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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 interrelationships 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,

– 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 are the subjects of this special issue: BEACHON-ROCS (Rocky Mountain Organic Carbon Study, 2010) and BEACHON-RoMBAS (Rocky Mountain Biogenic Aerosol Study, 2011).

1 Introduction

1.1 Motivation

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

The Bio-hydro-atmosphere interactions of Energy, Aerosols, Carbon, H_2O, Organics & Nitrogen (BEACHON) project was initiated by the National Center for Atmospheric Research (NCAR) as well as collaborators from the University of Colorado and Colorado State University to investigate ecosystem-atmosphere exchange of trace gases and aerosols and their potential feedbacks between biogeochemical and water cycles. BEACHON is now an ongoing component of atmospheric research sponsored by the National Science Foundation. This interdisciplinary research program integrates local and regional model simulations with remote sensing, regional network observations,

and canopy- to regional-scale field measurements. BEACHON includes investigations of atmospheric, ecological and hydrological processes including concentration and flux measurements of energy, CO_2, H_2O, volatile organic compounds, aerosols, nitrogen compounds, hydrological parameters and feedback processes that are relevant to at-
5   mospheric chemistry. Rocky Mountain ecosystems are important for providing water and other resources in the western United States, but contain only a limited number of long-term monitoring sites. This region is predominantly arid or semi-arid result-ing in biogeochemical cycles that are water-limited. Since the area contains some of the fastest growing population centers, water limitations (combined with a climate that
10 is projected to be warmer and potentially drier) pose significant societal vulnerabil-ities (Vorosmarty et al., 2010). The region's remote complex terrain leads to highly variable ecosystem characteristics, and it is unclear how this variability affects hydro-logical and atmospheric processes across larger geographical areas. The need for long-term land-ecosystem-atmosphere observation networks has been identified by
15 international research programs as a key need for advancing Earth System science (Guenther et al., 2011).

To address these challenges, the BEACHON project in collaboration with the United States Department of Agriculture (USDA) Forest Service established the Manitou Ex-perimental Forest Observatory (MEFO) in 2008, in an area representative of a middle-
20 elevation ($\sim$ 2000–2500 m a.s.l.), semi-arid, ponderosa pine ecosystem that is common throughout the Rocky Mountain West, but not adequately characterized. The BEA-CHON project and establishment of this site were designed to meet the following ob-jectives:

   – collect long-term measurements of meteorology, water, carbon dioxide (CO_2), and
25   energy fluxes, aerosol size distributions and fluxes, trace gas and cloud conden-sation nuclei concentrations;

   – monitor soil moisture, precipitation, snowpack, stable water isotopes, and other hydrological variables to provide input and lateral boundary conditions for Earth-

System models and as a basis for making more accurate water resource predictions for this and 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; Fig. 1a and 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 population 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 during these two fires, 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

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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.

The Manitou Experimental Forest's elevation ranges from 2280 to 2840 m a.s.l., 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 (Sect. 1.3). Leaf area index (LAI) measurements from representative trees resulted in a value of 3.0. The fractional coverage of the ponderosa pine surrounding the observatory is 0.38 resulting in an effective leaf area index for the site of 1.14 and average canopy height of 18.5 m. In 2009, core samples from a survey of 38 representative ponderosa pine showed that the median tree age was 49.5 yr (with average, minimum and maximum ages of 62.5, 27, and 201 yr respectively). Soils are mostly derived from weathered granite, are poorly developed, and prone to erosion. The National Weather Service has been monitoring precipitation at MEF since 1940 (Station Woodland Park 8 NNW, Coop ID: 059210), and US Forest Service staff have been collecting meteorological data including air and soil temperature, precipitation, and wind speed since 1998. These data indicate that 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.

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

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et al., 1985). Recent research is more diverse, and includes a long-term (> 30 yr) 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 wild-fire 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 (Fig. 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 Supplement. 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 a.g.l.

The micrometeorology tower (Fig. 1e) is a narrow 45 m triangular tower (Rohn 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 has 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 ≈ 18.5 m). The 22 m level contains a 4-component

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Kipp and Zonen CNR1 radiometer for measuring above-canopy incoming and outgoing shortwave and longwave radiation. Instrumentation on the other five levels include:

- Campbell-Scientific CSAT3 sonic anemometers to record the three orthogonal wind velocity components and temperature fluctuations;

- NCAR-Vaisala aspirated hygrothermometers to measure absolute temperature and relative humidity;

- LI-COR open-path infrared gas analyzers 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 (Fig. 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 equipped with 2-D and 3-D 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 include: CO, CO_2, H_2O vapor, NO, NO_2 and SO_2.

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Measurements from ponderosa pine (the primary vegetation) 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). 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 yr of CCN (cloud condensation nuclei) data during 2010–2011 measured from one of the 4 mobile laboratories adjacent to the chemistry tower (Fig. 1d). An additional month of CCN measurements was made above the canopy (25 m above ground) from the chemistry tower (Levin et al., 2012). Two large field campaigns were conducted during the summers of 2010 and 2011. The former was BEACHON ROCS (Rocky Mountain Organics Study) and the latter was BEACHON RoMBAS (Rocky Mountain Biogenic Aerosol Study). 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 Sect. 5. A more detailed summary of measurements at MEFO can be found in Table S1 in the Supplement. Long-term or campaign-specific data is available upon request.

1.4 Meteorology at Manitou Experimental Forest Observatory

Due to the area's complex topography, wind patterns are influenced by multiple factors, ranging from small-scale elevation gradients to regional-scale, topographically-induced flows. The observatory lies within a north-south drainage (draining to the north), leading to the formation of local mountain-valley flows. Nighttime flow above the canopy (28 m) is dominated by drainage from the south as can be seen in Fig. 2b (Summer) and f (Winter). Winds below the canopy are often westerly or southwesterly due to drainage flow from surrounding ridgelines (Fig. 2d). This height-dependent nocturnal pattern is dominant in all seasons. Daytime flows are much more variable. Although there is often a southerly flow during the day, other wind directions are also prevalent. When synoptic winds are strong (as during the winter), there is a higher frequency of westerly and

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southwesterly flow (Fig. 2e). These conditions tend to bring relatively unpolluted air to the site, as there is little anthropogenic influence to the west. During periods when more stagnant high pressure encompasses the region, locally-induced upslope flow from either the northeast or southeast becomes apparent. Below the canopy, these upslope flows are consistently observed during daylight hours (Fig. 2c). These periods are important in understanding the local chemistry as these flows transport air from Front Range cities (mainly Denver and Colorado Springs). Figure 3 shows two consecutive days during August 2010 that exemplify these typical patterns. Higher concentrations of NO_x (NO + NO_2) and O_3 accompany the upslope flow from the northeast on 14 August, whereas, much lower concentrations are observed during the southwesterly flow the next day (15 August). Regardless of the daytime wind patterns, southerly drainage flow usually develops soon after the daytime heating ceases and the more stable nocturnal boundary layer develops, which is often accompanied by a NO_x increase. Wind measurements as well as modeling results suggest that this is often due to air from the Denver area enhancing the total NO_x in the region during daytime upslope flow, which then drains towards the north and past the site at night. However, NO_x concentrations often increase at night even without any upslope flow (Fry et al., 2013). Some of this increase can be explained by the suppressed nocturnal boundary layer, but there are still other NO_x sources under investigation that also contribute to these enhancements. Nocturnal gradients of NO_x measured along the Chemistry tower show vary little variation (see Fig. 3b), which indicates that soil NO_x emissions are not significant.

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 the 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 augment the long-term records maintained by the USDA Forest Service mentioned in Sect. 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 Fig. 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 30 September of that year and a start date of 1 October 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 an extended dry period starting in the late summer and extending into early autumn. The average annual accumulated precipitation for 2010–2013 was ~ 430.5 mm with a range of 392 mm (in 2012) to 513 mm (in 2010). It should be noted that 2012 was among the driest years on record for most of the state, and the total precipitation for 2013 was similarly low. The latter year began with very low winter and spring snow fall, and stayed much drier than average until heavy September rains finally increased the total accumulated precipitation to about the same level observed in 2012. During most years, approximately 50 % of the total precipitation occurs during June–September. The maximum observed hourly rainfall recorded at the site from 2009–2013 was 57.9 mm, which occurred on 4 August 2010. Other thunderstorms with high rain fall rates (up to 25 mm h^{-1}) are common during the summer monsoon.

Seasonally-transient snowpack is an important feature of the hydrologic cycle as the snowpack can provide a lasting water source to the site during the spring melt period

and can also insulate the soil from freezing temperatures. Snow depth measurements (Jenoptik, Inc. SHM30 laser snow depth sensor) began during the winter of 2010–2011. Persistent patchy or complete snowpack is limited to December, January and February. Periodic snowstorms may also input appreciable moisture during the months of October, November, March and April although the snowpack rarely persists for more than 7 days.

Soil moisture (Decagon EC-5 probes) and temperature (Campbell Scientific T107 thermistor) profiles extending from the near surface to approximately 1 m depth are made at 3 different sites within the micrometeorology tower's footprint. The merged annual cycle of soil moisture from all sites is shown in Fig. 4b, and the annual soil temperature cycle is shown in Fig. 4c. The soil moisture cycle exhibits some interesting and classic features of western landscape hydrology, especially the tendency for persistent dryness and pulsed recharge of near-surface moisture, particularly in the warm season. Deeper into the soil, the moisture variability is significantly damped and there is evidence of persistent soil moisture there, regardless of extended summer dry periods. This deeper layer of persistent wet soil helps sustain some of the total evaporative flux from the ponderosa pine ecosystem during the summer. There are extended periods of winter soil temperatures several degrees below 0 °C, which extends to approximately 70 cm below the surface. These low soil temperatures indicate that significant amounts of soil water freeze (i.e., creates "soil frost") occasionally during the winter. The presence of soil frost is further evidenced by the sharp decline in recorded soil moisture values from December through late-February. Suppressed soil moisture values corresponding with sub-zero soil temperatures is a classic measurement artifact due to the significant change in soil dielectric permittivity as water undergoes phase change from liquid to ice and back again at the freezing point. This meltwater release and periodic melting of the transient snowpack impart additional water pulses to the site. As previously mentioned, MEFO typically experiences an early summer dry period before the onset of the monsoon rains, which is highly correlated with increased CO_2 and BVOC fluxes. The semi-arid climate creates very low mid-day stomatal conductance in pon-

derosa pine during the early- and late-summer dry periods, which protects the trees from water stress. These fluxes and stomatal conductance both increase substantially during the monsoon rains.

2.2 Water manipulation effects on ponderosa pine

Projected water limitations and higher temperatures are expected to put additional climate-induced physiological stresses on semi-arid forest ecosystems (Allen et al., 2010). To 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 Fig. 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

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the BEACHON project, and are necessary to address the ecological system processes for inclusion into Earth-System models as discussed in Sect. 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 ($\sim$ 10–20 % of 232-MBO concentrations). Anthropogenic VOC concentrations (which are typically transported into the area from the Colorado Springs or Denver metropolitan areas) are lower than the biogenic signals.

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) 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 PTR-MS 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. 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 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 instrument was used in

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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 measurements for determining EC fluxes of 232-MBO and isoprene (Karl et al., 2014). Figure 5 shows the vertical flux profiles for 232-MBO and total MT calculated from gradient measurements using the methodology described in Karl et al. (2004). It is evident that daytime MBO emissions follow a light-dependent pattern and that the fluxes increase with height up to 12 m. MT emission patterns were vertically more uniformly distributed suggesting that the understory (forest litter, bark and trunks) also contributed to the total emissions. Using site-specific leaf cuvette measurements as model inputs, MEGAN 2.1 estimates showed good agreement with the measured average daytime 232-MBO + isoprene fluxes of $1.84\,mg\,m^{-2}\,h^{-1}$. After the large rain and hail storm on 4 August 2010 (which produced 57.9 mm precipitation in an hour; Sect. 2.1), monoterpene fluxes increased to $4.7\,mg\,m^{-2}\,h^{-1}$ which is a factor 5–10 higher than what is normally observed ($0.5–1\,mg\,m^{-2}\,h^{-1}$) (Kaser et al., 2013b). Figure 6a shows the sum of MT and MBO + isoprene measurements starting on this day (4 August) and ending 1 week later (11 August). The increases in both emissions and fluxes, which continue for ~ 2 days after the event, are evident. The missing flux data on the first day (and periodically throughout the measurement period) is due to turbulence characteristics that are not amenable to EC calculations. Several other BVOC emissions such as cymene, camphor, nopinone, pinonaldehyde and sesquiterpenes were also enhanced after this disturbance of the vegetation.

The Trace Organic Gas Analyzer (TOGA, Apel et al., 2010) was deployed during the BEACHON ROCS campaign to measure concentrations of isoprene, 232-MBO, speciated MT and over 25 other targeted compounds. Results showed that the MT speciation is dominated by α-pinene, β-pinene and Δ-3-carene (approximately 25 % each). Other contributors include camphene (7 %), limonene (12 %), myrcene (5 %) and ocimene (1 %). Figure 6b (1–4) shows August 2010 ambient diel concentrations of 4 VOCs reported by TOGA. The concentrations of the biogenic compounds MBO and MT are much higher than those of typical anthropogenic compound (e.g. toluene)

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at this site, and the concentrations have different diurnal signatures. During the day, as the boundary layer grows and OH is present, MT concentrations are diminished even though their emissions are the greatest during this time. At night, the suppressed boundary layer height combined with decreased losses from O_3 and OH reactions leads to elevated MT concentrations that generally increase from 18:00 MST to midnight and remain elevated until 06:00–07:00 MST. MBO emissions from ponderosa pine are strongly light dependent (Harley et al., 1998; Kaser et al., 2013b) resulting in maximum emissions and ambient concentrations during midday with a secondary peak in early morning associated with initiation of emissions before the morning breakup of the nocturnal boundary layer. The combination of all 3 instruments used during BEACHON ROCS provided a unique opportunity to compare VOC measurement techniques under real-world conditions. The results were encouraging as the instruments agreed within ∼ 20 % for monoterpenes and ∼ 10 % for 232-MBO + isoprene with R^2 values of 0.85–0.97 (Kaser et. al. 2013a).

Branch- and needle-level BVOC measurements have been made by focusing emissions from cuvettes surrounding the vegetation on to solid adsorbents followed by thermal desorption gas chromatography with mass spectrometer and flame ionization (FID) detectors. These measurements confirm the dominance of MBO in the emission profile; during daylight hours, MBO comprises > 85 % of the emitted reactive BVOC mass. Similar to ambient observations, α-pinene, β-pinene, Δ-3-carene, camphene and limonene dominate the MT emissions, but a large number of other terpenoids are emitted at lower rates, including sabinene, myrcene, ocimene, α-terpinene, β-phellandrene, cymene, terpinolene, p-cymenene and the oxygenated monoterpenes linalool, terpineol and methyl chavicol. A number of sesquiterpenes, dominated by β-farnesene, also appear in emission samples. For model inputs, BVOC speciation is an important consideration as different compounds (such as MT isomers with the same chemical formula) have different reaction rate constants with OH, O_3 and NO_3, so their reaction products, pathways and atmospheric lifetimes can vary considerably. Additional soil BVOC flux measurements have been made using enclosures and a micrometeorological gradient

technique at the site (Greenberg et al., 2012). These results suggested that emissions from the litter were negligible, contributing less than 1 % of above-canopy emissions for all BVOCs measured.

A newly developed Thermal desorption Aerosol Gas chromatograph-Aerosol Mass Spectrometer (TAG-AMS) was deployed and analyzed semi-volatile VOCs ($\sim C_{14}$-C_{25}) on a bihourly timescale (Zhao et al., 2013). More than 70 semi-volatile gas-phase species were observed and quantified in the ambient atmosphere during August 2011. Source apportionment was used to identify the origin of these gas-phase species. Some were anthropogenic compounds (such as poly-aromatic hydrocarbons (PAH), oxygenated PAH and alkanes), but 23 species were identified to be terpenoid compounds of biogenic origin from a local source determined from Positive Matrix Factorization (PMF).

In addition to direct VOC emissions and transported species, it is also important to consider oxidation products. These compounds can influence tropospheric ozone formation, oxidative capacity of the atmosphere, and contribute to secondary organic aerosol. Concentrations and fluxes of two important oxygenated VOCs, formaldehyde (HCHO) and glyoxal (CHOCHO), were measured during the 2010 BEACHON-ROCS campaign (DiGangi et al., 2011, 2012) using Fiber Laser-Induced Fluorescence (FILIF; Hottle et al., 2009) and Laser-Induced Phosphorescence (Huisman et al., 2008). Ambient formaldehyde concentrations ranged between a minimum of ~ 0.5 ppb in the early morning hours (4:00 MST), and maximum values of 2–2.5 ppb in the evening ($\sim 20{:}00$ MST). Ambient glyoxal concentrations ranged between a minimum of ~ 18 ppt in the early morning hours (6:00 MST), and maximum values of 30–55 ppt in the evening ($\sim 17{:}00$ MST). The glyoxal : formaldehyde ratio maintained a stable diurnal cycle ratio with values of ~ 1.5–2 % in the early morning and at night, and rising to ~ 2.5–3 % in the middle of the days. In addition, to our knowledge, these are the first canopy-scale HCHO eddy flux measurements reported for any site. These results, coupled with enclosure measurements that showed minimal direct emissions, suggest a surprisingly large HCHO production source within the canopy air space. The mid-day HCHO fluxes

were positive (upward) ranging from 37 to 131 $\mu g\,m^{-2}\,h^{-1}$ (see Fig. 7b) and were correlated with temperature and radiation within the canopy. The missing HCHO source is thus consistent with oxidation of VOCs with light- and temperature-dependent emission profiles. The strength of HCHO fluxes cannot be accounted for by the oxidation of measured MBO and terpenes (also see Sect. 3.2).

3.2 Peroxy and hydroxyl radical observations

Numerous studies (e.g. Stone et al., 2012) have highlighted discrepancies between modeled and measured radical concentrations in forested environments suggesting an incomplete understanding of the chemical processes driving secondary pollutant formation. While most research has focused on regions dominated by isoprene emissions, results from several investigations indicate gaps in our understanding of BVOC oxidation in MBO- and monoterpene-dominated areas similar to MEFO (Kurpius and Goldstein, 2003; Day et al., 2008; Farmer and Cohen, 2008; Wolfe et al., 2011; Mao et al., 2012). Both the 2010 BEACHON-ROCS and 2011 BEACHON-ROMBAS campaigns included measurements of the hydroxyl radical (OH) and peroxy radicals (HO_2 and RO_2) (Table S1), providing a unique opportunity to test our understanding of the chemical reactions that link BVOC oxidation with production of ozone and secondary organic aerosol (SOA) precursors.

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

$$O_3 + h\nu \rightarrow O(^1D) + O_2 \tag{R1}$$
$$O(^1D) + H_2O \rightarrow 2OH \tag{R2}$$
$$HO_2 + NO \rightarrow OH + NO_2 \tag{R3}$$

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In a detailed analysis of OH observations, Kim et al. (2013) demonstrate that radical recycling via reaction (R3) is likely the dominant source of OH within the MEFO canopy. A 0-D box model under-predicts HO_x concentrations relative to observations, implying unidentified sources of HO_2. Using the same box model in a study focused on peroxy radical observations, Wolfe et al. (2013) confirm this result and identify several potential additional sources of both HO_2 and RO_2. Notably, it is suggested that oxidation of unmeasured, highly reactive BVOC could explain a significant portion of the missing peroxy radical source. Such a source may also explain the high HCHO fluxes observed during the BEACHON ROCS campaign (DiGangi et al., 2011; see Sect. 3.1). Figure 7a compares the hourly-averaged measured and modeled total peroxy radical mixing ratios for BEACHON-ROCS (August 2010). As described in Wolfe et al. (2013), the difference between measured and modeled values corresponds to a total "missing" peroxy radical production rate of as much as $130\,\text{ppt\,min}^{-1}$. For comparison, Fig. 7b shows measured and modeled HCHO fluxes (DiGangi et al., 2011). The additional HCHO production needed to reconcile modeled and measured formaldehyde fluxes is on the order of $65\,\text{ppt\,min}^{-1}$ at midday. Uncertainties in measurements and model results contribute to a significant overall uncertainty in these production rate estimates (approximately ±50 %). Nonetheless, the similarity between these results – obtained via two essentially independent methods – supports the conclusion that VOC oxidation within the canopy is much stronger than predicted by canonical chemical mechanisms.

Analysis of the role of anthropogenic influence on the oxidation of BVOCs, especially via the influence of NO_x on the fate of RO_2, is of great current interest (Orlando and Tyndall, 2012), and MEFO is well suited for such studies (see also Sect. 4.1). Figure 8a shows the measured HO_2, $HO_2 + RO_2$, NO and NO_2 concentrations during a representative day in BEACHON ROCS (24 August 2010), and Fig. 8c shows the corresponding wind speed and direction. On this day, upslope conditions (that can bring polluted urban air and are often seen at this site; see Fig. 3) were not observed, as the wind was generally out of the south or southwest where there is relatively little anthropogenic influence. During the mid-morning as the boundary layer developed, an

increase in NO_x (Fig. 8a) can be seen, which was likely due to downward transport of a residual layer. The anthropogenic influence on the fate of RO_2 is evident as the loss mechanism was initially dominated by the $RO_2 + NO$ channel (Fig. 8b), but during mid-day as NO_x concentrations decreased (due to the residual morning boundary layer breaking up and southwesterly flow to the site), the $RO_2 + HO_2$ channel became the major loss mechanism. While the patterns of these transitions do not appreciably affect the concentrations of biogenic and anthropogenic VOCs, the changes in the role of the different reaction channels are consistent with the measured HCHO and glyoxal concentrations (DiGangi et al., 2012) and measured and modeled $HO_2 + RO_2$ concentrations indicated in Fig. 7. This competition between NO_x and HO_2 for reaction with the peroxy radicals (RO_2) affects the composition of multigenerational reaction products formed during gas-phase radical cycling and thus dictates, to a large extent, the production of ozone and organic aerosol precursors.

3.3 Aerosol properties and composition

Particle size distribution measurements (covering diameters from 4 nm to 2.5 µm) were conducted for nearly 2 yr at MEFO starting in February 2010 and ending in January 2012. Frequent "small particle events" characterized by high concentrations of 4–20 nm particles were observed, especially during the summer season. The origin of these small particles is likely atmospheric nucleation (Kulmala et al., 2007), which is thought to be caused by reactions of gas-phase sulfuric acid with atmospheric bases such as ammonia and amines as well as oxidized organic compounds (Kirkby et al., 2011; Almeida et al., 2013). An example of three typical small particle events during July 2011 is shown in Fig. 9a, where the onset of each event is seen just prior to noon (MST). These events are common at MEFO in the summer, occurring 3–5 times per week during late morning or early afternoon, and typically coincide with changes in wind speed and direction. Figure 9b shows wind speed and wind direction at the top of the chemistry tower and sulfate aerosol mass loadings measured by the aerosol mass spectrometer. On each of these mornings the wind speed is fairly low ($\sim 1\,\mathrm{m\,s^{-1}}$) at

8:00 MST with wind direction shifting from the south to a more northerly or northeast-erly direction, indicating upslope transport from the Denver area (similar to the example shown in Fig. 3). Thermal desorption chemical ionization mass spectrometer (TDCIMS) measurements during these nucleation events demonstrated that sub-20 nm particles were composed of ∼ 60 % sulfate by mass whereas during non-event periods, sulfate contributed less than 40 % of the mass to these small particles. In both event and non-event periods, the bulk aerosol mass is not significantly affected by this sulfate mass, as the majority of the total aerosol mass is dominated by larger particles. The correlation with wind direction and the increase in sulfate aerosol indicates that these events are anthropogenically induced. The scarcity of particles smaller than 10 nm on 29 July suggests that nucleation is occurring away from the site, either aloft (Mirme et al., 2010; Schobesberger, et al., 2013) or in the mixed layer shortly (∼ 60 min or less) upwind of the site.

A Fast Mobility Particle Sizer (FMPS) was used during BEACHON-RoMBAS to measure size-dependent particle fluxes (Pryor et al., 2013). While the mean flux of both Aitken and nucleation mode (< 30 nm diameter) particles was downwards, upward fluxes were frequently observed. Based on quadrant and time-scale analyses using aerosol dynamics modeling, they found that the upward fluxes of nucleation mode particles were most strongly influenced by upward transport of particle-rich air from the canopy resulting from the growth of recently nucleated particles as well as coagulation processes. Downward fluxes of the Aitken mode were more commonly linked to breakdown of the nocturnal inversion and entrainment of particle-depleted air from above the canopy.

Average particle number concentrations at this site are typically less than $2 \times 10^3 \, \mathrm{cm}^{-3}$ and rarely exceed $10^4 \, \mathrm{cm}^{-3}$, which are typical values in rural continental environments. During the summertime 2011 BEACHON-RoMBAS study, AMS (Aerosol Mass Spectrometry) measurements showed average PM_1 mass loadings of $2.5 \, \mu\mathrm{g\,m}^{-3}$ (Fig. 10a). Also included in this figure is black carbon aerosol as measured with a single particle soot photometer (SP2, Droplet Measurement Technologies). Approximately

75 % of the total PM_1 aerosol mass was comprised of organic aerosol (OA), with the rest composed primarily of ammonium sulfate. Nitrate concentrations were low and were shown to be primarily composed of organic nitrates (Fry et al., 2013). Black carbon (BC) aerosol mass was of the order of a few percent of the total submicron mass and more variable, often increasing and decreasing by an order of magnitude on hourly timescales. Transport from urban areas, fires, and local traffic likely explain this high variability. Figure 10b shows the size-resolved composition for the same species and time period. Ammonium and sulfate size distributions were centered at 300–400 nm, while organics and nitrate aerosol size distributions were centered at $\sim$ 250 nm. The distinct size distributions of the chemical components indicate that these aerosols are not completely internally mixed. Figure 10c shows the month-long daily distributions indicating a subtle diurnal cycle in organic aerosol, peaking at night, but with considerable day-to-day variability. The peak in average sulfate (and associated ammonium) at $\sim$ 16:00–19:00 MST is primarily due to the influence of certain days where sulfate increased during late afternoon to early evening with corresponding SO_2 increases (see red spikes in Fig. 10a). The diurnal BC trend has two peaks. The larger of these was in the evening ($\sim$ 20:00 MST) coincident with the regular prolonged impact of the urban plume in afternoon through evening and was also seen in other anthropogenic species (e.g. NO_x, CO). The smaller, shorter-duration morning peak ($\sim$ 06:00 MST) was also correlated with NO_x and CO. The reason for this morning BC increase could be due to the break-up of the shallow nocturnal boundary layer causing mixing down of more pollution-rich residual layer air, or an increase of local emission sources into a shallow morning boundary layer. It should be noted that the diameter measured from BC aerosol is the mass equivalent diameter (D_{me}) which was obtained by assuming a density of 1.8 g cm^{-3} as recommended by Moteki et al. (2010). The vacuum aerodynamic diameter (D_{va}) shown in the size distributions (Fig. 10b) was computed by multiplying D_{me} by the density (1.8). D_{va} of the particles containing BC could be larger if the BC was internally mixed with other non-BC compounds (e.g. organic coatings), or smaller if the particles had irregular shapes (DeCarlo et al., 2004). BC diameters peaked at Dva

~ 200–300 nm, which is approximately 100 nm smaller than the peak of the organic and nitrate distributions.

PM$_{2.5}$ collection onto quartz fiber filters during the same campaign were analyzed for a variety of specific SOC (Secondary Organic Carbon) and carbon isotopic measurements as described in Geron (2011) and Lewandowski et al. (2013). These results estimated that 0.5 µg C m^{-3} could be attributed to specific SOC (Secondary Organic Carbon) precursors. Hemiterpene precursor compounds (isoprene + MBO) represented approximately half of the observed SOC, with monoterpenes contributing nearly the same amount to the total SOC. Isotopic measurements of these same filter samples found that the ^{14}C ratio was 0.71 ± 0.11 (range 0.52 to 0.88), indicating that roughly three quarters of the particulate carbon observed during BEACHON-RoMBAS was of modern, non-petrogenic origin. The fraction of modern carbon (70 %) at this site is less than values observed in eastern US forests. For example, Geron (2009) reported mean summer-time values of 83 % and with maximum values reaching 97 % for those forests. Similarly, during summer months near forests in the Eastern United States, Lewis et al. (2004) observed values between ~ 80–95 %. Organic tracer results (including isoprene, MT, and 232-MBO oxidation products) indicate that the lower fraction of contemporary carbon is primarily due to lower total biogenic emissions and lower organic mass loadings and not due to more traffic or other urban influences (Kleindienst et al., 2007). The modern carbon results from MEFO can also be compared to measurements at nine Interagency Monitoring for Protection of Visual Environments (IMPROVE) network sites. The values from the urban sites in this network averaged approximately 50 % (Bench et al., 2007).

Gas- and aerosol-phase organic nitrate concentrations were quantified with thermal dissociation, laser-included fluorescence (TD-LIF; Day et al., 2002; Rollins et al., 2010) during summer 2011 (Fry et al., 2013). Gas-phase organic nitrate classes showed diurnal cycles peaking mid-day at ~ 200 ppt (total alkyl and multifunctional nitrates) ~ 300 ppt (total peroxy acyl nitrates) while total particle-phase organic nitrates peaked at night or early morning. Formation rates of gas-phase organic nitrates within the

shallow nocturnal boundary layer were comparable to daytime formation rates. It was observed that total gas- and particle-phase organic nitrates had equilibrium-like responses to diurnal temperature changes, suggesting some reversible partitioning although thermodynamic modeling could not explain all of the repartitioning. Additionally, diurnal cycles of gas-particle partitioning supported model-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 the newly-developed Micro-Orifice Volatilization Impactor High-Resolution Time-of-Flight Chemical Ionization Mass Spectrometer (MOVI-HRToF-CIMS; Yatavelli et al., 2012, 2013). This technique provides a direct measurement of the gas-particle partitioning of individual and bulk organic acids. Bulk organic acids followed absorptive partitioning, responding to temperature changes on timescales of ~ 1–2 h, suggesting there were not major kinetic limitations to species evaporation. Species carbon number and oxygen content, together with ambient temperature, controlled the volatility of organic acids and were good partitioning predictors. Moreover, the relationship between observed and modeled 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 the 2011 BEACHON-RoMBAS study, although at levels signicantly lower than reported for a similar ponderosa pine-dominated site in California (Zhang et al., 2012). The reason for the lower organosulfates observed in the aerosol filter samples was tentatively attributed to the lower acidity of the pre-existing aerosol at BEACHON compared to the California site. 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 set of these measurements and data available. One key observation during the study was that rainfall events induced large increases in ambient fluorescent biological aerosol particle (FBAP) concentrations within the forest canopy (Huffman et al., 2013; Prenni et al., 2013), with concentrations remaining elevated for extended periods of time (> 12 h) due to increased humidity and surface wetness. The largest observed increases, of more than an order of magnitude relative to dry conditions, occurred in the size range of 2–6 µm. Microscopic observations showed that these particles were dominated by biological cells at sizes with characteristics of bacterial aggregates and fungal spores (Huffman et al., 2013). Concentration increases that occurred during the rain events likely resulted from mechanical ejection of biological particles from surfaces (Constantinidou et al., 1990; Jones and Harrison, 2004), while a second, larger mode (which occurred after the rain) was likely actively emitted from biota on vegetated surfaces near the site (Elbert et al., 2007; Huffman et al., 2013). Contrary to the expectation that large particles will be washed out during precipitation, these data showed a significant increase in concentration and net upward flux of primary, super-micron particles after rain, which demonstrates a direct and important link of airborne particles to the hydrological cycle. Longer term measurements continued for ten months (July 2011–June 2012) tracking the seasonal FBAP cycle at the site and observing trends with season, precipitation and other meteorological parameters (Schumacher et al., 2013).

3.4 Cloud condensation nuclei and ice nuclei

One of the primary goals of the BEACHON project was to determine the potential for biogenic emissions to serve as CCN and ice nuclei (IN), which can impact cloud properties and precipitation (e.g. Barth et al., 2005). It has been recently suggested that fungal spores may have large influences on SOA formation in the Amazonian forest (Pöhlker et al., 2012), and as discussed below, these biologically-influenced particles

can influence both CCN and IN. Changes in cloud properties and precipitation can, in turn, influence biogenic emissions, closing the loop on a potentially important feedback between the carbon and water cycles (Pöschl et al., 2010; Morris et al., 2014).

To better understand the influence of biogenic secondary organic aerosol on aerosol hygroscopicity and the seasonal variability of CCN, a continuous 14 month study (March 2010–May 2011) was performed at MEFO (Levin et al., 2012). This was followed by additional measurements during the 2011 BEACHON-RoMBAS intensive campaign, which allowed for direct comparison between aerosol hygroscopicity and aerosol chemical composition measurements (Levin et al., 2013). Aerosol hygroscopicity was described using the dimensionless hygroscopicity parameter, κ (Petters and Kreidenweis, 2007), with an annual averaged κ value of 0.16 ± 0.08. This value is similar to κ values measured in remote, forested regions, such as in Finland (Cerully et al., 2011) and the Brazilian Amazon (Gunthe et al., 2009), and is lower than the commonly assumed continental value of $\kappa = 0.3$ (Andreae and Rosenfeld, 2008). Aerosol composition derived from the hygroscopicity measurements at MEFO indicated a predominance of organic species in the aerosol, leading to the low κ measurement values. Direct comparison of organic mass fraction measured by aerosol mass spectrometry and filter measurements (discussed in Sect. 3.3) during BEACHON-RoMBAS agreed well with the composition derived from the hygroscopicity measurements. Organic mass fractions were found to be largest (up to 90 %) in the smallest particles (20–30 nm) as measured by a Thermal Desorption Chemical Ionization Mass Spectrometer (TDCIMS). This fraction decreased with increasing particle diameter as measured by the AMS (Fig. 10b; Levin et al., 2013), and is consistent with the smallest particles being composed primarily of oxidized organic species from forest emissions. Results from the year-long measurements showed that κ was slightly higher during the winter months when biogenic emissions (which are strongly temperature-dependent) are suppressed. The combination of these results suggests that secondary organic aerosol derived from biogenic emissions impact aerosol hygroscopicity and CCN number concentrations throughout the year.

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

4 Atmospheric processes at an urban-rural interface

4.1 Atmospheric chemistry

As mentioned in Sect. 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 $\sim$ 10–20 ppb at night. Nitrogen oxides (NO_x) are generally dominated by NO_2 with typical values $\sim$ 0.5 to 4 ppb, although occasional urban influences can cause the concentration to increase to 8–10 ppb. NO concentrations are much lower – typically less than 500 ppt, and rarely exceed 1 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 200 ppt, but concentrations can occasionally spike to $\sim$ 2 ppb. The average July 2011 CO concentration was 100 ppb (standard deviation of 5.2 ppb). These values increase when urban air is transported to the site, but rarely exceed 150 ppb. CO measurements taken at other times of year have shown similar consistent results. Figures 3 and 6 above demonstrate the concentrations of some of these gas-phase species. 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 Fig. 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 (24 August 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 $\sim 10{:}30$ a.m., 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 (Fig. 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-phase and aerosol chemistry as well as aerosol effects on radiation and clouds. Simulations were performed at 4 km horizontal grid spacing and compared to ground measurements during the intensive BEACHON-ROCS and BEACHON-RoMBAS measurement periods. These modeling studies focused particularly on organic aerosol (OA) formation from forest BVOC emissions, and the influence of anthropogenic pollutants transported to the site. Back-trajectory calculations based on WRF-Chem simulations confirm that these pollutants are advected from the Front Range urban (Fig. 11). Elevated concentrations of NO_2 (and SO_2, not shown) measured onsite coincide with the arrival of polluted air masses from Denver or Colorado Springs, whereas low concentrations are associated with cleaner air advected from the west. The effect of anthropogenic pollution on OA composition shows the predicted fraction of modern carbon is consistent with observations (Sect. 3.3). 30 % or more of OA is influenced by anthropogenic species (Fig. 12) through either the for-

mation of secondary organic aerosols by nighttime NO_3 chemistry, increased OH and O_3 oxidation, or the direct transport of anthropogenic OA to the site. NO_3 chemistry contributes to larger SOA concentrations at night when the boundary layer is shallow (Fry et al., 2013), but the overall contribution to the actual aerosol column relevant to radiative forcing is small (a 1 $\mu g\,m^{-3}$ mass concentration represents a 100 $\mu g\,m^{-2}$ column density in a 100 m nighttime boundary layer). Daytime aerosol mass loadings contribute much more to the regional aerosol mass due to the combination of the higher mass loadings and fully developed boundary layer (2 $\mu g\,m^{-3}$ corresponds to 4000 $\mu g\,m^{-2}$ in a 2 km daytime boundary layer; a forty-fold increase column height).

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

$$\text{NMD} = \frac{\sum_i Dp_i \times N_i}{\sum_i N_i} \tag{1}$$

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

The impact of biogenic aerosols on clouds and precipitation was also investigated as part of the BEACHON project. Figure 13c shows the effect of new particle formation

on cloud condensation nuclei (CCN) concentrations at the site during 5 days in August 2011. The observed CCN concentrations are compared with the predicted values, computed with and without accounting for particle nucleation in the model. These results show that modeled CCN concentration predictions (at 0.5 % supersaturation) sig-
5 nificantly under-predict the actual measured concentrations unless nucleation is taken into account. This demonstrates the importance of aerosol nucleation to accurately parameterize aerosol-cloud interactions. In future climate scenarios, it has been hypothesized that warmer temperatures (and thus higher biogenic emissions) could have a negative climate feedback (Paasonen et al., 2013). This is because more oxidation
10 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

15 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 hygro-
20 scopicity) 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
25 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 than primary emissions of unknown BVOC. The study also demonstrated

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

6 Conclusions

Observations at the Manitou Experimental Forest Observatory have provided important data for understanding terrestrial-atmosphere interactions in a semi-arid ponderosa pine forest that is typical of the Colorado Front Range urban–rural interface. Studies of biogenic emissions and their influence on gas-phase chemistry, aerosol properties and cloud condensation nuclei 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

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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

5 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.

Supplementary material related to this article is available online at http://www.atmos-chem-phys-discuss.net/14/1647/2014/
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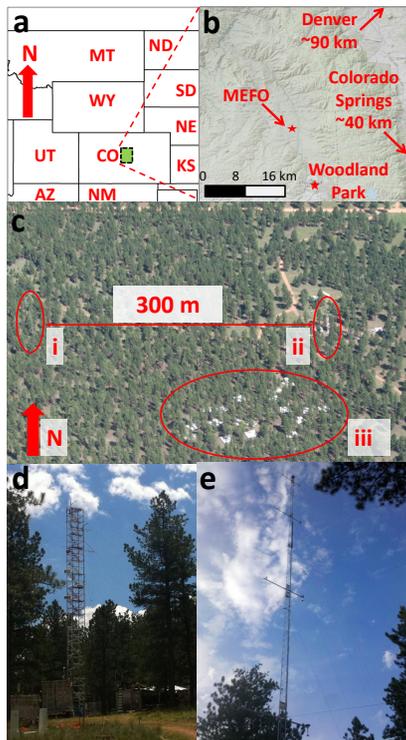
Fig. 1. Manitou Experimental Forest Observatory (MEFO). **(a)** Map showing general area within Colorado and its relationship to neighboring states. **(b)** Site location relative to the Front Range urban corridor including Denver and Colorado Springs. **(c)** Close-up aerial photograph showing the open-canopy ponderosa pine-dominated forest with the (i) micrometeorological tower, (ii) chemistry tower, and (iii) water manipulation experiment. **(d)** Close up picture of Chemistry tower. **(e)** Close of up picture of micrometeorological tower. The two towers shown in **(c)** are approximately 300 m apart. Maps in panels **(a)** and **(b)** were produced using ArcGIS software (ESRI Inc., Redlands, CA).

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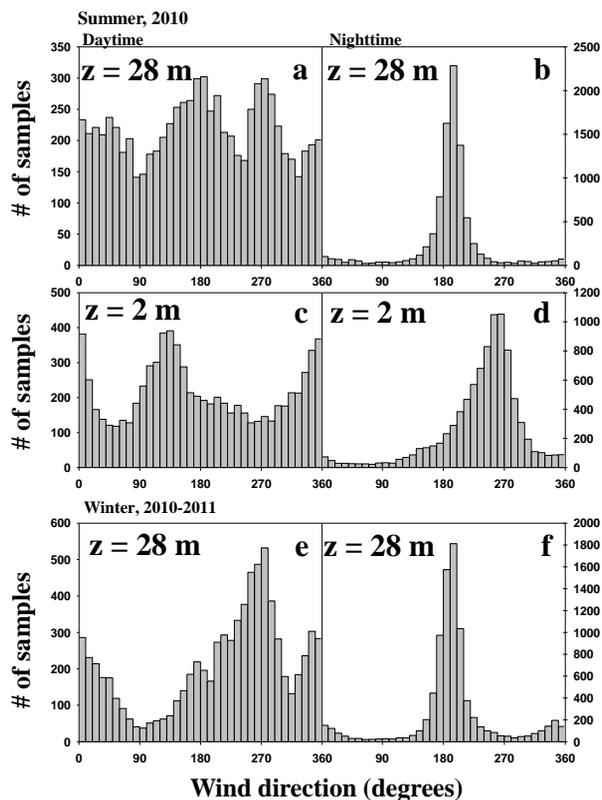
Fig. 2. Wind direction distributions (5 min averages binned every 10°) from the MEFO Chemistry tower. Panels **(a)**, **(c)** and **(e)** are daytime wind distributions (9:00–17:00 MST) whereas panels **(b)**, **(d)** and **(f)** are for nighttime hours (20:00 until 5:00 MST). Summer includes data from June–August 2010. Winter includes data from December 2010 to February 2011. Measurement height is noted on the panels.

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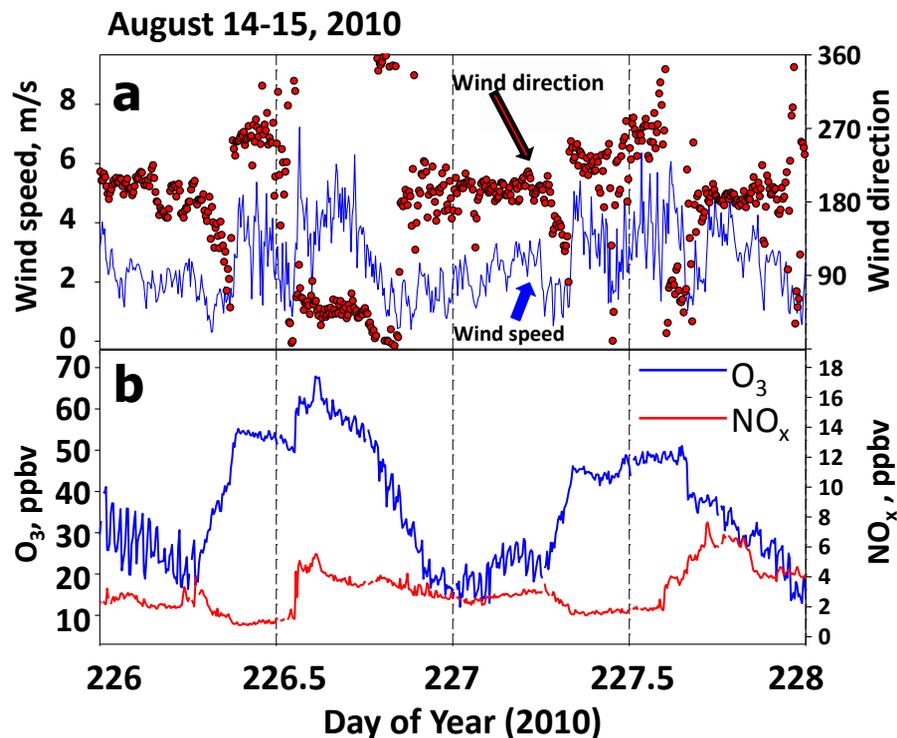
Fig. 3. Time series of wind speed, wind direction, ozone and NO_x as measured from the MEFO chemistry tower (14–15 August 2010) showing typical summertime patterns. Meteorological variables were measured at the top of the tower (25.1 m) and the trace gasses were measured using the 6 point gradient system (Table S1). Ozone deposition and resulting gradients lead to the nighttime variability. In contrast, NO_x is nearly constant through the canopy, implying negligible soil emissions.

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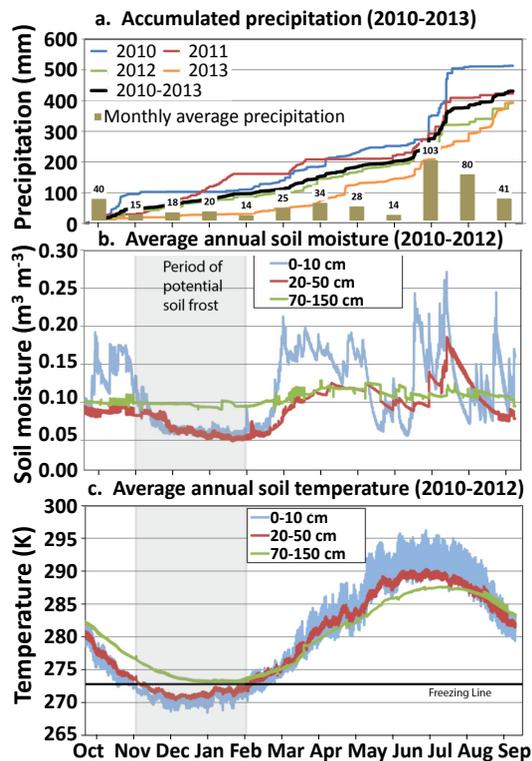
Fig. 4. Hydrological measurement summary at the Manitou Experimental Forest Observatory. Annual accumulated precipitation from rain and snow **(a)**, soil moisture at 3 depths **(b)**, and soil temperature at three different depths **(c)**. Note that the hydrological year is defined from as ending on 30 September with a start date of 1 October of the preceding year. Panel **(a)** includes data from hydrological years 2010–2013 whereas panels **(b)** and **(c)** include data from 2010–2012.

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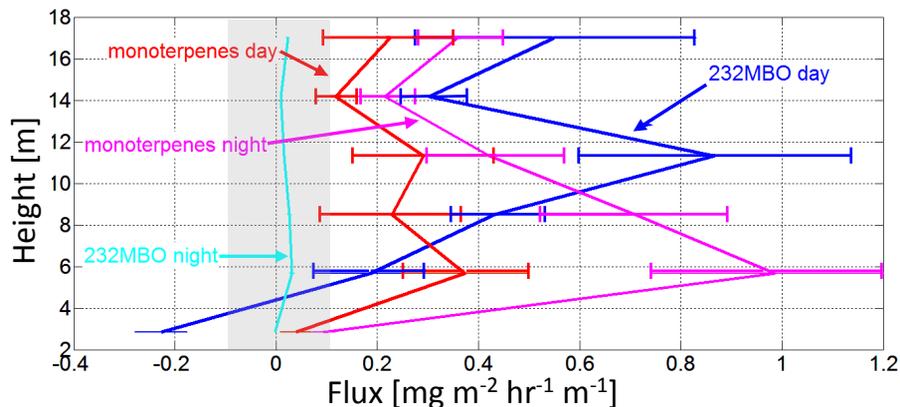
Fig. 5. Average daytime and nighttime vertical fluxes of monoterpenes ($C_{10}H_{16}$) and 2-methyl-3-buten-2-ol (232MBO, $C_5H_{10}O$) during August 2010. The average daytime integrated flux ratio of MBO : Monoterpenes is 1.65. Fluxes within $\pm 0.1\,\mathrm{mg\,m^{-2}\,h^{-1}\,m^{-1}}$ are shown within the shaded grey area to indicate the detection limit. Error bars indicate the standard deviation of all measurements for that chemical species and level.
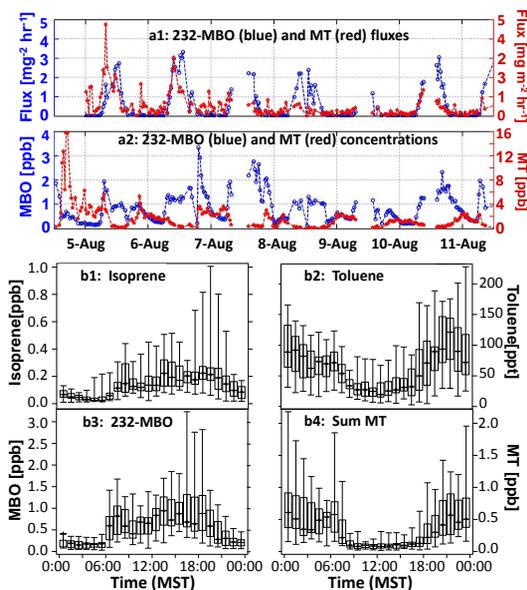
Fig. 6. (a) (adapted from Kaser et al., 2013b) shows the sum of MT and MBO + isoprene measurements as reported by the PTR-TOF-MS from 25.1 m on the chemistry tower from 4 August (DOY = 216) to 11 August 2010 (DOY = 223). Top panel **(a-1)** shows the above-canopy fluxes, while **(a-2)** shows the corresponding concentrations in ppbv. An intense hailstorm on the afternoon of 4 August 2010 (doy = 216) caused the anomalously high MT concentrations and fluxes that lasted for ~2 days after the event. This effect is due to mechanical disturbance, which released MT stored in pools within the needle structures. MBO, which is produced during photosynthesis and immediately emitted, was not noticeably affected by the event. Bottom panel **(b)** shows diurnal profiles of **(b-1)** isoprene, **(b-2)** toluene, **(b-3)** MBO, and **(b-4)** sum of monoterpenes during all of August 2010 as measured using TOGA. Box boundaries indicate inter-quartile range, median is indicated as the line through the box, and whisker lengths indicate the total measurement range.

Fig. 7. Average modeled and measured diurnal cycles of **(a)** within-canopy peroxy radical mixing ratios, and **(b)** above-canopy formaldehyde fluxes. The measured and modeled results for both compounds include the hourly averages from the August 2010 BEACHON ROCS intensive measurement campaign. Model calculations of HCHO fluxes and peroxy radicals are described in DiGangi et al. (2011) and Wolfe et al. (2013), respectively.

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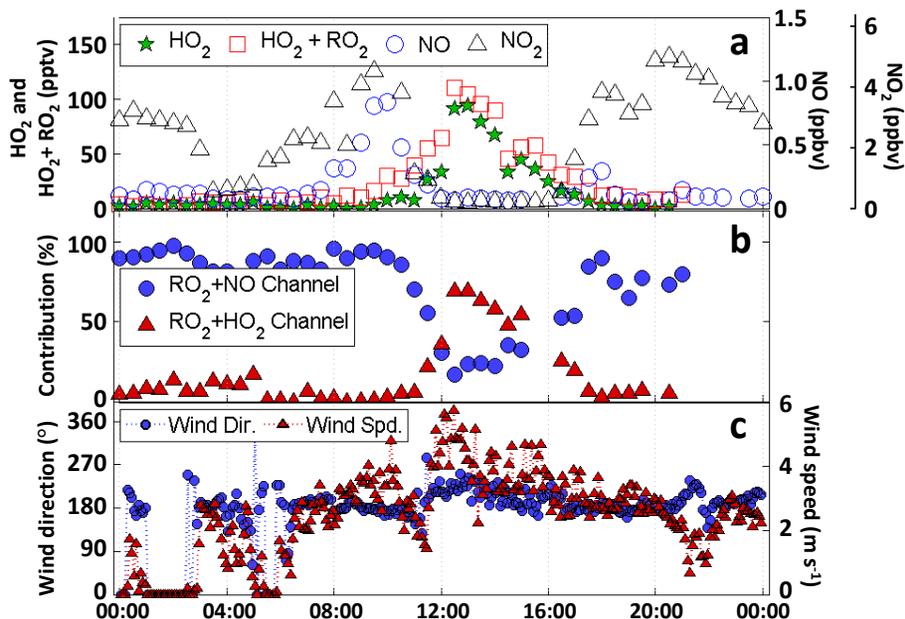
Fig. 8. Examination of RO_2 fate and its relation to anthropogenic influence on 24 August 2010 during BEACHON-ROCS. The first panel **(a)** shows median concentrations of NO, NO_2, HO_2, and $HO_2 + RO_2$ over the course of this day. Wind speed and direction **(c)** show the wind shifting from out of the south to out of the southeast just prior to noon indicating an anthropogenic-influence from the Colorado Springs area. This transition is also reflected in the NO increase in panel **(a)**. The middle panel **(b)** shows the calculated RO_2 loss percentage from reaction with NO or HO_2 based on measured NO and HO_2 concentrations and on rate constants obtained from the IUPAC database. Each symbol in **(b)** represents the median value from thirty minute time bins. Figure adapted from DiGangi et al. (2012).

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Fig. 9. Three representative days of particle size distributions **(a)**, wind speed, wind direction and sulfate aerosol mass **(b)** during 27–29 July 2011. In panel **(a)**, the mobility diameter is on the y axis, time is on the x axis, and the color bar indicates particle number concentration ($dN/d\log Dp$) in cm^{-3}. In panel **(b)**, the sulfate aerosol mass is multiplied by 4 and is listed on the 2nd y axis along with wind speed.

Fig. 10. Aerosol mass spectrometer (AMS) and Single Particle Soot Photometer (SP2) results of bulk PM_1 aerosol composition during July and August 2011. Black carbon (BC) is measured by the SP2 and all others (organics, nitrate, sulfate, and ammonium) are from the AMS. Panel **(a)** shows the mass loading time series, panel **(b)** shows the average size-resolved aerosol distributions, and panel **(c)** shows the diurnal trends of each of the individual species averaged over the study period. In **(c)** the lines represent the mean values, the box plot boundaries represent the 25th and 75th percentiles, and the whisker lengths indicate the 5th and 95th percentiles of the measurements. The center line through each box indicates the median and all statistical indicators are offset for some of the species by at most ±0.2 h for clarity. Note that the majority of the aerosol is composed of organic species, and that in all panels, black carbon mass has been multiplied by 6 and the other (sulfate, nitrate, and ammonium) species' masses have been multiplied by 3. The diameters for the BC measurements are estimated using an assumed density of $1.8\,\mathrm{g\,cm^{-3}}$ as indicated in the text (Sect. 3.3).

Fig. 11. Residence Time Analysis (RTA) from WRF-Chem estimates the amount of time that air masses originate from the various locations in the region. These simulations estimate 48 hour back-trajectories at MEFO (27 July to 26 August 2011). Three major Front Range cities (Denver, Colorado Springs, and Pueblo), are shown, and open circles indicate the cities' primary coal-fired power plants. The left panel indicates that the majority of the low NO_2 concentration results (0–50th percentile) are from air masses that originate from the west. The right panel shows that the highest 10 % of NO_2 concentrations originate from the Front Range cities and are advected to the site.

Modeled and measured total organic aerosol (TOA): July 16-August 25, 2011
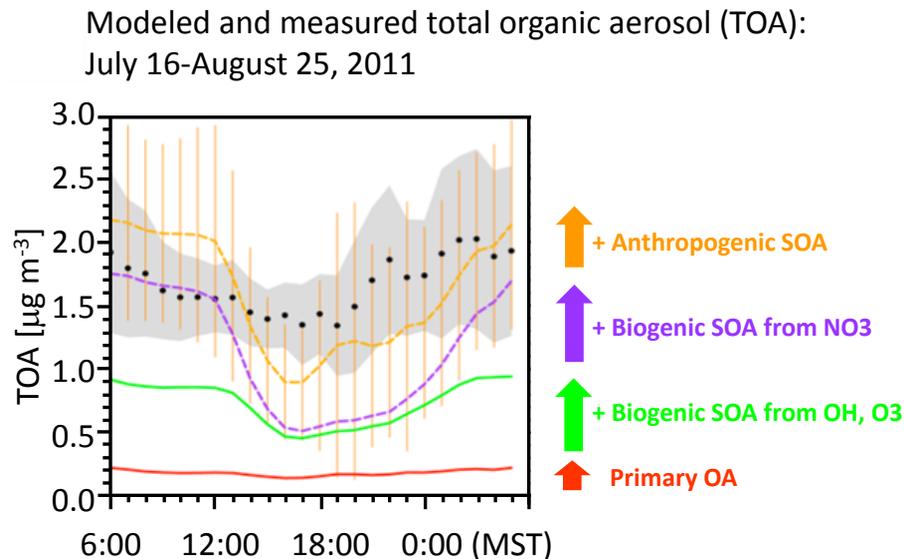
Fig. 12. Modeled and measured average diurnal profiles of total organic aerosol (TOA) mass concentrations at MEFO during BEACHON-RoMBAS-2011. Aerosol mass spectrometry (AMS) observations are shown as black circles (with 1σ variability shown in gray). Predicted TOA is indicated in yellow (with variability shown by the yellow bars). The predicted TOA is the sum of the contributions: primary OA (red), biogenic secondary organic aerosol (SOA) from OH and O_3 chemistry (green), biogenic SOA from NO_3 nighttime chemistry (purple) and anthropogenic SOA (yellow). Each plot (starting with green) is additive (equal to that process plus the sum of the processes below it): e.g. the purple plot shows the contributions from primary OA, biogenic SOA from OH and O_3 and biogenic SOA + NO_3. Biogenic SOA (both day and night) are the largest contributors to TOA, but anthropogenic species (gold) also make a significant contribution.
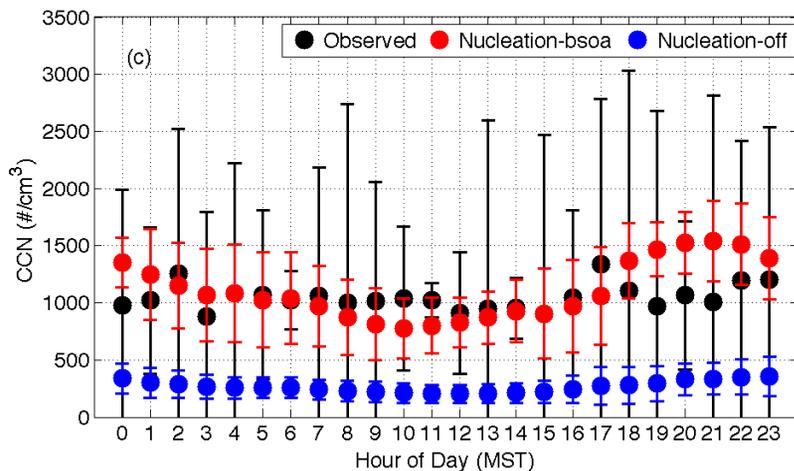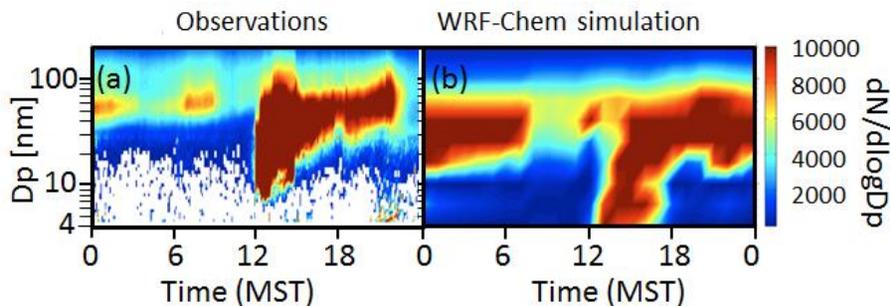
Fig. 13. 29 July 2011 particle size distributions observed **(a)** and modeled with WRF-Chem **(b)**. White areas in panel **(a)** indicate that no counts were observed for that diameter particle at that time. Panel **(c)** shows the observed (black) and predicted (red) CCN concentrations averaged over the 10–15 August 2011 time period. The blue circles are the simulations when nucleation is not included, which demonstrates the importance of particle nucleation for CCN formation.

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