Influence of oil and gas field operations on spatial and temporal distributions of atmospheric non-methane hydrocarbons and their effect on ozone formation in winter

	Robert A. Field ^{1,#} , Jeff Soltis ¹ , Michael C. McCarthy ² ,		
5	Shane Murphy ¹ , and Derek C. Montague ¹		
	¹ Department of Atmospheric Science, University of Wyoming, Laramie, WY, USA		
10	² Sonoma Technology Inc., Petaluma, CA, USA		
15			
20			
25			
	[#] Corresponding author: University of Wyoming, Department of Atmospheric Science,		
	1000 E. University Ave., Laramie, WY, 82071,		
	Tel.: 307-766-2180, Fax: 307-766-3269, e-mail: rfield1@uwyo.edu		

30 Abstract

Emissions from oil and natural gas development during winter in the Upper Green River Basin of Wyoming are known to drive episodic ozone (O₃) production. Contrasting O₃ distributions were observed in the winters of 2011 and 2012, with numerous episodes (hourly O₃ \geq 85 ppbv) in 2011 compared to none in 2012. The lack of O₃ episodes in 2012 coincided with a reduction in

- 35 measured ambient levels of total non-methane hydrocarbons (NMHC). Measurements of speciated NMHC, and other air quality parameters, were performed to better understand emission sources and to determine which compounds are most active in promoting O₃ formation. Positive Matrix Factorization (PMF) analyses of the data were carried out to help achieve these goals. PMF analyses revealed three contributing factors that were identified with different
- 40 emission source types: factor 1, combustion/traffic; factor 2, fugitive natural gas; and factor 3, fugitive condensate. Compositional signatures of three contributing factors were identified through comparison with independently derived emission source profiles. Fugitive emissions of natural gas and of condensate were the two principal emission source types for NMHC. A water treatment and recycling facility was found to be a significant source of NMHC that are abundant
- 45 in condensate, in particular toluene and m+p-xylene. Emissions from water treatment have an influence upon peak O₃ mixing ratios at downwind measurement sites.

1 Introduction

- 50 Oil and natural gas (O&NG) production in the US has grown significantly over the past decade and is expected to continue to grow through 2020 (US EIA, 2014). Improved production methods such as hydraulic fracturing and horizontal drilling technologies have enabled O&NG producers to access reservoirs that previously were economically infeasible (US Department of Energy, 2009). The US EIA (2013) estimates an increase in shale gas production from 5.0 trillion
- 55 cubic feet (tcf) per year in 2010 to 13.6 tcf per year by 2035, when shale gas is expected to account for half of total US gas production. Some of this new development is scheduled to take place in Wyoming, an energy rich state, ranked second in the US in total energy production for the 2012 data. In terms of proven natural gas reserves in the US for 2009, the Pinedale Anticline Project Area (Pinedale Anticline) and the Jonah Field, both in the Upper Green River Basin
- 60 (UGRB) of Sublette County, Wyoming, rank 3rd and 7th, respectively. These fields are both in the top 100 of proven US reserves for oil, with the Pinedale Anticline ranked 49th and Jonah ranked 65th (US EIA, 2010).

Adverse atmospheric impacts of the development and operation of O&NG fields include emissions of methane, a potent greenhouse gas (Allen et al., 2013; Karion et al., 2013; Brandt et

al., 2014; Caulton et al., 2014). A further concern is degraded local air quality, which can impact human health and well-being (Adgate et al., 2014; Colburn et al., 2014; McKenzie et al., 2012, 2014) through the emission of a range of air toxics and other pollutants (Pétron et al., 2012; Field et al., 2014; Helmig et al., 2014; Moore et al., 2014; Warneke et al., 2014) that can lead to the subsequent photochemical production of ozone (O₃) (Edwards et al., 2013; Gilman et al., 2013;

70 Oltmans et al., 2014).

Until recently the formation of high levels of O_3 in surface air was considered to be a summertime phenomenon in polluted urban areas. The discovery of O_3 mixing ratios exceeding 100 ppbv in 2005 in the rural UGRB in winter (Schnell et al., 2009), well above the pre-2008 National Ambient Air Quality Standard (NAAQS) of 85 ppbv for the fourth highest 8 hour

75 average, was therefore unexpected. Similar wintertime high O₃ episodes have subsequently reoccurred in the UGRB and, more recently, have also been observed in the nearby Uintah Basin of Utah. At both locations, O₃ formation has been directly linked to emissions from O&NG sources (Schnell et al., 2009; Martin et al., 2011; Oltmans et al., 2014), although specific details of the role played by non-methane hydrocarbons (NMHC) were initially not fully appreciated.

- 80 Studies show that development of elevated O₃ mixing ratios requires significant snow cover to facilitate both a high actinic flux and the formation of strong persistent shallow inversions. Inversions lead to the build up of adequate amounts of volatile organic compounds (VOC) and oxides of nitrogen (NO_x), the gaseous precursors of O₃. Episodes are most frequent later in winter (January March) when insolation is increasing, but before snow cover decreases.
- Since 2005, additional air quality network and meteorological monitoring stations have been deployed throughout the UGRB to determine the extent of O₃ episodes and their characteristics. Modeling studies have also been carried out (Carter and Seinfeld, 2012; Rappenglück et al., 2014). They point to the need for more definitive information on both the distribution and specific identity of O₃ precursor VOC compounds. These monitoring and
 modeling studies have led to significant progress in understanding the mechanisms and critical reaction pathways for wintertime O₃ formation, but questions remain. Notwithstanding the apparent importance of HONO for O₃ production (Rappenglück et al., 2014), the exact roles played by nitrogen-containing compounds and many individual VOCs, and, in consequence, the behavior of their radical derivatives, remain to be clarified. Many of these questions have
- 95 recently been answered for the Uintah Basin (Edwards et al., 2013, 2014), but the similarities and differences of wintertime O₃ formation chemistry in the different basins remains to be determined.

When wintertime ozone, measured at Wyoming Department of Environmental (WDEQ) monitoring stations in 2005 and 2008 in the UGRB, was first reported by Schnell et al. (2009)
the subtleties of photochemical production mechanisms were not clear. Modeling studies of 2011 wintertime ozone in the UGRB by Carter and Seinfeld (2012) and Rappenglück et al. (2014) have demonstrated that ozone production is critically dependent upon NMHC. These studies used some data from the University of Wyoming Boulder South Road (BSR) site as model input together with other available data in the UGRB. Here we present the entire speciated NMHC

105 dataset from BSR and explore intra-species correlations to investigate sources. Rather than photochemical modeling of ozone, we attempt to reconcile contributing emission sources with observed speciated NMHC. We also show the relationship of species sub-groups to O₃ during days with active wintertime photochemistry. Specifically, in this study we identify the most important speciated NMHC for O₃ formation, and by using Positive Matrix Factorization (PMF)

110 source apportionment (Brown et al., 2007; Buzcu and Fraser, 2008; McCarthy et al., 2013) determine the relative contributions of various emission sources to observed hydrocarbon levels.

2 Methodology

Fig. 1 shows well locations and monitoring locations in the Pinedale Anticline and Jonah Field developments. Table S2 gives more details of these locations and other sampling sites employed in the study. Summary statistics for the BSR site are given in Table S4. The UGRB, at an elevation of approximately 2150 m msl, is enclosed by the Wyoming mountain range to the west, the Gros Ventre range to the north, and the Wind River mountains to the northeast. To the south it broadens and opens onto lower elevation plains and the Interstate 80 corridor. It is

- located in Sublette County, Wyoming, where the population density, as reported by the US Census (2010), is a sparse 2.1 people per square mile (0.8 per km²). As the Pinedale Anticline and Jonah Field developments are both ranked within the top 10 of wet gas fields for proven reserves in the US (US EIA, 2010), the area has a high density of O&NG wells. Pollutant emissions in the UGRB are almost entirely from O&NG activities (WDEQ, 2014a) with minimal contributions from other sources (Schnell et al., 2009).
- Measurements characterizing air quality in the UGRB were carried out in and around the Pinedale Anticline. The principal monitoring site was at BSR, a location that experiences surface air containing relatively well-mixed trace gases representative of emissions from a variety of nearby O&NG development sources. This site was first used in 2009 as a comparative site (Soltis and Field, 2009) to WDEQ Boulder site (BLDR). As shown in Fig. 1 BSR (2142m msl) is located about 5 km to the southeast of BLDR (2162m msl) at a slightly lower elevation. Measurements of O₃, reactive nitrogen compounds (NO/NO₂/NO_x), total NMHC, methane (CH₄), and carbon monoxide (CO) mixing ratios, and standard meteorological parameters, were carried out continuously at BSR during the winters of 2010/11 and 2011/12. Table S1 in the
- 135 Supplementary Material lists the measurement uncertainties of these parameters and details of instrumentation employed.

Total NMHC measurements employed a Thermo Scientific 55i back-flush gas chromatographic system that provides direct measurements of CH₄ and total NMHC. The backflush method provides a direct measurement of total NMHC concentrations and this allows 140 accurate and precise measurement of low levels of total NMHC even if methane is at a much higher concentration.

The total NMHC peak consists of C_2 to C_{11} compounds, with the possibility of some C_{12} compound being captured. This upper range is due to sample losses on the walls of transport tubing with the analyzer designed for ambient sampling without a heated inlet (Francis, 2014).

145 While the Thermo Scientific model 55i analyzer measurement of total NMHC includes VOC containing halogens, nitrogen and oxygen, the sensitivity is anticipated to be lower for these classes compared to hydrocarbons. All compounds with C-bonds are detected, with a generally greater relative sensitivity for compounds with a higher number of C-H bonds. While sensitivity is proportional to carbon number, the replacement of C-H bonds with other functional groups typically results in a decrease in sensitivity.

2.1 Speciated NMHC Analyses

Hourly online measurements of speciated NMHC were performed at BSR during 2010/2011. Discontinuous speciated NMHC measurements at BSR in 2011/2012 and 2012/2013 155 were carried out using canister sampling (Entech silonite 6L canisters). Similar discontinuous measurements were made at other locations in all three winter periods (Fig. 1). Individual NMHC selected for this study are listed in Table 1. They include 15 alkanes, 10 alkenes, two alkynes and 10 aromatics. In 2010/11 and 2011/12, canister samples from locations other than BSR were collected for 24-hour periods, except when co-located diffusive samplers were 160 concurrently deployed, when sample times were extended to 72 hours. The results of diffusive sampling are the subject of a separate analysis to be reported elsewhere. Canister sampling duration was controlled using an Entech CS1200E flow regulation system. Sites close to emission sources were included in 2011/12 and in 2012/2013. Table S2 provides geographic coordinates of the monitoring sites and lists the number of samples at each site. Additional 165 details are given elsewhere (Soltis and Field, 2011a, 2011b, 2012a, 2012b).

Speciated NMHC analyses were carried out using a Perkin Elmer (PE) O₃ Precursor Analyzer (OPA) system that incorporates a Peltier cooled inlet adsorption sample concentrator within a TurboMatrix 300 Thermal Desorption system, a Nafion[®] dryer to remove water vapor, and a PE Clarus 500 Gas Chromatograph (GC) equipped with flame ionization detectors (FIDs).

170 The chromatograph utilizes two parallel columns for the separate analysis of lower (C_6 to C_{12})

and more (C_2 to C_6) volatile fractions in the sample. It was operated using ultrapure helium as the carrier gas. Further details of the OPA system are given elsewhere (Broadway and Tipler, 2012). During 2010/2011 canister samples were analyzed at the BSR field site. Consistent quality of the two sampling methods was ensured through recovery testing using span and zero gases. In

- 175 2011/2012 and 2012/2013, only canisters were used for sample collection, which were subsequently analyzed with minimal delay by the OPA at the University of Wyoming, using the same analytical protocol and data processing methods as those employed at BSR, thereby achieving equivalent analytical quality. Instrument calibrations were conducted with a custom trace gas standard mixture supplied by Apel-Riemer Environmental, Inc. The mole fraction of
- 180 reported compounds ranged from 3.6 ppbv to 44.6 ppbv. Calibration curves that encompassed the entire measurement range encountered in the field were achieved through varying the trapping time for analysis. Table S1 in the Supplementary Material lists the measurement uncertainties calculated for this study. Further details of monitoring sites, experimental sampling protocols, analytical instrumentation, and analysis techniques are given in the supplementary 185 material, and by Soltis and Field (2011a, 2011b, 2012a, 2012b).

2.1.1 Data Processing

The output data from the OPA was processed and validated with a data management system provided by Ricardo-AEA, Ltd., UK. This system, used by the UK Automatic
Hydrocarbon Network for more than 20 years (Dollard et al., 1995), analyzes batches of multiple chromatograms to yield an output file containing compiled time-stamped validated data, that include peak areas, widths, and retention times, for identified chromatogram eluents in each analyzed sample (Dernie and Dumitrean, 2013). Initialization of the processing software requires template calibration information that provides comparator data for the input chromatograms,

which in this study were grouped into one month long periods. Proprietary artificial intelligence (neural network) pattern recognition MatchFinder[®] software was employed to identify specific hydrocarbon peaks in the monthly batch analysis output files. Quality assurance and control procedures developed for the UK Automatic Hydrocarbon Network are then applied to ensure that peaks are correctly identified and without co-elution or peak merging issues (Derwent et al., 200 2014).

Conversion of chromatogram raw peak areas to mixing ratios was carried out using

response factors derived from calibration gas mixtures. Calibration responses were proportional to carbon number (from C₂ to C₁₀) with calculated accuracies given in Table S1. Response factor differences were observed, however, for ethyne, isoprene, and 1,3-butadiene, due to slow wallinduced heterogeneous loss of these compounds within the calibration gas mixture cylinder. Consequently, relative response factors were used to calculate mixing ratios of these gases. In addition, chromatographic problems resulting from measurable 'carry over' effects for decane, and the trimethylbenzenes in successive analyses, resulted in the derived mixing ratios for these compounds being removed from validated data sets used for subsequent interpretive analyses of ambient atmospheric behavior. The quality of validated data was demonstrated through a blind test of an unknown mixture with the support of the National Center for Atmospheric Research (NCAR) shown in Table S3.

2.2 Positive Matrix Factorization Analysis of Speciated NMHC

- 215 Positive Matrix Factorization (PMF) analyses of the BSR speciated NMHC data have been carried out to determine emission source characteristics and contributions. This analysis technique, developed by Paatero and Tapper (1994) and Paatero (1997), solves a bilinear receptor model that assumes that the dataset being analyzed is composed of contributions from a small number of factors, each with an unknown but constant source profile, that vary in
- 220 magnitude with time. PMF analysis aims to evaluate the optimum value of the chemical profile of each factor, and the mass contributions from each factor. It provides results as factors, or groups of compounds, each of which effectively constitutes a pattern or signature of an emission source or group of sources. The final output is analyzed to determine how well modeled results reproduce the input data by examining the residuals for each compound, scatter plots for
- 225 predicted and observed compound correlations, and mass recovery. The multivariate factor analysis EPA PMF tool, widely applied to ambient air quality data (Poirot et al., 2001; Song et al., 2001), was used for analysis of the BSR speciated NMHC data for the period October 2010 through March 2011. Uncertainties in the solution are estimated using a bootstrapping technique (Efron, 1982; Efron and Tibshirani, 1993; Norris et al., 2008). Each re-sampled dataset is
- 230 decomposed into profile and contribution matrices using PMF, and the results of each bootstrap run are then compared with the base run. If the original, base-run factors are consistently found or mapped with the re-sampled bootstrap runs, the factors are considered to be robust and the

data are not over-fit.

- PMF receptor modeling relies on data with known quality and accuracy, as measured by uncertainty. Uncertainties were calculated on both an absolute and relative basis to account for method detection limits and peak fitting imprecision. All speciated NMHC were assigned a conservative base uncertainty of 0.1 ppbv, plus 3% of the measured value of a given sample. For example, a measured value of 1 ppbv would have an uncertainty of 0.13 ppbv, while a measured value of 10 ppbv would have an uncertainty of 0.4 ppbv. Compounds were removed from the
- analysis if their signal-to-noise (S/N) ratios were below 1.3. Application of this criterion removed 1-butene, 1,3-butadiene, *t*-2-butene, *c*-2-butene, 1-pentene, isoprene, propyne, styrene, and propene from the analyses. Four consecutive samples on 11/26/2010 were also excluded from analysis because they contained high outlier values for toluene with values ranging from 28.5 pppv to 274.4 ppbv. Three outlier values for CO were removed on 11/23/2010. These
- 245 unrepresentative samples would not be effectively modeled using the PMF statistical technique. In addition to speciated NMHC, hourly data for total NMHC, background corrected CO, and background corrected CH_4 , were included in the analyses. NO_x is not included in the PMF analysis presented here as the focus of this study is source apportionment of speciated NMHC, and preliminary analyses revealed that NO_x was the only parameter in a separate factor.

250

3 Results and Discussion

3.1 Temporal variation of O₃, total NMHC and NO_x

- WDEQ ozone measurements at the BLDR site commenced in 2005 and have been 255 performed continuously since then. They reveal numerous occasions when hourly averaged O₃ levels were at or above 75 ppbv, and several occurrences during 2005, 2008, and 2011 when fourth highest 8-hour average values also exceeded 75 ppbv. In 2012, the UGRB was designated a non-attainment zone for the National Ambient Air Quality Standard for O₃. In 2011, daily 8hour ozone averages exceeded 75 ppbv at BLDR on 8 days. Similar exceedances occurred in
- 2011 at other UGRB WDEQ sites, albeit less frequently and at slightly lower O₃ levels. During 2011, measurements at BSR, also close to the Pinedale Anticline O&NG development (see Fig. 1), corroborated elevated ozone measurements at BLDR. At BSR, seven exceedances were observed in 2011. Of note however, is that in contrast to the significant number of ozone

episodes in 2011, there were only three days in 2012 during the January to March 'ozone season'

- when the hourly average ozone mixing ratio exceeded 75 ppbv, and a complete absence of days with non-compliant 8-hour ozone averages. Fig. 2 shows plots of hourly averaged mixing ratios of O_3 , NO_x , and total NMHC at BSR during the months January to March in 2011 and 2012. It is evident that both O_3 episodes (hourly $O_3 \ge 85$ ppbv) and high total NMHC values are significantly more frequent in 2011 than in 2012, while NO_x levels in these years are similar.
- 270 Species mixing ratios are influenced by their emission and/or formation rate(s), their removal rate, and by meteorological factors affecting dilution and dispersion. If meteorology were the only factor resulting in the year-to-year NMHC and O₃ differences shown in Fig. 2, then NO_x behavior should exhibit a similar pattern as NMHC. Observations at BLDR show similar behavior as those at BSR (MSI, 2012), with 16 hourly values of total NMHC greater than
- 275 2 ppmC in 2011 compared to none in 2012. In addition, a reduction in the average NMHC mixing ratio for the January to March period was found at both sites, from 0.34 ppmC in 2011 to 0.19 ppmC in 2012 at BLDR, and from 0.23 ppmC to 0.07 ppmC at BSR. For NO_x, similar reductions in the analogous mixing ratios were also observed, from 5 ppbv to 2 ppbv at BLDR and from 6 ppbv to 4 ppbv at BSR. These mixing ratio reductions may be linked to estimated
 280 emissions reductions of ~20% and ~50% for VOCs and NO_x respectively, reported in the winter emission inventory for Sublette County, from 2011 to 2012 (WDEQ, 2014a).

Snow cover and meteorological conditions, including temperature and wind speeds, at both BLDR and BSR in 2011 and 2012 were broadly similar, with no significant differences, suggesting that neither factor can solely account for the observed mixing ratio differences (MSI, 2012). Moreover, 8-hour average mixing ratio O₃ episodes were not only absent in 2012, but also in 2013 and 2014, at all UGRB sites, even though apparently favorable conditions (snow cover extent, 700 mb pressure, temperature, and wind speed) for O₃ formation prevailed (MSI 2012, 2012, 2014).

The weight of evidence suggests that the observed decreases in NMHC and NO_x mixing ratios and the concomitant lack of O₃ episode occurrence since 2011, likely result primarily from reduced O₃ precursor emission rates. However, factors associated with snow cover and meteorological conditions cannot be entirely discounted, because they can strongly affect ozone production rates. The influence of meteorology is recognized to affect year-to-year variability of O₃ levels. A lack of O₃ episodes in 2009 was for example linked with the absence of snow cover.

3.2 O₃ variations at BSR and BLDR

Similar O₃ mixing ratios were observed at BSR and BLDR in 2009, 2010, 2011 and 2012 during spring, summer, and fall. In November and December 2011, the average difference of hourly O₃ measurements at the two sites is 3 ppbv, and when values at BLDR exceed 40 ppbv, only 3 measurements differ from those at BSR by more than 10 ppbv, none of which occur

- 300 during afternoon hours. Similar behavior is found in November and December 2010. Afternoon maximum O₃ mixing ratios at the two sites are invariably similar. By contrast, the behavior observed in months associated with wintertime O₃ is different. For example, in February and March 2012, when O₃ values exceeded 40 ppbv at BLDR, 11 of the 12 measurements with a difference of greater than 10 ppbv are in the afternoon, 4 of which occur when O₃ is higher than
- 305 70 ppbv at BLDR. Wintertime differences were even more apparent in February and March 2011, when 91 afternoon hours differed by more than 10 ppbv, with 73 occurring when O₃ was higher than 70 ppbv at BLDR.

In the winter of 2011, O_3 episodes (average hourly $O_3 \ge 85$ ppbv) were observed on 13 days in the UGRB. Diurnal variations in O_3 mixing ratio observed at BSR and at BLDR (WDEQ

- 310 2014b), located some 5 km to the northwest, are illustrated by the 24-hour time-series plots on four days in 2011 in Fig. 3. These plots indicate the effect of variability in background levels, local production, and transport of O₃ to the different measurement sites. On February 26th 2011, when BSR O₃ mixing ratios increase by ~60 ppbv, peak O₃ at BSR exceeds that at BLDR by ~20 ppbv. However, on March 1st 2011, O₃ increased by ~120 ppbv at BLDR, but only by ~70 ppbv
- 315 at BSR. Similar behavior is evident on March 2nd 2011. Both of these days are associated with light southwesterly winds. By contrast on March 15th 2011, O₃ mixing ratios behave similarly at both BLDR and BSR, except for a short ~20 ppbv increase at BSR around 14:00. O₃ behavior for all 13 episode days are given in Fig. S5.

Fig. 2 plots suggest that high O₃ levels in 2011 are promoted by relatively high levels of
 total NMHC at relatively moderate NO_x levels. Understanding the observed differences in O₃
 episode variability is perhaps best achieved by examining the detailed composition and mixing
 ratios of the constituent NMHC, together with the concomitant levels of NO_x, at the two sites.

3.3 Relationship of O₃ to NMHC and NO_x

```
325
```

Surface NMHC measurements from October 2010 to March 2011 show diurnal and

seasonal variations, with the highest values during the coldest months and at night. Low surface temperatures in winter are associated with nocturnal radiation inversions that lead to pollutant trapping and accumulation, and consequential elevated mixing ratios (Schnell et al. 2009; Oltmans et al., 2014).

- An assessment of the fractional contribution of OPA detected hydrocarbons to the total NMHC measured by the Thermo 55i instrument (Table S1) was undertaken to understand the utility of total NMHC measurements, and to determine the contributions of speciated NMHC selected for this study. To achieve these aims a mass balance comparison of the total NMHC to the sum of the OPA identified speciated NMHC (C_2 to C_8) was performed. Total integrated
- 335 NMHC measured by the Thermo 55i includes both hydrocarbons and their halogenated, oxygenated, and nitrogen-containing derivatives, up to C₁₁ compounds. The mass balance comparison between total NMHC and the sum of the OPA identified speciated NMHC is shown in Fig. S6, for the period October 2010 to March 2011. A simple linear regression fit to the 2320 data points yields a best fit line of slope 0.57 and a coefficient of determination (R²) of 0.90.
- 340 While there is a strong correlation between the two NMHC data sets, using only identified OPA NMHC omits ~43% of the carbonaceous material included in the total NMHC measurement. Diurnal analyses reveal no significant differences by time of day. A second analogous comparison was carried out in which all of the unreported and unidentified carbonaceous material detected by the OPA was included in the NMHC summation. This additional material
- 345 increased the mass from identified $C_2 C_6$ aliphatic hydrocarbons by a factor of 1.1, and that from identified $C_7 - C_8$ aliphatic and $C_6 - C_9$ aromatic compounds by a factor of 2.0. The augmented summation of speciated NMHC mass resulted in both the slope and R² values of the regression line increasing, to 0.88 and 0.92 respectively. Measurement uncertainties, as outlined in Table S1, could account for the mass deficit implied by a regression fit slope less than unity.
- Wintertime measurements at BLDR from 2007 to 2014 reveal contributions of ~70% for alkanes, ~15% for aromatics, and >5% each for naphthalenes, alkenes and oxygenates to the observed VOCs (MSI, 2014). These measurements suggest that hydrocarbon classes dominate the total mass of VOC in the UGRB. Contributions of oxygenated VOCs not detected by the OPA are likely to be small, even though it is likely that they play an important role in wintertime photochemistry (Edwards et al., 2014), a contention supported by measurements of carbonyl

compounds at BLDR that suggests formaldehyde and acetaldehyde contribute significantly to VOC reactivity (MSI, 2014).

Identified C₂ to C₉ compounds contributing most to the total carbon NMHC mass measured by the OPA at BSR, namely ethane (26%), propane (15%), toluene (11%), m+p-

- 360 xylene and p-xylene (7%), *i*-butane (5%), and *n*-butane (5%), make up 69% of the identified carbonaceous mass. Similarly, analyses of 16 canister samples collected at BLDR in the winters of 2011/2012 and 2012/2013, during the Upper Green Winter O₃ Studies (UGWOS) (MSI, 2012, 2013) show that the three most important contributors are ethane (21%), propane (19%), and toluene (8%). The same dominant hydrocarbons are found at both measurement sites indicating
- that the hydrocarbon composition at BSR and BLDR is similar, as expected given their close proximity. This examination of the relative contributions of identified hydrocarbons showed that while missing mass is related to heavier NMHC, the most abundant NMHC in the C_2 to C_8 range are reported.
- Variations in the measured O₃ mixing ratio together with changes in total NMHC and
 NO_x at BSR are shown in Fig. 4, constructed from hourly averaged observations obtained
 between 11:00 and 20:00 during the three-month winter period from January to March 2011.
 Highest O₃ mixing ratios are associated with total NMHC mixing ratios above 0.2 ppmC, when
 NO_x mixing ratios are 6 20 ppbv, and decrease significantly as the mixing ratios of these
 precursors decline. As noted previously, O₃ production only occurs when actinic flux levels are
- high, and when this requirement is not met, O₃ mixing ratios remain low, irrespective of precursor concentrations. The data shown in Fig. 4 are undoubtedly influenced by a number of environmental parameters including meteorology, actinic flux intensity, and NMHC composition. An analogous plot constructed using BLDR measurements is shown in the supplementary information (Fig. S7). It exhibits the same trends evident in Fig. 4, but shows greater variability
- 380 of NO_x for high ozone values (80 120 ppbv). Thus, unlike at BSR, high O₃ mixing ratios are occasionally observed at BLDR when NO_x is low. Reported NO_x mixing ratios at BLDR frequently display erratic hour-to-hour variability throughout the period January to March 2011, during periods of both high and low O₃ mixing ratio. This suggests that the measurement uncertainties at BLDR may be larger than at BSR, and allows for the possibility that the greater
- 385 scatter evident in Fig. S7 compared to Fig. 4 results from these uncertainty differences. The figures reinforce the notion that high NMHC precursor mixing ratios are a necessary but

insufficient condition for O_3 formation. Other factors, as outlined above, must also be favorable. Thus for many daytime hours there are elevated precursor levels without high O_3 , suggesting that assuming constant emissions rates, favorable meteorological conditions required for O_3

390 formation are absent. Conducive conditions for high rates of ozone production were identified by WDEQ for ~15% of days in January through March 2011 (MSI, 2011). While the thresholds of required precursor mixing ratios, and consequently emissions, are as yet not determined definitively, the ambient data presented here show the importance of elevated levels of total NMHC to O₃ formation.

395

400

3.4 Source identification using PMF analysis

Hourly measurements at BSR, collected from October 2010 to March 2011, of speciated NMHC, and other selected parameters, allowed PMF analyses that explored the sensitivity of possible solutions for factor signatures of emission sources to be carried out. Other parameters included CO (with background subtracted), CH₄ (with background subtracted), total NMHC (measured by the Thermo Scientific model 55i analyzer) and NO_x. Preliminary PMF analyses showed that NO_x generated its own factor, unrelated to those for other species. As the analyses were primarily designed to identify the sources of speciated NMHC, NO_x was excluded from subsequent analyses.

- 405 Possible solutions to the PMF analyses were obtained for contributions from two, three, and four factors. Of these solutions, that for three factors was selected, because it yielded factors that are associated with likely emissions sources, was numerically stable using bootstrapping, and produced a solution for which the coefficients of determination (R^2) for all predicted compounds are greater than 0.8, with 21 out of 24 compounds predicted with $R^2 > 0.88$. All
- 410 solutions converged and were stable over multiple runs, and bootstrapping in each of 400 runs reproduced the same factor characteristics. The three-factor solution is also favored because while factors 1 and 2 show a positive correlation, contributions from factor 1, unlike those from factor 2, show no relationship to wind direction. By contrast, the four-factor solution is not stable with respect to bootstrapping, and the two-factor solution has significantly worse coefficients of determination for reproducing individual compound mixing ratios, with 15 of the 24 compounds.
- 415 determination for reproducing individual compound mixing ratios, with 15 of the 24 compounds predicted with R^2 of <0.88. The percentage contributions of each of the three derived factors to the mixing ratio of each constituent compounds are shown in Fig. 5.

The three PMF factor signatures each contain many common component compounds, but

- at different abundance levels. As previously noted, factors are not necessarily derived from
 specific emission sources, but can represent groups of sources. Oil and gas developments have
 numerous continuous and intermittent emission source types, many of which may well have their
 own unique compositional emissions pattern. Some sources are known to be difficult to
 quantitatively characterize and/or report, in particular flow-back from well completions and
 evaporative losses from produced water. Speciated NMHC emissions can, however, be broadly
- 425 classified as emanating from combustion, fugitive, or product handling sources, e.g. gas dehydration and condensate evaporation. Emission inventory data for the Pinedale Anticline development (February and March 2011 winter inventory) reveals that ~90% of total VOC emissions (~400 tons) are from "natural gas leakage", from source categories coded as tanks, dehydration units, pneumatic pumps, and fugitives (WDEQ, 2014a). Of the estimated ~70 tons
- 430 of BTEX emissions for the winter 2011 inventory, ~50 tons are assigned to dehydration units, and ~10 tons are assigned as fugitive emissions. Thus, based on the emission inventory, while VOC emissions are from many leakage sources, BTEX emissions are dominated by natural gas dehydration.
- Fig. 5 illustrates the average contribution of each PMF factor to the total derived mixing
 ratio for each compound across the entire monitoring period. For CO, factor 1 provides the
 dominant contribution. For speciated C₁ to C₆ non-aromatic hydrocarbons factor 2 dominates,
 whereas in the heavier hydrocarbon range (C≥7), up to *o*-xylene, factor 3 becomes dominant.
 Benzene and ethyne are the only two hydrocarbons that have roughly equivalent contributions
 from all 3 factors. The average percentage contribution of each factor to the measured mass of
 total NMHC are ~10%, ~50%, and ~40%, for factors 1, 2, and 3, respectively. However, for the
 14 speciated NMHC used for Fig. 6, this weighting is 25%, 60%, and 15%, respectively. Eight
- speciated NMHC are excluded from Fig. 6 as they are reported as grouped rather than individual compounds within emission profiles. The contribution of factor 3 weighting declines relative to the other factors due to the absence of these individual reported NMHC species (e.g. nonane).
- 445 Furthermore, factor 3 is also associated with heavier unidentified NMHC. Fig. 6 compares factor profiles with selected emission source profiles.

Designation of factor 1 as combustion (traffic) is supported by the significant contributions of background corrected CO, ethyne, benzene, *i*-octane, toluene, and *o*-xylene, all

characteristic of vehicle emissions. Contributions from other engines are possible. However, the

- diurnal profile for factor 1 shows a morning peak associated with peak traffic flow. Other combustion sources, e.g. drill rigs and compressor stations, in the Pinedale Anticline are reported to have relatively low CO emission rates while being important sources of NO_x (Livovitz et al., 2013). Of the three factors, factor 1 displays the least variability, with maximum contributions that are less than five times the average mass values, and also has the lowest overall impact on
- O₃ production, as discussed below. The profile for factor 1 resembles a combination of background, measured at the boundary of the UGRB, and traffic dominated profiles. The traffic profile in Fig. 6a is derived from a combination of profiles of gasoline and diesel vehicle exhaust (Schauer et al., 1999, 2002) with a weighting of 75% diesel derived from traffic surveys performed within the Pinedale Anticline and Jonah Field developments during 2009/2010. While
 emissions from traffic are likely to contribute to this factor, the roadside profile at the town of
- Pinedale also differs somewhat from the distribution derived for factor 1. This difference of factor 1 from profiles dominated by traffic is due to the additional contributions related to factor 2. Such smearing is anticipated to some extent from PMF analysis.
- The "fugitive natural gas" designation for factor 2 is largely suggested by the high
 contributions to its signature from background corrected methane, ethane and propane. The
 distribution of its component compounds, which closely resembles that for natural gas, includes
 significant contributions from butanes, pentanes, and several of the compounds also found in
 factor 1 (e.g. ethene, ethyne, and benzene). For some emission plumes, factor 2 ranges up to ~14
 times the average mass value. Compositional profiles for natural gas are from the Wyoming Oil
 and Gas Conservation Commission (WOGCC) for samples collected from 2001 to 2012
 (WOGCC, 2014). The WOGCC averaged profiles for 20 natural gas samples from both the
 Riverside and Mesa lease areas of the Pinedale Anticline shown in Fig. 6b, are in good
 agreement with each other and with factor 2, and clearly demonstrate that natural gas NMHC
 composition is dominated by light (≤ C₅) hydrocarbons. Measurements carried out at 190 natural
- 475 gas production sites in Appalachia, the Gulf Coast, and the Midcontinent and Rocky Mountain regions of the USA, indicate that at many sites pneumatic controllers and pumps are an important source of fugitive gas (Allen et al., 2013). Measurements of fugitive gas in the Pinedale Anticline, from 14 grab samples obtained in this study near operating pneumatic pumps, were used to derive a fugitive emissions profile. This profile, shown in Fig. 6b, matches WOGCC profiles of

- 480 natural gas. The gas profiles are very similar to factor 2. However, factor 2 has slightly elevated contributions from BTEX and this is likely due to emissions from dehydration activities being coincident with those of fugitive natural gas. Sources cannot be distinguished by PMF analysis when they are co-produced at each well site, however the compositional analysis shown in Fig 6 clearly identifies fugitive natural gas as the dominant emission source. While it is impossible to
- 485 differentiate emissions from specific well-pad components, their identity is well-known, e.g. pneumatic controllers and dehydration units. Observations show that fugitive natural gas emissions have the greatest impact on NMHC composition at BSR, with strong correlations between many of the light hydrocarbons, as shown in Fig. 7 for methane, ethane, propane, and *n*-butane.
- 490 The designation of factor 3 as "fugitive condensate" is supported by high contributions from C₇ to C₉ compounds, in particular benzene, toluene, ethylbenzene, and xylene isomers (BTEX). Factor 3 also includes significant contributions from nonane, octanes, *n*-heptane, and cyclohexane. The compound distribution closely resembles that for condensate, with the largest contribution from toluene and m+p-xylene. The impact of this factor on air samples measured at 495 BSR were most evident during air flow from the southwest. For some emission plumes, factor 3 reaches ~42 times average mass values. Also shown in Fig. 6c are WOGCC average profiles for condensate, derived from 20 samples, all with very similar compositions, from both the Riverside and Mesa lease areas. These condensate profiles are dominated by heavier (> C_5) NMHC constituents. This is also evident for factor 3, but there are differences in relative 500 contributions. These differences suggest the presence of a significant condensate source, proposed here to be a water treatment and recycling facility (Anticline Disposal facility), located 6 km west-southwest of the BSR monitoring site, as shown in Fig. 1. Figure 6c shows a strong similarity of the profile for factor 3 and that for fence line samples next to the water treatment facility.
- 505

3.5 Identification of emission source associated with PMF factor 3 at BSR

The Anticline Disposal facility was constructed to purify and recycle contaminated produced water and hydraulic fracturing flow back water, together with other drilling wastes from the Pinedale Anticline. Water treatment processes at this facility are described in detail by Schafer (2011) and Cox and Schafer (2010). Re-cycled water for use in hydraulic fracturing is

the result of API separator, anaerobic basin, aeration basin, clarifier, and sand filter treatment steps. Aeration of contaminated water within large heated ponds that are open to the environment is expected to enhance evaporative losses from the treated water. Further treatment steps, including a membrane bioreactor, reverse osmosis and electro-coagulation, produce water of

sufficient quality for re-injection. Discharge quality water is produced with an additional treatment step of boron ion exchange. Schafer (2011) reports that the contaminated water feed to the facility contains BTEX between 28,000 and 80,000 µg/L, gasoline organics in the range of 88,000 to 420,000 µg/L, and diesel organics that range from 77 to 1,100 µg/L. One of the three main Pinedale Anticline operators reports between three and four million barrels of their
produced water, including flow back water, are treated annually at this facility (US BLM, 2014).

An "in versus out" calculation of emissions is not possible due to a lack of process information. The WDEQ inventory estimates emissions for the 2011 calendar year from the facility as ~49 tons of VOC and ~21 tons of BTEX, of which ~18 tons is reported as benzene. Canister samples taken at the facility fence line indicate a speciated NMHC profile dominated by toluene and xylenes (70% of total hydrocarbon mass), as shown in Fig. 6c. The average composition distribution of the fence line water treatment facility samples are very similar to that of factor 3 suggesting this facility is the contributing source for factor 3. However, the possibility of some influence from other condensate emission sources to factor 3, e.g. flow back from completions, cannot be excluded. While quantification of the emission rate is not possible with this data, fence line measurements indicate a BTEX:benzene ratio of ~15:1, rather than ~1:1 as implied by inventory data. Additionally, fence line mixing ratios up to 992 ppbv of toluene and 911 ppbv of xylene isomers were measured suggesting significant emissions. An inventory

derived emission rate of 20 tons/year of BTEX for the water treatment facility (footprint of 0.08 miles²; 0.21 km²) corresponds to an emission intensity of ~250 tons/mile² (~95 tons/km²). This
value compares to a general intensity for the Pinedale Anticline (footprint of 312 miles²; 808 km²) of ~1 ton/ mile² (~0.39 ton/km²) when emissions from dehydration (258 tons/year), pneumatics (30 tons/year) and fugitives (73 tons/year) from the 2,045 operating wells in 2011 are combined. Emission inventory estimates therefore show that the facility has a far higher emission rate than the average value for the development. Factor 3 could equally well be labeled "water
treatment facility fugitive condensate". While the facility is an important point source of VOC and BTEX, the magnitude of emissions is uncertain. Overall, these data suggest that water

treatment operations may have a significant influence on ambient VOC composition and on O₃ formation.

545 **3.6 Spatial Variability of speciated NMHC in the UGRB**

Speciated NMHC distributions throughout the UGRB, and in particular in the Pinedale Anticline, were evaluated by carrying out canister sampling surveys. Twenty-eight sampling sites were identified, each of which was chosen to be representative of either background, boundary, downwind, upwind, or O&NG development conditions (Table S2). The surveys in 2010 and 2011 focused on determining differences between mixing ratios at background sites

- with those observed downwind and close to development activities. Mixing ratios varied significantly, both between sites in each survey and between surveys. Ethane and other speciated NMHC mixing ratios at sites near BLDR and BSR were generally more than twice those found at boundary sites upwind of the development area. At sites closer to development activities,
 reported ethane mixing ratios were higher, often between 3x and 10x those at BLDR and BSR.
 - Strong correlations of methane, propane and *n*-butane (Fig. 8) with ethane were observed in the data obtained from 255 canister samples collected at 27 sites throughout the UGRB during the period 2010 to 2013. (Samples close to the water treatment facility and production locations with pneumatic pump related fugitive natural gas emissions were excluded from this analysis).
- 560 These correlations suggest a commonality of contributing sources and are consistent with the dominance of fugitive natural gas emissions throughout the UGRB. The ratios between these light hydrocarbons are a close match to both those measured at BSR (Fig. 7) and those derived from natural gas composition profiles reported by the WOGCC (Fig. 6b) for samples collected at locations ranging from background sites to those downwind of drilling operations. While the
- 565 ratios of light hydrocarbons are relatively constant, ambient mixing ratios showed considerable variability, reflecting the local influence of meteorology and various O&NG operations. For example, in 2013 at Middle Crest (Table S2), a site within ~100 m of active drill rigs, fugitive natural gas signatures with ethane and toluene values of 485 ppbv and 11.3 ppbv, respectively, were observed. Similarly, measurements ~300 m downwind of flow back operations at Mesa
- 570 South Loop (Table S2) showed fugitive natural gas and condensate signatures with ethane and toluene up to 179 ppbv and 202 ppbv, respectively.

During 2011/2012 twelve surveys of 24-hour or three-day duration were performed at the

19

same 10 sites within and around the Pinedale Anticline boundary. Both Boulder sites are considered as well-mixed downwind sites, often with the lowest speciated NMHC values. While

- 575 the dominance of alkanes to the total speciated NMHC mass (C_2 to C_8) is consistent, there are enhanced aromatic contributions at three sites, namely Boulder Crest Road, Mesa North, and Mesa South, as shown in Fig. 9. Boulder Crest Road is located ~1.5 km to the northwest of the water treatment facility, which likely explains enhanced aromatics at this site. The two Mesa sites were in an area of intensive drilling, completion, and production activities. Inventory data
- 580 identifies dehydration as the most significant source of BTEX emissions, with enhancement relative to aliphatic hydrocarbons, leading, for example, to a much higher BTEX/*n*-hexane ratio than that for the condensate signature shown in Fig. 6c (WDEQ, 2014a). Over 80% of Pinedale Anticline BTEX production emissions are from dehydration units according to the 2011 winter inventory. Since dehydration emission sources are widely dispersed throughout the Pinedale
- 585 Anticline a somewhat uniform distribution of BTEX is anticipated. However, given the high level of activity on the Pinedale Mesa the influence of emissions from other activities is also possible. For example, completion and flow back operations, neither of which is represented adequately in current emission inventories, are likely to have contributed to elevated BTEX emissions. The Wyoming DEQ inventory reports emissions from the completion category in
- 590 2011 as zero for BTEX (WDEQ, 2014a). While the underlying causes of elevated BTEX on the Pinedale Mesa are uncertain, measurements at Boulder Crest and BSR suggest that a nearby water treatment facility causes a significant increase in contributions of higher molecular weight species to NMHC mixing ratios at these sites. Omission of water treatment and completions in inventories could therefore be a significant oversight.
- 595 Emission inventory source categories labeled as tanks, pneumatic pumps, and fugitives can be considered as contributing to 'fugitive natural gas'; while dehydration unit emissions can equate to 'fugitive condensate'. Combining estimates of these emissions rates according to this source categorization from the WDEQ emissions inventory for 2011 (Wyoming Department of Environmental Quality, 2014a) shows that ~75% of the inventory is assigned to 'fugitive natural gas' and ~25% to 'fugitive condensate'. Together, these categories comprise 93% of the 407 tons of VOC and 99% of the 68 tons of BTEX for February and March 2011 in the WDEQ inventory.
 - The predominance of fugitive gas emissions is consistent with the measurements reported here.

3.7 The importance of each PMF factor to episodic O₃ formation

- O₃ episodes at both Boulder sites are associated with high total NMHC mixing ratios.
 Despite being located only 5 km apart, peak O₃ differences of >50 ppbv were evident on both March 1st and 2nd 2011 (Fig. 3). These episode days are the least impacted by factor 3 at BSR. The BLDR site is located 7.5 km north of the water treatment facility (Fig.1). It is possible that, unlike at BSR, BLDR was impacted by emissions from this facility on these two days. The large differences in maximum O₃ mixing ratio at the two sites together with the observed hour by hour variations, indicates the localized nature of O₃ production and transport and the difficulties of modeling O₃ variability and its spatial distribution in the UGRB, particularly as flow patterns in the shallow surface layer below the inversion are as yet only partially characterized (Emery et al., 2014).
- Fig. 10 shows time series plots of the total OH reactivity of each PMF factor with the NO_x and O₃ mixing ratios, for four representative O₃ episode days. Reactivities for measured compounds with OH were calculated at standard temperature and pressure (298.15 K and 1013.25 hPa) using the recommended k_{OH} rate coefficients also employed by Gilman et al. (2009), derived from a variety of previous studies (Atkinson, 1986, 1990; Atkinson and Arey,
- 2003; Atkinson and Aschmann, 1988; DeMore et al., 1997). While the ozone mixing ratio is consistently scaled to 120 (ppbv), OH reactivity is scaled from 0 10 (s⁻¹) for March 2nd 2011, 0 20 (s⁻¹) for March 5th and 15th 2011, and 0 40 (s⁻¹) for February 18th 2011. Spiking of OH reactivity in Fig. 10 is most prevalent for factor 3. Individual rate coefficient (k_{OH}) values are listed in Table S9. Fig. S8 shows similar plots for all episode days. For factor 1, OH reactivity is dominated by contributions from CO. The contribution of local methane (total methane minus background methane in the unpolluted troposphere) for factors 1 and 2 accounted for ~2%, and ~5% of the factor 1 OH reactivity, respectively. Contributions from individual hydrocarbons in factor 2 to total OH reactivity are relatively uniform because with increasing carbon number, decreases in mixing ratio are offset by higher k_{OH} values. Factor 3 reactivity contributions are
- 630 dominated by those from the xylenes and toluene, both of which react relatively rapidly with OH. The plotted reactivities do not account for variations in actinic flux, so would perhaps be best described as potential reactivities that reflect the atmospheric composition.

The plots vary significantly from day to day, but common themes emerge, such as correlated increases in O₃ and factor 3 reactivity contributions, often resulting from increases in

m+p-xylene mixing ratio (and other compounds within the factor 3 profile). However, it is also clear that O₃ formation cannot be directly correlated with OH reactivity, and that NMHC species are mixed into the air parcels after O₃ has been formed.

On February 18th, NO_x levels are somewhat higher than usual so that accumulated O₃ is reduced before and after sunrise. A secondary spike in O₃ in early evening correlates with a rapid
increase in reactivity due to factor 3. Of the measured factor 3 hydrocarbons, *m+p*-xylene is the most important contributor to OH reactivity. The measured mixing ratio of *m+p*-xylene in this plume peaks at 37.9 ppbv. Factor 2 contributes most of the OH reactivity for much of the day on March 2nd 2011, when O₃ peaks some 50 ppbv higher at BLDR than at BSR, as noted in Fig. 3. Again, as on February 18th 2011, an increase in *m+p*-xylene late in the day, from 0.5 ppbv to 5.1 ppbv, coincides with an observed O₃ increase in early evening. The influence of two peak reactivity contributions from factor 3 on March 5th 2011 occur when *m+p*-xylene mixing ratios increase from 1.0 to 7.8 ppbv at 12:00 and then, after declining, increase of *m+p*-xylene from 0.4 to 12.3 ppbv at 13:00. Each of these elevated factor 3 contributions coincides with a

- 650 measured spike in O₃. Changes in wind direction could obviously advect factor 3 species to other locations, e.g. BLDR, and thereby affect O₃ production rates. Such an event may have occurred on March 1st and 2nd 2011, when southwesterlies (~210°) from the direction of the water treatment facility were reported at BLDR, and higher O₃ mixing ratios were observed.
- In summary, the time series plots in Fig. 10 (and Fig. S8) suggest that factor 3 emission sources, associated with high NMHC values, have a significant role in O₃ formation in surface air impacting the Boulder area downwind of the Pinedale Anticline. Toluene and the xylenes are the principal compounds that lead to increases in factor 3 total reactivity and hence in O₃ production potential. These compounds alone frequently contribute more than 50% of OH reactivity for factor 3. It should be noted that other unreported compounds are likely to be
- 660 present within this emission source. Trimethylbenzenes are also expected to add significantly to factor 3 reactivity, but unfortunately, though known to be present in the air samples that contain xylenes, their mixing ratios could not be accurately assessed. Numerical values of applied reactivities are listed in Table S9 for two 18:00 time periods, one on February 20th when both O₃ and factor 3 contributions were low, and one on February 18th, during the O₃ episode illustrated
- 665 in Fig. 10. The listed values also lead to the conclusion that neither CO nor CH₄ are important

contributors to OH reactivity during O₃ episodes.

Wintertime O_3 episodes in the UGRB and the Uintah Basin share many important common characteristics (Oltmans et al., 2014). Episodic O_3 production in both basins is associated with high NMHC levels and moderate NO_x . A key difference is that unlike the Uintah

- 670 basin, O₃ in the UGRB can be spatially highly variable with large gradients over small distances. In the UGRB, our results show that fugitive condensate material, and in particular its methylated aromatic constituents, frequently plays an important role in determining NMHC reactivity towards OH. A similar conclusion, derived from a numerical modeling study, has recently been reported for the Uintah Basin (Ahmadov et al 2014).
- 675

680

4 Summary and Conclusions

The pollutant profile observed in the winter of 2011 at a monitoring site close to the Pinedale Anticline natural gas field in Sublette County, Wyoming, differs from that measured in winter 2012, when significantly lower ambient total NMHC mixing ratios are associated with a lack of O₃ episodes. During 2011, numerous localized O₃ episodes were evident in the Boulder area of the UGRB, sometimes with significant gradients in O₃ mixing ratios over relatively short distances.

- Total NMHC mixing ratios are dominated by compounds associated with fugitive emissions of natural gas and condensate. C_2 to C_4 alkanes and C_7 to C_8 aromatics are the most abundant speciated NMHC. PMF analyses revealed three contributing factors that were identified with different emission source types: factor 1, combustion/traffic; factor 2, fugitive natural gas; and factor 3, fugitive condensate. The attribution of the PMF factors is supported by their close similarity to independent emission source profiles, in particular, for sources related to O&NG activities. In addition to fugitive natural gas, factor 2 includes emissions from
- 690 dehydration emissions, indicated by BTEX contributions. While factor 3 is noted as fugitive condensate, it could equally well be designated as water treatment emissions. Factor profile and meteorological data suggest that the water treatment facility is a point source for emissions of factor 3. Sampling surveys downwind of this facility show a condensate type signature that matches factor 3 with significantly elevated levels of toluene and m+p-xylene.
- 695 Surveys of speciated NMHC within the UGRB reveal fugitive emission of natural gas to be the dominant source of both methane and C_2 to C_4 NMHC for all of the 28 sampling sites. At

some sites the relative contribution from alkanes (fugitive natural gas) to total NMHC mass is reduced due to enhanced aromatic contributions. Two areas had relatively elevated levels of aromatic compounds, an area of intensive exploration activity on the Pinedale Mesa, and close to a water treatment facility. Elevated levels of aromatics at the Pinedale Mesa may have resulted

- 700 a water treatment facility. Elevated levels of aromatics at the Pinedale Mesa may have resulted from a variety of sources including dehydration and flow back operations during well completions. Emissions from a water treatment facility can influence NMHC measurements at the BSR site, and other sampling locations in the Boulder area of the Pinedale Anticline.
- 705 Author contribution: R.A. Field designed the experimental approach for the study. R.A. Field and J. Soltis performed data collection and validation activities. M. C. McCarthy performed the PMF analysis. R.A. Field interpreted the results of the study and prepared the manuscript with support from all co-authors, in particular D.C. Montague.
- 710 Acknowledgments: Our sincere thanks goes to Peter Dumitrean for assistance when setting-up the VOC system. Financial support from the University of Wyoming School of Energy Resources and the Pinedale Anticline Project Office for the PASQUA study, whose results we present here, are appreciated. We also acknowledge WDEQ, which provided data, external auditors for routine parameter measurements, and PASQUA administrative oversight, as well as
- 715 funding of the MAPA project. We thank all the individuals and their respective organizations involved in canister deployment, namely: Sublette County Conservation District (Meghann Durbrow and Loren Racich); Sublette County Health District (Keith Raney); Wyoming BLM (Tim Zebulske, Kyle Schumacher, Brian Roberts, Cindi Etcheverry and Janet Bellis); USFS (Ted Porwoll); Citizens United for Responsible Energy Development (Perry Walker, Bev Sharp,
- 720 Carmel Kail, Tina Rock, Elaine Crumpley, and Mary Lynn Worl); WDEQ (Jennifer Frazier, Ken Rairigh and Brandi O'Brien); Town of Pinedale (Patty Racich, Dave Racich, and Dave Hohl); Shell (Nancy Feck, Jasmine Allison, and Aimee Davidson); BP (Don Brooks); and QEP (Kevin Williams). Thanks also to ShihMing Huang for producing maps for the manuscript. Finally the comments and support of Dr. Richard (Dick) Derwent are appreciated.

References

Adgate, J. L., Goldstein, B. D., and McKenzie, L. M.: Potential public health hazards, exposures

- and health effects from unconventional natural gas development, Environ. Sci. Technol., 48,
 8307-8320, doi:10.1021/es404621d, 2014.
 - Ahmadov, R., McKeen, S., Trainer, M., Banta, R., Brewer, A., Brown, S., Edwards, P. M., deGouw, J. A., Frost, G. J., Gilman, J., Helmig, D., Johnson, B., Karion, A., Koss, A., Langford,A., Lerner, B., Olson, J., Oltmans, S., Peischl, J., Pétron, G., Pichugina, Y., Roberts, J. M.,
- Ryerson, T., Schnell, R., Senff, C., Sweeney, C., Thompson, C., Veres, P., Warneke, C., Wild,
 R., Williams, E. J., Yuan, B., and Zamora, R.: Understanding high wintertime ozone pollution events in an oil and natural gas producing region of the western US, Atmos. Chem. Phys. Discuss., 14, 20295-20343, doi:10.5194/acpd-14-20295-2014, 2014.

Allen, D. T., Torres, V. M., Thomas, J., Sullivan, D. W., Harrison, M., Hendler, A., Herndon, S.

- C., Kolb, C. E., Fraser, M. P., Hill, A. D., Lamb, B. K., Miskimins, J., Sawyer, R. F., and Seinfeld, J. H.: Measurements of methane emissions at natural gas production sites in the United States, Proc. Nat. Acad. Sci., 110, 17768-17773, 10.1073/pnas.1304880110, 2013.
 Atkinson, R.: Kinetics and mechanisms of the gas-phase reactions of the hydroxyl radical with organic-compounds under atmospheric conditions, Chem. Rev., 86, 69–201, 1986.
- 745 Atkinson, R.: Gas-phase tropospheric chemistry of organic compounds. A review, Atmos. Environ., 24A, 1-41, 1990.

Atkinson, R., and Arey J.: Atmospheric degradation of volatile organic compounds, Chem. Rev., 103, 4605 – 4638, 2003.

- and structurally related aromatic compounds with OH and NO₃ radicals, N_2O_5 and O_3 at 296 ± 2 K, Int. J. Chem. Kinet., 20, 513–539,1988.
 - Brandt, A. R., Heath, G. A., Kort, E. A., O'Sullivan, F. O., Pétron, G., Jordaan, S. M., Tans, P.,
 Wilcox, J., Gopstein, A. M., Arent, D., Wofsy, S., Brown, N. J., Bardley, R., Stucky, G. D.,
 Eardley, D., Harris, R.: Methane leaks from North American natural gas systems, Science, 343, 733-735, 2014.

755

Broadway, G. and Tipler, A.: Ozone precursor analysis using a Thermal Desorption-GC system, PerkinElmer Gas Chromatography White Paper No. 008880B_01, Perkin Elmer, 2012.

Atkinson, R. and Aschmann S. M.: Kinetics of the reactions of acenaphthene and acenaphthylene

Brown, S. G., Frankel, A., and Hafner, H. R.: Source apportionment of VOCs in the Los Angeles area using positive matrix factorization, Atmos. Environ. 41, 227–237, 2007.

- Buzcu, B. and Fraser, M. P.: Comparison of VOC emissions inventory data with source apportionment results for Houston, TX., Atmos. Environ., 42, 5032-5043, 2008.
 Carter, W. P. and Seinfeld, J. H., Winter ozone formation and VOC incremental reactivities in the Upper Green River Basin of Wyoming, Atmos. Environ., 50, 255-266, 2012.
 Caulton, D. R., Shepson, P. B., Santoro, R. L., Sparks, J. P., Howarth, R. W., Ingraffea, A. R.,
- Cambaliza, M. O. L., Sweeney, C., Davis, K. J., Stirm, B. H., Montzka, S. A., and Miller, B.
 R.: Toward a better understanding and quantification of methane emissions from shale gas development, Proc. Nat. Acad. Sci., 111, 6237-6242, 2014.

Colburn, T., Schultz, K., Herrick, L., and Kwiatkowski, C.: An exploratory study of air quality near natural gas operations, Human Ecol. Risk Assess: Int. J., 20,1, 86-105,

- doi:10.1080/10807039.2012.749447, 2014.
 - Cox, L. and Shafer, L.: A working model for oil and gas produced water treatment. Energy resources and produced waters conference, May 25th to 26th 2010, Laramie Wyoming.
 Accessed through the University of Wyoming WyoCast On-Demand interface at http://wyocast.uwyo.edu/WyoCast/Play/27449dccec254addb46c72528606a76d.
- DeMore, W. B., Sander S. P., Golden D. M., Hampson R. F., Kurylo M. J., Howard C. J.,
 Ravishankara A. R., Kolb C. E., and Molina M. J.: Chemical kinetics and photochemical data for use in stratospheric modeling: Evaluation number 12, JPL Publ. 97–4, 1 266, NASA,
 Pasadena, California, 1997.
 - Dernie, J. and Dumitrean, P.: UK hydrocarbon network annual report for 2012, Report by AEA Technology ED 47833/ED46645, 2013.
 - Derwent R.G., Dernie, J., Dollard, G. J., Dumitrean, P., Mitchell R.F. Murrells T.P., Telling S.P., and Field R.A.: Twenty years of continuous high time resolution volatile organic compound monitoring in the United kingdom from 1993 to 2012, Atmos. Environ., 99, 239-247, 2014.
 Dollard, G. J., Davies, T. J., Jones, B. M. R., Nason, P. D., Chandler, J., Dumitrean, P., Delaney,
- M., Watkins, D. and Field, R. A., The UK hydrocarbon monitoring network, Chap. 3, 37-50,
 Volatile organic compounds in the atmosphere, ISBN 0-85404-215-61995, ed. Hester, R. E.
 and Harrison, R. M., Royal Society of Chemistry, Cambridge UK, 1995.

Edwards, P. M., Young, C. J., Aikin, K., de Gouw, J., Dubé, W. P., Geiger, F., Gilman, J., Helmig, D., Holloway, J. S., Kercher, J., Lerner, B., Martin, R., McLaren, R., Parrish, D. D.,

Peischl, J., Roberts, J. M., Ryerson, T. B., Thornton, J., Warneke, C., Williams, E. J., and Brown, S. S.: Ozone photochemistry in oil and natural gas extraction region during winter: simulations of a snow-free season in the Uintah Basin, Utah, Atmos. Chem. Phys., 13, 8955-8971, doi:10.5194/acp-13-8955-2013, 2013.

Edwards, P. M., Brown, S.S., Roberts, J.M., Ahmadov, R., Banta, R.M, de Gouw, J.A., Dubé,

- W.P., Field, R.A., Flynn, J.H., Gilman, J.B., Graus, M., Helmig, D., Koss, A., Langford, A.O.,
 Lefer, B.L., Lerner, B.M., Li, R., Li, S.M., McKeen, S.A., Murphy, S.M., Parrish, D.D., Senff,
 C.J., Soltis, J., Stutz, J., Sweeney, C., Thompson, C.R., Trainer, M.K., Tsai, C., Veres, P.R.,
 Washenfelder, R.A., Warneke, C., Wild, R.J., Young, C.J., Yuan, B., Zamora, R.:
 Unconventional photochemistry underlying winter ozone in an oil and gas producing region,
- Nature, 514, 351–354, doi:10.1038/nature13767, 2014.
 Efron, B.: The jackknife, the bootstrap and other resampling plans, Society for Industrial and Applied Mathematics, Philadelphia, PA, ISBN 978-0-89871-179-0, 1982.
 - Efron, B. and Tibshirani, R.J.: An introduction to the bootstrap, Chapman & Hall, New York, ISBN-13: 978-041204231, 1993.
- Emery, B. R., Montague, D. C., Field, R. A., and Parish, T. R.: Barrier wind formation and influence on pollutant distributions during elevated ozone episodes in the Upper Green River Basin of Sublette County, Wyoming, submitted to J. Appl. Meteor. Climatol., November, 2014.
 Field, R. A., Soltis, J., and Murphy, S.: Air quality concerns of unconventional oil and natural gas production, Environ. Sci. Processes Impacts, 16, 954-969, 2014.
- 810 Francis, R.: Personal Communication regarding performance of Thermo Scientific model 55i analyzer, Thermo Scientific, 2014.
 - Gilman, J. B., Kuster, W. C., Goldan, P. D., Herndon, S. C., Zahniser, M. S., Tucker, S. C.,Brewer, W. A., Lerner, B. M., Williams, E. J., Harley, R. A., Fehsenfeld, F. C., Warneke, C.,and de Gouw, J. A.: Measurements of volatile organic compounds during the 2006
- TexAQS/GoMACCS campaign: Industrial influences, regional characteristics, and diurnal dependencies of the OH reactivity, J. Geophys. Res., 114, D00F06, doi:10.1029/2008JD011525, 2009.

Gilman, J. B, Lerner, B. M, Kuster, W. C, de Gouw, J. A.: Source signature of volatile organic

compounds from oil and natural gas operations in Northeastern Colorado, Environ. Sci.

- 820 Technol. 47, 1297-1305, 2013.
 - Helmig, D., Thompson, C. R., Evans, J., Boylan, P., Hueber, J., and Park, J.-H.: Highly elevated atmospheric levels of volatile organic compounds in the Uintah Basin, Utah, Environ. Sci. Technol., 48(9), 4707-4715, 2014.

Karion, A., Sweeney, C., Pétron, G., Frost, G., Hardesty, R. M., Kofler, J., Miller, B. R.,

- Newberger, T., Wolter, S., Banta, R., Brewer, A., Dlugokencky, E. J., Lang, P. M., Montzka, S. A., Schnell, R., Tans, P., Trainer, M., Zamora, R., and Conley, S.: Methane emissions estimate from airborne measurements over a western United States natural gas field, Geophys. Res. Letters, 40(16), 4393-4397, doi: 10.1002/grl.50811, 2013.
 - Litovitz, A. Cutright A., Abramzon S., Burger N., Samaras C., Estimation of regional air-quality
- damages from Marcellus Shale natural gas extraction in Pennsylvania, Environ. Res. Lett., 8, 014017, 1-8, 2013.
 - Martin, R., Moore, K., Mansfield, M., Hill, S., Harper, K. and Shorthill, H.: Uintah Basin winter ozone and air quality study, Report, University of Utah, 2011, <u>http://rd.usu.edu/files/uploads/ubos_2010-11_final_report.pdf</u>
- McCarthy M.C., Aklilu Y.A., Brown S.G., Lyder D.A., Source apportionment of volatile organic compounds measured in Edmonton, Alberta, Atmos. Environ., 81, 504-516, 2013.
 McKenzie, L. M., Witter, R. Z., Newman, L. S., and Adgate, J. L.: Human health risk assessment of air emissions from development of unconventional natural gas resources, Sci. Total Environ., 424, 79-87, 2012.
- 840 McKenzie, L. M., Guo, R., Witter, R. Z., Savitz, D. A., Newman, L. S., Adgate, J. L.: Birth outcomes and maternal residential proximity to natural gas development in rural Colorado, Environ. Health Persp., 122,4, 412-417, 2014.
 - Moore, C. W., Zielinska, B., Pétron, G., and Jackson, R. B.: Air impacts of increased natural gas acquisition, processing, and use: a critical review, Environ. Sci. Technol.,
- doi:10.1021/es4053472, 2014.
 - MSI, (Meteorological Solutions, Inc.), Final Report, 2011 Upper Green River Winter Ozone Study,

http://sgirt.webfactional.com/filesearch/content/Air%20Quality%20Division/Programs/Ozone/ Winter%20Ozone-Winter%20Ozone%20Study/2011_UGWOS-Monitoring-Final-Report.pdf,

850 Report, 2011.

MSI (Meteorological Solutions, Inc.), Final Report, 2012 Upper Green River Winter Ozone Study,

http://sgirt.webfactional.com/filesearch/content/Air%20Quality%20Division/Programs/Ozone/ Winter%20Ozone-Winter%20Ozone%20Study/2012_UGWOS-Monitoring-Final-Report.pdf,

855 Report, 2012.

MSI (Meteorological Solutions, Inc.), Final Report, 2013 Upper Green River Winter Ozone Study, MSI and T&B Systems,

http://sgirt.webfactional.com/filesearch/content/Air%20Quality%20Division/Programs/Ozone/Winter%20Ozone-Winter%20Ozone%20Study/2013_UGWOS-Monitoring-Final-Report.pdf,

860 Report, 2013.

MSI, (Meteorological Solutions, Inc.), Final Report, 2014 Upper Green River Winter Ozone Study,

http://sgirt.webfactional.com/filesearch/content/Air%20Quality%20Division/Programs/Ozone/Winter%20Ozone-Winter%20Ozone%20Study/2014_UGWOS-Monitoring-Final-Report.pdf,

865 Report, 2014.

Norris, G., Vedantham, R., Wade, K. S., Brown, S. G., Prouty, J. D., and Foley, C., EPA positive matrix factorization (PMF) 3.0 fundamentals and user guide. Report by the National Exposure Research Laboratory, Sonoma Technology Inc. and Lockheed Martin Systems Engineering Center, EP-D-05-004; STI-907045.05-3347-UG, 2008.

870 Oltmans, S., Schnell, R., Johnson, B., Pétron, G., Mefford, T. and Neely, R.: Anatomy of wintertime ozone associated with oil and natural gas extraction activity in Wyoming and Utah, Elem. Sci. Anth., 2: 000024, doi: 10.12952/journal.elementa.000024, 2014.

Paatero, P.: Least squares formulation of robust non-negative factor analysis, Chemometr. Intellig. Lab., 37, 23-35, doi:10.1016/S0169-7439(96)00044-5, 1997.

875 Paatero, P. and Tapper, U.:Positive matrix factorization: a non-negative factor model with optimal utilization of error estimates of data values, Environmetrics 5, 111-126, 1994.

Pétron, G., Frost, G., Miller, B. R., Hirsch, A. I., Montzka, S. A., Karion, A., Trainer, M.,
Sweeney, C., Andrews, A. E., Miller, L., Kofler, J., Bar-Ilan, A., Dlugokencky, E. J., Patrick,
L., Moore, Jr., CT., Ryerson, T. B., Siso, C., Kolodzey, W., Lang, P. M., Conway, T., Novelli,

880 P., Masarie, K., Hall, B., Guenther, D., Kitzis, D., Miller, J., Welsh, D., Wolfe, D., Neff, W.,

and Tans, P.: Hydrocarbon Emissions Characterization in the Colorado Front Range: A Pilot Study, J. Geophys. Res., 117(D4), doi:10.1029/2011JD016360, 2012.

- Poirot, R. L., Wishinski, P. R., Hopke, P. K., and Polissar, A. V.: Comparative application of multiple receptor methods to identify aerosol sources in northern Vermont, Environ. Sci.
- 885 Technol. 35,23, 4622-4636, 2001.
 - Rappenglück, B., Ackermann, L., Alvarez, S., Golovko, J., Buhr, M., Field, R. A., Soltis, J.,
 Montague, D. C., Hauze, B., Adamson, S., Risch, D., Wilkerson, G., Bush, D., Stoeckenius, T.,
 and Keslar, C., Strong wintertime ozone events in the Upper Green River Basin, Wyoming,
 Atmos. Chem. Phys., 14, 4909–4934, 2014.
- 890 Rodriguez, M., Reed, J., Chien, C-J., Taylor, C. Reid, S. and Craig, K.: Ozone modeling results and analyses for winter in Sublette County, Sweetwater County and Lincoln County Wyoming; Interim Report from AECOM to the Wyoming Department of Environmental Quality, April 2014.

- air pollution sources C₁ through C₃₀ organic compounds from medium duty diesel trucks,
 Environ. Sci. Technol. 33(10), 1578-1587, 1999.
 - Schauer, J. J., Fraser, M. P., Cass, G. R., and Simoneit, B. R. T., Measurement of emissions from air pollution sources C₁ C₃₂ organic compounds from gasoline-powered motor vehicles, Environ. Sci. Technol., 36(6), 1169-1180, 2002.
- 900 Schafer, L.: Water recycling and purification in the Pinedale Anticline Field: Results from the Anticline Disposal Project, SPE 141448, paper presented at Society of Petroleum Engineers Conference, Houston, TX, March 21-23, 2011.
 - Schnell, R. C., Oltmans, S. J., Neely, R. R., Endres, M. S., Molenar, J. V., White, A. B.: Rapid photochemical production of ozone at high concentrations in a rural site during winter, Nature
- Geosci. 2, 120-122, 2009.
 Soltis, J. and Field, R. A.: Pinedale Anticline Spatial Air Quality Assessment (PASQUA), mobile laboratory monitoring of ozone precursors at Boulder South Road site 2010-2011, Report, University of Wyoming, 2011a, <u>http://www-das.uwyo.edu/ozone/index.html</u>
 Soltis, J. and Field, R. A.: Pinedale Anticline Spatial Air Quality Assessment (PASQUA), 2010-
- 910 2011 spatial distribution surveys, Report, University of Wyoming, 2011b, <u>http://www-das.uwyo.edu/ozone/index.html</u>

Schauer, J. J., Kleeman, M. J., Cass, G. R., Simoneit, B. R. T.: Measurement of emissions from

Soltis, J. and Field, R. A.: Pinedale Anticline Spatial Air Quality Assessment (PASQUA), mobile laboratory monitoring of ozone precursors at Boulder South Road site 2011-2012, Report, University of Wyoming, 2012a, <u>http://www-das.uwyo.edu/ozone/index.html</u>

915 Soltis J. and Field R.A.: Pinedale Anticline Spatial Air Quality Assessment (PASQUA), 2011-2012 spatial distribution surveys, Report, University of Wyoming, 2012b, <u>http://wwwdas.uwyo.edu/ozone/index.html</u>

Song, X. H., Polissar, A. V., and Hopke, P. K.: Sources of fine particle composition in the northeastern U.S., Atmos. Environ. 35 (31), 5277-5286, 2001.

- US BLM (US Bureau of Land Management), Annual Operator Meetings, 2014 http://www.blm.gov/wy/st/en/field_offices/Pinedale/anticline/airwatermtg.html.
 US Census Bureau, American Community Survey, 2010.
 - US Department of Energy, Modern shale gas development in the United States: A primer, Contract DE-FG26-04NT15455, 2009, Report by Office of Fossil Energy National Energy

925 Technology Laboratory, 2009.

- US Energy Information Administration, 2009 U.S. Crude Oil, Natural Gas and Natural Gas Liquids Proved Reserves, Report top100 fields, 2010.
- US Energy Information Administration, 2012 Annual energy outlook, Report, 2013.
- US Energy Information Administration, Annual energy outlook 2014 Early Release Overview,

930 Report, 2014.

Warneke, C., Geiger, F., Edwards, P. M., Dubé, W., Pétron, G., Kofler, J., Zahn, A., Brown, S.
S., Graus, M., Gilman, J., Lerner, B., Peischl, J., Ryerson, T. B., de Gouw, J. A., and Roberts, J.
M., Volatile organic compound emissions from the oil and natural gas industry in the Uinta basin, Utah: point sources compared to ambient air composition, Atmos. Chem. Phys. Discuss.,

935 14, 11895-11927, 2014.

Wyoming Department of Environmental Quality, Actual Emission Inventories, http://deq.wyoming.gov/aqd/emission-inventories/resources/annual-and-winter-ugrbemissions/, 2014a.

Wyoming Department of Environmental Quality, Wyoming Visibility Monitoring Network,

 940 <u>http://www.wyvisnet.com</u>, 2014b.
 WOGCC (Wyoming Oil and Gas Conservation Commission),: Gas/Water Analysis, <u>http://wogcc.state.wy.us/AnalysisMenu.cfm?Skip='Y'&oops=ID42520</u>, 2014.

Alkane	Alkene (&Alkyne)	Aromatic	
ethane	ethene (ethylene)	benzene	
propane	propene (propylene)	toluene	
butane (<i>n</i> -butane)	trans-but-2-ene (t-2-butene)	ethylbenzene	
2-methylpropane (<i>i</i> -butane)	but-1-ene (1-butene)	<i>m</i> + <i>p</i> -xylene	
pentane (<i>n</i> -pentane)	cis-but-2-ene (<i>c</i> -2-butene)	<i>o</i> -xylene	
2-methylbutane (<i>i</i> -pentane)	1,3-butadiene	styrene	
cyclopentane	pent-1-ene (1-pentene)	1,2,3-trimethylbenzene*	
hexane (<i>n</i> -hexane)	trans-pent-2-ene (t-2-pentene)	1,2,4-trimethylbenzene*	
2-methylpentane (<i>i</i> -hexane)	cis-pent-2-ene (c-2-butene)	1,3,5-trimethylbenzene*	
3-methylpentane	2-methyl-1,3-butadiene (isoprene)		
heptane (<i>n</i> -heptane)			
octane (<i>n</i> -octane)	ethyne (acetylene)		
cyclohexane	prop-1-yne (propyne)		
nonane			
decane*			
*not reported during 2011-2012 or 2012-2013; during 2010 – 2011 indicative only			

Table 1 Speciated NMHC measured with the Perkin Elmer Ozone Precursor Analyzer



Figure 1 Map of study area including principal monitoring sites and locations of oil and natural gas wells within the Jonah Field and the Pinedale Anticline



Figure 2 Time series of O₃, NO_x, and NMHC at Boulder South Road (BSR) for the period January through March during 2011 and 2012



Figure 3 O₃ mixing ratios during 4 episodes at Boulder sites February to March 2011





Figure 5 Percentage contribution of PMF factors to the average mixing ratio of each analyzed pollutant (-b signifies minus background) from the whole sampling period at Boulder South Road (BSR)











Figure 6c Comparison of factor 3 with emission source profiles as percentage contribution by mass for selected NMHC



1035 Figure 7 Correlation of methane, propane and *n*-butane with ethane at Boulder South Road (BSR) from 2010 to 2011



Figure 8 Correlation of methane, propane and *n*-butane with ethane for locations within and around the Pinedale Anticline during 2010 - 2013 surveys



1055 Figure 9 NMHC class distributions for 2011-2012 surveys at 10 sites within and around the Pinedale Anticline (Average mass are scaled as shown relative to the key value of $100 \ \mu g/m^3$)



Figure 10 Relationship of PMF factor OH reactivity, NO_x and O_3 during selected episodes at Boulder South Road (BSR)