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Physiochemical and Molecular Insights into the Boundary Layer and Free Troposphere Aerosol Interactions Over the Southern Great Plains

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Abstract

Ambient aerosols' vertical profiles are critical for evaluating the role of aerosols in atmospheric chemistry and radiative transfer, but limited data on these profiles hinders our ability to fully assess their impact on the Earth's radiative balance. Here, we investigated the size-, time-, and altitude-resolved composition of individual particles and bulk molecular composition of particle samples collected by an uncrewed aerial system—ArcticShark over the Southern Great Plains. Single particle microanalysis shows that, the free tropospheric (FT) samples are dominated (56-66%) by carbonaceous sulfate particles, while boundary layer (BL) samples are dominated (57-74%) by carbonaceous particles. Back trajectory simulations suggest that FT particles are likely influenced by long-range transport and have undergone aqueous-phase processing. Conversely, in-situ size distribution data shows evidence of particle growth in the upper BL and just below the FT. This observation may indicate vertical transport of particles from an elevated aerosol layer in the FT, possibly linked to a new particle formation event. This observation is further supported by high-resolution molecular composition data, which reveals particle volatility increasing with increasing size, which aligns with the growth event. This study aids in fundamental understanding of the compositional and molecular specificity of vertically resolved organic aerosols to provide insights into particle size evolution for future atmospheric models.

KEYWORDS

ArcticShark, vertically-resolved, single particle, molecular composition, aqueous phase processing

SYNOPSIS STATEMENT

The molecular composition of organic aerosol offers valuable insights into particle growth and atmospheric processing.

1. Introduction

Atmospheric aerosols play a critical role in the Earth's energy systems, influencing global radiative budget, regional air quality, and human health¹⁻³. Aerosols can affect Earth's radiation balance by scattering and absorbing sunlight and by modifying the properties and lifetimes of clouds⁴⁻⁶. The effects of aerosols on Earth's energy system are quantified by direct radiative forcing (DRF), which is strongly influenced by the vertical distribution of ambient aerosols and their physicochemical properties. For example, aerosol populations with higher concentration of light absorbing species such as black carbon and organic carbon like brown carbon have considerably higher DRF⁷ than particle populations with light scattering species. For example, inorganic salt aerosols, like sea salt, can be light-scattering particles and effective cloud condensation nuclei (CCN), which can primarily have a cooling effect⁸. Moreover, for the same type of particles, size resolved data is crucial for understanding how aerosols contribute to cloud condensation nuclei (CCN), which affects indirect radiative forcing by altering cloud properties⁵. Additionally, the size of the aerosol affects its scattering properties thereby modifying its DRF^{5, 8, 9}. Without size and molecularly resolved data, accurately estimating the aerosol DRF will remain a challenge.

Further, aerosol chemical composition and morphology can vary rapidly with time and altitude¹⁰ due to rapid and dynamic processes, such as new particle formation (NPF), particle growth, transport, and deposition, which leads to high chemical and vertical variability^{11, 12}. Thus, it is essential to have high time resolution measurements to capture the rapid evolution of aerosols to improve our knowledge of their role in interacting with solar radiation and clouds. Additionally, dynamic atmospheric processes are not confined to isolated layers but often involve interactions across multiple atmospheric layers¹³ such as between the boundary layer (BL) and free troposphere (FT). For example, FT particles can be transported to the BL via entrainment¹⁴, and other events in which cold, dry air rapidly descends from the FT down to the BL¹⁵⁻¹⁸, and the influence on BL aerosol composition is not well studied. Therefore, understanding of aerosol transport between different atmospheric layers can further benefit the modeling of aerosol DRF.

However, observations of aerosol vertical distribution remain limited, despite its critical importance for accurately representing aerosol impacts on Earth's energy system in models^{19, 20}. There have been expansive aerial campaigns (e.g., CAIPEEX, ATom)²¹⁻²⁴ that have investigated vertically resolved atmospheric properties (e.g., aqueous phase processing, seasonal variability). Despite their successes, there is still an overall lack of sampling efforts that have facilitated vertically resolved interrogation of increasingly specific particle properties, namely single particle elemental and molecular-level compositions. Most particle measurements and observations have been conducted at the ground level and might not provide vertical profile measurements. Ground-based remote sensing instruments, such as radiometers and lidars, typically provide either aerosol total column measurements or lack detailed size-resolved and chemical composition information²⁵. For example, the Atmospheric Radiation Measurement (ARM) facility uses a Raman lidar in many of their field campaigns that gives vertical aerosol extinction profiles²⁶. While understanding how the aerosol extinction coefficient varies with altitude is important, these data still lack in detailed particle chemical composition. Furthermore, ARM conducted many years of routine aircraft flights during various seasons to understand the temporal and spatial variability of aerosol optical properties²⁷. Scattering and absorption profiles

showed significant seasonal differences, with highest aerosol loading in the summer, and lowest in winter, however, these measurements did not include molecular insights. While these remote sensing techniques and flight measurements are valuable, they may not accurately represent aerosols vertical profile with size resolved particle chemical composition.

Moreover, there is limited availability of vertically resolved data with molecular insights, specifically between the BL and FT. One study found that in near-cloud environments in samples taken aloft, there was an increase in the size mode of the carbonaceous sulfate (CNOS) particles⁹. This study featured the vertical profile of various aerosol types, however molecularly resolved data was not reported. Moreover, a separate study found an abundance of organonitrate molecular formulae (CHNO MF) in samples taken aloft versus ground samples with cloudy conditions in the Southern Great Plains²⁸. While this study featured molecularly resolved data, it does not feature vertical profiling. In addition, both studies utilized the Tethered Balloon System (TBS) to collect sample measurements, thus, data was limited to the BL and therefore cannot account for the interaction between atmospheric layers. Furthermore, previous research reported on molecular insights of aircraft measurements from cloud water and below-cloud particles, finding evidence of hydrolysis of CHNO compounds in cloud water, highlighting chemical evolution during aqueous-phase processing²⁹. While these studies offer valuable insights into chemically and molecularly resolved aerosol data, there are very few studies²⁸⁻³⁰ which involve molecularly resolved data with vertical profiling.

In this study, we utilize the U.S. Department of Energy's (DOE) ARM ArcticShark uncrewed aerial system, which provides a unique opportunity to study the interactions between BL and FT with high temporal and spatial resolution^{2, 30}. We present size-resolved aerosol composition and molecular insights into summertime ambient aerosols over the Southern Great Plains (SGP) region with vertical profiling. Based on the in-situ measurements coordinated with the comprehensive offline analysis, we report that our FT aerosol samples may be particles processed by aqueous phase processing during long-range transport, and the BL samples may have experienced particle growth and/or an interaction between the FT and BL based on the size evolution observed. This work uniquely demonstrates these interconnected microphysical and chemical processes by applying a suite of complementary techniques on co-located samples across a vertical atmospheric profile.

2. Materials and Methods

2.1 Ambient measurements and field sampling site

This study focuses on the ArcticShark² flight on June 19, 2023 over the ARM SGP central facility site, which began at 14:41 UTC and ended at 19:55 UTC. The ArcticShark collected samples at six altitudes for 20 minutes each: 1829 ± 10 m, 1676 ± 11 m, 1372 ± 13 m, 1067 ± 12 m, 762 ± 13 m, and 610 ± 11 m above mean sea level (AMSL). Further details on sample altitude and collection time can be found in Table S1 and the 3D flight path can be found in Figure S1. Ambient particles were collected on Transmission Electron Microscopy (TEM) Carbon type-B film grids, lacey grids, and silicon nitride substrates loaded on home-built four-stage (A, B, C, and D) cascade impactors³¹. We selected to analyze only D-stage substrates because particle concentrations were consistently highest on this stage and contained a greater fraction of organics than the other stages.

As a result, this stage provided the most statistically representative samples for single-particle analysis and ensured sufficient aerosol loading for bulk molecular composition measurements.

The Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT)^{32, 33} model simulation was performed to simulate the air masses transport pattern and relative humidity profiles seven days prior to sampling time for all altitudes (Figure S2a-d).

2.2 In situ and remote sensing measurements of particle number concentration and meteorological conditions

A Portable Optical Particle Spectrometer (POPS) measured aerosol size distribution from 135 to 3,000 nm optical size (1Hz)³⁴ with concentration counting limits as 3000 cm^{-3} , an Advanced Mixing Condensation Particle Counter (mCPC) measured aerosol total number concentration between 7 at 2,000 nm (1Hz)³⁵ with concentration counting limits as 10^5 cm^{-3} , and an Aircraft Integrated Meteorological Measurement System (AIMMS) instruments measured aircraft altitude, latitude, longitude, and meteorological information (e.g., static temperature (1 Hz), relative humidity (3 Hz), and 3-D winds². These in situ instruments were mounted onboard the UAS ArcticShark.

Additionally, a doppler lidar operating at a wavelength of 1548 nm from the SGP central facility was used to measure backscattered light intensity and vertical wind speed, providing insights into BL mixing and turbulence²⁵. Lidar measures light backscattering, and higher backscattering than background indicates the presence of cloud or aerosol layers³⁵. The specific characteristics of the backscattered light, such as its intensity and spatial distribution, can also provide information about cloud properties such as cloud height, thickness, and type (e.g., water droplet clouds versus ice crystal clouds)²⁵. Lastly, the scanning mobility particle sizer (SMPS) located at the SGP ground site central facility was used to monitor the size distribution of particle in the diameter range from 10 to 500 nanometers³⁶.

2.3 Microscopy analysis of individual particles for chemical composition and carbon speciation

Samples collected on carbon B-film TEM grids were analyzed by an Environmental Scanning Electron Microscope (ESEM) (Quanta 3D, Thermo Fisher) equipped with an FEI Quanta digital field emission gun operated at 20 kV and 480 pA at 293 K under vacuum conditions ($\sim 2 \times 10^{-6}$ Torr). The Computer Controlled Scanning Electron Microscope (CCSEM) equipped with an energy-dispersive X-ray spectroscopy (EDX, Oxford, Inc.) was used to automatically probe the size and elemental composition of individual particles. EDX spectra were used to determine the elemental compositions of the particles by quantifying the relative percentages of 15 elements (C, N, O, Na, Mg, Al, Si, P, S, Cl, K, Ca, Mn, Fe, and Zn)³⁷. Based on the elemental composition, each particle was classified into CNO, CNOS, K_2SO_4 , and ‘Others’ categories (Figure S3).

Scanning Transmission X-Ray Microscopy with Near Edge X-Ray Absorption and Fine Structure Spectroscopy (STXM-NEXAFS) was performed at beamline 5.3.2.2 of the Advanced Light Source (ALS) at the Lawrence Berkeley National Laboratory to probe the chemical bonding of carbon functional groups of individual particles^{38, 39}. STXM-NEXAFS uses a focused

monochromatic soft X-ray beam generated by the synchrotron light source using a zone plate with 25 nm outer zones. Detailed STXM-NEXAFS analysis has been discussed in previous studies^{40, 41}. Briefly, we probed individual particles to provide classification based on carbon functionalities like organic carbon (OC), elemental carbon mixed with OC (EC + OC), OC mixed with inorganic (IN + OC), and particles containing mixtures of OC, EC, and IN (OC + EC + IN). We calculate the total carbon absorbances (TCA) and the organic volume fraction (OVF) based on the STXM-NEXAFS data, and values for altitude resolved samples are shown in Table S2⁴¹.

2.4 High resolution mass spectrometry analysis of bulk organic aerosol

For analysis of the organic molecular composition of the particles, we used nanospray desorption electrospray ionization with high-resolution mass spectrometry (nano-DESI-HRMS)⁴²⁻⁴⁴. Samples were collected on and desorbed from a silicon nitride substrate (4×4 mm). The source was scanned along the XY plane at 50 $\mu\text{m/s}$ within a 2 mm radius of the substrate center. Substrate setup can be found in figure S4. All nano-DESI experiments were coupled with a LTQ Velos Orbitrap high-resolution mass spectrometer (Thermo Scientific, Waltham) operated in negative ion mode. More information on sample acquisitions, processing, and formula assignments can be found in SI. The limited sample loading only permitted untargeted, MS1 level information to be acquired by nano-DESI HRMS.

3. Results and Discussion

3.1 In-situ and remote sensing measurements distinguish Free Tropospheric Layer from Boundary Layer

Lidar data from Figure 1a and 1b shows backscattering of light and vertical wind turbulence, respectively. The BL consists of the mixed layer characterized by high ($>10 \text{ m}^2/\text{s}^2$) vertical wind variance, and the entrainment zone approaching the BL top, where it becomes less well mixed. The large vertical variance in the lower BL indicates the BL has strong updrafts and downdrafts, which will make the boundary layer well mixed. Likewise, if a convective boundary layer is topped by a stable layer, turbulent mixing can lead to the formation of a well-mixed BL layer such as the one observed at the sampling site. Such BL are common over land during the day when surface heating is strong, such as during the summertime in the SGP, where the surface temperature becomes over 30°C during the daytime. During sampling time, data from the Infrared Thermometer at the SGP central facility showed that the ground surface temperature at the SGP site was between 32-35°C (Figure S5). Figure 1a-b shows the BL top at around 1100 m during sampling time, which indicates that 1829m, 1676m, and 1372m samples were collected in the FT, and 1067m, 762m, and 610m samples were collected within the BL near the entrainment zone. Furthermore, the lidar data shown in Figure 1a suggests the presence of a thin cloud layer above the 1829m sample.

In-situ measurements from mCPC and POPS particle number concentration relative humidity (%) and temperature (°C) are shown in Figures 1c-f, respectively. In general, particle number concentrations from mCPC and POPS steadily decrease from 3000 to 2000 cm^{-3} and from 300 to 200 cm^{-3} , respectively, with increasing altitude within the BL from 200-1000m. This differs from

the FT, where mCPC significantly increased (200%) from the bottom of the FT to the elevated aerosol layer (EAL) from 1200-1700m, but POPS did not change proportionately (36%) in this range. This suggests that the particle size increase occurred most in smaller size ranges (<135 nm), which cannot be detected by POPS. Within the FT, particle number concentrations increase, with the most marked increase in both mCPC (from 1000 to 3300cm⁻³) and POPS (from 250 to 350cm⁻³) concentrations from 1372m sampling altitude to 1676m. The observed increase in particle concentration was noted as an elevated aerosol layer (EAL), which is a period marked by a significant increase in particle number concentration. The increase in mCPC at the EAL in the FT is more significant in smaller size ranges (<135nm), which could be explained by NPF⁴⁵.

Furthermore, within the well-mixed BL, relative humidity trends slightly upwards from 50% to 60% with increasing altitudes from 200-600m. However, as it reaches the entrainment zone, RH% decreases to 40%. RH% decreases to 30% at the altitude associated with the transition to the FT from 1000-1100m, where it remains relatively unchanging throughout the FT. Ambient temperature profiles steadily decrease from 27°C to 18°C with an increasing altitude from 610m to 1829m.

While this study showcases data from a single day, it is important to note that this data is representative for typical summertime ambient conditions at the SGP site. The size distribution measurements align with broader trends observed within the ARM dataset at the SGP (Figure S6). For example, the other flights at the SGP site that were conducted in June 09 shows similar vertical profile pattern (Figure S7). Likewise, ground SMPS data frequently indicate particle growth events occurring in the mid-morning or early afternoon across several days in June. Furthermore, Mei et al⁴⁶ summarized the vertical profiles of in-situ particle concentration and size distribution measurements conducted in June 2023. Their results suggest that our sampling day is representative of typical conditions during that month.

3.2 Discrepancy of the physiochemical profiles of the Free Troposphere and Boundary Layer

Figure 2 presents the chemical composition of the collected samples, highlighting single-particle elemental profiles and organic molecular signatures derived from microscopy and high-resolution mass spectrometry analyses. As shown in Figure 2, the FT and BL showed considerable differences in size-resolved chemical composition, particle mixing and molecular composition. Within the FT, the dominant particle type was CNOS (61%) followed by CNO (37%) (Table S3). Contrarily, in the BL, 39% of particles are CNOS and 58% of particles in our samples are CNO. A small fraction (2%) of K₂SO₄ particles is observed in both the FT and BL. The dominant molecular formulae in both the FT and BL were CHO (52% and 62%, respectively). However, there are more CHNO and CHOS molecular formulae in the FT (32% and 16%, respectively) versus BL (25% and 13%, respectively). The STXM-NEXAFS data also presented differences in particle type between the FT and BL (Table S4). The largest difference observed was within the OC and OCIN. The FT contained 56% OCIN and 41% OC versus 63% and 34%, respectively in the BL. IN (2%) and OCEC (1%) made up the minority of particles in the FT, while OCINEC (2%) and OCEC (1%) dominated the minority of particles in the BL. Figure S8 and Figure S9 show normalized size distribution for CCSEM-EDX and STXM-NEXAFS, respectively for the FT and BL samples. Table S5 shows the TCA and OVF of each sampling altitude. The average TCA value for the FT

was 0.015 versus 0.028 in the BL. A similar trend was observed in the OVF values, where the FT average value was 0.323 vs the BL value of 0.553. The BL was therefore richer in organics than the FT, and reportedly showed more total carbon absorbance per particle than the FT.

3.3 Evidence of aqueous-phase processing in long-range transported FT aerosols

CCSEM-EDX data showed samples collected in the FT are dominated by CNOS (55-66%) particles (Figure 2). Large CNOS particles $>0.5\mu\text{m}$ dominated (60.1%) the 1829m sample (Figure S8). These large CNOS ($>0.5\mu\text{m}$) particles are often associated with cloud residuals. Lata et al found that aerosols that crossed the cloud layer contained large CNOS particles⁹. These results suggest that a substantial fraction of the particles in our FT sample may have been influenced by aqueous phase processes during transit. Additionally, a previous study reported that aloft aerosols in the Southern Great Plains contained a large proportion of MF containing CHNO²⁸. The high abundance (25.8- 36.4%) of nitrogen-containing organics (CHNO), with increasing altitude in this study may indicate that these particles could have been influenced by aqueous phase processing²⁹. However, RH% remains low ($<40\%$) during FT samples collection time and altitude. Although Doppler Lidar data shows the presence of very thin clouds from 2000-3000m in altitude approximately one hour prior to sampling at 1829m, HYSPLIT back trajectory simulation did not show an interaction between sample air masses and the cloud layer (Figure S2a). Thus, this excludes the possibility of local aqueous phase reactions for generating these large aqueous phase particles.

Conversely, HYSPLIT back trajectory simulation in Figure S2a shows air mass traveled from more than 4km in altitude 72 hours before they descended to the sampling site and were in high RH% conditions ($>80\%$ RH) 24 hours before sampling. Likewise, the three FT samples remained above 3km in altitude 8 hours before sampling and remained in high RH conditions ($>80\%$) 18 hours prior to sampling. Therefore, the observed size and chemical evolution of sulfate and nitrogen-containing organics may be due to aqueous phase processing during long-range transport.

3.4 Size evolution of BL aerosols suggests particle growth events

Here, we describe our observations of a particle growth event that may have originated as a new particle formation (NPF) event in the EAL in the FT. Since SMPS measurements were not available aloft, only at the ground site (Figure S10), we rely on data from the CPC and the POPS to explain the event. Additionally, we use molecular composition data to help explain the subsequent particle growth observed within the BL. Within the BL at the 1067m sample, the POPS data shows a clear increase in concentration from 200 to 300 cm^{-3} , whereas the mCPC did not change proportionally (11 %) in this region (Figure S11). Since the top of the BL layer is within the entrainment zone, and Doppler lidar wind data in Figure S12 suggests airmasses are being transported down, there may be some influence from the lower FT to the top of the BL. Specifically, the possible NPF event in the EAL may be transporting particles that are continuously growing into the top of the BL via the entrainment zone. These new particles that may have formed in the FT, which are detectable by mCPC, could have been transported down into the BL via the entrainment zone¹. During their transport, they continuously grow until reaching a size threshold ($>135\text{nm}$) that can be captured by POPS. A similar observation of particle transport during a NPF event from FT to

the BL was found at the SGP site in April 2016 during the HI-SCALE campaign¹. Specifically, fine aerosols from the lower free troposphere were entrained into the cleaner boundary layer, where they grew further as they descended toward the surface.

To investigate the influence of FT particles on BL particle composition, we probed their organic MF via HRMS. Figure 3b shows volatility values of the lowest FT sample (1372 m) and the BL sample post suspected particle growth event (762 m). From sample 1372 m, of the unique MF assigned, a total of 67% of the MF were assigned as LVOC (49%), and ELVOC (18%). In contrast, the 762m sample shows a broader distribution of volatility overall, but only 44% of MF assigned were assigned LVOC (35%) and ELVOC (9%). Therefore, there are more MF with lower volatility at the 1372m sampling altitude versus the 762m sampling altitude. These results suggest samples collected at 1372m are less volatile compared to those collected at 762m. This is consistent with the theory that particle growth events are initially driven by the condensation of low volatility species, and as particle size increases, they can incorporate a wider range of SVOCs and VOCs⁴⁷. Therefore, our results suggest that particle transport from FT to BL might contribute to the growth event observed in the top BL. These two samples showed the largest number of unique MF compared to all other samples, and the change in particle size between them was the most noticeable. The unique feature data can be found in Figure S13.

Furthermore, we postulate that the lower BL from 200-700m may have been influenced by ground emissions. First, ground measurements from SMPS instruments at the sampling site indicate that new particle formation events were occurring prior to sampling time from 13:00 to 15:00 UTC (Figure S10) due to the 250% increase in particle size mode from 50nm to 100nm. Since Doppler lidar data shows that the 610m sample is within the well-mixed layer (figure 1b), it is possible that ground emissions were mixed within the airmass sampled at this altitude. Likewise, HYSPLIT data shows that particles below 610m were likely influenced by local emissions during ground NPF, which was 6 hours prior to sampling time. To conclude, our results suggest that the particle growth event observed at the top of the BL was most likely influenced by the FT via entrainment, and particles at the lowest two altitudes could be influenced by ground emissions.

3.5 Association between hydrolysis reactions and relative humidity as a function of altitude

As an additional means of demonstrating the value of the vertically-resolved molecular-level information obtained through this study, Figure 4 presents an application of these data streams to inform mechanistic processes. Specifically, we interrogated our annotated MF lists per altitude-resolved sample for MFs consistent with the hydrolysis of nitrate functional groups as suggested by the scheme in Figure 4 (*i.e.*, identifying both $(\text{CHO})_x(\text{NO})_y$ and $(\text{CHO})_x(\text{NO})_{(y-1)}$ MFs in a single sample list may represent a precursor/product pair for nitrate hydrolysis). A similar analysis strategy was previously used by O'Brien *et al.* for interrogating imine formation.⁴⁸ We acknowledge that this approach is qualitative and that particle phase nitrate hydrolysis is highly dependent upon particle acidity.^{49, 50} Nevertheless, when both RH and percent hydrolysis (*i.e.*, percentage of all CHNO MF for which a corresponding CHO hydrolysis product was identified) are plotted against altitude, both trends are remarkably similar. Given the known association of RH with hydrolysis reactions in atmospheric aerosols.⁵¹ Figure 4 therefore provides foundational

evidence for using untargeted annotation lists to investigate a variety of other vertically-resolved phenomena/mechanisms in future applications (heterogeneous chemistry, nitrate oxidation, etc.).

Despite the limitations of HRMS only identifying molecular formula and not specific compounds, a clear observable trend was found between assumed hydrolysis reactions and relative humidity. Figure 4 shows the altitude-resolved hydrolysis reactions with respect to RH. With increasing RH%, the percentage of reactant/product CHNO/CHO pairs increases. Namely, within the BL, the sampling altitudes of 610m, 762m, and 1067m have a relative humidity between 40-50%. Of the 475, 597, and 525 MF assigned at these altitudes respectively, the percentage of hydrolysis was between 30-40%. Likewise, with increasing altitude, particularly at the planetary BL, RH% decreases significantly, below 30%, and the percentage of hydrolysis reactions follows this trend, decreasing to within 1.5-8%. Free tropospheric samples 1372m, 1676m and 1829m had 589, 581, and 355 assigned MF, respectively. These samples were found to have hydrolysis reactions in 1.4%, 7.7%, and 5% of assigned MF, respectively. For this particular study, hydrolysis reactions were found to be occurring most readily closer to the ground where the RH% was higher. Our data shows a correlation between hydrolysis reactions and relative humidity, with a decrease in RH and hydrolysis with increasing altitude, especially near the BL. The sharp decrease in hydrolysis with altitude highlights the importance of RH-resolved chemical mechanisms in modeling vertical aerosol transformation and their implications for air quality and climate forcing.

4. Implications

Our study provides a vertical profile of the size-resolved chemical composition and molecular composition of organic aerosols in the lower troposphere over the Southern Great Plains, a widely studied region essential for understanding aerosol processes in agriculturally influenced areas. Vertically resolved single-particle chemical composition, combined with particle size distribution measurements, enables estimation of hygroscopicity parameters and CCN concentrations. Future study with more samples that represent BL and FT samples can be used to derive volatility distribution of organic aerosols from molecular composition data. Moreover, the influence of RH-dependent hydrolysis on SOA formation and reactive nitrogen partitioning has significant implications for particle growth and CCN activation. These chemical mechanisms can modify aerosol phase states and alter their ability to act as CCN under varying atmospheric conditions.

Individual particle analyses and their mixing with different species within the BL and FT may provide insights into their cloud formation potential and optical properties^{52, 53}. These data and findings are critical for enhancing accuracy of single particle resolved models which are pivotal for understanding the role of aerosols in cloud formation and precipitation processes. Furthermore, molecular information of organic aerosols can improve the prediction of particle growth and evolution in future regional models such as WRF-CHEM^{54, 55}. The insights gained from our physiochemical and molecularly resolved measurements can refine the representation of dynamic vertical processes in atmospheric models by including a broader representation of particle types with chemical and molecular specificity, thereby improving the predictions of cloud condensation nuclei concentrations and their subsequent impact on cloud properties⁵⁶.

Associated Content

The Supporting Information is available free of charge.

Constant volatility values (Table S1); Sampling information (Table S2); CCSEM (Table S3) and STXM (Table S4) Particle class and fraction with standard error for each sample; Total Carbon Absorption from STXM-NEXAFS (Table S5); 3D flight pattern of sampling time (Figure S1); HYSPLIT Back Trajectory Simulations (Figure S2); CCSEM-EDX Classification (Figure S3); HRMS setup (Figure S4); Ground Temperature data for SGP site (Figure S5); . Ground SMPS data in June at the SGP site (Figure S6); Vertical profile of total aerosol number concentration from CPC and POPS during June 09 (Figure S7); CCSEM-EDX Normalized size distribution (Figure S8); STXM-NEXAFS Normalized size distribution (Figure S9); POPS and SMPS data for sampling time and prior to sampling time (Figure S10); Particle number concentration data for sampling period (Figure S11); Doppler Lidar data for sampling day (Figure S12); Unique features data from HRMS (Figure S13).

Notes

The authors declare no competing financial interest. In-situ aerosol and remote sensing measurements data used in this study are available in ARM data archive (<https://www.arm.gov/data/data-sources>).

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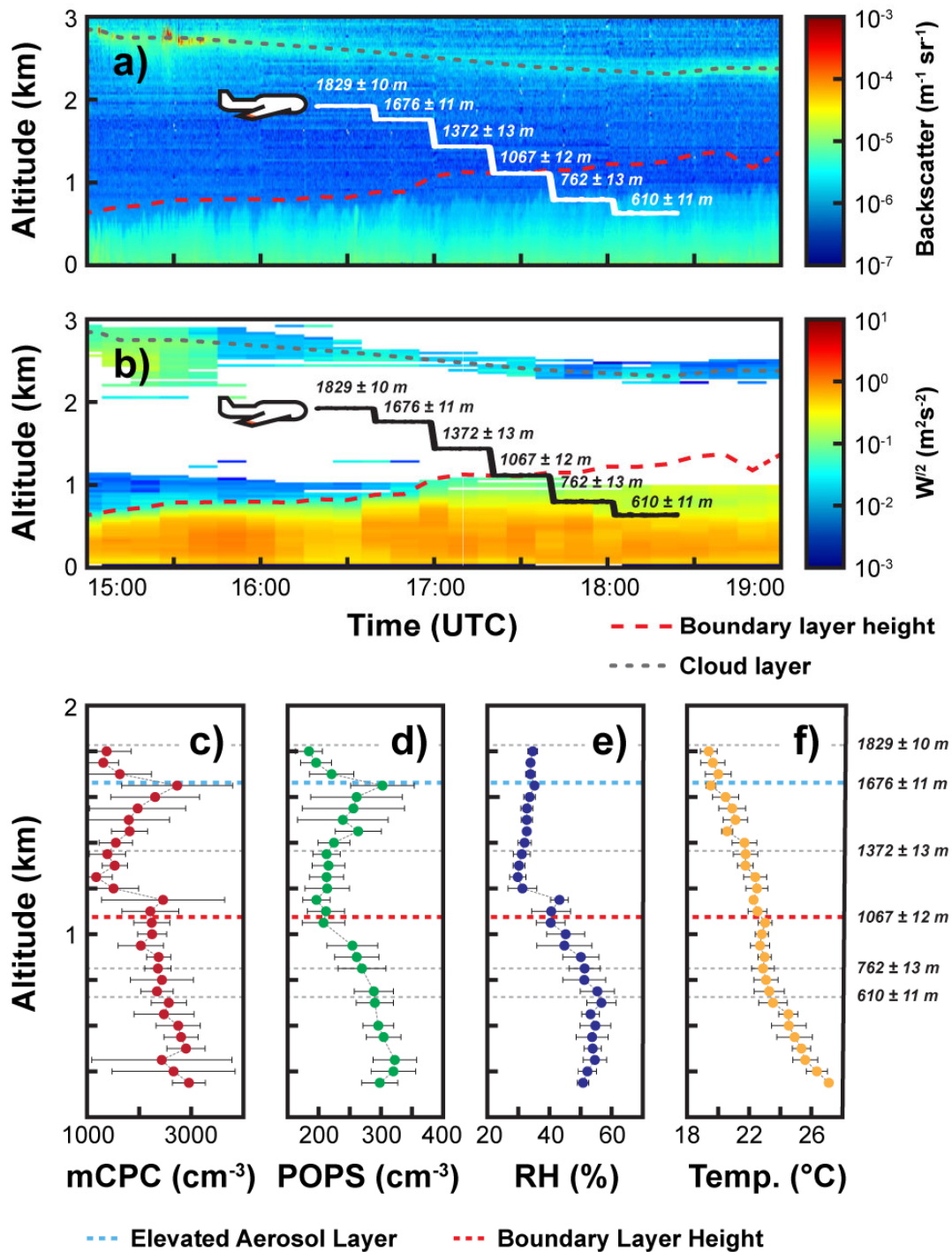


Figure 1. Doppler Lidar shows (a) particle backscatter at the wavelength of 1548 nm, and (b) vertical wind variance. Staircase pattern overlaid on lidar data in (a) and (b) highlights each sampling altitude. Red dotted line marks where the BL height is during sampling time, and a thin cloud layer is represented in lidar data by a gray dashed line. Total particle number concentration

is shown from (c) mCPC and (d) POPS instruments. Vertical profile of (e) relative humidity and (f) ambient temperature.

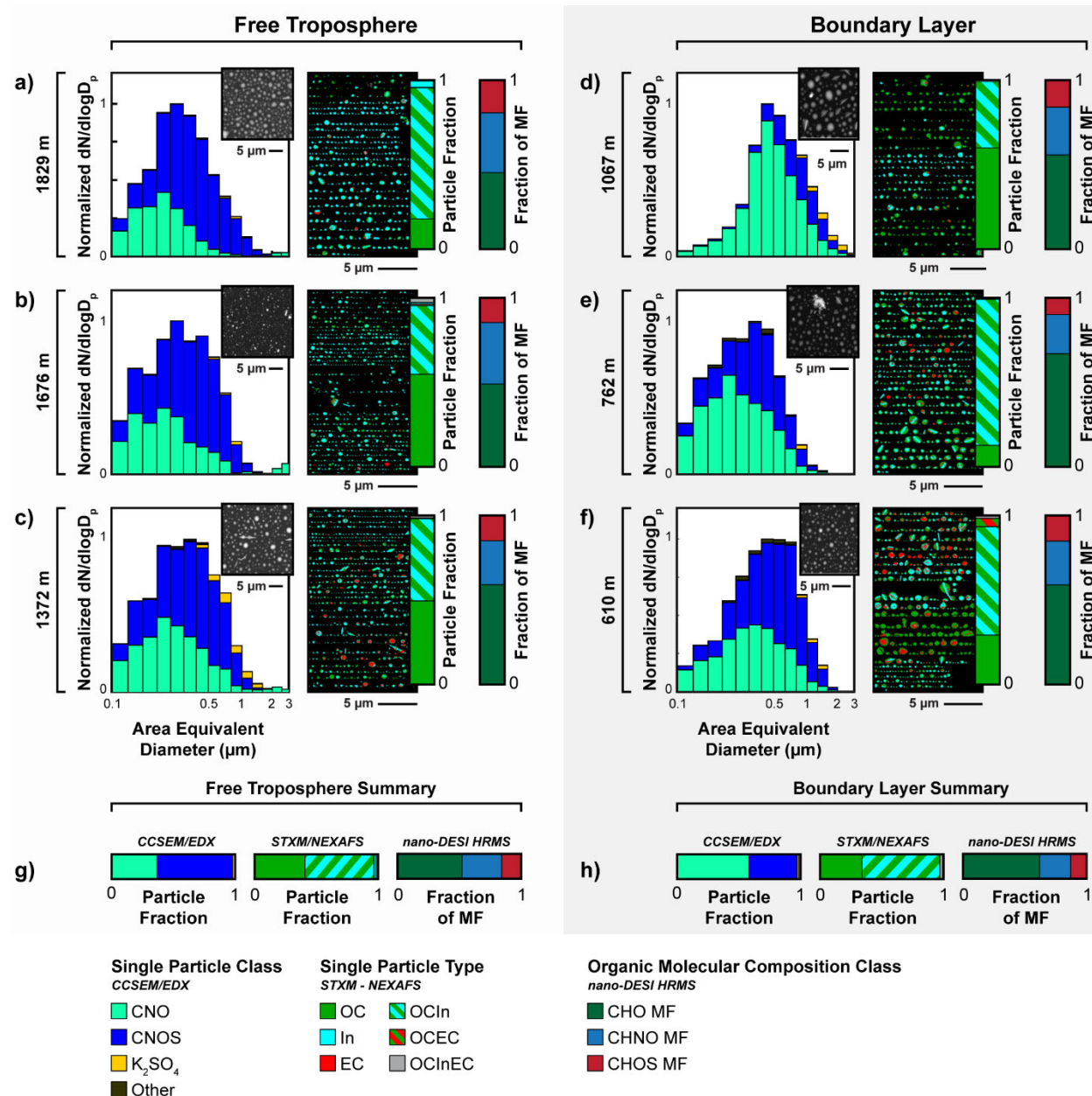


Figure 2. Offline chemical analysis results for samples collected during UAS ArcticShark campaign on June 19th, 2023. Each altitude resolved sample (a-f) shows CCSEM-EDX derived chemically resolved size distribution plots (left panel), individual particle mixing state from STXM-NEXAFS (middle panel), and carbon speciation maps, and percent contribution of organic molecular formulae from nano-DESI-HRMS analysis (right panel). Samples shown in (a-c) were collected in the free troposphere and (d-f) in the BL. Summary bars of CCSEM/EDX, STXM/NEXAFS, and nano-desi-HRMS are shown for the FT (g) and the BL (h).

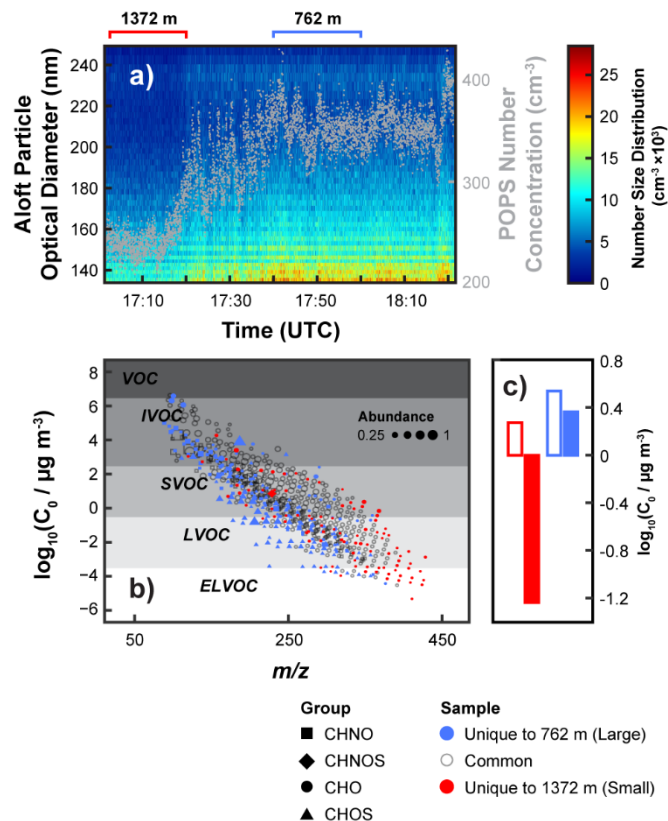


Figure 3. Particle number concentration and size distribution (a) from POPS measurements. Red 1372m box indicates sampling altitude before particle growth event (small particle size), and blue 762m box indicates sampling times after growth event (large particle size). Volatility plot (b) for particles from both sampling altitudes is shown. (c) bar charts that show the average parametrized volatility (i.e., $\log_{10}(C_0)$) for MFs commonly found in both samples (empty bars), as well as for MFs found uniquely in each sample (filled bars), further illustrating the lower volatility contributions to the 1372 m sample and higher volatility contributions to the 762 m sample.

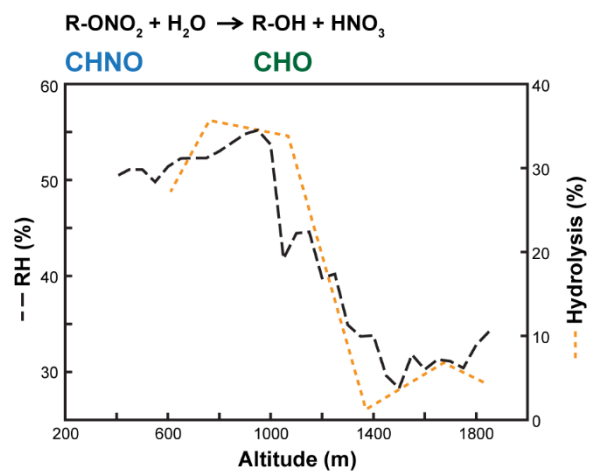


Figure 4. Percent of hydrolysis reactions of organonitrate groups with relative humidity and altitude in the UAS-ArcticShark campaign on June 19th, 2023 in the Southern Great Plains. Reaction shows a general reaction scheme of an organonitrate hydrolysis reaction during aqueous phase processing.

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