Formation of p-cymene from the Oxidation of Biogenic Sources during NACHTT 2011

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Abstract
A comprehensive suite of vertically-resolved volatile organic compound (VOC) measurements were conducted at the Bolder Atmospheric Observatory (BAO) in Erie, Colorado from 18 February to 13 March 2011 as part of the Nitrogen, Aerosol Composition, and Halogens on a tall tower (NACHTT) campaign. The main purpose of this experiment was to investigate and quantify the contribution of monoterpene oxidation to the secondary production of aromatic hydrocarbons. A limited number of studies have been performed regarding this area of research, but recent laboratory experiments have suggested that BVOC oxidation should be considered as an important source to the production of aromatic hydrocarbons. Gratien et al. (2011) established that p-cymene is a product of the oxidation of α-pinene in air and its yield is greater at higher RH and in the presence of acids. The BAO tower was an ideal location to conduct research because of the potential gas phase precursor sources and the comprehensive suite of measurements during NACHTT. The vertically-resolved measurements have provided insight on biogenic emissions and their subsequent chemical transformations. Two different scenarios were observed in the individual vertical profiles. Scenario 1 suggests normal conditions on 25 February 2011. The vertical profiles increase with height from 50-150 meters, but decrease from 150-250 meters. Scenario 2 can be observed on 6 March 2011; the vertical profiles show an increase in p-cymene and a decrease in α-pinene and other aromatics indicating the formation of p-cymene from chemical processing in the atmosphere. Both scenarios have an acidic atmosphere, but the colder temperatures and higher relative humidity on 25 February 2011 is facilitating particle formation as opposed to the heterogeneous processing of α-pinene to form p-cymene. The drier air and ample surface area observed on 6 March 2011 allows the heterogeneous reactions to take place, which facilitates the formation of p-cymene.

1.0 Introduction
Volatile organic compounds (VOCs) are emitted into the atmosphere from both biogenic and anthropogenic sources [1]. Emissions of VOCs from biogenic sources are approximately 1150 Tg/year-1 carbon per year and anthropogenic sources constitute about 140 Tg per year [2,3]. Biogenic sources include monoterpenes, which are an important class of biogenic volatile organic compounds (BVOCs) emitted from vegetation [4,5]. Other biogenic sources include isoprene, sesquiterpenes, and oxygenated hydrocarbons [3,6]. Among the monoterpenes are the gases α-pinene, p-cymene, and β-pinene, with α-pinene being the most abundant monterpene [3,7]. In the troposphere, these compounds react with hydroxyl radicals (OH), ozone (O3), and nitrate radicals (NO3) to form an array of oxidation products [8].

Globally, monoterpenes constitute 10-50% of BVOC emissions from vegetation with approximately ~30-130 Tg/year [3,9]. It has been widely assumed that aromatic hydrocarbons only arise from anthropogenic sources; however, studies have shown that they have also been recently associated with biogenic emissions [10,11,12,13,14]. The compounds p-cymene and toluene are not only released from motor vehicle exhaust, solvent evaporation, and industrial wastewater, but direct emissions from
plants have also been reported [15,16,3]. Also, p-cymene concentrations were reported to increase as a function of altitude above a forest canopy that consisted of significant emissions of α-pinene, suggesting that it might be formed by in situ reactions [8,12]. In a study performed by Gratien et al. (2011) [8], p-cymene formation was observed from the oxidation of α-pinene by OH, O3, or NO3 in air. These experiments established (for the first time) that p-cymene is a product of the oxidation of α-pinene in air, and its yield is greater at higher RH and in the presence of acids [8]. Gratien et al. (2011) [8] concluded that the sources of aromatic hydrocarbons in air may not only include direct emissions from anthropogenic sources and plants, but also the conversion of some biogenic hydrocarbons via atmospheric reactions.

Many aromatics and their oxidation products have adverse health effects and have been shown to be mutagenic [17,18]. Not only are they problematic to human health, but aromatic hydrocarbons provide a significant contribution to photochemical air pollution [19]. The homogeneous gas phase oxidation of monoterpenes and aromatics has two significant impacts on air quality and climate. First, monoterpenes and aromatics are precursors to the production of O3; second, their oxidation products act as precursors to secondary organic aerosols (SOA) [20,21]. The photochemical production of O3 and SOA can potentially cause detrimental effects on human health, vegetation and crops, and visibility. In order to study the production of O3 and SOA, their VOC precursors must be accurately identified and quantified.

The main purpose of this experiment was to investigate and quantify the contribution of monoterpene oxidation to the secondary production of aromatic hydrocarbons. Several laboratory and field studies have been performed that suggest that BVOC oxidation should be considered as an important source of aromatic hydrocarbons – these include: observation of toluene emissions from vegetation, a biogenic contribution to spring/summer ambient toluene mixing ratio enhancements, and toluene emissions from alfalfa and loblolly pine trees [11,13,22,23]. Recently, Gratien et al. (2011) [8] observed a direct correlation between the loss of α-pinene following the OH oxidation and the production of p-cymene in a laboratory chamber experiment. This was the first study to report the direct production of an aromatic compound from the oxidation of a biogenic hydrocarbon. These studies suggest that monoterpenes should be considered as a source of aromatics to the atmosphere, with increasing significance in forested areas.

Monoterpene’s mixing ratios vary throughout the year and their emissions are both light and temperature dependent. Therefore, most studies have been conducted during the growing season (i.e., summer), but some studies have observed the highest monoterpene emission rates during the springtime [5,24,25,26,27,28,29]. Measurements have also been conducted at the Thompson Farm field site in Durham, NH that show elevated monoterpene mixing ratios during the winter, with levels comparable to those in the summer [23]. These results demonstrate that monoterpene emission capacity significantly varies throughout the year [24,28,29].

The measurements reported here were conducted at the Boulder Atmospheric Observatory in Weld County, Colorado as part of the Nitrogen, Aerosol Composition, and Halogens on a Tall Tower (NACHTT) campaign. The experiment was conducted from 18 February 2011 through 13 March 2011. This was an ideal location to conduct the work because of the diverse potential gas phase precursor sources and the comprehensive suite of measurements. The vertically-resolved measurements provide insight on biogenic emissions and their subsequent chemical transformations.

2.0 Methods

Research was conducted at the Boulder Atmospheric Observatory (BAO) from 18 February through 13 March 2011 during the NACHTT campaign. The BAO research facility is located in Weld County, Colorado (40.05 °N, -105.01 °W, elevation 1584 m). The facility is 33 km north of the city center of Denver and 23 km east of the city center of Boulder (see Figure 1). A 300-meter research tower is located at the observatory and is equipped with meteorological instruments and is used for atmospheric chemical sampling. The site is surrounded by grasslands, fields, and forests with vegetation species including pine, lodgepole pine, Douglas fir, Rocky Mountain fir, and Engelmann spruce [30]. These vegetation species are all known to be monoterpene emitters [4,5]. The BAO is an excellent site for measuring VOCs and gauging their potential contribu-
tion to secondary aromatic hydrocarbon product formation because of the numerous sources coming into the area. These sources originate from the wide range of air mass types and compositions, including urban emissions from Boulder and Denver to the south and west, respectively, and clean air that comes from the north and east. Overnight, the air masses are primarily transported from the west, which is a region with high monoterpene emissions (see Figure 2).

Whole air samples were collected hourly in 2-liter electropolished stainless steel canisters. Sampling took place at the top of each hour, beginning at noon on 18 February and continuing through noon on 13 March 2011. Before the sample was collected, the canister was flushed with ambient air 5 times and then the canisters were pressurized to ~30 psig, using a single head metal bellows pump. In addition to the samples collected hourly, a portable sampling manifold was used to fill the canisters to 30 psig ~2-3 times per day at heights of 50, 100, 150, 200, and 250 meters on the tower to obtain vertical profiles of the VOC distributions. A personnel elevator on the

Figure 1. Map of the Front Range urban corridor of Colorado, showing major urban areas, major roads, power plants, oil and gas wells, and major agriculture facilities. The large red diamond marks the location of the Bolder Atmospheric Observatory.

Figure 2. Monoterpene emission rates surrounding the BAO site.
tower was used to reach these heights. A total of 550 hourly canister samples and 168 vertical profile samples were collected during the NACHTT campaign.

Immediately following the campaign, the canister samples were returned to the Sive laboratory at the University of New Hampshire and were analyzed for a suite of VOCs. Each sample was analyzed within one month of collection. Gas chromatography, using flame ionization and electron capture detection in conjunction with mass spectrometry, was used for the analysis of the canister samples. The analytical system used three gas chromatographs (GC), two flame ionization detectors (FIDs), two electron capture detectors (ECDs), and one mass spectrometer (MS) to quantify a suite of C2-C10 nonmethane hydrocarbons, C1-C2 halocarbons, C1-C5 alkyl nitrates, oxygenated volatile organic compounds, and reduced sulfur gases. A total of 90 VOCs were reported for the canister sample analysis.

For each canister sample, a 1785 cm² (at STP) aliquot of air was trapped on a glass bead-filled loop immersed in liquid nitrogen. After the sample was trapped, the loop was isolated, warmed to ~80°C, and injected. A carrier gas (ultra-high purity helium) was used to flush the contents of the loop and the stream was split into five, with each substream feeding a separate GC column/detector pair. Multiple standards were used during the sample analysis, including working standards (analyzed every 10 samples) and absolute standards (analyzed once daily). A 1785 cm³ (at STP) aliquot from one of the two working standards was analyzed every 10th analysis. The measurement precision for each compound was 3-15% for halocarbons, 1-10% for the NMHCs, 3-5% for the alkyl nitrates, 3-8% for the sulfur compounds, and 8-10% for the OVOCs.

### 3.0 Results and Discussion

Canister samples were collected each hour from 17 February to 15 March 2011 at an inlet height of 20 meters on the BAO tower. The time periods for the vertical profiling were determined using the in situ measurements as a guide. During these periods, a canister sample was collected at five heights (every ~50 meters from 50-250) four times throughout the day (00:00, 06:00, 12:00, and 18:00 local time) to obtain diurnal cycles of the vertical gradient. Several events occurred during the NACHTT campaign where levels of monoterpenes were enhanced. During these periods, wind speeds were low (<2 m s⁻¹) and the events with the highest monoterpene mixing ratios (pptv) tended to be transported in air masses from the west to the southeast corridor. Time series plots of various aromatics from 20 m at the BAO tower are shown in Figure 3. The alkanes dominated the overall OH reactivity at the site, but there were significant and persistent levels of aromatics throughout the campaign. Monoterpenes levels were small compared to the aromatics and only made up ~1% of the OH reactivity (see Figure 4).

Figure 5 shows vertical profiles of selected monoterpenes and aromatic hydrocarbons. The profiles represent the average mixing ratio at each height (from 50-250 m). From a first look, it appears as though the formation of p-cymene is occurring; however, individual vertical profiles (particularly of p-cymene and α-pinene) provide a better analysis of the processes occurring in the atmosphere. The individual vertical profiles of selected monoterpenes and aromatic hydrocarbons are shown in Figures 5-9.

Two different scenarios are occurring in the individual vertical profiles. Scenario 1 can be seen on 25 February 2011 from 8:15 pm to 8:50 pm, which shows normal distributions of monoterpenes and aromatics (see Figures 6, 7). Each vertical profile conveys a similar V-like shape. At first, the mixing ratio (pptv) increases with increasing height, but at approximately 150 meters the mixing ratio starts to decrease as the height increases. Scenario 2 can be observed on 6 March 2011 at 10:00 am and will be considered for the case study vertical profiles. The mixing ratio of p-cymene increases with increasing height, but at approximately 150 meters the mixing ratio starts to decrease as the height increases. Scenario 2 can be observed on 6 March 2011 at 10:00 am and will be considered for the case study vertical profiles. The mixing ratio of p-cymene increases with increasing height (see Figure 9). The other aromatic hydrocarbons stay constant or decrease with increasing height and α-pinene also decreases with increasing height (see Figures 8, 9). Since p-cymene levels are elevated and α-pinene is decreasing, the formation of p-cymene can be observed on 6 March 2011.

Aerosol, nitric acid, temperature, and relative humidity distributions were analyzed for both scenarios to determine the drivers for p-cymene formation. The presence of nitric acid in the atmosphere can be observed in both scenarios (see Figures 10, 11). Since there is plenty of acid in the atmosphere for both scenarios, this is not a limiting factor to the formation of p-cymene on 6 March 2011. Cold temperatures and high relative humidity can be observed on 25 February 2011, which is facilitating particle formation.
Figure 3. Time series plots of various aromatics from 20 m at the BAO tower. While the alkanes dominated the overall OH reactivity at the site, there were significant and persistent levels of aromatics throughout the campaign.
Figure 4. A stacked area time series plot of the monoterpenes during NACHTT. This figure highlights the fact that total monoterpenes levels were small compared to the aromatics and only made up ~1% of the OH reactivity.

Figure 5. Vertical profiles of selected monoterpenes and aromatic hydrocarbons. These profiles show an average distribution of each gas throughout NACHTT.
**Figure 6.** Individual vertical profiles conducted from 8:15 pm to 8:50 pm on 25 February 2011. The profiles show a normal distribution with a distinct V-shape profile. The mixing ratio increases at first, but eventually decreases with an increase in height.

**Figure 7.** Individual vertical profiles conducted from 8:15 pm to 8:50 pm on 25 February 2011. The profiles show a normal distribution with a distinct V-shape profile. The mixing ratio increases at first, but eventually decreases with an increase in height.
Figure 8. Individual vertical profiles conducted at 10:00 am on 6 March 2011. These are case study profiles that either stay constant or increase with increasing height. The increasing profiles show the formation of p-cymene.

Figure 9. Individual vertical profiles conducted at 10:00 am on 6 March 2011, showing mixing ratio distribution at various heights (50 – 250 meters). These are case study profiles that either appear fairly straight or increase with increasing height. P-cymene levels are elevated with increasing altitude and α-pinene shows a decrease.
Figure 10. Aerosol, nitric acid, temperature (°C), and relative humidity distribution from 50-250 meters from 8:15 pm to 8:50 pm on 25 February 2011. The colder temperatures and higher relative humidity is facilitating particle formation as opposed to the heterogeneous processing of α-pinene to form p-cymene.
as opposed to the heterogeneous processing of α-pinene to form p-cymene (see Figure 10). Warmer temperatures and a lower relative humidity can be observed on 6 March 2011, which indicates drier air in the atmosphere (see Figure 11). The combination of dry air along with acids and ample surface area facilitate the heterogeneous processing of α-pinene to form p-cymene.

Figure 11. Aerosol, nitric acid, temperature (˚C), and relative humidity distribution from 50-250 meters at 10:00 am on 6 March 2011. The dry air in the atmosphere plus ample surface area facilitates the formation of p-cymene.

4.0 Summary
The main purpose of this experiment was to investigate and quantify the contribution of monoterpene oxidation to the secondary production of aromatic hydrocarbons. Measurements were conducted at the Bolder Atmospheric Observatory (BAO) in Erie, Colorado from 18 February to 13 March 2011 as part of the Nitrogen, Aerosol Composition, and Halogens on a tall tower (NACHTT) campaign. Individual vertical profiles conducted showed normal conditions on 25 March 2011 and the formation of p-cymene through heterogeneous processing of α-pinene on 6 March 2011. An acidic atmosphere can be observed during both scenarios, but the colder temperatures and higher relative humidity on 25 February 2011 is facilitating particle formation as opposed to the heterogeneous processing of α-pinene to form p-cymene. The drier air and
ample surface area observed on 6 March 2011 allows the heterogeneous reactions to take place, which facilitates the formation of p-cymene.

These results along with other research conducted during NACHTT have helped to improve the understanding of BVOC emissions and heterogeneous processes occurring in the atmosphere and its influences on aromatic hydrocarbon and monoterpene distributions. This information is essential for determining air quality and the overall composition of the atmosphere and changes in Earth’s climate.

Acknowledgements
Financial support for this research was provided by the National Science Foundation through RAPID award ANT-1127774 to Appalachian State University. We thank Peter Mine (NSF Program manager) for his support of this work, in addition to Gerd Hübler (NOAA), Bill Dube (NOAA), Dan Wolfe (NOAA), Nick Wagner (NOAA), Andrew Young (UNH), Steve Brown (NOAA), Brian Lemer (NOAA), Eric Williams (NOAA), Bill Keene (UVA), and Alex Pszenny (UNH) and the BAO staff for their assistance and support during the field campaign. A special thanks to Dr. Barkley Sive for his help and dedication to this manuscript.

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Volume 3, 1st Edition • Spring/Fall 2013


