Overview of the Manitou Experimental Forest Observatory: Site description and selected science results from 2008-2013

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Abstract

The Bio-hydro-atmosphere interactions of Energy, Aerosols, Carbon, H_2O, Organics & Nitrogen (BEACHON) project seeks to understand the feedbacks and inter-relationships between hydrology, biogenic emissions, carbon assimilation, aerosol properties, clouds and associated feedbacks within water-limited ecosystems. The Manitou Experimental Forest Observatory (MEFO) was established in 2008 by the National Center for Atmospheric Research to address many of the BEACHON research objectives, and it now provides a fixed field site with significant infrastructure. MEFO is a mountainous, semi-arid ponderosa pine-dominated forest site that is normally dominated by clean continental air, but is periodically influenced by anthropogenic sources from Colorado Front Range cities. This article summarizes the past and ongoing research activities at the site, and highlights some of the significant findings that have resulted from these measurements. These activities include:

- soil property measurements,
- hydrological studies,
- measurements of high-frequency turbulence parameters,
- eddy covariance flux measurements of water, energy, aerosols and carbon dioxide through the canopy,
- determination of biogenic and anthropogenic volatile organic compound emissions and their influence on regional atmospheric chemistry,
- aerosol number and mass distributions,
- chemical speciation of aerosol particles,
- characterization of ice and cloud condensation nuclei,
- trace gas measurements, and

- model simulations using coupled chemistry and meteorology.

In addition to various long-term continuous measurement, three focused measurement campaigns with state-of-the-art instrumentation have taken place since the site was established, and two of these studies are the subjects of this special issue: BEACHON-ROCS (Rocky Mountain Organic Carbon Study; 2010) and BEACHON-RoMBAS (Rocky Mountain Biogenic Aerosol Study; 2011).

111 **1. Introduction**

112 1.1 Motivation

113 Development of Earth-System models is driven by the need to improve the
114 predictability of atmospheric chemical and physical processes over time scales ranging from
115 minutes to decades. Accurate model predictions are contingent on process-level understanding
116 and detailed numerical descriptions of the coupling between water, energy and biogeochemical
117 cycles across temporal and spatial scales (Denman et al., 2007, Alo and Wang 2008, Heald et al.,
118 2009). A number of studies have discussed some of these processes and associated feedbacks
119 (e.g. Barth et al., 2005, Carslaw et al., 2010, Mahowald et al., 2011), but more detailed
120 observations and coordinated modeling efforts are required for improved representation in Earth-
121 System models.

122 The Bio-hydro-atmosphere interactions of Energy, Aerosols, Carbon, H_2O, Organics &
123 Nitrogen (BEACHON) project was initiated by the National Center for Atmospheric Research
124 (NCAR) as well as collaborators from the University of Colorado and Colorado State University
125 to investigate ecosystem-atmosphere exchange of trace gases and aerosols and their potential
126 feedbacks between biogeochemical and water cycles. BEACHON is now an ongoing component
127 of atmospheric research sponsored by the National Science Foundation. This interdisciplinary
128 research program integrates local and regional model simulations with remote sensing, regional
129 network observations, and canopy- to regional-scale field measurements. BEACHON includes
130 investigations of atmospheric, ecological and hydrological processes including concentration and
131 flux measurements of energy, CO_2, H_2O, volatile organic compounds, aerosols, nitrogen
132 compounds, hydrological parameters and feedback processes that are relevant to atmospheric
133 chemistry. Rocky Mountain ecosystems are important for providing water and other resources in

134 the western United States, but contain only a limited number of long-term monitoring sites. This
135 region is predominantly arid or semi-arid resulting in biogeochemical cycles that are water-
136 limited. Since the area contains some of the fastest growing population centers, water limitations
137 (combined with a climate that is projected to be warmer and potentially drier) pose significant
138 societal vulnerabilities (Vorosmarty et al., 2010). The region's remote complex terrain leads to
139 highly variable ecosystem characteristics, and it is unclear how this variability affects
140 hydrological and atmospheric processes across larger geographical areas. The need for long-
141 term land-ecosystem-atmosphere observation networks has been identified by international
142 research programs as a key need for advancing Earth System science (Guenther et al., 2011).
143 To address these challenges, the BEACHON project in collaboration with the United
144 States Department of Agriculture (USDA) Forest Service established the Manitou Experimental
145 Forest Observatory (MEFO) in 2008, in an area representative of a middle-elevation (~2000 –
146 2500 m a.s.l.), semi-arid, ponderosa pine ecosystem that is common throughout the Rocky
147 Mountain West, but not adequately characterized. The BEACHON project and establishment of
148 this site were designed to meet the following objectives:

149 • Collect long-term measurements of meteorology, water, carbon dioxide (CO_2), and
150 energy fluxes, aerosol size distributions and fluxes, trace gas and cloud condensation
151 nuclei concentrations;
152 • Monitor soil moisture, precipitation, snowpack, stable water isotopes, and other
153 hydrological variables to provide input and lateral boundary conditions for Earth-System
154 models and as a basis for making more accurate water resource predictions for this and
155 other semi-arid regions;

- Provide infrastructure for collaborative research among government laboratories, universities and private companies;
- Carry out intensive measurement campaigns;
- Provide training for undergraduate and graduate students and promote multidisciplinary research.

This article describes the Manitou Experimental Forest Observatory, presents on-going research at the site and highlights some initial findings. More specific scientific results and publications can be found in the publication list (Table S2) and within the individual articles as part of this special issue of Atmospheric Chemistry and Physics.

1.2 Site description and meteorological overview

The Manitou Experimental Forest (39.1006° N, 105.0942° W; Figure 1A,B), in the Front Range of the Colorado Rocky Mountains, has been managed as a research facility by the USDA Forest Service's Rocky Mountain Research Station since 1938. It contains approximately 6760 ha and exemplifies the Colorado Front Range wildland-urban interface where semi-arid montane forest ecosystems are in close proximity to larger urban centers. These interface areas, which also contain a number of small residential communities, are prone to wild fires from lightning as well as human causes. Two particularly large nearby fires (the 560 km^2 Hayman fire in 2002 and the 74 km^2 Waldo Canyon Fire in 2012) were among the most ecologically and economically damaging in the state's history. Although the primary study areas were not burned, areas within several km to the south and west of the site were affected by the 2002 fire. The landscape has thus been dramatically affected in both appearance and in the vegetation's ability to slow soil erosion from surface run-off during monsoon rains. Fire-damaged portions of the forest can change aspects of the atmospheric chemistry measured at the site through changes in gas- and

aerosol-phase emissions from nearby fire-scarred vegetation and soil. Wildfires are ubiquitous in the semi-arid forested American West, of which this area can be considered representative.

This forest's elevation ranges from 2,280 to 2,840 meters above sea level, and vegetation is primarily composed of forests of ponderosa pine, Douglas-fir, mixed conifer and aspen. The forest stands surrounding the observatory are relatively young, uneven-aged stands dominated by ponderosa pine (Section 1.3). In 2009, core samples from a survey of 38 representative ponderosa pine showed that the median tree age was 49.5 years (with average, minimum and maximum ages of 62.5, 27, and 201 years respectively).

Soils underlying the tower site and the surrounding area are classified as deep, well-drained sandy loams and sandy gravelly loams originating from alluvial deposits weathered from underlying arkosic sandstone formations as well as nearby granite formations (Soil Conservation Service, 1992). Although numerous outcroppings of partially-weathered sandstone exist around the site, the average depth to bedrock is estimated to be between 1-1.8 m (36-60 inches) below ground surface. The soil ranges from slightly acidic to moderately alkaline (pH 6.1-7.8) with little organic matter content (1-4%) and rooting depths reported to be in excess of 1.3 m (40 inches). Soil permeability on undisturbed soils is moderately rapid (approx. 50-150 mm hr^{-1}). Rapid runoff generation and sediment transport occurs on compacted road surfaces, and other areas void of significant ground vegetation. The tower site is on an alluvial bench, formed by the erosion of underlying granite. It is situated in a broad, shallow valley approximately 1 km west of an intermittent creek, which flows towards the north. The terrain slope is asymmetric across this valley with the east side of the valley being steeper and the west side more gradual (gradient between 3-8%).

The National Weather Service has been monitoring precipitation at MEF since 1940 (Station Woodland Park 8 NNW, Coop ID: 059210), and U.S. Forest Service staff have been collecting meteorological data including air and soil temperature, precipitation, and wind speed since 1998. The climate is cool (mean temperature is 19°C in July and -2°C in January) and dry with an average annual precipitation for 2010-2013 of 430.5 mm (16.94 inches). Approximately 50% of the precipitation falls as rain during the summer season (June – September) primarily during afternoon thunderstorms characterized by brief but intense periods of rainfall and lightning. Winter snowfall is typically light, and a persistent snowpack rarely develops.

Like much of Colorado, the site has a high frequency of sunny days during most of the year. During mid-day in July, approximately 80% of the days have PAR values (photosynthetically active radiation between 400 and 700 nm) above the canopy that exceed 440 W m^{-2}, and part of nearly every day reaches PAR values greater than 400 W m^{-2} (~2000 μmol m^{-2} s^{-1}). The average PAR calculated from 1998-2012 was 72 W m^{-2}. Frequent afternoon thunderstorms can temporarily reduce the solar insolation, but rarely for more than three hours. Figure 2 shows the diel cycle of total longwave and shortwave radiation of four representative months during 2011. The total radiation is calculated from the difference between the downwelling radiation and the upwelling radiation from the radiometers at the top of the chemistry tower at 28 m.

Numerous studies have been conducted here by researchers from a wide range of federal agencies, academic institutions, and non-governmental organizations. Early research focused on range management, including re-vegetation of abandoned fields, grazing management in native and seeded pastures, watershed management in gully control, stream sedimentation, surface runoff, bacterial pollution, and infiltration (Gary et al., 1985). Recent research is more diverse,

and includes a long-term (> 30 years) study on the flammulated owl (Linkhart et al., 2006, 2007), studies assessing the impacts of forest restoration and fuel reduction techniques (Battaglia et al., 2010, Massman et al., 2010, Rhoades et al., 2012), silviculture studies (Lezberg et al., 2008), and wildfire recovery studies (Fornwalt et al., 2010). Additional information about the site (including long-term weather, tree growth data and a bibliography of publications) can be found at: http://www.fs.usda.gov/manitou.

1.3 Measurements at the Manitou Experimental Forest Observatory (MEFO) under the auspices of BEACHON

In 2008, with cooperation with the USDA Forest Service, NCAR established the infrastructure at the site and named it the Manitou Experimental Forest Observatory (MEFO). The site includes four (4) mobile steel containers each having 160 ft^2 of laboratory floor space, numerous sampling ports, temperature-control and 20 kW power. Two research towers that extend through the canopy were constructed approximately 300 m apart (Figure 1C) and are referred to here as the micrometeorology and chemistry towers. Detailed information on these towers' measurements is listed in Table S1 in the supplementary materials section. A third (smaller) eddy-covariance measurement tower was deployed in a large clearing or 'forest gap' from 2011-2012. The purpose of this smaller tower was to make 4-way radiation measurements, surface skin temperature, and sensible and latent heat flux measurements over the grass and forb vegetation that is found beneath and in between the ponderosa pine. These measurements were taken at 1 and 3 m above ground level.

The micrometeorology tower (Figure 1E) is a narrow 45 m triangular tower (Rohn Products, Peroria, IL, USA; model 45G; 425 mm per side) designed to facilitate the analysis of the impact of canopy elements (needles, branches, trunks) on turbulent exchange between the surface,

canopy layers, and the overlying atmosphere. This tower had instruments deployed at six different levels (2, 8, 16, 22, 30, and 43 m), thus allowing several measurements within and above the canopy (average canopy height ≈ 16 m). The 22 m level contained a 4-component radiometer (Kipp and Zonen, The Netherlands, model CNR1) for measuring above-canopy incoming and outgoing shortwave and longwave radiation. Instrumentation on the other five levels include:

- Sonic anemometers (Campbell Scientific, Logan, UT, model CSAT3) to record the three orthogonal wind velocity components and temperature fluctuations;
- NCAR-Vaisala (Vantaa, Finland) aspirated hygrothermometers to measure absolute temperature and relative humidity;
- Open-path infrared gas analyzers (LiCOR, Lincoln, NE, model 7500) to measure water vapor and carbon dioxide.

The instruments on the micrometeorology tower operated nearly continuously from July 2009 until July 2012 when they were removed as a precaution due the proximity of the Waldo Canyon Fire. This multi-season dataset is being used to:

- Quantify the importance of canopy-induced modifications to turbulence in predicting whole-ecosystem exchange in regional and global climate models,
- Partition water fluxes into transpiration and evaporation components, and
- Investigate impacts of spatially heterogeneous canopy distributions on evapotranspiration using additional information from the chemistry and understory towers.

The chemistry tower is a 28 m walk-up type tower that is equipped with meteorological sensors as well as a variety of flux and gradient concentration measurements for gasses and aerosols (Figure 1D). The platform on each level is 1.78 m × 1.27 m and is suitable for heavier

instruments that require more space, power and maintenance. It can also support gradient sampling systems, which can move vertically along the tower. This tower is also equipped with 2D and 3D sonic anemometers, temperature, and radiation probes for continuous meteorological measurements and for calculating fluxes using the closed-path eddy covariance method. Other continuous gas-phase measurements from this tower have included: CO, CO_2, H_2O vapor, NO, NO_2 and SO_2. The Waldo Canyon fire in June 2012 forced the removal of the trace gas instruments from the chemistry tower and all of the instruments from the micrometeorological tower. Fortunately, the fire did not directly affect the site, and meteorological measurements from the chemistry tower have operated continuously (see Table S1). Since the two towers had generated 3-4 years of data and some of the instruments were required for other projects and field sites, it was decided to adjust the sampling strategy. Future core measurements of trace gases (CO, O3, SO2, NOx) and aerosol number size distributions will be operated 4 times per year (for 4-6 weeks in duration) to capture the seasonal variability of these key species..

The suitability of these towers for making eddy covariance flux measurements in the surrounding landscape was analyzed by Kaser et al. (2013b). Briefly, the flux footprint was found to extend to 900 m for unstable boundary layer conditions and to 2500 m for stable conditions. However, because there is more heterogeneity in the forest composition and proximity to former burn areas inside the 2500 m radius, a practical limit of 1850 m beyond the tower was used as one of the criteria for valid flux data. A paved road ~ 500 m to the site caused data to be eliminated if wind direction was from that sector.

Measurements from ponderosa pine (the only significant woody vegetation around the observatory) include leaf- and branch-level photosynthesis, respiration and biogenic volatile organic compound (BVOC) emissions as well as sap flow using the compensation heat pulse

method as described by Burgess et al. (2001). Leaf-level gas exchange was measured during peak sun exposure (9:00 – 14:00) on sunlit needles ~ 10m above the ground. Each measurement was made on 6-10 mature needles. Mature needles were defined as needles that been on the branch through at least one winter. Gas exchange measurements were made using an LI-6400 portable gas exchange system (LI-COR Biosciences, Lincoln, NE) and photosynthesis, stomatal conductance, and transpiration calculations were made using total leaf area (measurement as described in Eller et al., 2013). The high solar insolation just prior to monsoon precipitation is demonstrated by the low stomatal conductance and photosynthesis values in July.

Table 1: Mean values for needle-level gas exchange measured on mature *P. ponderosa* needles at the Manitou Experimental Forest Observatory. All calculations are based on total, rather than projected, leaf area. Values in parentheses give the range of measurement dates (2011 day of year). Standard deviations are given in italics (n=3).

	May (136-149)	June, July (178-185)	August (230-233)	September (263-265)
Net Phosynthesis (A) [μmol CO_2 m^{-2} s^{-1}]	2.9 *0.6*	0.9 *0.6*	3.2 *0.8*	3.5 *0.2*
Stomatal conductance(g_s) [mmol H_2O m^{-2} s^{-1}]	28 *9*	7 *5*	29 *12*	30 *6*
Transpiration [mmol H_2O m^{-2} s^{-1}]	0.49 *0.13*	0.35 *0.28*	1.00 *0.22*	0.64 *0.07*

A suite of hydrological measurements for total precipitation, soil moisture, leaf wetness and snow depth have been measured nearly continuously since 2009. Aerosol measurements include two years of particle size distributions from 4 nm to 2 μm and 1 year of CCN (cloud condensation nuclei) data during 2010-2011 measured from one of the 4 mobile laboratories adjacent to the tower (Figure 1D). An additional month of CCN measurements was made above the canopy (25 m above ground) from the chemistry tower (Levin et al., 2012). BEACHON

ROCS (Rocky Mountain Organics Study, 2010) and BEACHON RoMBAS (Rocky Mountain Biogenic Aerosol Study, 2011) were two large intensive measurement campaigns that occurred at the site. Selected results from these two campaigns as well as the initial 2008 Southern Rocky Mountain (SRM) study are discussed in this article and are summarized in Section 5. A more detailed summary of measurements at MEFO can be found in Table S1 in the Supplementary Material section. Campaign-specific data has been quality checked, archived and put into ICARTT format when possible. This data is publicly available for the 2 major campaigns at the following website: http://www2.acd.ucar.edu/campaigns
Other long-term data is available upon request from the corresponding author.

1.4 Meteorology at Manitou Experimental Forest Observatory

As mentioned in section 1.2, the observatory lies within a north-south drainage (draining to the north), leading to the formation of diurnal mountain-valley flows. Nighttime flow above the canopy (28 m) is dominated by drainage from the south as can be seen in Figures 3B and 3F. Winds below the canopy are often westerly or southwesterly due to drainage flow from surrounding ridgelines (Figure 3D). This height-dependent nocturnal pattern is dominant in all seasons. Daytime wind directions are much more variable. Although there is often a southerly flow during the day, other wind directions are also prevalent. Synoptic winter winds lead to a higher frequency of westerly and southwesterly flow (Figures 3A and 3E). These conditions tend to bring relatively unpolluted air to the site from the west. Stagnant high pressure conditions lead to locally-induced upslope flow from either the northeast or southeast, which are consistently observed during daylight hours (Figure 3C). These periods are important in understanding the local chemistry as these flows transport air from Front Range cities (mainly Denver and Colorado Springs). Regardless of the daytime wind patterns, southerly drainage

flow usually develops soon after the stable nocturnal boundary layer develops, which is often accompanied by an an increase in anthropogenic pollutants. Wind measurements as well as modeling results suggest that this is often due to air from the Denver area during daytime upslope flow, which then drains towards the north and past the site at night.

2. Footprint hydrology in a water-limited ecosystem

2.1 Overview of hydrological measurements

Intensive hydrological measurements of total precipitation (rain and snow), soil moisture and snow depth as well as soil temperatures have been collected at MEFO since the summer of 2009. These complement the vertical flux measurements of water vapor for a complete accounting of the site's water budget. The precipitation measurements also augment the long-term records maintained by the USDA Forest Service mentioned in Section 1.2. A network of 11 tipping bucket rain gauges as well as an alter-shielded, weighing-type total precipitation gauge provide high time resolution, year-round precipitation measurements in a network distributed within the chemistry tower footprint in order to characterize the high spatial variability of precipitation. More details about these measurements are given in Table S1. The 2010-2013 annual accumulation of hourly precipitation is shown in Figure 4A. These time series are bias-corrected merged data products between the site's sensors in order to cover periodic data gaps. The site's annual precipitation measurements for a given year are defined by an end date of September 30 of that year and a start date of October 1 in the preceding year. The patterns observed have been fairly consistent. Periodic precipitation episodes occur throughout the principal cool season of October through May followed by a brief dry season from late May through mid-June. This is followed by a summer period of rather intense precipitation episodes associated with the regional incursion of the North American Monsoon system. Finally there is

362 an extended dry period starting in the late summer and extending into early autumn. The average
363 annual accumulated precipitation for 2010-2013 was 430.5 mm with a range of 392 mm (in
364 2012) to 513 mm (in 2010). It should be noted that 2012 was among the driest years on record
365 for most of Colorado, and the total precipitation for 2013 was similarly low. The latter year
366 began with very low winter and spring snow fall, and stayed much drier than average until heavy
367 September rains increased the total accumulated precipitation to about the same level observed in
368 2012. During most years, approximately 50% of the total precipitation occurs during June-
369 September. The maximum observed hourly rainfall recorded at the site from 2009-2013 was
370 57.9 mm, which occurred on Aug. 4, 2010. Other thunderstorms with high rain fall rates (up to
371 25 mm per hour) are common during the summer monsoon.
372 Seasonally-transient snowpack is an important feature of the hydrologic cycle as the
373 snowpack can provide a lasting water source to the site during the spring melt period and can
374 also insulate the soil from freezing temperatures. Snow depth measurements (Jenoptik, Inc.,
375 Jena, Germany, model SHM30 laser snow depth sensor) began during the winter of 2010-2011.
376 Persistent patchy or complete snowpack is limited to December, January and February. Periodic
377 snowstorms may also input appreciable moisture during the months of October, November,
378 March and April although the snowpack rarely persists for more than 7 days.
379 Soil moisture probes (Decagon Devices, Pullman, WA, USA, model EC-5) and
380 temperature profiles (Campbell Scientific, Logan, UT, USA, model T107 thermistor) extending
381 from the near surface to approximately 1 meter depth are made at 3 different sites within the
382 micrometeorology tower's footprint. The merged annual cycle of soil moisture from all sites is
383 shown in Figure 4B, and the annual soil temperature cycle is shown in Figure 4C. The soil
384 moisture cycle exhibits some interesting and classic features of western landscape hydrology,

385 especially the tendency for persistent dryness and pulsed recharge of near-surface moisture,
386 particularly in the warm season. Deeper into the soil, the moisture variability is significantly
387 damped and there is evidence of persistent soil moisture there, regardless of extended summer
388 dry periods. This deeper layer of persistent wet soil helps sustain some of the total evaporative
389 flux from the ponderosa pine ecosystem during the summer. There are extended periods of
390 winter soil temperatures several degrees below 0 °C, which extends to approximately 70 cm
391 below the surface. These low soil temperatures indicate that significant amounts of soil water
392 freeze (i.e., creates 'soil frost') occasionally during the winter. The presence of soil frost is
393 further evidenced by the sharp decline in recorded soil moisture values from December through
394 late-February. Suppressed soil moisture values corresponding with sub-zero soil temperatures is
395 a classic measurement artifact due to the significant change in soil dielectric permittivity as water
396 undergoes phase change from liquid to ice and back again at the freezing point. This meltwater
397 release and periodic melting of the transient snowpack impart additional water pulses to the site.
398 As previously mentioned, MEFO typically experiences an early summer dry period before the
399 onset of the monsoon rains, which is highly correlated with increased CO_2 and BVOC fluxes.
400 The semi-arid climate creates very low mid-day stomatal conductance in ponderosa pine during
401 the early- and late-summer dry periods, which protects the trees from water stress. When the
402 monsoon rains start, these fluxes and stomatal conductance both increase substantially.
403
404 2.2 Water manipulation effects on ponderosa pine
405 Projected water limitations and higher temperatures are expected to put additional
406 climate-induced physiological stresses on semi-arid forest ecosystems (Allen et al., 2010). To
407 test hypotheses related to future climates, manipulation experiments must be carefully designed

to ensure that data are representative of larger ecosystems responses (Beier et al., 2012). With these considerations in mind, another study at MEFO during 2010-2011 was designed to quantify the effect of different water treatments on the photosynthesis and respiration rates as well as BVOC emissions from mature trees (at least 10 m in height). Up to 50% of the incoming precipitation (snow and rain) was systematically diverted from the root zones (10 m × 10 m area) around targeted trees using an array of troughs (see iii in Figure 1C). The intercepted water was collected into barrels and then added to nearby trees resulting in a water continuum delivered to the various trees from 0.5 to 1.5 times the total precipitation such that the total amount of water delivered to the entire plot remained constant. Physiological parameters (e.g. sapflow, photosynthesis, and BVOC emissions) were measured on all trees within the experimental plot. Similar to the speciation seen in ambient air, branch-level measurements showed that the BVOCs emitted in the highest concentrations were methanol, 2-methyl-3-buten-2-ol, and monoterpenes. Initial observations showed that seasonality in plant physiological processes and weather dynamics interact to produce complex controls over climate-dependent emissions of these compounds with a strong dependence on soil moisture and precipitation. If the climate in this region shifts to a drier summer regime, total BVOCs emitted from needles of this forest are likely to decrease, which will have implications for modeling both gas- and liquid-phase regional chemistry. Studies such as this exemplify the interdisciplinary research questions addressed by the BEACHON project, and are necessary to address the ecological system processes for inclusion into Earth-System models as discussed in Section 1.1.

3. Volatile organic compounds, oxidants and aerosol properties

3.1 Volatile organic compound observations

Volatile organic compounds (VOCs) at MEFO are a mixture of biogenic and anthropogenic compounds. The summertime VOC signals are dominated by biogenic emissions, primarily methanol, ethanol, acetone, monoterpenes ($C_{10}H_{16}$, abbreviated by MT) and 2-methyl-3-buten-2-ol ($C_5H_{10}O$, abbreviated by 232-MBO or MBO). Isoprene (C_5H_8) is also observed during summer, but to a much lesser extent (~10-20% of 232-MBO concentrations). Anthropogenic VOC concentrations are lower than the biogenic compounds and are typically transported into the area from the Colorado Springs or Denver metropolitan areas.

A variety of techniques have been used to measure VOCs from different levels on the chemistry tower, individual branches from the dominant vegetation (ponderosa pine), and from the ground. A quadrupole proton transfer reaction mass spectrometer (PTR-MS; Ionicon, Analytik, Innsbruck, Austria) measured a suite of selected VOCs (including methanol, acetonitrile, acetaldehyde, acetone+propanal, 232-MBO+isoprene, benzene, monoterpenes and sesquiterpenes) during portions of each of the 2008-2012 growing seasons. Under normal operating conditions, 232-MBO undergoes a dehydration reaction in the PTR-MS drift tube leading to a molecular ion of m/z = 69. This is the same ion as protonated isoprene, which is why they are reported as the sum of both species. Tower-based measurements alternated between a six point gradient system (1.6, 5, 8.5, 12, 17.7 and 25.1 m above ground) and an eddy covariance (EC) flux system at the top level (25.1 m). In addition, a time-of-flight (TOF) PTR-MS (University of Innsbruck, Austria) was deployed for EC and concentration measurements above the ponderosa pine canopy in 2010 and 2011 (Kaser et al., 2013a,b). A Selective Reagent Ion (SRI) PTR-TOF-MS (Ionicon Analytik, Innsbruck, Austria) instrument was used in 2011 to selectively distinguish 232-MBO from isoprene concentrations by using NO^+ as the reagent ion (Karl et al., 2012). This configuration was also used for one week in 2012 to continue these

454 measurements for determining EC fluxes of 232 -MBO and isoprene (Karl et al., 2013). Figure 5
455 shows the vertical flux profiles for 232-MBO and total MT calculated from gradient
456 measurements using the methodology described in Karl et al. (2004). It is evident that MBO
457 emissions follow a light-dependent pattern and that the fluxes increase with height up to 12 m.
458 MT emission patterns were vertically more uniformly distributed suggesting that the understory
459 (forest litter, bark and trunks) also contributed to the total emissions. Using site-specific leaf
460 cuvette measurements as model inputs, MEGAN 2.1 estimates showed good agreement with the
461 measured average daytime 232-MBO + isoprene fluxes of 1.84 mg m^{-2} h^{-1}. After the large rain
462 and hail storm on August 4th 2010 (which produced 57.9 mm precipitation in an hour; Section
463 2.1), monoterpene fluxes increased to 4.7 mg m^{-2} h^{-1} which is a factor 5-10 higher than what is
464 normally observed (0.5-1mg m^{-2} h^{-1}) (Kaser et al., 2013b). Figure 6A shows the sum of MT and
465 MBO+isoprene concentrations and fluxes starting on this day (August 4) and ending 1 week later
466 (August 11). The increases in both emissions and fluxes, which continue for ~2 days after the
467 event, are evident. The missing flux data on the first day (and periodically throughout the
468 measurement period) is due to turbulence characteristics that are not amenable to EC calculations
469 as described in section 1.3. The PTR-MS showed that ambient concentrations of several other
470 BVOC (including cymene, camphor, nopinone, pinonaldehyde and sesquiterpenes) were also
471 elevated after this vegetation disturbance.

472 The Trace Organic Gas Analyzer (TOGA, Apel et al., 2010) was deployed during the
473 BEACHON ROCS campaign to measure concentrations of isoprene, 232-MBO, speciated MT
474 and over 25 other targeted compounds. Results showed that the MT speciation is dominated by
475 α-pinene, β-pinene and Δ-3-carene (approximately 25% each). Other quantified monoterpenes
476 include camphene (7%), limonene (12%), myrcene (5%) and ocimene (1%). Figure 6B(1-4)

477 shows August 2010 ambient diel concentrations of 4 selected VOCs reported by TOGA. The
478 concentrations of the biogenic compounds MBO and MT are much higher than those of a typical
479 anthropogenic compound (e.g. toluene) at this site, and the concentrations have different diurnal
480 signatures. During the day, as the boundary layer grows and OH is present, MT concentrations
481 are diminished even though their emissions are the greatest during this time. At night, the
482 suppressed boundary layer height combined with decreased losses from O_3 and OH reactions
483 leads to elevated MT concentrations that generally increase from 18:00 to midnight and remain
484 elevated until 06:00-07:00. MBO emissions from ponderosa pine are strongly light dependent
485 (Harley et al 1998, Kaser et al., 2013b) resulting in maximum emissions and ambient
486 concentrations during midday with a secondary peak in early morning associated with initiation
487 of emissions before the morning breakup of the nocturnal boundary layer. The combination of
488 all 3 instruments used during BEACHON ROCS provided a unique opportunity to compare
489 VOC measurement techniques under real-world conditions. The results were encouraging as the
490 instruments agreed within ~20% for monoterpenes and ~10% for 232-MBO + isoprene with R^2
491 values of 0.85-0.97 (Kaser et. al. 2013a).

492 Consistent with ambient concentration measurements, branch- and needle-level BVOC
493 emission measurements confirm the dominance of MBO in the emission profile; during daylight
494 hours, MBO comprises >85% of the emitted reactive BVOC mass. Similar to ambient
495 observations, α-pinene, β-pinene, Δ-3-carene, camphene and limonene dominate the MT
496 emissions, but a large number of other terpenoids are emitted at lower rates, including sabinene,
497 myrcene, ocimene, α-terpinene, β-phellandrene, cymene, terpinolene, p-cymenene and the
498 oxygenated monoterpenes linalool, terpineol and methyl chavicol. A number of sesquiterpenes,
499 dominated by β-farnesene, also appear in emission samples. For model inputs, BVOC speciation

500 is an important consideration as different compounds (such as MT isomers with the same
501 chemical formula) have different reaction rate constants with OH, O_3 and NO_3, so their reaction
502 products, pathways and atmospheric lifetimes can vary considerably. Additional soil BVOC flux
503 measurements have been made using enclosures and a micrometeorological gradient technique at
504 the site (Greenberg et al., 2012). These results suggested that emissions from the litter were
505 negligible, contributing less than 1% of above-canopy emissions for all BVOCs measured.

506 A newly developed Thermal desorption Aerosol Gas chromatograph - Aerosol Mass
507 Spectrometer (TAG-AMS) was deployed and analyzed semi-volatile VOCs (~C_{14}-C_{25}) on a
508 bihourly timescale. The sample collection, thermal desorption and chromatography systems
509 have been described previously by Zhao et al. (2013), however the 2011 BEACHON-RoMBAS
510 campaign was one of the first to couple it to the AMS as a detector (Williams et al., 2014). More
511 than 70 semi-volatile gas-phase species were observed and quantified in the ambient atmosphere
512 during the campaign. Source apportionment was used to identify the origin of these gas-phase
513 species. Some were anthropogenic compounds (such as poly-aromatic hydrocarbons (PAH),
514 oxygenated PAH and alkanes), but 23 species were identified to be terpenoid compounds of
515 biogenic origin from a local source determined from Positive Matrix Factorization (PMF).

516 In addition to direct VOC emissions and transported species, it is also important to
517 consider oxidation products. These compounds can influence tropospheric ozone formation,
518 oxidative capacity of the atmosphere, and contribute to secondary organic aerosol.
519 Concentrations and fluxes of two important oxygenated VOCs, formaldehyde (HCHO) and
520 glyoxal (CHOCHO), were measured during the 2010 BEACHON-ROCS campaign (DiGangi et
521 al., 2011, 2012) using Fiber Laser-Induced Fluorescence (FILIF; Hottle et al., 2009) and Laser-
522 Induced Phosphorescence (Huisman et al., 2008). Ambient formaldehyde concentrations ranged

523 between a minimum of ~0.5 ppb in the early morning hours (4:00 MST), and maximum values
524 of 2-2.5 ppb in the evening (~20:00 MST). Ambient glyoxal concentrations ranged between a
525 minimum of ~18 ppt in the early morning hours (6:00 MST), and maximum values of 30-55 ppt
526 in the evening (~17:00 MST). The glyoxal:formaldehyde ratio maintained a stable diurnal cycle
527 ratio with values of ~1.5-2% in the early morning and at night, and rising to ~2.5-3% in the
528 middle of the days. In addition, to our knowledge, these canopy-scale HCHO eddy flux
529 measurements are the first reported for any site. These results, coupled with enclosure
530 measurements that showed minimal direct emissions, suggest a surprisingly large HCHO
531 production source within the canopy air space. The mid-day HCHO fluxes were positive
532 (upward) ranging from 37 to 131 $\mu g\ m^{-2}\ h^{-1}$ (see Figure 7b) and were correlated with temperature
533 and radiation within the canopy. The missing HCHO source is thus consistent with oxidation of
534 VOCs with light and temperature dependent emission profiles. The strength of HCHO fluxes
535 cannot be accounted for by the oxidation of measured MBO and terpenes (also see section 3.2).
536 A detailed analysis regarding HCHO sources and oxidation is discussed in DiGangi et al. (2011).
537
538 3.2 Peroxy and hydroxyl radical observations
539 Numerous studies (e.g. Stone et al., 2012) have highlighted discrepancies between
540 modeled and measured radical concentrations in forested environments suggesting a lack of
541 understanding of the chemical processes driving secondary pollutant formation. While most
542 research has focused on regions dominated by isoprene emissions, results from several
543 investigations indicate gaps in our understanding of BVOC oxidation in MBO- and
544 monoterpene-dominated areas similar to MEFO (Kurpius and Goldstein, 2003; Day et al., 2008;
545 Farmer and Cohen, 2008; Wolfe et al., 2011; Mao et al., 2012). Both the 2010 BEACHON-

546 ROCS and 2011 BEACHON-ROMBAS campaigns included measurements of the hydroxyl
547 radical (OH) and peroxy radicals (HO_2 and RO_2) (see Table S1), providing a unique opportunity
548 to test our understanding of the chemical reactions that link BVOC oxidation with production of
549 ozone and secondary organic aerosol (SOA) precursors.

550 Discrepancies between modeled and measured HO_x (= OH + HO_2) in regions with high
551 BVOC levels have been primarily attributed to "missing" sources of OH (Thornton et al., 2002;
552 Lelieveld et al., 2008; Hofzumahaus et al., 2009; Peeters et al., 2009). In the boundary layer, OH
553 is produced both via "primary" sources, such as photolysis of ozone in the presence of water
554 vapor, and via radical cycling reactions, such as reaction of HO_2 with NO.

555 $$O_3 + h\nu \rightarrow O(^1D) + O_2 \quad \text{(R1)}$$

556 $$O(^1D) + H_2O \rightarrow 2OH \quad \text{(R2)}$$

557 $$HO_2 + NO \rightarrow OH + NO_2 \quad \text{(R3)}$$

558 In a detailed analysis of OH observations, Kim et al. (2013) demonstrate that radical recycling
559 via (R3) is likely the dominant source of OH within the MEFO canopy. A 0-D box model under-
560 predicts HO_x concentrations relative to observations, implying unidentified sources of HO_2.
561 Using the same box model in a study focused on peroxy radical observations, Wolfe et al. (2013)
562 confirm this result and identify several potential additional sources of both HO_2 and RO_2.
563 Notably, it is suggested that oxidation of unmeasured, highly reactive BVOC could explain a
564 significant portion of the missing peroxy radical source. Such a source could also explain the
565 high HCHO fluxes observed during the same campaign (DiGangi et al, 2011; see Section 3.1).
566 Figure 7a compares the hourly-averaged measured and modeled total peroxy radical mixing
567 ratios for BEACHON-ROCS (August 2010). As described in Wolfe et al. (2013), the difference
568 between measured and modeled values corresponds to a total "missing" peroxy radical

569 production rate of as much as 130 ppt/min. For comparison, Figure 7b shows measured and
570 modeled HCHO fluxes (DiGangi et al., 2011). The additional HCHO production needed to
571 reconcile modeled and measured formaldehyde fluxes is on the order of 65 ppt/min at midday.
572 Uncertainties in measurements and model results contribute to a significant overall uncertainty in
573 these production rate estimates (approximately ± 50%). Nonetheless, the similarity between
574 these results—obtained via two essentially independent methods—supports the conclusion that
575 VOC oxidation within the canopy is much stronger than predicted by canonical chemical
576 mechanisms.

577 Analysis of the role of anthropogenic influence on the oxidation of BVOCs, especially
578 via the influence of NO_x on the fate of RO_2, is of great current interest (Orlando and Tyndall,
579 2012), and MEFO is well suited for such studies (see also section 4.1). Figure 8A shows the
580 measured HO_2, HO_2+RO_2, NO and NO_2 concentrations during a representative day in
581 BEACHON ROCS (August 24, 2010), and Figure 8C shows the corresponding wind speed and
582 direction. On this day, upslope conditions (that can bring polluted urban air and are often seen at
583 this site) were not observed, as the wind was generally out of the south or southwest where there
584 is relatively little anthropogenic influence. During the mid-morning as the boundary layer
585 developed, an increase in NO_x (Figure 8A) can be seen, which was likely due to downward
586 transport of a residual layer. The anthropogenic influence on the fate of RO_2 is evident as the
587 loss mechanism was initially dominated by the RO_2 + NO channel (Figure 8B), but during mid-
588 day as NO_x concentrations decreased (due to the residual morning boundary layer breaking up
589 and southwesterly flow to the site), the RO_2+HO_2 channel became the major loss mechanism.
590 While the patterns of these transitions do not appreciably affect the concentrations of biogenic
591 and anthropogenic VOCs, the changes in the role of the different reaction channels are consistent

592 with the measured HCHO and glyoxal concentrations (DiGangi et al., 2012) and measured and
593 modeled HO_2+RO_2 concentrations indicated in Figure 7. This competition between NO_x and
594 HO_2 for reaction with the peroxy radicals (RO_2) affects the composition of multigenerational
595 reaction products formed during gas-phase radical cycling and thus dictates, to a large extent, the
596 production of ozone and organic aerosol precursors.
597
598 3.3 Aerosol properties and composition
599 Particle size distribution measurements (covering diameters from 4 nm to 2.5 μm) were
600 conducted for nearly 2 years at MEFO starting in February 2010 and ending in January 2012.
601 The instrument used for these measurements consists of the following components:
602 • Optical Particle Counter (200 – 2500 nm); Lasair model 1002 from Particle
603 Measurement Systems (Boulder, CO, USA),
604 • Regular scanning mobility particle sizer (SMPS; 30-300 nm): Custom sheath air
605 and HV control unit combined with TSI model 3081 Differential Mobility
606 Analyzer (DMA) and TSI model 3760 Condensation Particle Counter (CPC; TSI
607 Inc., Shoreview, MN, USA), and
608 • Nano SMPS (4-30 nm): Custom sheath air and HV control unit combined with
609 TSI model 3085 DMA, and TSI model 3025a CPC.
610 Particle size distributions started at midnight at exact 5 minute intervals for a total of 288
611 size distributions per day. Frequent "small particle events" characterized by high concentrations
612 of 4 – 20 nm particles were observed, especially during the summer season. The origin of these
613 small particles is likely atmospheric nucleation (Kulmala et al., 2007), which is thought to be
614 caused by reactions of gas-phase sulfuric acid with atmospheric bases such as ammonia and

615 amines as well as oxidized organic compounds (Kirkby et al., 2011, Almeida et al., 2013). An
616 example of three typical small particle events during July 2011 is shown in Figure 9A, where the
617 onset of each event is seen just prior to noon (MST). These events are common at MEFO in the
618 summer, occurring 3-5 times per week during late morning or early afternoon, and typically
619 coincide with changes in wind speed and direction. Figure 9B shows wind speed and wind
620 direction at the top of the chemistry tower and sulfate aerosol mass loadings measured by an
621 aerosol mass spectrometer (described below). On each of these mornings the wind speed is
622 fairly low (~1 m/s) at 8:00 MST with wind direction shifting from the south to a more northerly
623 or northeasterly direction, indicating upslope transport from the Denver area. Thermal
624 Desorption Chemical Ionization Mass Spectrometer (TDCIMS) measurements during these
625 nucleation events demonstrated that sub-20 nm particles were composed of ~60% sulfate by
626 mass whereas during non-event periods, sulfate contributed less than 40% of the mass to these
627 small particles (Cui et al., 2014). In both event and non-event periods, the bulk aerosol mass is
628 not significantly affected by this sulfate mass, as the majority of the total aerosol mass is
629 dominated by larger particles. The correlation with wind direction and the increase in sulfate
630 aerosol indicates that these events are anthropogenically induced, The scarcity of particles
631 smaller than 10 nm on July 29 suggests that nucleation is occurring away from the site, either
632 aloft (Mirme et al., 2010, Schobesberger,et al., 2013) or in the mixed layer shortly (~60 minutes
633 or less) upwind of the site.
634 A Fast Mobility Particle Sizer (FMPS, Model 3091, TSI Inc., Shoreview, MN, USA) was
635 used during BEACHON-RoMBAS to measure size-dependent particle fluxes (Pryor et al., 2013).
636 While the mean flux of both Aitken and nucleation mode particles was downwards, upward
637 fluxes were frequently observed. Based on quadrant and time-scale analyses using the University

638 of Helsinki Multicomponent Aerosol (UHMA) model (Korhonen et al., 2004). They found that
639 the upward fluxes of nucleation mode (< 30 nm diameter) particles were most strongly
640 influenced by upward transport of particle-rich air from the canopy resulting from the growth of
641 recently nucleated particles as well as coagulation processes. Downward fluxes of the Aitken
642 mode particles were more commonly linked to breakdown of the nocturnal inversion and
643 entrainment of particle-depleted air from above the canopy.

644 Average particle number concentrations at this site are typically less than 2×10^3 cm^{-3}
645 and rarely exceed 10^4 cm^{-3}, which are typical values in rural continental environments. During
646 the August 2011 BEACHON-RoMBAS study, chemical speciation and mass loadings of non-
647 refractory PM_1 aerosol were measured using a high resolution time-of-flight aerosol mass
648 spectrometer (HR-ToF-AMS, Aerodyne Research, Inc., Billerica, MA; DeCarlo et al., 2006).
649 Average mass loadings during the campaign were 2.5 μg m^{-3} (Figure 10). Also included in this
650 figure is black carbon aerosol as measured with a single particle soot photometer (Droplet
651 Measurement Technologies, Boulder, CO, model SP2). Approximately 75% of the total PM_1
652 aerosol mass was comprised of organic aerosol (OA), with the rest composed primarily of
653 ammonium sulfate. Nitrate concentrations were low and were shown to be primarily composed
654 of organic nitrates (Fry et al., 2013). Black carbon (BC) aerosol mass was of the order of a few
655 percent of the total submicron mass and more variable, often increasing and decreasing by an
656 order of magnitude on hourly timescales. Transport from urban areas, fires, and local traffic
657 likely explain this variability. Figure 10b shows the size-resolved composition for the same
658 species and time period. Ammonium and sulfate size distributions were centered at 300-400 nm,
659 while organics and nitrate aerosol size distributions were centered at ~250 nm. The distinct size
660 distributions of the chemical components indicate that these aerosols are not completely

661 internally mixed. Figure 10c shows the month-long daily distributions indicating a subtle diurnal
662 cycle in organic aerosol, peaking at night, but with considerable day-to-day variability. The peak
663 in average sulfate (and associated ammonium) at ~16:00-19:00 is primarily due to the influence
664 of certain days where sulfate increased during late afternoon to early evening with corresponding
665 SO_2 increases (see spikes in Figure 10a). The diurnal BC trends showed two peaks. The larger
666 of these was in the evening (~20:00) coincident with the regular prolonged impact of the urban
667 plume in afternoon through evening and was also seen in other anthropogenic species (e.g. NO_x,
668 CO). The smaller, shorter-duration morning peak (~06:00 MST) was also correlated with NO_x
669 and CO. The reason for this morning BC increase could be due to the break-up of the shallow
670 nocturnal boundary layer causing mixing down of more pollution-rich residual layer air, or an
671 increase of local emission sources into a shallow morning boundary layer. It should be noted
672 that the diameter measured from BC aerosol is the mass equivalent diameter (D_{me}) which was
673 obtained by assuming a density of 1.8 g cm^{-3} as recommended by Moteki et al. (2010). The
674 aerodynamic diameter is estimated to be at least 1.8 times larger than the D_{me} shown in Figure
675 10b and could be larger than this if the BC was internally mixed with other non-BC compounds
676 (e.g. organic coatings), or smaller if the particles had irregular shapes (DeCarlo et al., 2004).
677 $PM_{2.5}$ collection onto quartz fiber filters during the same campaign were analyzed for a
678 variety of specific SOC (Secondary Organic Carbon) and carbon isotopic measurements as
679 described in Geron (2011) and Lewandowski et al. (2013). These results estimated that 0.5 μgC
680 m^{-3} could be attributed to specific SOC (Secondary Organic Carbon) precursors. Hemiterpene
681 precursor compounds (isoprene + MBO) represented approximately half of the observed SOC,
682 with monoterpenes contributing nearly the same amount to the total SOC. Isotopic
683 measurements of these same filter samples found that the ^{14}C ratio was 0.71 ± 0.11 (range 0.52 to

684 0.88), indicating that roughly three quarters of the particulate carbon observed during
685 BEACHON-RoMBAS was of modern, non-petrogenic origin. The fraction of modern carbon
686 (70%) at this site is less than values observed in eastern U.S. forests. For example, Geron (2009)
687 reported mean summer-time values of 83% and with maximum values reaching 97% for those
688 forests. Similarly, during summer months near forests in the Eastern United States, Lewis et al.
689 (2004) observed values between ~80-95%. Organic tracer results (including isoprene, MT, and
690 232-MBO oxidation products) indicate that the lower fraction of contemporary carbon is
691 primarily due to lower total biogenic emissions and lower organic mass loadings and not due to
692 more traffic or other urban influences (Kleindienst et al., 2007). The modern carbon results from
693 MEFO can also be compared to measurements at nine Interagency Monitoring for Protection of
694 Visual Environments (IMPROVE) network sites. The values from the urban sites in this
695 network averaged approximately 50% (Bench et al., 2007).
696 Gas- and aerosol-phase organic nitrate concentrations were quantified with thermal
697 dissociation, laser-included fluorescence (TD-LIF; Day et al., 2002, Rollins et al., 2010) during
698 summer 2011 (Fry et al., 2013). Gas-phase organic nitrate classes showed diurnal cycles
699 peaking mid-day at ~200 ppt (total alkyl and multifunctional nitrates) ~300 ppt (total peroxy acyl
700 nitrates) while total particle-phase organic nitrates peaked at night/early morning. Rates of
701 formation of gas-phase organic nitrates within the shallow nocturnal boundary layer were
702 comparable to daytime rates of formation. It was observed that total gas- and particle-phase
703 organic nitrates had equilibrium-like responses to diurnal temperature changes, suggesting some
704 reversible partitioning although thermodynamic modeling could not explain all of the
705 repartitioning. Additionally, diurnal cycle of gas-particle partitioning supported modeled-
706 predicted nighttime formation of lower volatility products, compared to daytime, from NO_3

radical-initiated oxidation of monoterpenes. Aerosol-phase organic nitrates were also measured by AMS and showed good agreement with TD-LIF (Fry et al., 2013).

Hundreds of acids in the gas and aerosol phases were quantified in real-time during summer 2011 using a newly-developed technique: the Micro-Orifice Volatilization Impactor High-Resolution Time-of-Flight Chemical Ionization Mass Spectrometer (MOVI-HRToF-CIMS; Yatavelli et al., 2012; 2014). It allowed for direct measurement of the gas-particle partitioning of individual and bulk organic acids. Comparisons to absorptive partitioning modeling demonstrated that bulk organic acids seemed to follow absorptive partitioning, responding to temperature changes on timescales of <1-2 hours, suggesting there were not major kinetic limitations to species evaporation. It was shown that species carbon number and oxygen content, together with ambient temperature, controlled the volatility of organic acids and are good predictors for partitioning. Moreover, the relationship between observed and model partitioning with carbon number and oxygen content pointed toward the likely importance of different classes of multifunctional organic acids that comprised the bulk of the acid groups (e.g. hydroxyacids, hydroperoxyacids, or polyacids but not ketoacids).

A newly identified 232-MBO-derived organosulfate was identified in aerosol samples during BEACHON-RoMBAS, although at levels lower than reported for a previous California study (Zhang et al., 2012). The difference was tentatively attributed to the lower acidity of the pre-existing aerosol at BEACHON, as acidity is thought to greatly enhance the formation of this organosulfate. This species has the potential to be used as a tracer of SOA formation from 232-MBO.

Part of BEACHON-RoMBAS included the collection of time- and size-resolved biological aerosol properties. To our knowledge, this is the most extensive and comprehensive

730 set of these measurements and data available. One key observation during the study was that
731 rainfall events induced large increases in ambient fluorescent biological aerosol particle (FBAP)
732 concentrations within the forest canopy (Huffman et al., 2013; Prenni et al., 2013), with
733 concentrations remaining elevated for extended periods of time (> 12 hr) due to increased
734 humidity and surface wetness. The largest observed increases, of more than an order of
735 magnitude relative to dry conditions, occurred in the size range of 2-6 μm. Microscopic
736 observations showed that these particles were dominated by biological cells at sizes with
737 characteristics of bacterial aggregates and fungal spores (Huffman et al., 2013). Concentration
738 increases that occurred during the rain events likely resulted from mechanical ejection of
739 biological particles from surfaces (Constantinidou et al. 1990; Jones and Harrison, 2004), while a
740 second, larger mode (which occurred after the rain) was likely actively emitted from biota on
741 vegetated surfaces near the site (Elbert et al., 2007; Huffman et al., 2013). Contrary to the
742 expectation that large particles will be washed out during precipitation, these data showed a
743 significant increase in concentration and net upward flux of primary, super-micron particles after
744 rain, which demonstrates a direct and important link of airborne particles to the hydrological
745 cycle. Longer term measurements continued for ten months (July 2011 – June 2012) tracking the
746 seasonal FBAP cycle at the site and observing trends with season, precipitation and other
747 meteorological parameters (Schumacher et al., 2013).
748
749 3.4 Cloud condensation nuclei and ice nuclei
750 One of the primary goals of the BEACHON project was to determine the potential for
751 biogenic emissions to serve as CCN and ice nuclei (IN), which can impact cloud properties and
752 precipitation (e.g. Barth et al., 2005). It has been recently suggested that fungal spores may have

753 large influences on SOA formation in the Amazonian forest (Pöhlker et al., 2012), and as
754 discussed below, these biologically-influenced particles can influence both CCN and IN.
755 Changes in cloud properties and precipitation can, in turn, influence biogenic emissions, closing
756 the loop on a potentially important feedback between the carbon and water cycles (Pöschl et al,
757 2010, Morris et al., 2013).

758 To better understand the influence of biogenic secondary organic aerosol on aerosol
759 hygroscopicity and the seasonal variability of CCN, a continuous 14 month study (March 2010 -
760 May 2011) was performed at MEFO (Levin et al., 2012). This was followed by additional
761 measurements during the summer 2011 BEACHON-RoMBAS intensive campaign, which
762 allowed for direct comparison between aerosol hygroscopicity and aerosol chemical composition
763 measurements (Levin et al., 2013). Aerosol hygroscopicity was described using the
764 dimensionless hygroscopicity parameter, κ (Petters and Kreidenweis, 2007), showing an annual
765 averaged κ value of 0.16 ± 0.08. This value is similar to κ values measured in remote, forested
766 regions, such as in Finland (Cerully et al., 2011) and the Brazilian Amazon (Gunthe et al., 2009),
767 and is lower than the commonly assumed continental value of $\kappa = 0.3$ (Andreae and Rosenfeld,
768 2008). Aerosol composition derived from the hygroscopicity measurements at MEFO indicated
769 a predominance of organic species in the aerosol, leading to the low κ measurement values.
770 Direct comparison of organic mass fraction measured by aerosol mass spectrometry and filter
771 measurements (discussed in Section 3.3) during BEACHON-RoMBAS agreed well with the
772 composition derived from the hygroscopicity measurements. Organic mass fractions were found
773 to be largest (up to 90%) in the smallest particles (20-30 nm as measured by the TDCIMS. This
774 fraction decreased with increasing particle diameter as measured by the AMS (Figure 10B; Levin
775 et al., 2013), and is consistent with the smallest particles being composed primarily of oxidized

776 organic species from forest emissions. Results from the year-long measurements showed that κ
777 was slightly higher during the winter months when biogenic emissions (which are strongly
778 temperature-dependent) are suppressed. The combination of these results suggests that
779 secondary organic aerosol derived from biogenic emissions impact aerosol hygroscopicity and
780 CCN number concentrations throughout the year.

781 In addition to the CCN measurements, IN have also been characterized. Ice nucleating
782 particles induce ice formation in clouds and are thought to be critical in initiating precipitation
783 from mixed phase clouds (DeMott et al., 2010). During BEACHON-RoMBAS, IN number
784 concentrations were characterized at temperatures between -34 ˚C and -9 ˚C. In addition, the
785 particle sizes that induced freezing at temperatures greater than -20 ^{o}C were characterized via the
786 droplet freezing technique. These particles as well as IN were both positively correlated with
787 number concentrations of FBAP (Huffman et al., 2013; Prenni et al., 2013, Tobo et al., 2013).
788 Similar to the precipitation-induced increases observed in biological particle concentrations, IN
789 also increased during rain. The most dramatic example of this increase occurred on August 2,
790 2011, when a thunderstorm produced 19.6 mm of precipitation (maximum rainfall rate of 30 mm
791 hr^{-1}). During this storm, IN concentrations at -25 °C increased from 2 L^{-1} to nearly 200 L^{-1}
792 (Prenni et al., 2013). Correlation between IN and FBAP across the temperature range, coupled
793 with DNA analysis of a portion of the residual IN, suggests that a significant fraction of the IN
794 near the ground surface is composed of biological particles, particularly during and after rain
795 events (Huffman et al., 2013, Prenni et al., 2013, Tobo et al., 2013). When lofted to altitudes
796 where mixed-phase clouds persist, these biologically-influenced IN can influence subsequent
797 precipitation, providing yet another feedback between biogenic emissions and the hydrologic
798 cycle, and further linking the biosphere, hydrosphere and atmosphere.

4. Atmospheric processes at an urban-rural interface

4.1 Atmospheric chemistry

As mentioned in Section 2.2, the MEFO site is primarily influenced by clean continental air, but is periodically impacted by polluted air advected from the Colorado Front Range urban areas. This makes the site a suitable location to investigate interactions between biogenic and anthropogenic emissions, and a variety of interesting questions can be addressed. For example, how are the oxidation pathways of locally emitted BVOC influenced by oxidant levels (NO_3, OH and O_3) during clean and polluted conditions? In addition, to what extent does the transport of SO_2, oxidants and VOCs from urban areas affect particle nucleation and growth? Model simulations can be initialized and parameterized using long-term and campaign-specific measurements of aerosols, VOCs, trace gasses, and meteorology. Results from these simulations can then be compared to observations. Local emissions are dominated by 232-MBO and monoterpenes, but these can be augmented by transport of anthropogenic species from the Front Range cities. Typical summertime ozone concentrations are 50-60 ppb during the afternoon, and decrease to ~10-20 ppb at night. Nitrogen oxides (NO_x) are generally dominated by NO_2 with typical values ~0.5 to 4.0 ppb, although occasional urban influences can cause the concentration to increase to 8-10 ppb. NO concentrations are much lower – typically less than 0.5 ppb, and rarely exceed 1.0 ppb. Since the area is relatively rural with low NO_x concentrations, ozone is not titrated away at night as would typically happen in an urban environment. Average SO_2 concentrations are quite low year-round, averaging less than 0.2 ppb, but concentrations can occasionally spike to ~2.0 ppb. The average August 2011 CO concentration was 123 ppb (standard deviation of 27 ppb). These values increase when urban air is transported to the site, but rarely exceed 150 ppb. Periodic CO measurements at other times of year have shown similar

consistent results. These direct measurements provide valuable insight into the range of atmospheric conditions that the site experiences, and can be used as initial inputs and provide constraints in modeling efforts. The relatively clean conditions combined with periodic, well-defined urban perturbations make it an ideally situated location for studying atmospheric processes at the rural-urban interface. An example of this was demonstrated in Figure 8 (adapted from DiGangi et al., 2012), which shows the ambient concentrations of HO_2, RO_2, NO and NO_2 in 8A and the corresponding wind speed and direction in 8C during a representative BEACHON-ROCS day (August 24, 2010). In the early morning, both HO_2 and RO_2 are very low (< 20 ppt), accompanied by low wind speeds. During the day, the wind speed increases and becomes south-easterly with an accompanying increase in NO (likely from the Colorado Springs area, ~40 km SE of the site). At ~10:30 AM, there is an abrupt change in wind direction with air coming from the SW (where there is little anthropogenic influence) accompanied by a sharp decrease in NO concentrations. Concentrations of HO_2+RO_2 then reach maximum values during the early afternoon at which point the HO_2 concentrations become maximized and the loss mechanism for RO_2 is through the RO_2+HO_2 channel (Figure 8B). These observations demonstrate that the fate of RO_2 radicals at the site is dominated by reaction with HO_2 under clean-air conditions and by reaction with NO when influenced by urban air. The transitions between the two regimes can be quite sharp, making the site well-suited for studying these types of transitions.

4.2 Coupled weather and chemistry modeling

Three-dimensional coupled meteorology and chemistry simulations of MEFO and the surrounding region have been conducted using the Weather Research and Forecasting model with chemistry (WRF-Chem; Grell et al., 2005, Fast et al., 2006). These model runs include gas-

846 phase and aerosol chemistry as well as aerosol effects on radiation and clouds. Simulations were
847 performed at 4 km horizontal grid spacing and compared to ground measurements during the
848 intensive BEACHON-ROCS and BEACHON-RoMBAS measurement periods. These modeling
849 studies focused particularly on organic aerosol (OA) formation from forest BVOC emissions,
850 and the influence of anthropogenic pollutants transported to the site. To study OA formation, the
851 WRF-Chem model was configured as described in Fry et al. (2013) using the SOA module based
852 on Hodzic and Jimenez (2011) for anthropogenic precursors and Shrivastava et al. (2011) for
853 biogenic precursors. To study the influence of anthropogenic pollution on aerosol formation, the
854 WRF-Chem model was configured as described in Cui et al. (2014). Back-trajectory
855 calculations based on WRF-Chem simulations confirm that these pollutants are advected from
856 the Front Range urban area (Figure 11). Elevated concentrations of NO_2 (and SO_2, not shown)
857 measured onsite coincide with the arrival of polluted air masses from Denver or Colorado
858 Springs, whereas low concentrations are associated with cleaner air advected from the west. The
859 effect of anthropogenic pollution on predicted OA composition suggests a fraction of modern
860 carbon that is of the order of that measured. 30% or more of OA is influenced by anthropogenic
861 species (Figure 12) through either the formation of secondary organic aerosols by nighttime NO_3
862 chemistry, increased OH and O_3 oxidation, or the direct transport of anthropogenic OA to the
863 site. NO_3 chemistry contributes to larger SOA concentrations at night when the boundary layer
864 is shallow (Fry et al., 2013), but the overall contribution to the actual aerosol column relevant to
865 radiative forcing is small (a 1 $\mu g\ m^{-3}$ mass concentration represents a 100 $\mu g\ m^{-2}$ column density
866 in a 100 m nighttime boundary layer). Daytime aerosol mass loadings contribute much more to
867 the regional aerosol mass due to the combination of the higher mass loadings and fully

868 developed boundary layer (2 μg m^{-3} corresponds to 4000 μg m^{-2} in a 2 km daytime boundary
869 layer; a forty-fold increase column height).

870 Small particle events (see section 3.3) were correlated with elevated SO_2 concentrations.
871 Figure 13 shows the onset and subsequent growth of particles at the site during one of these
872 events (July 29, 2011) as observed (panel a) and the corresponding WRF-Chem simulation
873 (panel b). Model results indicate that initial particle formation is triggered by anthropogenic
874 SO_2, whereas subsequent particle growth is driven by condensation of BVOC oxidation products
875 (Cui et al., 2014) as discussed in section 3.3. Growth rates were calculated using the number
876 mean diameter defined by (Matsui et al., 2011):

877 $$NMD = \frac{\sum_i Dp_i \times N_i}{\sum_i N_i} \quad (1)$$

878 where Dp_i and N_i are the diameter (nm) and number concentration respectively. The model
879 simulations estimated that the average particle growth rates during these events (from 4-40 nm
880 mobility diameter) were 3.4 nm hr^{-1}. The observed values calculated from SMPS measurements
881 (average = 2.0 nm hr^{-1}) are less than the simulated values, but in reasonable agreement with other
882 reports from forested regions in Indiana, USA (2.5 nm hr^{-1}; Pryor et al., 2010) and Finland (2.9
883 nm hr^{-1}; Jaatinen et al., 2009). It should also be noted that there is considerable variability in
884 reported growth rates, and this value is highly dependent upon the chosen diameter range.

885 The impact of biogenic aerosols on clouds and precipitation was also investigated as part
886 of the BEACHON project. Figure 13c shows the effect of new particle formation on cloud
887 condensation nuclei (CCN) concentrations at the site during 5 days in August 2011. The
888 observed CCN concentrations are compared with the predicted values, computed with and
889 without accounting for new particle formation in the model. These results show that modeled

CCN concentration predictions (at 0.5% supersaturation) significantly under-predict the actual measured concentrations unless nucleation is taken into account. This demonstrates the importance of aerosol nucleation parameterization to accurately parameterize aerosol-cloud interactions. In future climate scenarios, it has been hypothesized that warmer temperatures (and potentially higher biogenic emissions) could have a negative climate feedback (Paasonen et al., 2013). This is because more oxidation products from BVOC emissions will be available for condensation, resulting in higher CCN concentrations and consequently increased cloud cover. Other regional modeling efforts utilizing BEACHON-ROCS and RoMBAS data are still underway to explore a variety of bio-hydro-atmosphere relationships.

5. Key findings from 2008-2011 field campaigns.

The Manitou Experimental Forest Observatory has hosted three multi-investigator intensive measurement campaigns, each designed to focus on specific aspects of bio-hydro-atmosphere interactions. Measurements made during the BEACHON-SRM08 (Southern Rocky Mountains 2008) study provided an initial characterization of the site, provided data (specifically aerosol number and mass concentrations, CCN and hygroscopicity) for evaluation of regional-scale model simulations examining aerosol-cloud interactions, and enabled the identification of key scientific questions that could be addressed during subsequent field campaigns. The 2010 BEACHON-ROCS (Rocky Mountain Organic Carbon) study focused on BVOC oxidation and associated implications for oxidant cycling and distributions. The results showed that while there are compounds in the ambient air not typically measured by standard techniques, there is evidence that missing OH sinks are associated with oxidation products of known BVOC rather

912 than primary emissions of unknown BVOC. The study also demonstrated that considerable
913 BVOC oxidation takes place within the canopy air space. The following year (2011) the
914 BEACHON-RoMBAS (Rocky Mountain Biogenic Aerosol Study) took place to characterize a
915 multitude of aerosol processes at the site and incorporate the findings from the gas-phase
916 measurements of BEACHON-ROCS into modeling efforts. Among the many measurements
917 performed were IN, CCN, particle size distributions, chemical speciation of bulk aerosol and
918 small (<30 nm) particles, gas- and particle-phase partitioning, black carbon, elemental:organic
919 carbon (EC:OC) ratios, gas-phase nitrate and NO_x, and super-micron biological particles. This
920 campaign also included many of the same gas-phase measurements from 2010 to further
921 characterize BVOC emissions, oxidant levels and oxidation products. Many of long-term
922 seasonal observations (see Table S1) have been valuable in characterizing the site, and for
923 interpreting measurements taken during the intensive measurement campaigns. Table S2 in the
924 supplementary materials section lists the publication results from the past 5 years based on
925 MEFO observations. Future investigations and data analysis from past measurements are
926 expected to result in further publications, additional observations, and more collaborative
927 research. This is not intended to be an exhaustive list, but rather provide context for the research
928 site and further information for past, present and future researchers.

929 **6. Conclusion**

930 Observations at the Manitou Experimental Forest Observatory have provided important
931 data for understanding terrestrial-atmosphere interactions in a semi-arid ponderosa pine forest
932 that is typical of the Colorado Front Range urban-rural interface. Studies of biogenic emissions
933 and their influence on gas-phase chemistry, aerosol properties and cloud condensation nuclei
934 have led to a number of interesting conclusions – some of which have been summarized herein.

High-frequency turbulence measurements coupled with corresponding CO_2, water, and energy fluxes at the site are now being incorporated into the land-surface schemes of climate models to more accurately represent canopy influences. The unique observational data are available for other model parameterization and evaluation studies. The infrastructure exists to enable additional measurements and future scientific measurement campaigns as well as for testing new instruments, measurement inter-comparisons, graduate and undergraduate student development and other studies involving terrestrial-atmospheric exchange processes. MEFO is a collaborative facility that is maintained through a cooperative agreement between NCAR and the USDA Forest Service and is available to the scientific community for training, model development and evaluation and scientific discovery.

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