

1 **Investigating Types and Sources of Organic Aerosol in Rocky Mountain National**
2 **Park Using Aerosol Mass Spectrometry**

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1 **Abstract**

2 The environmental impacts of atmospheric particles are highlighted in remote areas where
3 visibility and ecosystem health can be degraded by even relatively low particle concentrations.
4 Submicron particle size, composition, and source apportionment were explored at Rocky
5 Mountain National Park using a High-Resolution Time-of-Flight Aerosol Mass Spectrometer.
6 This summer campaign found low average, but variable, particulate mass (PM) concentrations
7 (max = 93.1 $\mu\text{g}/\text{m}^3$, avg. = $5.13 \pm 2.72 \mu\text{g}/\text{m}^3$) of which $75.2 \pm 11.1\%$ is organic. Low-volatility
8 oxidized organic aerosol (LV-OOA, 39.3% of PM_{10} on average) identified using Positive Matrix
9 Factorization appears to be mixed with ammonium sulfate (3.9% and 16.6% of mass,
10 respectively), while semi-volatile OOA (27.6%) is correlated with ammonium nitrate (nitrate:
11 4.3%); concentrations of these mixtures are enhanced with upslope (SE) surface winds from the
12 densely populated Front Range area, indicating the importance of transport. A local biomass
13 burning organic aerosol (BBOA, 8.4%) source is suggested by mass spectral cellulose
14 combustion markers (m/z s 60 and 73) limited to brief, high-concentration, polydisperse events
15 (suggesting fresh combustion), a diurnal maximum at 22:00 local standard time (LST) when
16 campfires were set at adjacent summer camps, and association with surface winds consistent with
17 local campfire locations. The particle characteristics determined here represent typical
18 summertime conditions at the Rocky Mountain site based on comparison to ~10 years of
19 meteorological, particle composition, and fire data.

20 **1. Introduction**

21 From alpine meadows to stark peaks, Rocky Mountain National Park (RMNP) hosts abundant
22 wildlife, an important water catchment, and roughly 3 million visitors per year (Annual Park
23 Visitation Report, NPS Public Use Statistics Office). Recent studies chronicle visibility reduction
24 in RMNP, a Clean Air Act Class I protected environment, due to fine particles, especially in the
25 summer when concentrations are higher (Levin et al., 2009; Malm et al., 2009b). Environmental
26 impacts from increased nutrient - and particularly nitrogen - deposition are also documented in
27 the Colorado Rocky Mountains (Baron et al., 2000), where mountain-valley circulations
28 periodically transport ammonium, nitrate, and other particulate species from agricultural and
29 urban sources to the east (Benedict et al., 2013a&b). However, organic compounds contribute the
30 majority of fine-particle mass and attendant visibility impairment at RMNP during summer

1 months (average July 1991-2006 PM_{2.5} organic mass fraction = $51 \pm 6\%$, Levin et al., 2009);
2 unfortunately, beyond indications that contemporary carbon (denoting biomass burning and/or
3 biogenic VOC condensation) and organic nitrogen contribute to organic mass (Benedict et al.,
4 2013a; Schichtel et al., 2008), local organic aerosol (OA) types and sources are unknown. In fact,
5 studies concerning remote environments are infrequent despite the myriad health, environmental,
6 and climate effects of fine particles (Solomon et al., 2007) and the fact that such sites comprise
7 the atmospheric ‘background’ that contextualizes our developing understanding of atmospheric
8 chemistry. Those that do exist indicate a range of particle sources from transported urban
9 particles (e.g. Sun et al., 2009) to biomass burning (e.g. Corrigan et al., 2013) and secondary OA
10 formation involving biogenic VOCs (e.g. Chen et al., 2009); efficient mitigation strategies clearly
11 require a sophisticated understanding of OA sources.

12 This study explores particle sources and composition at a remote site in Rocky Mountain
13 National Park during 2 July-31 August 2010 as part of the Rocky Mountain Atmospheric
14 Nitrogen and Sulfur (RoMANS) Study. The Time-of-Flight Aerosol Mass Spectrometer (HR-
15 ToF-AMS or ‘AMS’) analyzes submicron, non-refractory particles quantitatively for size and
16 composition with high mass- and time- resolution (Decarlo et al., 2006); Positive Matrix
17 Factorization (PMF) is used to deconvolve a matrix containing 2-5 minute average organic mass
18 spectra into a number of spectrally-static organic ‘factors’ whose contributions to total organic
19 mass vary over time (Paatero & Tapper, 1994).

20 PMF-derived factor mass spectra (MS) may reveal particle sources through comparison with MS
21 profiles of various compounds and aerosol types (Alfarra et al., 2007; Lanz et al., 2007; Zhang et
22 al., 2011). Correlating factors with inorganic tracers by particle size and concentration may also
23 support source identification (Zhou et al., 2005). For instance, biomass burning organic aerosol
24 (BBOA) may be identified by fragments of levoglucosan (C₆H₁₀O₅) and other anhydrosugars -
25 products of cellulose and hemi-cellulose combustion - in the ambient mass spectra at m/z 60
26 (C₂H₄O₂⁺), m/z 73 (C₃H₅O₂⁺), etc. (Simoneit et al., 1999; Weimer et al., 2008); BBOA is
27 sometimes, but not always, correlated with potassium (K), another known combustion tracer
28 (Echalar et al., 1995; Sullivan et al., 2008).

29 Other common classifications are based on organic compounds’ degrees of oxidation.
30 Hydrocarbon-like Organic Aerosol (HOA) is produced chiefly by fuel combustion and
31 distinguished by hydrocarbon chains at m/z 57 (C₄H₉⁺, Lanz et al., 2007; Zhang et al., 2005). The

1 spectrum of Semi-Volatile Oxidized Organic Aerosol (SV-OOA or OOA-II) is characterized by
2 the predominance of hydrocarbons and/or carbonyls at m/z 43 ($C_3H_7^+$ or CH_3CO^+) over more
3 oxidized fragments at m/z 44 (mostly CO_2^+ , Lanz et al. 2007; Ulbrich et al. 2009). Lastly,
4 enhanced signal at m/z 44 indicates highly oxidized Low-Volatility Oxidized Organic Aerosol
5 (LV-OOA or OOA-I, Lanz et al. 2007; Ulbrich et al. 2009); oxidized OA is often observed in
6 rural and remote areas (Zhang et al., 2007). Using particle composition with factor analysis,
7 particle size, and meteorological data, this work constructs a comprehensive description of
8 submicron particle sources and suggests, through comparison to historical data, that these
9 represent ‘typical’ summer conditions at Rocky Mountain National Park.

10 **2. Methods**

11 Particles were sampled in a valley on the SE side of Rocky Mountain National Park at ~2740 m
12 (Lat: 40.2778, Long: 105.5453; Figure 1). The sampling site is adjacent to the Salvation Army
13 High Peak, Covenant Heights, Timberline, and Aspen Lodge Resort camps, but removed from
14 urban centers and considered rural; traffic on the nearby Colorado Hwy 7 is light. The AMS was
15 co-located with meteorological, CASTNet, and IMPROVE (designator: ROMO) stations, a
16 particle-into-liquid sampler (PILS-IC, Orsini et al., 2003), Hi-Vol filter samplers, URG annular
17 denuders, a differential mobility particle sizer (DMPS; TSI 3085), an optical particle counter, an
18 aerodynamic particle sizer, and an automated precipitation sampler. Beem et al. (2010), Levin et
19 al. (2009), and Benedict et al. (2012) present results from measurements using some of the above
20 instrumentation. Rigorous AMS calibration and data quality assurance protocols were used,
21 including weekly or bi-weekly ionization efficiency calibrations and HEPA filtration periods. For
22 this study, a DMPS study-average submicron size distribution shows that the AMS aerodynamic
23 lens transmits ~98.7% of submicron mass (Ezra Levin, personal communication, 22 November,
24 2011; Liu et al., 2007). Data analysis utilized SQUIRREL (v1.51H), PIKA (v1.10H, Sueper et al.,
25 2011), and the PMF2 algorithm (Paatero & Tapper, 1994) in PET (v2.03A, Ulbrich et al., 2009) in
26 Igor Pro 6.22A (WaveMetrics Inc., Lake Oswego, OR). Elemental analysis of high-resolution
27 mass spectra utilized the updated AMS fragmentation table for ambient OA in Aiken et al.
28 (2008). Data preparation for the PMF analysis followed Zhang et al. (2011) and Ulbrich et al.
29 (2009) and included fragments m/z 12-110; solutions for 1-5 factors were explored with varying
30 rotational parameters ($-1 \leq FPEAK \leq 1$, in increments of 0.2). A three-factor solution was

1 selected based on criteria presented in Ulbrich et al. (2009) and Zhang et al. (2011), as discussed
2 in more detail in Section 3.2. Diagnostic information for this PMF solution can be found in the
3 supplement, along with 2- and 4-factor solutions (Figures S1, S5, and S6).

4 Chemical source apportionment is often supported by meteorological information; many studies
5 have used wind direction, HYSPLIT, and other back-trajectory products to map source regions
6 and transport (Chan et al., 2011; Sun et al., 2010). Here, complex flow over mountainous terrain
7 produces back-trajectories that may be useful in aggregate but lack the specificity needed to study
8 individual events (Gebhart et al., 2011); fortunately, links between increased NO_x concentrations
9 and low-level upslope flow from the Front Range indicate that less complex meteorological
10 analysis may aid source apportionment (Parrish et al., 1990). Thermally-induced afternoon
11 upslope (NE-S, 45°-180°) and nighttime downslope (SW-N, 225°-360°) winds are well
12 established in the Rocky Mountains and may transport urban plumes toward or away from the
13 RMNP site, respectively (Figures 1 and 2; Bossert & Cotton, 1994); the co-located ROMO met
14 station records hourly surface observations.

15 The Conditional Probability Function (CPF) identifies wind directions contributing high
16 constituent concentrations and is well supported in the literature (Kim & Hopke, 2004; Xie &
17 Berkowitz, 2007); the CPF equals the number of concentration points greater than a threshold
18 (here, the concentration average plus one standard deviation) measured in a given wind sector
19 divided by the number of data points in that sector.

20 **3. Results**

21 **3.1 General Particle Composition and Concentration**

22 Submicron aerosol mass concentrations during these summer measurements were fairly low, with
23 an average (\pm one sd) of $5.13 \pm 2.72 \mu\text{g}/\text{m}^3$, and comparable to average PM_{2.5} measurements from
24 the IMPROVE network during July and August from 2005 to 2012 ($5.13 \pm 4.36 \mu\text{g}/\text{m}^3$, CIRA
25 2013). Total organics dominate with frequent higher-concentration events manifested in both
26 brief, high-amplitude spikes and longer-duration, lower-intensity increases (max. = $93.1 \mu\text{g}/\text{m}^3$,
27 avg. $3.86 \pm 2.66 \mu\text{g}/\text{m}^3$, Figure 3); organics contribute $75.2 \pm 11.1\%$ of total non-refractory
28 submicron mass on average, which is consistent with the organic contribution to 24-hour average
29 PM_{2.5} found in the summer of 2006 ($60 \pm 12\%$; Hand et al., 2012; Levin et al., 2009). Sulfate

1 concentrations are lower and less variable (max. = $7.45 \mu\text{g}/\text{m}^3$, avg. $0.85 \pm 0.48 \mu\text{g}/\text{m}^3$); nitrate
2 and ammonium concentrations are also low on average but with some higher concentration
3 episodes (Figure 3, NO_3 : max. = $5.37 \mu\text{g}/\text{m}^3$, avg. $0.22 \pm 0.24 \mu\text{g}/\text{m}^3$; NH_4 : max. = $2.05 \mu\text{g}/\text{m}^3$,
4 avg. $0.20 \pm 0.14 \mu\text{g}/\text{m}^3$). These values are statistically similar to concentrations in previous
5 datasets covering 2005-2012, showing low inter-annual variability in major species and total
6 particulate mass (Table 1). Time-series correlations indicate ammonium-nitrate ($r^2 = 0.89$) and
7 ammonium-sulfate ($r^2 = 0.97$) mixtures; ammonium nitrate and ammonium sulfate commonly
8 arise in ambient particles produced from ageing of agricultural, industrial, and other
9 anthropogenic sources. The low correlation between nitrate and sulfate ($r^2 = 0.34$, Table 2) may
10 indicate that they are not regularly internally mixed in the local aerosol. Formation mechanisms
11 and/or upwind source types and locations for particulate ammonium nitrate and ammonium
12 sulfate may differ: ammonium nitrate may arise from reaction of gaseous nitric acid and
13 ammonia, while the presence of sulfate may reflect in-cloud or gas phase oxidation of sulfur
14 dioxide (Barth et al., 2000; Lelieveld & Heintzenberg, 1992; Seinfeld & Pandis, 2006); this will
15 be explored further in following sections.

16 Diurnal average concentration patterns are shown in Figure 4. Nighttime increases in inorganics
17 may be caused by thermal partitioning and/or boundary layer compression, and mirror those seen
18 in oxidized OA PMF factors, as discussed later. Diurnal means of inorganic species increase
19 sharply in the afternoon, in contrast to the 25th and 75th percentiles, which are similar in profile to
20 the oxidized organics (next section); this indicates that the mean values are influenced
21 disproportionately by fewer, high-concentration events and may not indicate ‘typical’ behavior.
22 The afternoon increases in the means of sulfate and ammonium have a pattern different than that
23 of nitrate, supporting the suggestion that events and/or mechanisms driving concentrations of
24 ammonium sulfate differ from those influencing nitrate. Nitrate has a bi-modal mean similar to
25 total organics and presaging the organic nitrogen content explored in Section 3.3. Concentrations
26 of total organics and all inorganic species begin to increase at ~10:00-12:00 LST, approximately
27 2-4 hours after the ~8:00 LST initiation of upslope winds (Figure 2), consistent with typical lags
28 observed in episode analysis (Section 3.7).

3.2 PMF-Derived Organic Aerosol Factors

The selection of number of PMF factors is based on factors' spectral and timeline dissimilarities, comparison to 'established' factor types, and correlation with tracers such as inorganic species. The supplement to this work details the PMF analysis. Positive Matrix Factorization suggests a three-factor solution with Biomass Burning Organic Aerosol (BBOA, Figure 5; Simoneit et al. 1999) and two types of oxidized organics, Low-Volatility Oxidized Organic Aerosol (LV-OOA) and Semi-Volatile Oxidized Organic Aerosol (SV-OOA; Lanz et al. 2007; Ng et al. 2010) as defined in the introduction. All of these factors are quite oxidized, with oxygenated fragments often dominating signal at a given m/z (note fragment families $C_xH_yO_1$ and $C_xH_yO_{n>1}$ in Figure 5) and significant CH_3CO^+ (at m/z 43) and CO_2^+ (at m/z 44).

PMF solutions are subjective since they involve qualitative user inputs such as number of factors; indeed, we hypothesize that some 'BBOA' mass may be misallocated to the SV-OOA factor by the algorithm. The most compelling evidence is that the SV-OOA mass spectrum contains some m/z 60 and m/z 73, but average mass spectra of all high-SV-OOA periods with no commensurate increase in BBOA do not contain mass at m/z 60 and m/z 73 (Fig. S4); therefore, an SV-OOA mass spectrum containing these biomass burning markers does not represent the vast majority of elevated-SV-OOA periods.

Secondly, timeline and meteorological data indicate that the OOA factors are transported with inorganics from the Front Range (Section 3.5); dilution during transport tends to yield gradual, sustained, and moderate (~2-3 times average) concentration increases (Fig. 3). The appearance, then, of brief, high-amplitude SV-OOA events commensurate with BBOA but not with inorganics is inconsistent with the likely behavior of transported, aged SV-OOA (see example: period A, Fig. 11). This is not conclusive, of course, as real increases in particulate SV-OOA could also arise from semivolatile organic carbon (SVOC) condensation onto the newly available biomass burning particle surface area. However, diurnal patterns echo these timeline idiosyncrasies; the 22:00 LST increase in BBOA is mirrored in the diurnal modes of m/z 60 and SV-OOA (Fig. 4), but in a PMF run excluding periods with BBOA events (defined as $f_{60} > 0.003$, the ambient background), SV-OOA increases only slightly at night and is similar to LV-OOA in amplitude and pattern (Fig. S4). Apportionment of some BBOA mass to SV-OOA would account for enhanced m/z 60 mass in the SV-OOA mass spectrum and the increased SV-OOA concentration during BBOA events.

1 In PMF, the FPEAK parameter is used to explore linear transformations, or ‘rotations,’ of the
2 solution matrix that redistribute mass between the factors, presenting alternate solutions (Ulbrich
3 et al., 2009). Positive FPEAK allocates less m/z 60 and m/z 73 to SV-OOA and more to BBOA,
4 but also re-allots mass at other m/z s to BBOA; this renders the BBOA time line increasingly like
5 that of SV-OOA, which is unphysical because it suggests that BBOA increases during periods
6 when no biomass burning markers are present in the mass spectra, as explained above. A six-
7 factor solution with subsequent recombination to three factors produced better-resolved BBOA
8 and SV-OOA factors (Fig. S2), for which increases in f_{60} are commensurate with increases in
9 BBOA but not with SV-OOA (Fig. S2). This solution produced the conclusions, as above, that
10 LV-OOA is associated with ammonium sulfate, SV-OOA with ammonium nitrate, and BBOA
11 has sporadic, high amplitude events (Table S1). However, since this recombination technique is
12 more subjective and yields the same conclusions about the local aerosol, the original 3-factor
13 PMF analysis with FPEAK=0 is presented here. The LV-OOA factor is generally most abundant
14 (average = $2.15 \pm 1.11 \mu\text{g}/\text{m}^3$), and features longer duration (~6-11 hour), low amplitude (2-3
15 times average) elevated-concentration events. The LV-OOA time series is correlated with sulfate
16 and ammonium (Table 2), similar to studies with LV-OOA factors from anthropogenically-
17 influenced secondary aerosol formation (Zhang et al., 2011). Internal mixing of sulfate and low-
18 volatility OA may arise from similar oxidation pathways; the advanced oxidative processing that
19 produces low-volatility OA will also tend to produce S(VI) if S(IV) species are present in the
20 same air mass (Jimenez et al., 2009). For instance, aqueous processing is known to efficiently
21 produce both low-volatility organic compounds and S(VI) species.

22 The LV-OOA factor increases consistently in the afternoon (diurnal mean mode at 14:00-15:00
23 LST) and nighttime (mode at 22:00 LST, Fig. 4). The afternoon increase may arise from transport
24 with upslope winds, as will be explored later; the nighttime concentration maximum begins to
25 form at ~16:00 LST, when temperatures start to drop (Fig. 2), which may indicate effects from
26 boundary layer compression and/or thermal partitioning. Both OOA factors also feature a subtle
27 8:00 LST minimum, which could be attributed to thermal boundary layer expansion before an
28 influx of particles associated with afternoon upslope winds.

29 While the SV-OOA factor is lower in general, it is more variable (average = $1.51 \pm 1.63 \mu\text{g}/\text{m}^3$);
30 the SV-OOA timeline is punctuated by longer duration, low amplitude concentration increases
31 similar to (and often accompanied by) LV-OOA increases, but also short, high-amplitude (4-10

1 times average, max. = $64 \mu\text{g}/\text{m}^3$) periods commensurate with increasing BBOA as discussed
2 above. Like LV-OOA, SV-OOA has two modes in the diurnal average; however, the evening
3 increase is more pronounced than that of LV-OOA (from misallocation of BBOA, as discussed
4 above). SV-OOA is correlated with ammonium and, more weakly, nitrate (Table 2), suggesting
5 influence from urban areas and/or agriculture.

6 The BBOA factor is generally very low (average $0.46 \pm 0.21 \mu\text{g}/\text{m}^3$), but has brief (~1-2 hour),
7 higher-concentration episodes; these events occur in the evenings and the occasional afternoon,
8 producing a consistent diurnal mode at ~22:00 LST commensurate with nighttime campfires at
9 adjacent summer camps and an outlier-driven mean increase at ~16:00 LST (Fig. 4, High Peak
10 Camp manager Russ Chandler, personal communication, 9 September 2012). BBOA is not
11 correlated with other AMS-determined aerosol components or 17-minute PILS-IC potassium ($r^2 =$
12 0.01); however, the K^+ timeline periodically tracks BBOA. Because K^+ is emitted mainly during
13 the fire flaming phase (versus smoldering), it often lacks correlation with anhydrosugar fragments
14 (e.g., m/z 60), which are more consistent biomass burning markers across burn and fuel types
15 (Lee et al., 2010; Sullivan et al., 2008).

16 PMF factors are mass-spectrally static; to explore the behavior of and variability within each type
17 of OA, periods dominated by a given factor were subjected to elemental, size, and meteorological
18 analyses which will be presented below. "LV-dominated" periods are indicated when $[\text{LV}] \geq$
19 $2 \cdot [\text{SV}]$, "SV-dominated" periods when $[\text{SV}] > [\text{LV}]$, and "BBOA-dominated" episodes when
20 $[\text{BB}] \geq 2 \cdot 0.46 \mu\text{g}/\text{m}^3$ (twice the average BBOA factor concentration).

21 **3.3 Elemental Analysis and Organic Nitrogen**

22 The ratio of organic mass to organic carbon (OM:OC) averages 1.99 ± 0.16 and indicates highly
23 oxidized OA consistent with other non-urban sites (Aiken et al., 2008; Turpin & Lim, 2001); O:C
24 averages 0.66 ± 0.13 and H:C averages 1.27 ± 0.09 . N:C is determined from CHN and CHON
25 fragments, excluding nominally inorganic fragments such as NO_2^+ that may also arise from
26 fragmentation of organic nitrogen (ON) molecules; N:C averages 0.01 ± 0.01 (max = 0.55).

27 On the van Krevelen-triangle diagram (Fig. 6), the data position in the apex of the 'ambient
28 triangle' space (higher O:C and lower H:C) indicates highly oxidized particles consistent with
29 similar datasets (Ng et al. 2011; Heald et al. 2010); data points are colored by the dominant PMF
30 factor as defined above. SV-OOA- and BBOA-dominated periods occupy similar ranges, while

1 LV-OOA-dominated periods are more oxidized with lower H:C. During BBOA-dominated
2 periods, O:C ranges from ~0.2 to ~0.65, which is a greater range than often observed in the
3 literature (usually ~0.3-0.4, Aiken et al., 2007, 2008; Heringa et al., 2012); the higher maximum
4 degree of oxygenation may arise from the ubiquity of OOA at the site, and/or from additional
5 partitioning of oxidized organics onto the new biomass burning particles. The total dataset also
6 demonstrates consistent high oxidation (i.e. there are no points in the 'HOA/POA' region of the
7 graph indicated by a grey ellipse). The overlap in van Krevelen space between data points from
8 high-concentration LV- and SV-OOA episodes and the concomitance of SV- and LV-OOA time-
9 series ($r^2 = 0.59$) suggest that, *purely in terms of oxidation*, SV- and LV-OOA are somewhat
10 arbitrary delineations between air masses whose aerosol oxidation state varies continuously.
11 However, the different inorganic mixtures (and particle sizes, Section 3.4) associated with LV-
12 OOA and SV-OOA validate treating them separately. Linear regressions of O:C/H:C are
13 sometimes used to investigate oxidation mechanisms (Heald et al., 2010). While the reaction
14 mechanisms producing these slopes are best constrained when observing air masses isolated
15 during reaction, a doubtful assumption for this lengthy ambient dataset, these values are provided
16 for reference in the supplement.

17 Quantification of organic nitrogen from AMS data is prevented by fragmentation of ON to
18 nominally inorganic fragments (NO_n^+), the inconsistency of this fragmentation between
19 instruments, and the vast array of possible ON parent compounds in ambient particles (Farmer et
20 al., 2010). However, a lower bound on organic nitrogen mass can be estimated using $\text{ON}_{\min} =$
21 $(\text{Org}/\text{OM}:\text{OC}) * \text{N}:\text{C} * (14/12)$ where 'Org' is total organic mass; ON mass may be underestimated
22 using this method because N:C includes only N from CHON and CHN fragments, disregarding
23 NO_n^+ and/or NH_n^+ produced by ON fragmentation. ON_{\min} is small and comprised mostly of CHN
24 fragments (max = $1.04 \mu\text{g}/\text{m}^3$; average = $0.02 \pm 0.02 \mu\text{g}/\text{m}^3$). The few, modest ON_{\min} events are
25 accompanied by BBOA (although not all BBOA increases are accompanied by ON_{\min}) and total
26 nitrate with no commensurate sulfate or ammonium increases (Fig. 7); ON such as nitrophenols
27 (Iinuma et al., 2007), urea (Mace et al., 2003), nitriles, and amines/amides (Simoneit et al., 2003)
28 have been associated with biomass burning in the literature. Although the half-width/half-max
29 fitting rule was always maintained, CHN fragments are often neighbor to larger organic fragment
30 peaks, which generally complicates identification or quantification of the smaller peak; however,
31 our assertion that these fragments represent real CHN content is supported by contemporaneous,

1 co-located filter-based measurements of water-soluble organic nitrogen, which was enhanced
2 during biomass-burning episodes and contained organic bases, as observed here (Benedict, 2012).
3 Though fragmentation in the AMS precludes identification of parent organic molecules, series of
4 CHN fragments at m/z s 30 and 58 (with additional peaks at m/z s 72, 86, and 100) have been
5 observed in 70eV mass spectra from laboratory and field aerosols with amine content (Murphy et
6 al., 2007; Silva et al., 2008); CH_4N^+ (m/z 30) may result from amine re-arrangement after electron
7 impact ionization (Murphy et al., 2007). Here, prominent CHN fragments are noted at m/z s 30,
8 41, 53, 58, 63, 67, 77, 79, 81, 91, and 95 and are organized into the ‘wave’ pattern often seen in
9 organic spectra (m/z s 53, 67, 81, and 95, ‘Series 1’ in Fig. 8), which arises from the tendency of
10 organic molecules to lose CH_2 groups sequentially during fragmentation and results in peaks
11 separated by 14 amu. Empirical formulae at m/z s 53, 67, 81, and 95 belong overwhelmingly to
12 nitrile and/or pyrrole (heterocyclic) molecules, suggesting that these are (or fragment from)
13 important ON compounds in the local particulate matter; however, because a mixture of amine
14 compounds is possible, molecular structure cannot be determined through fragmentation ratios.
15 Fragments at m/z s 63, 77, and 91 form another methylene-subtraction series (‘Series 2,’ Fig. 8),
16 for which empirical formulae also suggest nitriles and/or heterocyclic compounds, including
17 pyridine, which is often used to stabilize agricultural fertilizers and is produced in small amounts
18 in biomass burning (McKenzie et al., 1995).

19 This CHN series, while not found in the literature, is similar to fragments observed in a similar
20 high-altitude site near Grand Teton National Park (m/z s 30, 41, 55, 58, 67, 79, 91; Schurman,
21 2014). The average CHN mass spectrum for elevated- ON_{min} periods (not shown) has higher CHN
22 signal than average total, LV-OOA, and SV-OOA spectra, but no appreciable difference in
23 fragment patterns, indicating a concentration increase but likely minimal change in CHN
24 composition. The concurrence of increases in ON_{min} and BBOA suggests that ON content, and
25 especially nitrile and/or hetero-aromatics, is enhanced in biomass burning plumes. Although
26 CHON fragments (nominally, ‘organonitrates’) were fit in the high-resolution analysis, they
27 contained very little mass and no clear fragmentation patterns.

28 **3.4 Particle Size**

29 While low particle concentrations and therefore signal prevent continuous size determination for
30 many observed species (notably inorganics), size determination of marker m/z s and time periods

1 heavily dominated by a given organic factor can elucidate ‘average’ particle behavior and perhaps
2 atmospheric processing as discussed below. Lognormal fits of average aerosol component mass
3 size distributions allow better statistical comparison of factor-dominated periods and were
4 constructed using the Igor fitting algorithm; lognormal fits also allow size mode estimation in
5 species such as ammonium and nitrate that suffer from lower signal:noise in the raw size
6 distributions.

7 High-LV-OOA events have larger particles (~380 nm geometric mean diameter) than SV-OOA
8 episodes (~300 nm), while BBOA may be slightly smaller (~280 nm, Fig. 9). As indicated by σ_g
9 (the geometric sd), LV-OOA events are also more monodisperse than SV-OOA; the tendency of
10 condensation and coagulation during oxidation to make particles larger and more monodisperse
11 suggests that the OOA factors spend time in transit from their source (Seinfeld & Pandis, 2006),
12 and further that LV-OOA particles undergo more oxidative processing than SV-OOA particles, as
13 mean radius is observed to increase continuously with ageing (Reid et al., 2005).

14 The similar size distributions and time-series of LV-OOA, ammonium, and sulfate suggest that an
15 internal mixture of these components is common. While SV-OOA and LV-OOA are often
16 coincident, SV-OOA-dominated periods feature smaller particle sizes and a correlation with
17 ammonium nitrate. As mentioned earlier, differences in atmospheric processing of the given
18 components may lead to these distinct mixtures. SV-OOA and ammonium nitrate, all semivolatile
19 species, may arise in the particle phase through condensation of vapors. In contrast, the
20 correlation between LV-OOA and sulfate suggests a possible common aqueous production route.
21 Size distributions of cloud/fog-processed particles tend to be larger than observed here (Hering &
22 Friedlander, 1982; Meng & Seinfeld, 1994), but many of these studies feature heavy, prolonged
23 cloud/fog cover and meteorology and chemistry (e.g. higher aerosol precursor concentrations)
24 which may differ from brief convective cloud processing in the Front Range. Aqueous reactions
25 in wetted particles are also feasible; the deliquescence relative humidity of mixed ammonium
26 sulfate-organic particles is ~30-70% (depending on organic fraction and type) and the ambient
27 surface RH varied from 4-100% during this study with an average of $59 \pm 31\%$ (Smith et al.,
28 2012; Takahama et al., 2007). These RH values are consistent with the historical July-August
29 average RH of ~50%, based on monthly-average data (during 1991-2012, CIRA 2013).

30 BBOA events are smaller and more polydisperse than other organic factors, higher in amplitude,
31 and not coincident with inorganic species, reflecting a fresher, local particle population given less

1 time to grow by condensation and/or coagulation. With an average organic mode of ~280 nm, the
2 biomass burning aerosol at this site is consistent with fresh BB plumes from temperate forests,
3 which range in volume mean diameter from 86-300 nm (volume and mass distributions being
4 analogous assuming constant density; Reid et al., 2005 and references therein). 2-D time and size
5 images for some BBOA events at RMNP (not shown) reveal growth of total organics from 100-
6 200 nm to ~350 nm over the course of the event, consistent with observations in the literature and
7 explained by rapid coagulation and condensation (Adler et al., 2011). The level of oxidation
8 (average $f_{44} = 0.09 \pm 0.02$ during BB-dominated periods) is consistent with literature SV-OOA;
9 together, the relatively large size (in comparison to some biomass combustion, e.g. mode = 100
10 nm in Adler et al. 2011, though mode may vary with burn type) and advanced oxidation may be
11 explained by the presence of 'background' OOA and/or rapid condensation of semivolatile VOCs
12 onto the increased particle surface area provided by the BB plume.

13 **3.4 Source/Transport Analysis**

14 The particle composition and size data indicate that oxidized organic aerosol is mixed in varying
15 combinations with inorganic anthropogenic tracers nitrate, sulfate, and ammonium. The level of
16 oxidation argues for prolonged reaction time in the atmosphere; also, limited local habitation
17 precludes high local emissions of inorganic anthropogenic tracers. Together, these suggest
18 transported, anthropogenically-influenced OOA particles, which could arise from either
19 anthropogenic OA and SOA precursors, and/or anthropogenic OA and oxidation products of
20 biogenic organics, such as BVOC oxidation in the presence of NO_x (Kiendler-Scharr et al., 2009).
21 Correlations between secondary OA mass and temperature may indicate which precursors and
22 mechanisms are at play: in many urban/downwind ambient observations, a negative correlation
23 arises from thermodynamically-driven partitioning effects, but in heavily forested areas,
24 increased SOA-precursor BVOC emissions from increasing temperature can overwhelm
25 thermodynamic partitioning reduction, causing an overall increase in secondary mass (Leitch et
26 al., 2011). These studies are usually episode-focused and establish the connectivity of the
27 measured air masses using meteorology and anthropogenic trace gases; at Rocky Mountain, the
28 average relationship between temperature and SOA concentration is determined for periods with
29 up-slope and down-slope winds. Concentrations of LV-OOA, SV-OOA, 'SOA' (defined here as
30 LV+SV), and BBOA have no relationship with ambient temperature during either upslope or

1 downslope winds ($r^2=0.00$, $m=0.00$); this could a) indicate a balance, on average, between
2 thermodynamic partitioning and BVOC precursor emission effects on SOA mass, and/or b) be a
3 product of the inconsistent lag between wind direction and concentration changes (see below).
4 Fragmentation within the AMS prevents the molecular specificity needed to determine which of
5 these mechanisms is at play. However, co-located carbon isotope work conducted in a year with
6 total burned area and fire contributions to surface $PM_{2.5}$ similar to that herein indicates that ~88%
7 of summer $PM_{2.5}$ carbon is contemporary (Schichtel et al., 2008; Val Martin et al., 2013). From
8 the PMF factors, biomass burning OA (which contains contemporary carbon) contributes a study
9 average of ~11% of submicron OC. Thus, biomass burning does not appear to provide all of the
10 observed contemporary C. This suggests that biogenic VOCs may contribute substantially to
11 local OA formation. Levin et al. (2012) described particle growth from condensation of organics
12 in summer at a similar forested Colorado site; concomitant size increase and κ (hygroscopicity
13 parameter) decrease during particle formation events is an indicator of organic condensation.
14 Associating meteorology with component concentrations and diurnal patterns supports these
15 source indications. Surface winds are funneled by the valley topography and are predominantly
16 down-valley from the WNW (48%) or up-valley from the SE (16%); this pattern is consistent
17 inter-annually, with similar wind roses produced by data from 1995-2005 (Malm et al., 2009a).
18 Raw and directionally averaged concentrations of aerosol components plotted against surface
19 wind direction over sixteen $22^\circ30'$ wind direction bins are shown with conditional probability
20 functions (CPFs) in Fig. 10. High inorganic concentrations are associated with local SE winds
21 indicating up-valley movement from the Front Range and are very similar in both CPF value and
22 meteorological association to co-located $PM_{2.5}$ measurements (note that CPFs are multiplied by
23 10 to share a scale with concentration; Benedict et al. 2013b). CPFs for OOA factors also have an
24 association with southeasterly winds, and higher average concentrations are associated with S-SE
25 winds for all components (including BBOA, though from a different source; see below).
26 However, unlike organics, OOA factors also have above-average concentrations associated with
27 NW winds (though not above the CPF threshold). This may indicate regional OOA content (i.e.
28 “background” organics), possibly aged biogenic SOA from forest emissions, which could
29 originate from the west and be unassociated with Front Range emissions; aqueous processing in
30 orographic clouds arising from westerly flow over the mountains could also contribute to this
31 oxidized OA.

1 High BBOA concentrations are usually associated with NW or SW-to-S surface winds. The
2 closest campfire source is ~200m WNW of the sampling site; the shorter transport (and therefore
3 dilution) time may explain the higher concentrations in BBOA events from the WNW. Three
4 other camps are placed ~0.5-1 km due south; the increased number and distance of the fires
5 explains the higher average but lower maximum concentrations associated with SW-to-S winds.

6 **3.5 Episode Analysis**

7 The aerosol characteristics summarized previously are demonstrated in a series of alternating
8 high- and low-concentration periods during July 7-11, which clearly show the transport of OOA
9 and inorganics by SE surface winds (Fig. 11). Initiation of SE flow is followed by marked
10 concentration increases after ~3 hours, suggesting a 3-hour transport time between the Front
11 Range and RMNP during this period. A similar lag applies between down-valley flow initiation
12 and concentration decreases; the fact that 1-3 hour offsets did not improve correlation between
13 wind direction and species concentrations indicates that transport time is, not surprisingly,
14 variable. The abrupt decreases in all components' concentrations following NW wind initiation
15 reveals the relative cleanliness of the air coming over the mountains during these periods. Lastly,
16 note the apparent discrepancy during period A, where ~NW winds are accompanied by sharp
17 spikes in SV-OOA; this is thought to be an entanglement of BBOA mass with SV-OOA (Section
18 3.2) as evidenced by the short, high-amplitude concentration increase, enhancement of m/z 60 in
19 the mass spectrum (not shown), and lack of attendant increase in anthropogenic inorganics. This
20 hypothesis is corroborated by an increase in BBOA in the recombinant-factor PMF analysis (not
21 shown) and the NW placement of the campfire source (as winds are from the north).

22 **4. Summary and Conclusions**

23 The ambient submicron aerosol at the Rocky Mountain National Park ROMO site during 2 July -
24 31 August 2010 is low in average concentration (total average $PM_{10} = 5.13 \pm 2.72 \mu\text{g}/\text{m}^3$),
25 dominated by highly oxidized organics (LV-OOA and SV-OOA), and punctuated by short
26 biomass burning (BBOA) episodes. Mixtures of LV-OOA with ammonium sulfate and SV-OOA
27 with ammonium nitrate are indicated by consistent size distributions and time-series correlation.
28 Inorganic species (nitrate, sulfate, and ammonium) are established anthropogenic emission tracers
29 for which no strong local sources are apparent; high inorganic concentrations are concurrent with

1 southeasterly surface winds that indicate upslope flow from the Front Range. A biogenic
2 contribution, possibly from oxidation of BVOCs as Front Range oxidant-rich pollution plumes
3 are transported over forest, is suggested by the fact that contemporary carbon contributed by local
4 biomass burning may not account for total contemporary carbon at the site (though datasets are
5 not contemporaneous, Schichtel et al., 2008). Organic nitrogen fragments are associated with
6 BBOA and may indicate amine, nitrile, and/or heterocyclic aromatic content, but are low in mass
7 (omitting nominally inorganic fragments from ON calculations); BBOA is not correlated with any
8 measured inorganic species.

9 Transport of oxidized organic aerosols from the Front Range is indicated by advanced oxidation
10 and relative monodispersity (both indicative of ageing), association with inorganic anthropogenic
11 tracers, and concentration correlation with surface upslope flow from the urban and agriculture
12 emissions-rich Front Range; the presence of sulfate, periodic high relative humidity and cloud
13 cover, larger particle sizes, and advanced oxidation of the LV-OOA suggest possible contributions
14 from aqueous processing, while growth by vapor condensation is more likely for SV-
15 OOA/ammonium nitrate particles. A local BBOA source is suggested by biomass combustion
16 markers (*m/z*s 60 and 73) limited to brief, high-concentration, polydisperse events (suggesting
17 fresh combustion emission), association with local S or NW winds consistent with campfire
18 locations, and an unequivocal diurnal maximum at 22:00 LST, when campfires were set at
19 adjacent summer camps.

20 Lastly, the particle characteristics and sources determined here appear to be typical of summer
21 conditions at the Rocky Mountain site, based on the historical meteorological patterns,
22 IMPROVE (total PM_{2.5}, sulfate, nitrate, ammonium, and OC), PILS-IC (PM_{2.5} sulfate, nitrate,
23 and ammonium), filter (PM_{2.5} sulfate, nitrate, and ammonium), and fire (burned area, contribution
24 to surface PM_{2.5}) data analyzed here.

25 **Author Contributions**

26 T. L. and M. I. S. conducted field experiments; Y. S. and T. L. consulted during data analysis; B.
27 A. S., S. M. K., and J. L. C., Jr. designed the field campaign and provided support and conceptual
28 guidance; and M. I. S. performed data analysis and wrote the manuscript. All authors collaborated
29 on data interpretation and provided continual feedback during the writing process.

30 **Acknowledgements**

1 This study was supported by NPS #H237009400. We would like to thank Amy Sullivan, Christian
2 Carrico, Katherine Benedict, and Ezra Levin for their extensive support in the field, and the
3 Salvation Army High Peak Camp for site access and logistical assistance.

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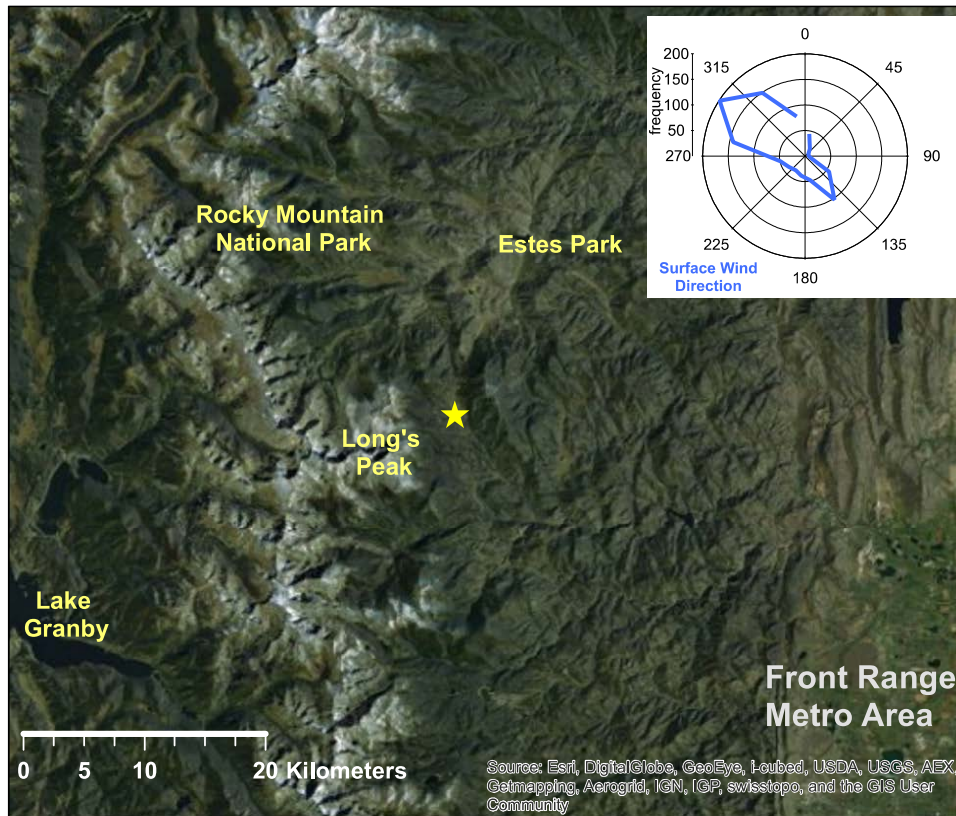
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1 Table 1. July-August average \pm standard deviation concentrations of particulate species in $\mu\text{g}/\text{m}^3$.
2 The IMPROVE network collects 24-hour PM_{2.5} nylon-filter samples for nitrite, nitrate, sulfate,
3 and chloride, and quartz filters for organic matter and elemental carbon analysis. IMPROVE data
4 are averaged over July and August during 2005-2012 (“IMPROVE”) or over July and August
5 during 2010 (“IMPRV 2010”), and were accessed via the VIEWS database on 22 January 2014.
6 **Bold** text indicates significant difference (using Wilcoxon Rank test) between IMPROVE 2010
7 and AMS data averaged to the 24-hr IMPROVE time-resolution. *Benedict et al. (2013). **
8 IMPROVE does not measure ammonium; it is calculated as the amount needed to neutralize
9 sulfate and nitrate.

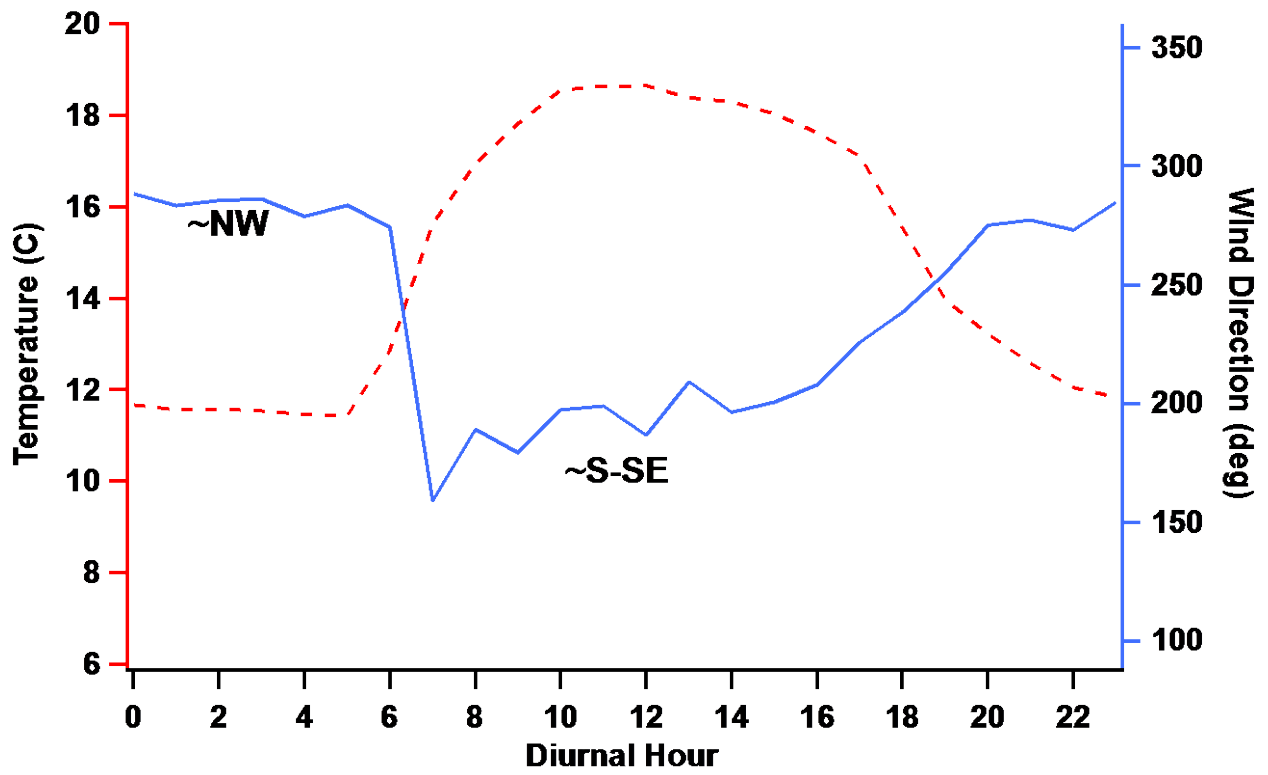
	NO ₃	SO ₄	NH ₄	OM	PM _{2.5}
This study	0.22 \pm 0.24	0.85 \pm 0.48	0.20 \pm 0.14	3.86 \pm 2.66	PM ₁ : 5.13 \pm 2.72
Summer 2006*	0.12	0.99	0.32		
Summer 2010*	0.08 \pm 0.06	0.31 \pm 0.14	0.18 \pm 0.07		
IMPROVE	0.08 \pm 0.10	0.42 \pm 0.19	0.02 \pm 0.03**	3.90 \pm 6.11	5.13 \pm 4.36
IMPRV 2010	0.12 \pm 0.13	0.53 \pm 0.27	0.04 \pm 0.04**	1.48 \pm 0.64	3.13 \pm 1.29

- 1 Table 2. Time-series coefficients of determination (r^2) between inorganic species and organic
- 2 factors calculated using the IGOR linear regression algorithm.

	LVOOA	SVOOA	BBOA	SO ₄	NO ₃
SO ₄	0.77	0.18	0.05		
NO ₃	0.33	0.41	0.02	0.34	
NH ₄	0.76	0.72	0.03	0.97	0.89



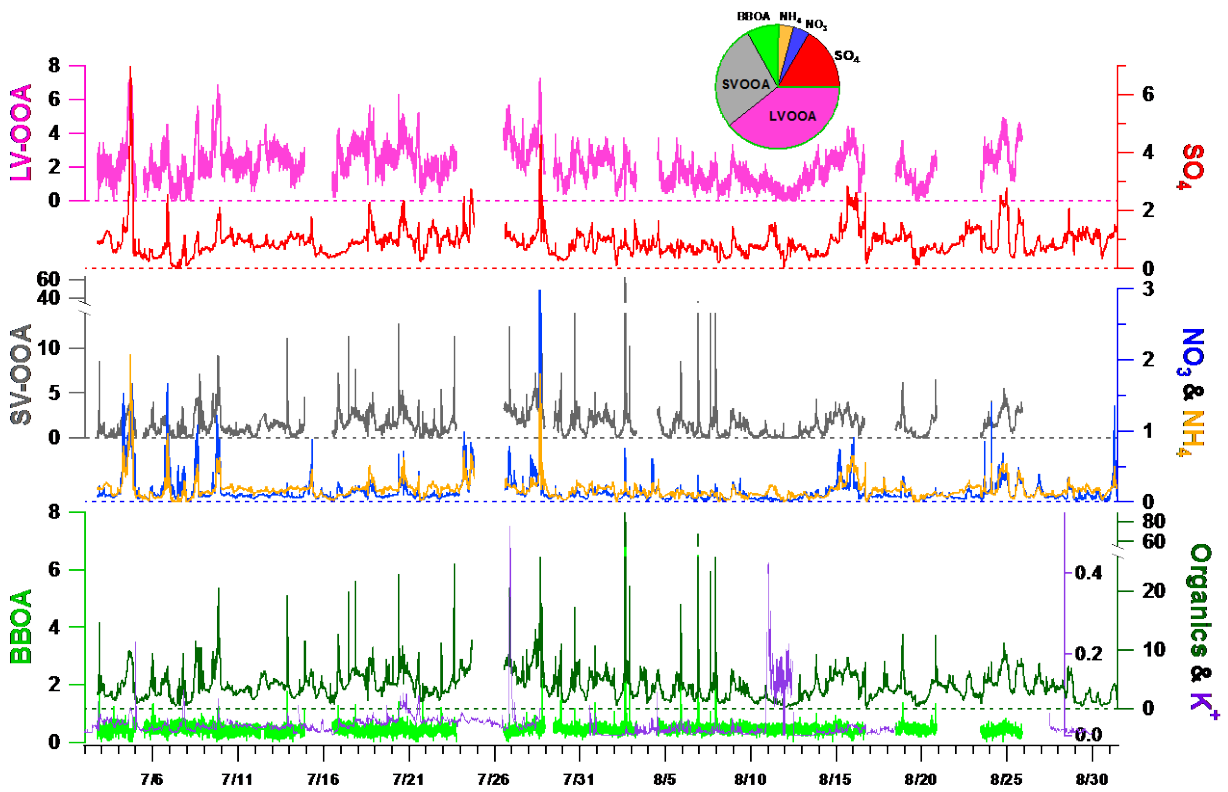
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 3 Figure 1. Map showing the Rocky Mountain National Park sampling site (yellow star). Boulder,
 4 Denver, and other cities form the Front Range metro area to the east (ARCgis map generation:
 5 Zitely Tzompa, 15 March 2014). The wind rose shows a histogram of wind directions
 6 measurements during the study.



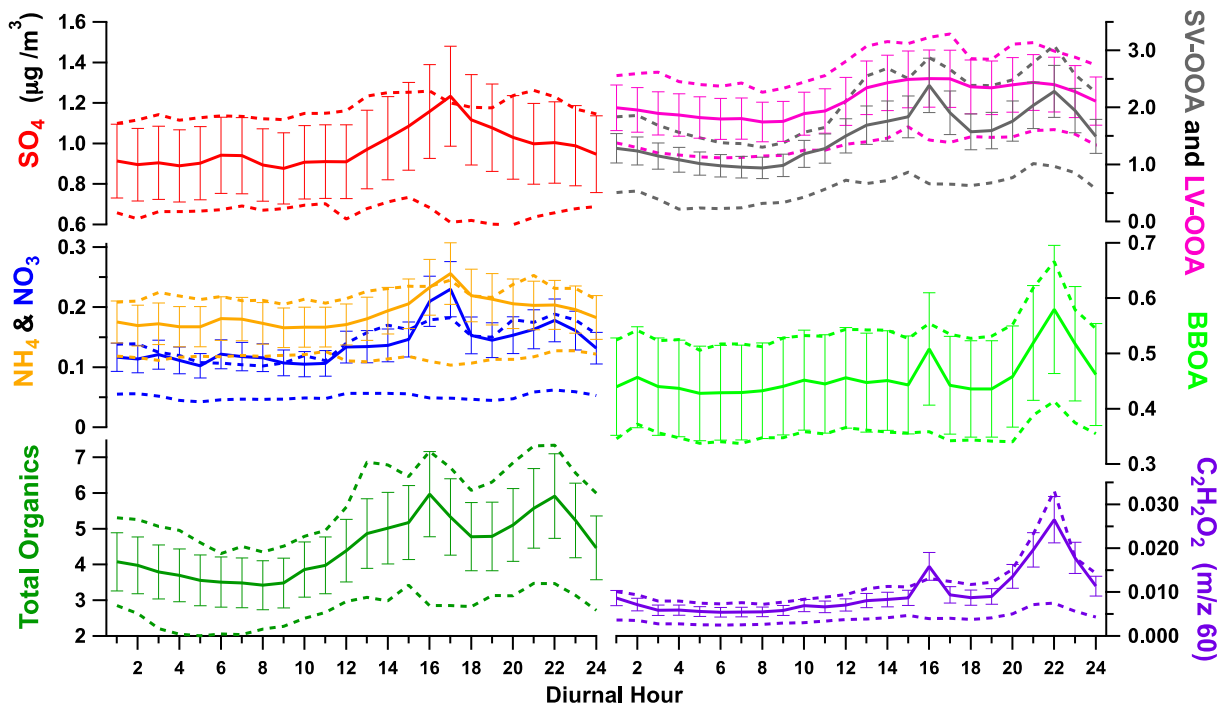
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3 Figure 2. Study-average diurnal variation of ambient temperature (red dashed line, left axis) and
 4 surface wind direction (blue line, right axis).



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 3 Figure 3. Time series of inorganic components, total organics, and organic factors (LV-OOA,
 4 SV-OOA, and BBOA) in $\mu\text{g}/\text{m}^3$. Potassium (K^+) is from 17-minute-average PILS-IC samples.
 5 Pie chart shows study-average contributions for each component; the dark green outline contains
 6 total organics.

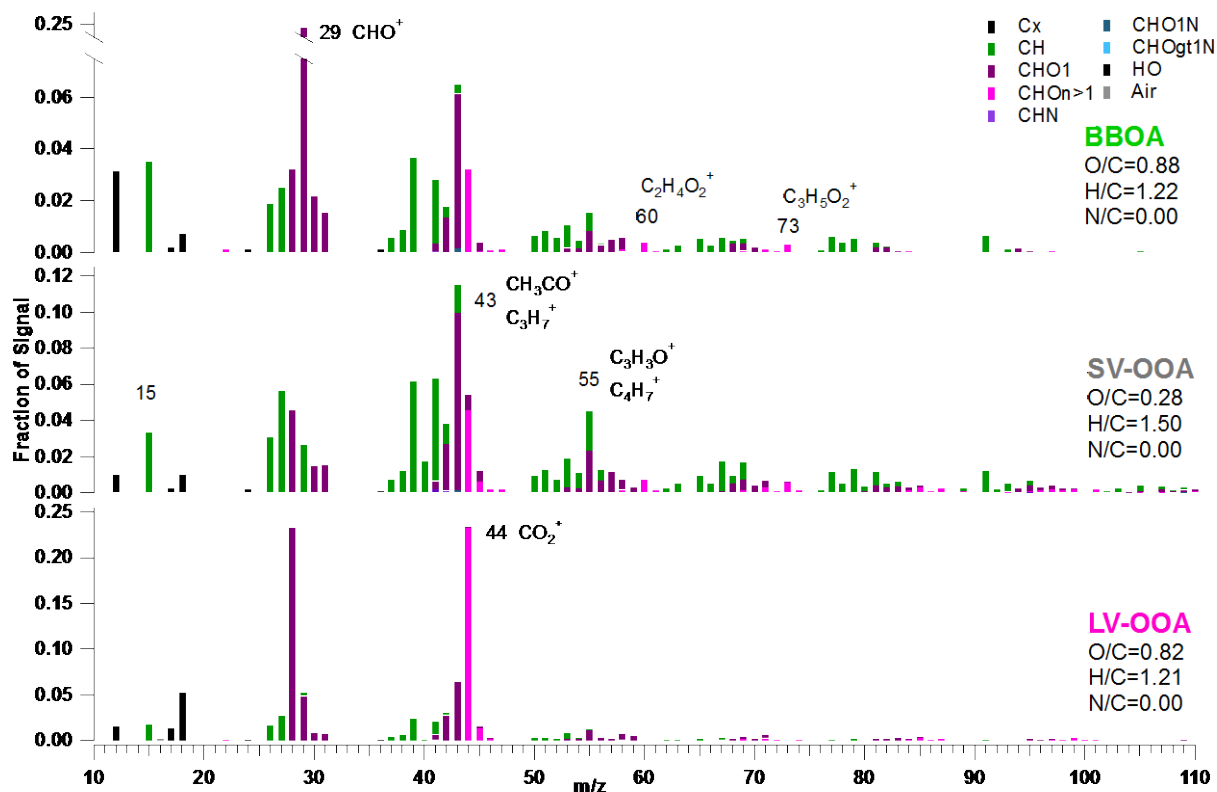


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3 Figure 4. Study-average diurnal concentrations of particulate sulfate, nitrate, ammonium, total
 4 organics, BBOA, LV-OOA, SV-OOA, $\text{C}_3\text{H}_3\text{O}^+$ (m/z 55), and $\text{C}_2\text{H}_4\text{O}_2^+$ (m/z 60, levoglucosan).

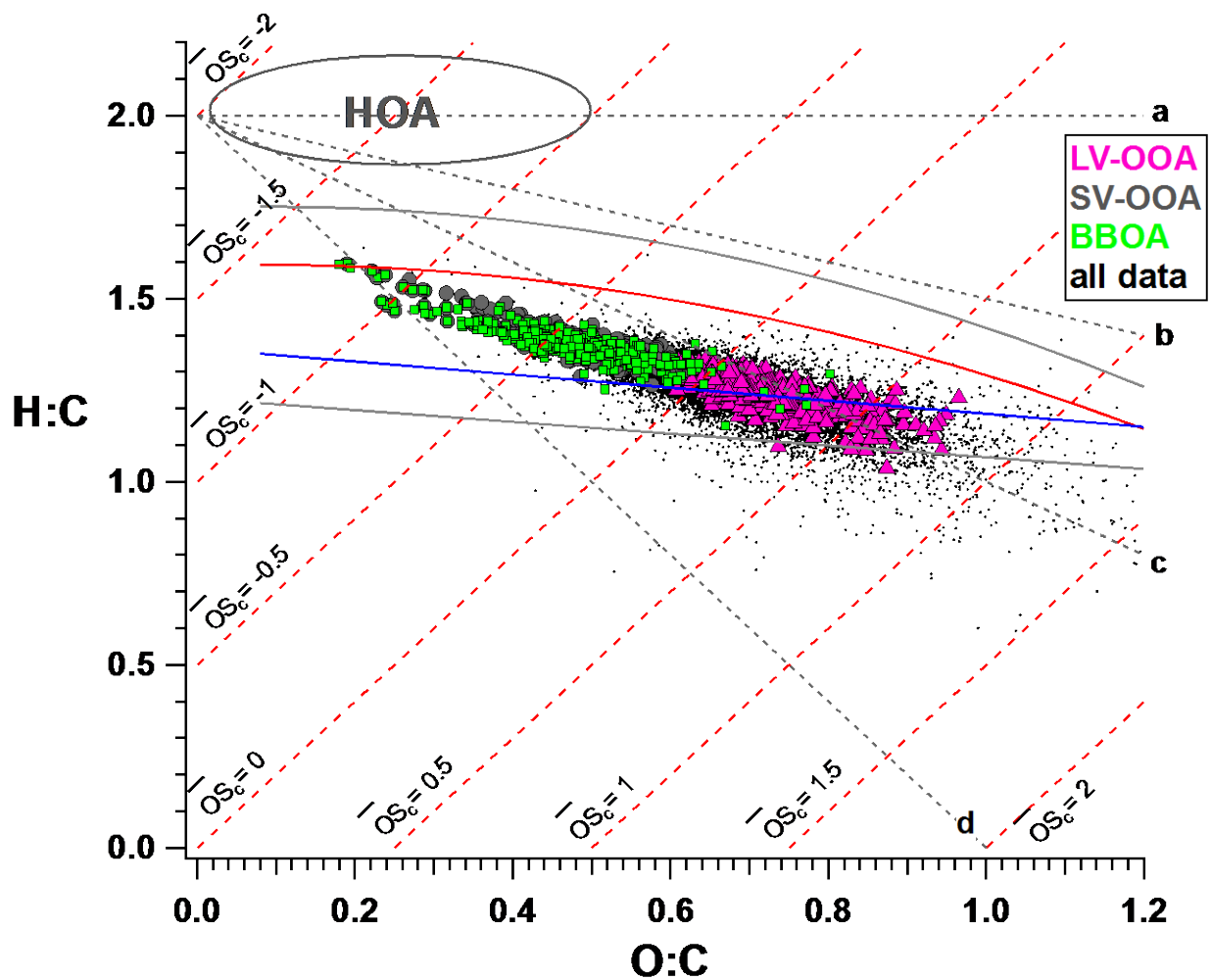
5 Solid lines are means, with $\pm 20\%$ error bars reflecting AMS quantitation error. Dashed lines are
 6 25th and 75th percentiles.



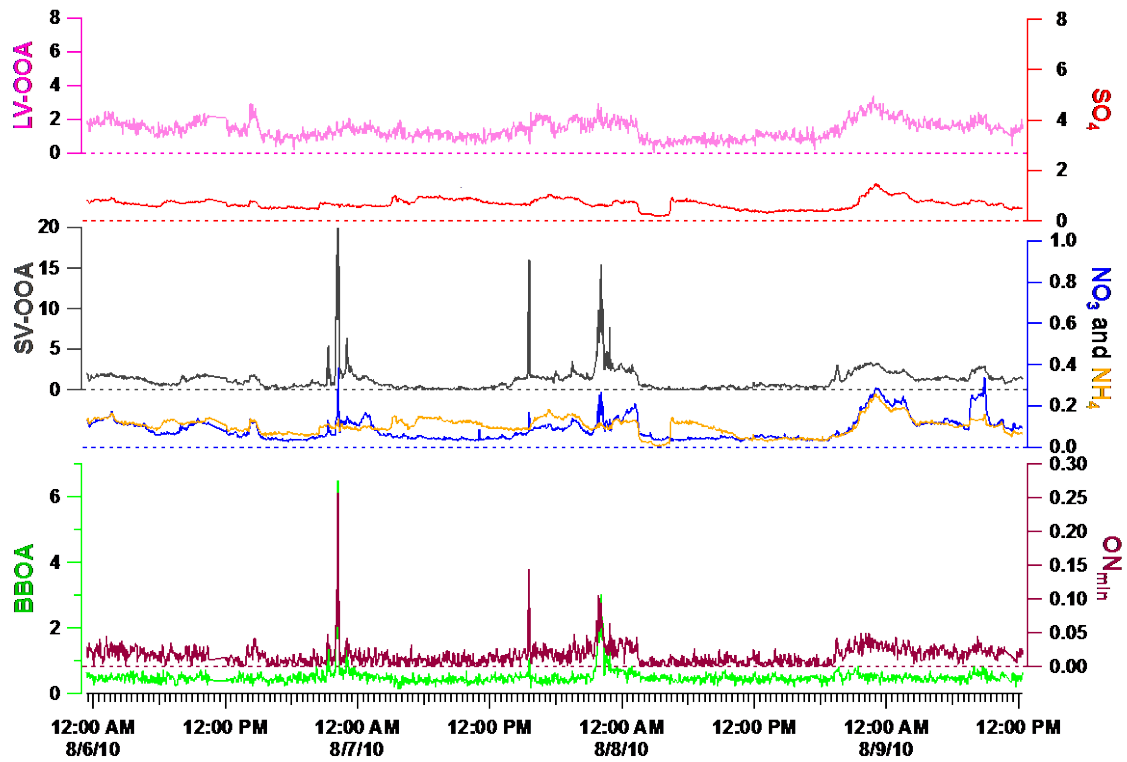
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3 Figure 5. Normalized mass spectra of organic aerosol types determined by Positive Matrix
 4 Factorization (Paatero and Tapper, 1994): Biomass Burning Organic Aerosol (BBOA), Semi-
 5 Volatile Oxidized Organic Aerosol (SV-OOA), and Low Volatility Oxidized Organic Aerosol
 6 (LV-OOA). O/C values are calculated for the given factor mass spectrum.



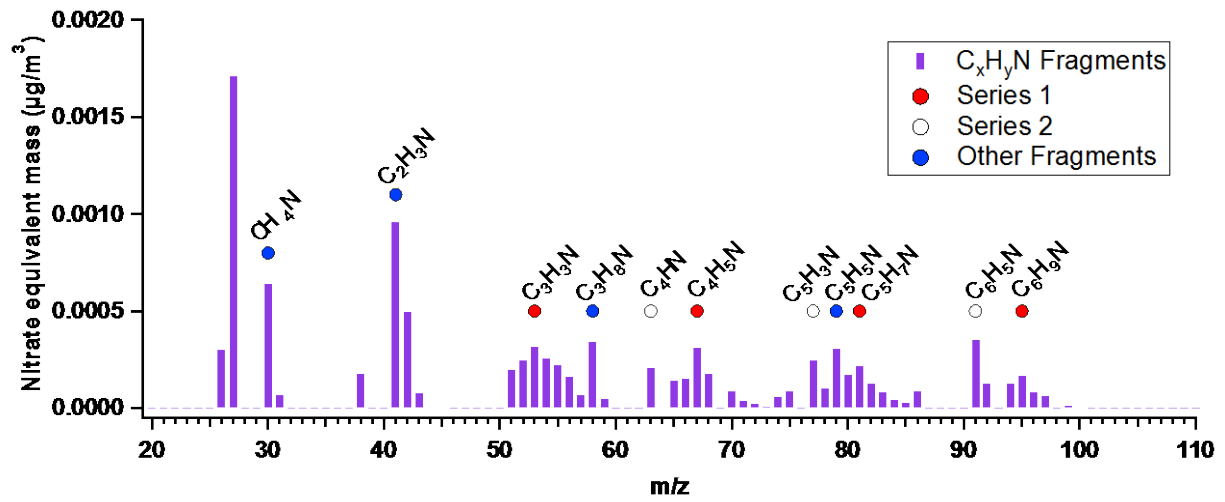
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 3 Figure 6. Van Krevelen-triangle diagram for time periods dominated by the given factor (as
 4 defined in Section 3.3) and for all data points. Estimated oxidation state, $\overline{OS}_c \approx 2 * O:C - H:C$ (Kroll
 5 et al., 2011). Red and blue lines indicate the region usually inhabited by ambient data in the *f43*
 6 vs. *f44* plot; grey lines represent 10% error. Grey ellipse shows typical HOA values. a:
 7 +alcohol/peroxide, $m = 0$; b: carboxylic acid + fragmentation, $m = -0.5$; c: +carboxylic acid (no
 8 fragmentation), $m = -1$; d: +ketone/aldehyde, $m = -2$ (Ng et al. 2011).



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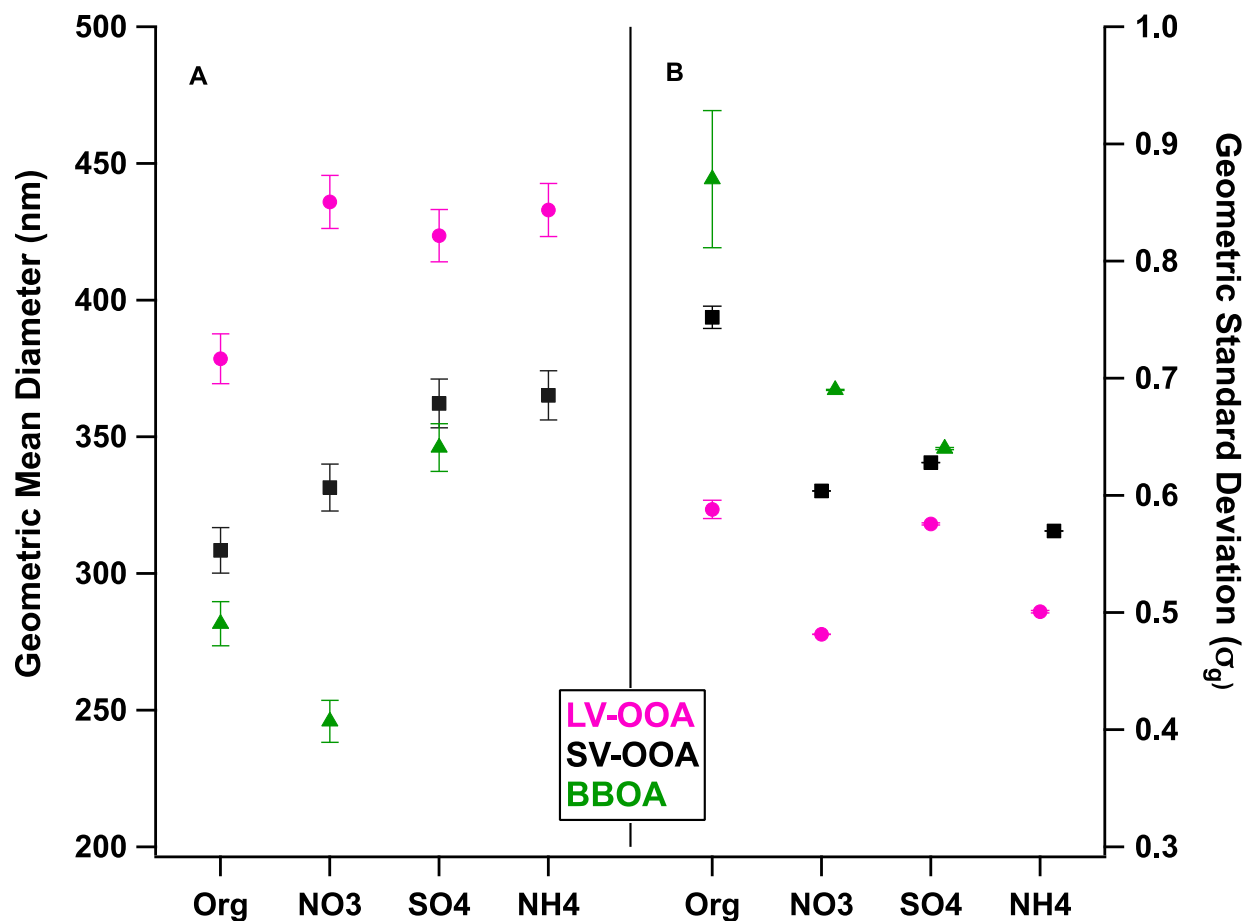
3 Figure 7. Time series showing select elevated- ON_{min} periods with inorganics and other organic
 4 factors from the Rocky Mountain National Park site.



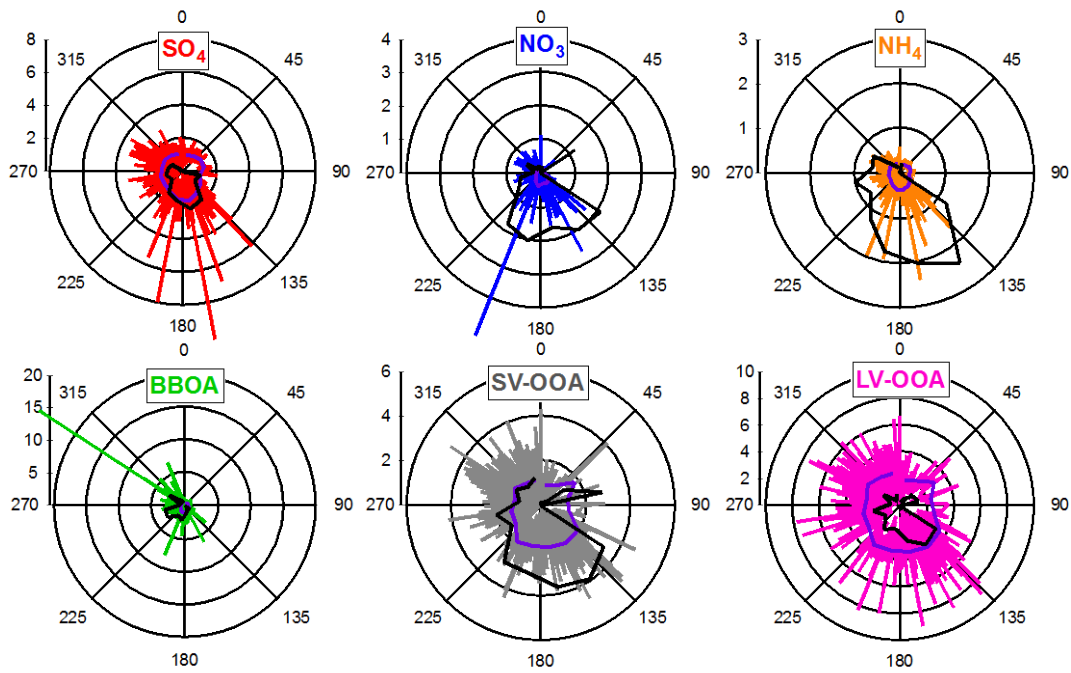
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3 Figure 8. Rocky Mountain study-average mass spectrum of CHN fragments.



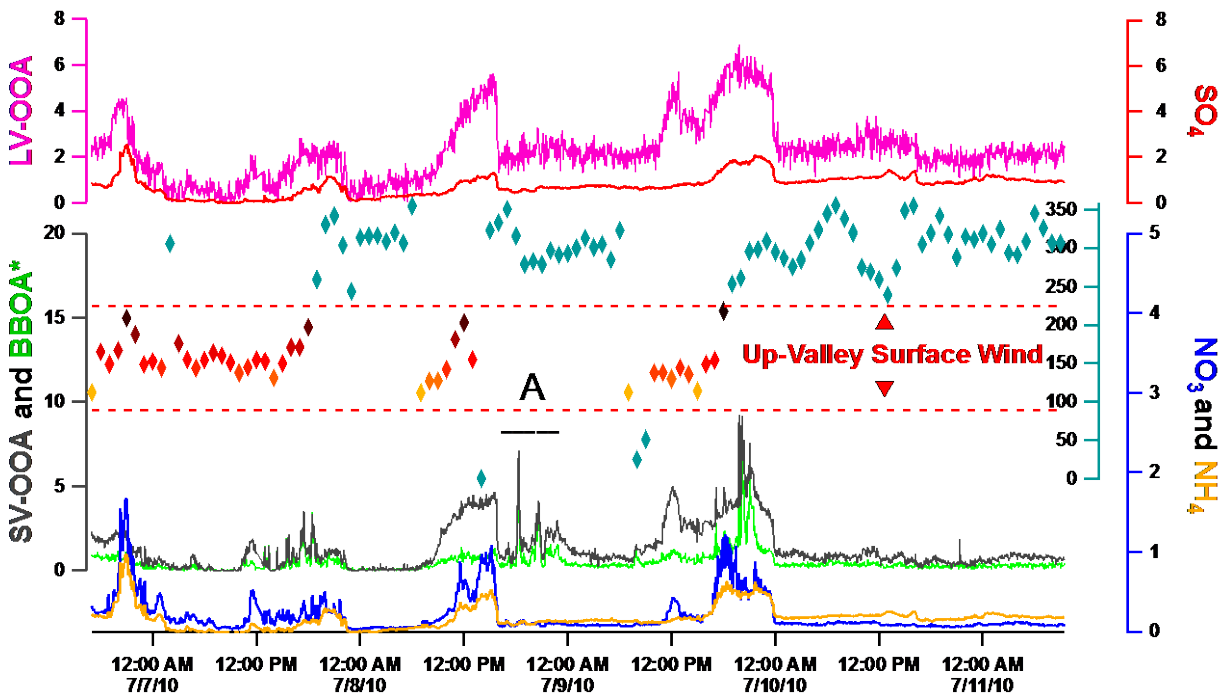
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 3 Figure 9. A) Geometric mean diameter of the log normal mass size distribution fit for the
 4 indicated species or total organics for the average of time periods dominated by the color-
 5 designated organic factor; error bars are estimations of size-dependent PToF error, compounding
 6 chopper broadening and calibration-particle size standard deviation (Supplement). B) Geometric
 7 standard deviation of the lognormal fit, with error bars equaling the reduced chi-squared value.
 8 Ammonium concentrations were too low during BBOA events for size determination.



1

2

3 Figure 10. 1-hour average concentrations ($\mu\text{g}/\text{m}^3$) of organic aerosol types with surface wind
 4 direction. Raw data are colored by species; average concentrations over the sixteen $22^\circ30'$ wind
 5 direction bins are shown in purple; and black lines indicate the Conditional Probability Function
 6 (CPF multiplied by 10).



1
 2
 3 Figure 11. Timeline of species and relevant organic factor concentrations for 7-11 July 2010,
 4 plotted with 1-hour surface wind direction at the site (diamonds). Wind directions 90 through 180
 5 degrees denote up-valley winds and are demarcated by dashed red lines and warm-colored
 6 diamonds. BBOA* is calculated using the six-factor PMF reconstructions outlined in the
 7 supplement.