settling (accounts for the effect of sedimentation) resistances comparison for low and high friction velocities. Resistance comparison assumes a 1 micron particle diameter.

4 Conclusions

In this study, source apportionment of OA using separate PMF analyses on inlets situated above and below a forest canopy resulted in three OA factors at a site in northern Michigan. Similarity in OA composition, concentration, and diurnal profiles was observed between the two inlets, suggesting that turbulent transport efficiently mixes OA across the canopy. However, OA factor vertical differences between the two inlets were observed during four separate episodes. During these episodes, vertical differences were both positive (greater concentrations above the canopy) and negative (greater concentrations below canopy). NR-PM$_1$ composition amongst these episodes was unique (Episode #1: MO-OOA dominant, Episode #2: SO$_4$ dominant, Episode #3: 91Fac dominant, Episode #4: IEPOX-OA dominant). Furthermore, the vertical difference concentrations can be 35% of the total available SO$_4$ or OA at the site. It has also been shown that relative vertical differences in SO$_4$ and OA are linearly associated, suggesting the role of regional SO$_4$ in vertical profiles of NR-PM$_1$ in forested environments.

Using micrometeorological measurements, it has been shown in this work that periods of low in-canopy mixing conditions can be associated with the timing of vertical difference episodes where above-canopy concentrations are larger than those below. The opposite scenario is hypothesized to be associated with transport of air from aloft or with accumulation of material below canopy more rapidly than it is deposited. Either way, these results suggest that canopy mixing impacts particle levels. However, under low-mixing scenarios, it appears that enhancements as defined here depend on both these conditions and the presence of transported O$_3$ or SO$_4$ to enhance IEPOX-OA and 91Fac levels.

To the knowledge of the author, this is one of only a few studies that have assessed vertical profiles in OA factors above and below a forest canopy, and the first study to observe episodes of vertical differences in OA factors above and below a forest canopy. This work adds to the existing literature on aerosol chemistry in a forest canopy environment presented by Rizzo et al. (2010) and Whitehead et al. (2010) and to literature on vertical profiles of OA in an urban environment by Özturk et al. (2013).

To investigate the effects of forest canopies on SOA formation, small-scale models, such as those described in Schulze et al. (2017) and Ashworth et al. (2015), have been developed. The OA data from this work can be used to validate such models and are particularly relevant to these modeling efforts, as the models were developed using campaign data from the PROPHET site in 2009. Vertical transport and horizontal advection are both sources of uncertainty in current forest canopy-atmosphere exchange models, which are designed to focus on local processes. Ultimately, the vertical similarity in

NR-PM$_1$ OA composition observed in this study implies that it may be valid to assume that below-canopy OA composition is generally representative of the OA composition in the atmospheric layer directly above the canopy and vice versa. However, this work highlights that advection of regional pollution into forested regions can lead to in-canopy gradients that are not present under purely local conditions.

Data Availability

Data are available through contacting the corresponding author.

Author Contributions

A.A.T.B. prepared the manuscript with input from all authors. A.A.T.B., H.W.W. and R.J.G. conceived of the study and operated and analyzed the data from the HR-ToF-AMS. S.K. and A.L.S. investigated friction velocity and in-canopy mixing. H.D.A. and D.B.M. collected and analyzed VOC data. J.H.F., M.H.E. and S.A. collected and analyzed trace gas data and operated the MAQL.

Competing Interests

The authors declare they have no conflict of interest.

Acknowledgements

The assistance of all staff and collaborators at UMBS is gratefully acknowledged. We would like to thank Wei Wang at University of Colorado Boulder for assistance in collecting O$_3$ data at the AmeriFlux tower and the Murphy group at the University of Toronto for provision of nitrogen oxide data. This work was funded by the National Science Foundation (NSF) under grant AGS-1552086. PTR-QiToF measurements during PROPHET-AMOS were also supported by NSF (grants AGS-1428257+AGS-1148951). Trace gas and meteorological measurements on board the MAQL were also supported by NSF (grant AGS-1552077).

References

Alwe, H.D., Millet, D.B., Chen, X., Raff, J.D., Payne, Z.C., Fledderman, K., 2019. Oxidation of Volatile Organic Compounds as the Major Source of Formic Acid in a Mixed Forest Canopy. Geophysical Research Letters 0. https://doi.org/10.1029/2018GL081526

Ashworth, K., Chung, S.H., Griffin, R.J., Chen, J., Forkel, R., Bryan, A.M., Steiner, A.L., 2015. FORest Canopy Atmosphere Transfer (FORCAsT) 1.0: a 1-D model of biosphere–atmosphere chemical exchange. Geoscientific Model Development 8, 3765–3784. https://doi.org/10.5194/gmd-8-3765-2015

Baldocchi, D., Guenther, A.B., Harley, P., Klinger, L., Zimmerman, P., Lamb, B., Westberg, H., 1995. The fluxes and air chemistry of isoprene above a deciduous hardwood forest. Philosophical Transactions: Physical Sciences and Engineering 351, 279–296.

Bergen, K.M., Dronova, I., 2007. Observing succession on aspen-dominated landscapes using a remote sensing-ecosystem approach. Landscape Ecology 22, 1395–1410. https://doi.org/10.1007/s10980-007-9119-1

Berkowitz, C.M., Fast, J.D., Springston, S.R., Larsen, R.J., Spicer, C.W., Doskey, P.V., Hubbe, J.M., Plastridge, R., 1998. Formation mechanisms and chemical characteristics of elevated photochemical layers over the northeast United States. J. Geophys. Res. 103, 10631–10647. https://doi.org/10.1029/97JD03751

898   Bondy, A.L., Wang, B., Laskin, A., Craig, R.L., Nhliziyo, M.V., Bertman, S., Pratt, K.A., Shepson, P.B., Ault, A.P., 2017.
899   Inland Sea Spray Aerosol Transport and Incomplete Chloride Depletion: Varying Degrees of Reactive Processing
900   Observed during SOAS. Environ. Sci. Technol. https://doi.org/10.1021/acs.est.7b02085
901   Brown, S.S., Osthoff, H.D., Stark, H., Dubé, W.P., Ryerson, T.B., Warneke, C., de Gouw, J.A., Wollny, A.G., Parrish, D.D.,
902   Fehsenfeld, F.C., Ravishankara, A.R., 2005. Aircraft observations of daytime NO_3 and N_2O_5 and their implications
903   for tropospheric chemistry. Journal of Photochemistry and Photobiology A: Chemistry 176, 270–278.
904   https://doi.org/10.1016/j.jphotochem.2005.10.004
905   Bryan, A.M., Bertman, S.B., Carroll, M.A., Dusanter, S., Edwards, G.D., Forkel, R., Griffith, S., Guenther, A.B., Hansen,
906   R.F., Helmig, D., Jobson, B.T., Keutsch, F.N., Lefer, B.L., Pressley, S.N., Shepson, P.B., Stevens, P.S., Steiner,
907   A.L., 2012. In-canopy gas-phase chemistry during CABINEX 2009: sensitivity of a 1-D canopy model to vertical
908   mixing and isoprene chemistry. Atmospheric Chemistry and Physics 12, 8829–8849. https://doi.org/10.5194/acp-
909   12-8829-2012
910   Budisulistiorini, S.H., Nenes, A., Carlton, A.G., Surratt, J.D., McNeill, V.F., Pye, H.O.T., 2017. Simulating Aqueous-Phase
911   Isoprene-Epoxydiol (IEPOX) Secondary Organic Aerosol Production During the 2013 Southern Oxidant and
912   Aerosol Study (SOAS). Environmental Science & Technology 51, 5026–5034.
913   https://doi.org/10.1021/acs.est.6b05750
914   Canagaratna, M.R., Jimenez, J.L., Kroll, J.H., Chen, Q., Kessler, S.H., Massoli, P., Hildebrandt Ruiz, L., Fortner, E.,
915   Williams, L.R., Wilson, K.R., Surratt, J.D., Donahue, N.M., Jayne, J.T., Worsnop, D.R., 2015. Elemental ratio
916   measurements of organic compounds using aerosol mass spectrometry: characterization, improved calibration, and
917   implications. Atmospheric Chemistry and Physics 15, 253–272. https://doi.org/10.5194/acp-15-253-2015
918   Carlton, A.G., Baker, K.R., 2011. Photochemical Modeling of the Ozark Isoprene Volcano: MEGAN, BEIS, and Their
919   Impacts on Air Quality Predictions. Environmental Science & Technology 45, 4438–4445.
920   https://doi.org/10.1021/es200050x
921   Carroll, M.A., Bertman, S.B., Shepson, P.B., 2001. Overview of the Program for Research on Oxidants: PHotochemistry,
922   Emissions, and Transport (PROPHET) summer 1998 measurements intensive. Journal of Geophysical Research
923   106.
924   Chang, Y., Deng, C., Cao, F., Cao, C., Zou, Z., Liu, S., Lee, X., Li, J., Zhang, G., Zhang, Y., 2017. Assessment of
925   carbonaceous aerosols in Shanghai, China – Part 1: long-term evolution, seasonal variations, and meteorological
926   effects. Atmos. Chem. Phys. 17, 9945–9964. https://doi.org/10.5194/acp-17-9945-2017
927   Cooper, O.R., Moody, J.L., Thornberry, T.D., Town, M.S., Carroll, M.A., 2001. PROPHET 1998 meteorological overview
928   and air-mass classification. Journal of Geophysical Research 106.
929   Cubison, M.J., Ortega, A.M., Hayes, P.L., Farmer, D.K., Day, D., Lechner, M.J., Brune, W.H., Apel, E., Diskin, G.S.,
930   Fisher, J.A., Fuelberg, H.E., Hecobian, A., Knapp, D.J., Mikoviny, T., Riemer, D., Sachse, G.W., Sessions, W.,
931   Weber, R.J., Weinheimer, A.J., Wisthaler, A., Jimenez, J.L., 2011. Effects of aging on organic aerosol from open
932   biomass burning smoke in aircraft and laboratory studies. Atmospheric Chemistry and Physics 11, 12049–12064.
933   https://doi.org/10.5194/acp-11-12049-2011
934   DeCarlo, P.F., Kimmel, J.R., Trimborn, A., Northway, M.J., Jayne, J.T., Aiken, A.C., Gonin, M., Fuhrer, K., Horvath, T.,
935   Docherty, K.S., others, 2006. Field-deployable, high-resolution, time-of-flight aerosol mass spectrometer.
936   Analytical Chemistry 78, 8281–8289.
937   Ditto, J.C., Barnes, E.B., Khare, P., Takeuchi, M., Joo, T., Bui, A.A.T., Lee-Taylor, J., Eris, G., Chen, Y., Aumont, B.,
938   Jimenez, J.L., Ng, N.L., Griffin, R.J., Gentner, D.R., 2018. An omnipresent diversity and variability in the chemical
939   composition of atmospheric functionalized organic aerosol. Communications Chemistry 1, 75.
940   https://doi.org/10.1038/s42004-018-0074-3
941   Draxler, R.R., Hess, G.D., 1998. An overview of the HYSPLIT_4 modeling system for trajectories, dispersion, and
942   deposition. Australian meteorological magazine 47.
943   El-Sayed, M.M.H., Ortiz-Montalvo, D.L., Hennigan, C.J., 2018. The effects of isoprene and NO_x on secondary organic
944   aerosols formed through reversible and irreversible uptake to aerosol water. Atmospheric Chemistry and Physics
945   18, 1171–1184. https://doi.org/10.5194/acp-18-1171-2018

946 Farmer, D.K., Chen, Q., Kimmel, J.R., Docherty, K.S., Nemitz, E., Artaxo, P.A., Cappa, C.D., Martin, S.T., Jimenez, J.L.,
947   2013. Chemically Resolved Particle Fluxes Over Tropical and Temperate Forests. Aerosol Science and Technology
948   47, 818–830. https://doi.org/10.1080/02786826.2013.791022
949 Fehsenfeld, F.C., Calvert, J.G., Fall, R., Goldan, P., Guenther, A., Hewitt, C.N., Lamb, B., Shaw, L., Trainer, M., Westberg,
950   H., Zimmerman, P., 1992. Emissions of volatile organic compounds from vegetation and the implications for
951   atmospheric chemistry. Global Biogeochemical Cycles 6.
952 Finnigan, J., 2000. Turbulence in plant canopies. Annual Review of Fluid Mechanics 32, 519–571.
953 Foken, T., Meixner, F.X., Falge, E., Zetzsch, C., Serafimovich, A., Bargsten, A., Behrendt, T., Biermann, T., Breuninger, C.,
954   Dix, S., Gerken, T., Hunner, M., Lehmann-Pape, L., Hens, K., Jocher, G., Kesselmeier, J., Lüers, J., Mayer, J.-C.,
955   Moravek, A., Plake, D., Riederer, M., Rütz, F., Scheibe, M., Siebicke, L., Sörgel, M., Staudt, K., Trebs, I.,
956   Tsokankunku, A., Welling, M., Wolff, V., Zhu, Z., 2012. Coupling processes and exchange of energy and reactive
957   and non-reactive trace gases at a forest site – results of the EGER experiment. Atmospheric Chemistry and Physics
958   12, 1923–1950. https://doi.org/10.5194/acp-12-1923-2012
959 Fuentes, J.D., Wang, D., Bowling, D.R., Potosnak, M., Monson, R.K., Goliff, W.S., Stockwell, W.R., 2007. Biogenic
960   Hydrocarbon Chemistry within and Above a Mixed Deciduous Forest. Journal of Atmospheric Chemistry 56, 165–
961   185. https://doi.org/10.1007/s10874-006-9048-4
962 Gao, W., Wesely, M.L., Doskey, P.V., 1993. Numerical modeling of the turbulent diffusion and chemistry of NO_x, O_3,
963   isoprene, and other reactive trace gases in and above a forest canopy. Journal of Geophysical Research:
964   Atmospheres 98, 18339–18353. https://doi.org/10.1029/93JD01862
965 Geron, C., Rasmussen, R., R. Arnts, R., Guenther, A., 2000. A review and synthesis of monoterpene speciation from forests
966   in the United States. Atmospheric Environment 34, 1761–1781. https://doi.org/10.1016/S1352-2310(99)00364-7
967 Goldstein, A.H., Galbally, I.E., 2007. Known and unexplored organic constituents in the earth's atmosphere. Environmental
968   Science & Technology.
969 Gordon, M., Staebler, R.M., Liggio, J., Vlasenko, A., Li, S.-M., Hayden, K., 2011. Aerosol flux measurements above a
970   mixed forest at Borden, Ontario. Atmospheric Chemistry and Physics 11, 6773–6786. https://doi.org/10.5194/acp-
971   11-6773-2011
972 Guenther, A., Geron, C., Pierce, T., Lamb, B., Harley, P., Fall, R., 2000. Natural emissions of non-methane volatile organic
973   compounds, carbon monoxide, and oxides of nitrogen from North America. Atmospheric Environment 34, 2205–
974   2230.
975 Guenther, A., Hewitt, C.N., Erickson, D., Fall, R., Geron, C., Graedel, T., Harley, P., Klinger, L., Lerdau, M., McKay, W.A.,
976   Pierce, T., Scholes, B., Steinbrecher, R., Tallamraju, R., Taylor, J., Zimmerman, P., 1995. A global model of natural
977   volatile organic compound emissions. Journal of Geophysical Research 100.
978 Gunsch, M.J., May, N.W., Wen, M., Bottenus, C.L.H., Gardner, D.J., VanReken, T.M., Bertman, S.B., Hopke, P.K., Ault,
979   A.P., Pratt, K.A., 2018. Ubiquitous influence of wildfire emissions and secondary organic aerosol on summertime
980   atmospheric aerosol in the forested Great Lakes region. Atmospheric Chemistry and Physics 18, 3701–3715.
981   https://doi.org/10.5194/acp-18-3701-2018
982 Holzinger, R., Lee, A., Paw, K.T., Goldstein, U.A.H., 2005. Observations of oxidation products above a forest imply
983   biogenic emissions of very reactive compounds. Atmospheric Chemistry and Physics 5, 67–75.
984 Hu, W.W., Campuzano-Jost, P., Palm, B.B., Day, D.A., Ortega, A.M., Hayes, P.L., Krechmer, J.E., Chen, Q., Kuwata, M.,
985   Liu, Y.J., de Sá, S.S., McKinney, K., Martin, S.T., Hu, M., Budisulistiorini, S.H., Riva, M., Surratt, J.D., St. Clair,
986   J.M., Isaacman-Van Wertz, G., Yee, L.D., Goldstein, A.H., Carbone, S., Brito, J., Artaxo, P., de Gouw, J.A., Koss,
987   A., Wisthaler, A., Mikoviny, T., Karl, T., Kaser, L., Jud, W., Hansel, A., Docherty, K.S., Alexander, M.L.,
988   Robinson, N.H., Coe, H., Allan, J.D., Canagaratna, M.R., Paulot, F., Jimenez, J.L., 2015. Characterization of a real-
989   time tracer for isoprene epoxydiols-derived secondary organic aerosol (IEPOX-SOA) from aerosol mass
990   spectrometer measurements. Atmospheric Chemistry and Physics 15, 11807–11833. https://doi.org/10.5194/acp-15-
991   11807-2015
992 IPCC (Ed.), 2007. Climate change 2007: the physical science basis: contribution of Working Group I to the Fourth
993   Assessment Report of the Intergovernmental Panel on Climate Change. Cambridge University Press, Cambridge ;
994   New York.

Jimenez, J.L., Canagaratna, M.R., Donahue, N.M., Prevot, A.S.H., Zhang, Q., Kroll, J.H., DeCarlo, P.F., Allan, J.D., Coe, H., Ng, N.L., Aiken, A.C., Docherty, K.S., Ulbrich, I.M., Grieshop, A.P., Robinson, A.L., Duplissy, J., Smith, J.D., Wilson, K.R., Lanz, V.A., Hueglin, C., Sun, Y.L., Tian, J., Laaksonen, A., Raatikainen, T., Rautiainen, J., Vaattovaara, P., Ehn, M., Kulmala, M., Tomlinson, J.M., Collins, D.R., Cubison, M.J., Dunlea, E., Huffman, J.A., Onasch, T.B., Alfarra, M.R., Williams, P.I., Bower, K., Kondo, Y., Schneider, J., Drewnick, F., Borrmann, S., Weimer, S., Demerjian, K., Salcedo, D., Cottrell, L., Griffin, R., Takami, A., Miyoshi, T., Hatakeyama, S., Shimono, A., Sun, J.Y., Zhang, Y.M., Dzepina, K., Kimmel, J.R., Sueper, D., Jayne, J.T., Herndon, S.C., Trimborn, A.M., Williams, L.R., Wood, E.C., Middlebrook, A.M., Kolb, C.E., Baltensperger, U., Worsnop, D.R., 2009. Evolution of Organic Aerosols in the Atmosphere. Science 326, 1525–1529. https://doi.org/10.1126/science.1180353

Jokinen, T., Berndt, T., Makkonen, R., Kerminen, V.-M., Junninen, H., Paasonen, P., Stratmann, F., Herrmann, H., Guenther, A.B., Worsnop, D.R., Kulmala, M., Ehn, M., Sipilä, M., 2015. Production of extremely low volatile organic compounds from biogenic emissions: Measured yields and atmospheric implications. Proceedings of the National Academy of Sciences 112, 7123–7128. https://doi.org/10.1073/pnas.1423977112

Kanakidou, M., Seinfeld, J.H., Pandis, S.N., Barnes, I., Dentener, F.J., Facchini, M.C., Dingenen, R.V., Ervens, B., Nenes, A., Nielsen, C.J., others, 2005. Organic aerosol and global climate modelling: a review. Atmospheric Chemistry and Physics 5, 1053–1123.

Kroll, J.H., Donahue, N.M., Jimenez, J.L., Kessler, S.H., Canagaratna, M.R., Wilson, K.R., Altieri, K.E., Mazzoleni, L.R., Wozniak, A.S., Bluhm, H., Mysak, E.R., Smith, J.D., Kolb, C.E., Worsnop, D.R., 2011. Carbon oxidation state as a metric for describing the chemistry of atmospheric organic aerosol. Nature Chemistry 3, 133–139. https://doi.org/10.1038/nchem.948

Kruijt, B., Malhi, Y., Lloyd, J., Norbre, A.D., Miranda, A.C., Pereira, M.G.P., Culf, A., Grace, J., 2000. Turbulence Statistics Above And Within Two Amazon Rain Forest Canopies. Boundary-Layer Meteorology 94, 297–331. https://doi.org/10.1023/A:1002401829007

Leong, Y.J., Sanchez, N.P., Wallace, H.W., Cevik, B.K., Hernandez, C.S., Han, Y., Flynn, J.H., Massoli, P., Floerchinger, C., Fortner, E.C., Herndon, S., Bean, J.K., Ruiz, L.H., Jeon, W., Choi, Y., Lefer, B., Griffin, R.J., 2017. Overview of surface measurements and spatial characterization of submicrometer particulate matter during the DISCOVER-AQ 2013 campaign in Houston, TX. Journal of the Air & Waste Management Association 67, 854–872. https://doi.org/10.1080/10962247.2017.1296502

Makar, P.A., Staebler, R.M., Akingunola, A., Zhang, J., McLinden, C., Kharol, S.K., Pabla, B., Cheung, P., Zheng, Q., 2017. The effects of forest canopy shading and turbulence on boundary layer ozone. Nature Communications 8, 15243, https://doi.org/10.1038/ncomms15243

Marais, E.A., Jacob, D.J., Jimenez, J.L., Campuzano-Jost, P., Day, D.A., Hu, W., Krechmer, J., Zhu, L., Kim, P.S., Miller, C.C., Fisher, J.A., Travis, K., Yu, K., Hanisco, T.F., Wolfe, G.M., Arkinson, H.L., Pye, H.O.T., Froyd, K.D., Liao, J., McNeill, V.F., 2016. Aqueous-phase mechanism for secondary organic aerosol formation from isoprene: application to the southeast United States and co-benefit of SO$_2$ emission controls. Atmospheric Chemistry and Physics 16, 1603–1618. https://doi.org/10.5194/acp-16-1603-2016

Middlebrook, A.M., Bahreini, R., Jimenez, J.L., Canagaratna, M.R., 2012. Evaluation of Composition-Dependent Collection Efficiencies for the Aerodyne Aerosol Mass Spectrometer using Field Data. Aerosol Science and Technology 46, 258–271. https://doi.org/10.1080/02786826.2011.620041

Millet, D.B., Alwe, H.D., Chen, X., Deventer, M.J., Griffis, T.J., Holzinger, R., Bertman, S.B., Rickly, P.S., Stevens, P.S., Léonardis, T., Locoge, N., Dusanter, S., Tyndall, G.S., Alvarez, S.L., Erickson, M.H., Flynn, J.H., 2018. Bidirectional Ecosystem–Atmosphere Fluxes of Volatile Organic Compounds Across the Mass Spectrum: How Many Matter? ACS Earth and Space Chemistry 2, 764–777. https://doi.org/10.1021/acsearthspacechem.8b00061

Miyazaki, Y., Fu, P., Ono, K., Tachibana, E., Kawamura, K., 2014. Seasonal cycles of water-soluble organic nitrogen aerosols in a deciduous broadleaf forest in northern Japan. J. Geophys. Res. Atmos. 119, 1440–1454. https://doi.org/10.1002/2013JD020713

Mohr, C., DeCarlo, P.F., Heringa, M.F., Chirico, R., Slowik, J.G., Richter, R., Reche, C., Alastuey, A., Querol, X., Seco, R., Peñuelas, J., Jiménez, J.L., Crippa, M., Zimmermann, R., Baltensperger, U., Prévôt, A.S.H., 2012. Identification

1044   and quantification of organic aerosol from cooking and other sources in Barcelona using aerosol mass spectrometer
1045   data. Atmospheric Chemistry and Physics 12, 1649–1665. https://doi.org/10.5194/acp-12-1649-2012
1046 NADP, 2016. National Atmospheric Deposition Program, National Trends Network (NTN) Site Details [WWW Document].
1047   URL http://nadp.slh.wisc.edu/data/sites/siteDetails.aspx?net=NTN&id=MI09 (accessed 6.21.18).
1048 Ng, N.L., Canagaratna, M.R., Zhang, Q., Jimenez, J.L., Tian, J., Ulbrich, I.M., Kroll, J.H., Docherty, K.S., Chhabra, P.S.,
1049   Bahreini, R., Murphy, S.M., Seinfeld, J.H., Hildebrandt, L., Donahue, N.M., DeCarlo, P.F., Lanz, V.A., Prévôt,
1050   A.S.H., Dinar, E., Rudich, Y., Worsnop, D.R., 2010. Organic aerosol components observed in Northern
1051   Hemispheric datasets from Aerosol Mass Spectrometry. Atmospheric Chemistry and Physics 10, 4625–4641.
1052   https://doi.org/10.5194/acp-10-4625-2010
1053 Öztürk, F., Bahreini, R., Wagner, N.L., Dubé, W.P., Young, C.J., Brown, S.S., Brock, C.A., Ulbrich, I.M., Jimenez, J.L.,
1054   Cooper, O.R., Middlebrook, A.M., 2013. Vertically resolved chemical characteristics and sources of submicron
1055   aerosols measured on a Tall Tower in a suburban area near Denver, Colorado in winter. J. Geophys. Res. Atmos.
1056   118, 2013JD019923. https://doi.org/10.1002/2013JD019923
1057 Paatero, P., 1997. Least squares formulation of robust non-negative factor analysis. Chemometrics and Intelligent Laboratory
1058   Systems 37, 23–35.
1059 Paatero, P., Tapper, U., 1994. Positive matrix factorization: A non-negative factor model with optimal utilization of error
1060   estimates of data values. Environmetrics 5, 111–126.
1061 Polissar, A., 1999. The aerosol at Barrow, Alaska: long-term trends and source locations. Atmospheric Environment 33,
1062   2441–2458. https://doi.org/10.1016/S1352-2310(98)00423-3
1063 Polissar, A.V., Hopke, P.K., Harris, J.M., 2001. Source Regions for Atmospheric Aerosol Measured at Barrow, Alaska.
1064   Environ. Sci. Technol. 35, 4214–4226. https://doi.org/10.1021/es0107529
1065 Pryor, S.C., Larsen, S.E., Sørensen, L.L., Barthelmie, R.J., Grönholm, T., Kulmala, M., Launiainen, S., Rannik, Ü., Vesala,
1066   T., 2007. Particle fluxes over forests: Analyses of flux methods and functional dependencies. Journal of
1067   Geophysical Research 112. https://doi.org/10.1029/2006JD008066
1068 Pugh, T. a. M., MacKenzie, A.R., Hewitt, C.N., Langford, B., Edwards, P.M., Furneaux, K.L., Heard, D.E., Hopkins, J.R.,
1069   Jones, C.E., Karunaharan, A., Lee, J., Mills, G., Misztal, P., Moller, S., Monks, P.S., Whalley, L.K., 2010.
1070   Simulating atmospheric composition over a South-East Asian tropical rainforest: performance of a chemistry box
1071   model. Atmospheric Chemistry and Physics 10, 279–298. https://doi.org/10.5194/acp-10-279-2010
1072 Rannik, Ü., Zhou, L., Zhou, P., Gierens, R., Mammarella, I., Sogachev, A., Boy, M., 2016. Aerosol dynamics within and
1073   above forest in relation to turbulent transport and dry deposition. Atmospheric Chemistry and Physics 16, 3145–
1074   3160. https://doi.org/10.5194/acp-16-3145-2016
1075 Rizzo, L.V., Artaxo, P., Karl, T., Guenther, A.B., Greenberg, J., 2010. Aerosol properties, in-canopy gradients, turbulent
1076   fluxes and VOC concentrations at a pristine forest site in Amazonia. Atmospheric Environment 44, 503–511.
1077   https://doi.org/10.1016/j.atmosenv.2009.11.002
1078 Schulze, B.C., Wallace, H.W., Bui, A.T., Flynn, J.H., Erickson, M.H., Alvarez, S., Dai, Q., Usenko, S., Sheesley, R.J.,
1079   Griffin, R.J., 2018. The impacts of regional shipping emissions on the chemical characteristics of coastal submicron
1080   aerosols near Houston, TX. Atmospheric Chemistry and Physics 18, 14217–14241. https://doi.org/10.5194/acp-18-
1081   14217-2018
1082 Schulze, B.C., Wallace, H.W., Flynn, J.H., Lefer, B.L., Erickson, M.H., Jobson, B.T., Dusanter, S., Griffith, S.M., Hansen,
1083   R.F., Stevens, P.S., VanReken, T., Griffin, R.J., 2017. Differences in BVOC oxidation and SOA formation above
1084   and below the forest canopy. Atmospheric Chemistry and Physics 17, 1805–1828. https://doi.org/10.5194/acp-17-
1085   1805-2017
1086 Seinfeld, J.H., Pandis, S.N., 2006. Atmospheric chemistry and physics : from air pollution to climate change. Hoboken, N.J. :
1087   John Wiley, ©2006.
1088 Sheesley, R.J., Schauer, J.J., Bean, E., Kenski, D., 2004. Trends in Secondary Organic Aerosol at a Remote Site in
1089   Michigan's Upper Peninsula. Environmental Science & Technology 38, 6491–6500.
1090   https://doi.org/10.1021/es049104q
1091 Sirois, A., Bottenheim, J.W., 1995. Use of backward trajectories to interpret the 5-year record of PAN and O_3 ambient air
1092   concentrations at Kejimkujik National Park, Nova Scotia. Journal of Geophysical Research 100, 2867.
1093   https://doi.org/10.1029/94JD02951

Stein, A.F., Draxler, R.R., Rolph, G.D., Stunder, B.J.B., Cohen, M.D., Ngan, F., 2015. NOAA's HYSPLIT Atmospheric Transport and Dispersion Modeling System. Bulletin of the American Meteorological Society 96, 2059–2077. https://doi.org/10.1175/BAMS-D-14-00110.1

Steiner, A.L., Pressley, S.N., Botros, A., Jones, E., Chung, S.H., Edburg, S.L., 2011. Analysis of coherent structures and atmosphere-canopy coupling strength during the CABINEX field campaign. Atmospheric Chemistry and Physics 11, 11921–11936. https://doi.org/10.5194/acp-11-11921-2011

Stroud, C., Makar, P., Karl, T., Guenther, A., Geron, C., Turnipseed, A., Nemitz, E., Baker, B., Potosnak, M., Fuentes, J.D., 2005. Role of canopy-scale photochemistry in modifying biogenic-atmosphere exchange of reactive terpene species: Results from the CELTIC field study. Journal of Geophysical Research: Atmospheres 110. https://doi.org/10.1029/2005JD005775

Thomas, C., Foken, T., 2007. Flux contribution of coherent structures and its implications for the exchange of energy and matter in a tall spruce canopy. Boundary-Layer Meteorology 123, 317–337. https://doi.org/10.1007/s10546-006-9144-7

Thornberry, T., Carroll, M.A., Keeler, G.A., Sanford, S., Bertman, S.B., Pippin, M.R., Ostling, K., Grossenbacher, J.W., Shepson, P.B., Cooper, O.R., Moody, J.L., Stockwell, W.R., 2001. Observations of reactive oxidized nitrogen and speciation of NO_y during the PROPHET summer 1998 intensive. Journal of Geophysical Research 106, 359–386.

Toma, S., Bertman, S., 2012. The atmospheric potential of biogenic volatile organic compounds from needles of white pine (Pinus strobus) in Northern Michigan. Atmospheric Chemistry and Physics 12, 2245–2252. https://doi.org/10.5194/acp-12-2245-2012

Ulbrich, I.M., Canagaratna, M.R., Zhang, Q., Worsnop, D.R., Jimenez, J.L., 2009. Interpretation of organic components from Positive Matrix Factorization of aerosol mass spectrometric data. Atmospheric Chemistry and Physics 9, 2891–2918.

US Census Bureau, 2018. City and Town Population Totals: 2010-2016 [WWW Document]. URL https://www.census.gov/data/tables/2016/demo/popest/total-cities-and-towns.html (accessed 1.24.18).

VanReken, T.M., Mwaniki, G.R., Wallace, H.W., Pressley, S.N., Erickson, M.H., Jobson, B.T., Lamb, B.K., 2015. Influence of air mass origin on aerosol properties at a remote Michigan forest site. Atmospheric Environment 107, 35–43. https://doi.org/10.1016/j.atmosenv.2015.02.027

Wallace, H.W., Sanchez, N.P., Flynn, J.H., Erickson, M.H., Lefer, B.L., Griffin, R.J., 2018. Source apportionment of particulate matter and trace gases near a major refinery near the Houston Ship Channel. Atmospheric Environment 173, 16–29. https://doi.org/10.1016/j.atmosenv.2017.10.049

Wang, Y.Q., 2014. MeteoInfo: GIS software for meteorological data visualization and analysis: Meteorological GIS software. Meteorological Applications 21, 360–368. https://doi.org/10.1002/met.1345

Wang, Y.Q., Zhang, X.Y., Draxler, R.R., 2009. TrajStat: GIS-based software that uses various trajectory statistical analysis methods to identify potential sources from long-term air pollution measurement data. Environmental Modelling & Software 24, 938–939. https://doi.org/10.1016/j.envsoft.2009.01.004

Whitehead, J.D., Gallagher, M.W., Dorsey, J.R., Robinson, N., Gabey, A.M., Coe, H., McFiggans, G., Flynn, M.J., Ryder, J., Nemitz, E., Davies, F., 2010. Aerosol fluxes and dynamics within and above a tropical rainforest in South-East Asia. Atmospheric Chemistry and Physics 10, 9369–9382. https://doi.org/10.5194/acp-10-9369-2010

Wiedinmyer, C., Greenberg, J., Guenther, A., Hopkins, B., Baker, K., Geron, C., Palmer, P.I., Long, B.P., Turner, J.R., Pétron, G., Harley, P., Pierce, T.E., Lamb, B., Westberg, H., Baugh, W., Koerber, M., Janssen, M., 2005. Ozarks Isoprene Experiment (OZIE): Measurements and modeling of the "isoprene volcano." Journal of Geophysical Research: Atmospheres 110. https://doi.org/10.1029/2005JD005800

Wolfe, G.M., Thornton, J.A., 2011. The Chemistry of Atmosphere-Forest Exchange (CAFE) Model – Part 1: Model description and characterization. Atmospheric Chemistry and Physics 11, 77–101. https://doi.org/10.5194/acp-11-77-2011

Xu, L., Pye, H.O.T., He, J., Chen, Y.L., Murphy, B.N., Ng, N.L., 2018. Experimental and model estimates of the contributions from biogenic monoterpenes and sesquiterpenes to secondary organic aerosol in the southeastern United States. Atmospheric Chemistry and Physics 18, 12613-12637. https://doi.org/10.5194/acp-18-12613-2018

Xu, L., Suresh, S., Guo, H., Weber, R.J., Ng, N.L., 2015. Aerosol characterization over the southeastern United States using high-resolution aerosol mass spectrometry: spatial and seasonal variation of aerosol composition and sources with a

focus on organic nitrates. Atmospheric Chemistry and Physics 15, 7307–7336. https://doi.org/10.5194/acp-15-7307-2015

Zhang, Q., Jimenez, J.L., Canagaratna, M.R., Allan, J.D., Coe, H., Ulbrich, I., Alfarra, M.R., Takami, A., Middlebrook, A.M., Sun, Y.L., Dzepina, K., Dunlea, E., Docherty, K., DeCarlo, P.F., Salcedo, D., Onasch, T., Jayne, J.T., Miyoshi, T., Shimono, A., Hatakeyama, S., Takegawa, N., Kondo, Y., Schneider, J., Drewnick, F., Borrmann, S., Weimer, S., Demerjian, K., Williams, P., Bower, K., Bahreini, R., Cottrell, L., Griffin, R.J., Rautiainen, J., Sun, J.Y., Zhang, Y.M., Worsnop, D.R., 2007. Ubiquity and dominance of oxygenated species in organic aerosols in anthropogenically-influenced Northern Hemisphere midlatitudes: Ubiquity and dominance of oxygenated OA. Geophysical Research Letters 34, 6. https://doi.org/10.1029/2007GL029979

Zhang, Q., Jimenez, J.L., Canagaratna, M.R., Ulbrich, I.M., Ng, N.L., Worsnop, D.R., Sun, Y., 2011. Understanding atmospheric organic aerosols via factor analysis of aerosol mass spectrometry: a review. Analytical and Bioanalytical Chemistry 401, 3045–3067. https://doi.org/10.1007/s00216-011-5355-y

Zhang, Q., Worsnop, D.R., Canagaratna, M.R., Jimenez, J.L., 2005. Hydrocarbon-like and oxygenated organic aerosols in Pittsburgh: insights into sources and processes of organic aerosols. Atmospheric Chemistry and Physics 5, 3289–3311.