



**Influence of oil and gas operations on atmospheric hydrocarbons and ozone**

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# 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

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Received: 16 September 2014 – Accepted: 17 September 2014 – Published: 30 September 2014

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Published by Copernicus Publications on behalf of the European Geosciences Union.

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## Abstract

Emissions from oil and natural gas development during winter in the Upper Green River Basin of Wyoming are known to drive episodic ozone (O<sub>3</sub>) production. Contrasting O<sub>3</sub> distributions were observed in the winters of 2011 and 2012, with numerous episodes in 2011 compared to none in 2012. During 2011 wintertime O<sub>3</sub> episodes at two sites near Boulder Wyoming, situated ~ 5 km apart, were observed to sometimes differ. In 2012 the lack of O<sub>3</sub> episodes coincided with a reduction in 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 O<sub>3</sub> 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 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 condensate range NMHC, in particular toluene and *m* + *p*-xylene. Emissions from water treatment have an influence upon peak O<sub>3</sub> mixing ratios at downwind measurement sites.

## 1 Introduction

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

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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 O<sub>3</sub> 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 O<sub>3</sub> precursor VOC compounds. These monitoring and modeling studies have led to significant progress in understanding the mechanisms and critical reaction pathways for wintertime O<sub>3</sub> formation, but questions remain. Notwithstanding the apparent importance of HONO for O<sub>3</sub> 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 recently been answered for the Uintah Basin (Edwards et al., 2013, 2014), but it remains to be determined how similar the chemistry compares between various basins impacted by wintertime O<sub>3</sub> formation.

In this study, extensive non-methane hydrocarbon (NMHC) measurements were made in the UGRB in an effort to identify the compounds that are most important for O<sub>3</sub> formation. Positive matrix factorization (PMF) source apportionment has been applied to the speciated non-methane hydrocarbon (NMHC) air quality data (Brown et al., 2007; Buzcu and Fraser, 2008; McCarthy et al., 2013), thereby allowing the relative contributions of various sources to ambient observed hydrocarbon levels to be assessed.

## 2 Methodology

Measurements characterizing air quality in the UGRB were carried out in and around the Pinedale Anticline. The principal monitoring site was at Boulder South Road (BSR), a location that experiences surface air containing relatively well-mixed trace gases representative of emissions from a variety of nearby O & NG development

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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.

### 2.3 Positive matrix factorization analysis of speciated NMHC

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 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 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 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

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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. Additionally, ten samples were also excluded from analysis because they contained extremely high outlier values, most notably for either toluene or ethyne. These 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<sub>4</sub>, were included in the analyses.

### 3 Results and discussion

Figure 1 shows well locations in the Pinedale Anticline and Jonah Field developments, together with selected monitoring locations, all within the UGRB of Wyoming. 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 m.s.l., 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 km<sup>2</sup>). 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



composition and mixing ratios of the constituent NMHC, together with the concomitant levels of  $\text{NO}_x$ , at the two sites.

### 3.3 Relationship of $\text{O}_3$ to NMHC and $\text{NO}_x$

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 ( $\text{C}_2$  to  $\text{C}_8$ ) was performed. Total integrated NMHC measured by the Thermo 55i includes both hydrocarbons and their halogenated, oxygenated, and nitrogen-containing derivatives, up to  $\text{C}_{11}$  compounds. The mass balance comparison 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 ( $R^2$ ) of 0.90. While there is a strong correlation between the two NMHC data sets, using only identified OPA NMHC omits  $\sim 43\%$  of the carbonaceous material included in the total NMHC measurement. A second analogous comparison was therefore 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 increased the mass from identified  $\text{C}_2$ – $\text{C}_6$  aliphatic hydrocarbons by a factor of 1.1, and that from identified  $\text{C}_7$ – $\text{C}_8$  aliphatic and  $\text{C}_6$ – $\text{C}_9$  aromatic compounds by a factor of 2.0. Using the augmented summation of speciated NMHC mass resulted in the slope and  $R^2$  values of the regression line both increasing, to 0.88 and 0.92 respectively. Measurement uncertainties, as outlined in Table S1, may account for the mass deficit implied by a regression fit slope

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less than unity. Contributions from oxygenated and other compounds not detected by the OPA can only be small however, suggesting that VOC total mass in the UGRB is dominated by hydrocarbons.

Identified C<sub>2</sub> to C<sub>9</sub> compounds contributing most to the total carbon NMHC mass measured by the OPA at BSR, namely ethane (26%), propane (15%), toluene (11%), *m* + *p*-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 2011/12 and 2012/13, during the Upper Green Winter O<sub>3</sub> 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<sub>2</sub> to C<sub>8</sub> range are reported.

Variations in the measured O<sub>3</sub> mixing ratio together with changes in total NMHC and NO<sub>x</sub> at BSR are shown in Fig. 4, constructed from hourly averaged observations obtained between 11:00 and 20:00 MST during the three-month winter period from January to March 2011. Highest O<sub>3</sub> mixing ratios are associated with total NMHC mixing ratios above 0.2 ppmC, when NO<sub>x</sub> mixing ratios are 6–20 ppbv, and decrease significantly as the mixing ratios of these precursors decline. Data point scatter, shown in Fig. 4, is likely to be influenced by a number of environmental parameters including meteorology, actinic flux intensity, and NMHC composition. An analogous plot constructed using BLDR measurements for the same O<sub>3</sub> episode days, is shown in the Supplement (Fig. S7). It exhibits the same trends evident in Fig. 4, but suggests that similarly high O<sub>3</sub> levels can occur when NO<sub>x</sub> mixing ratios are depressed to lower values.

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### 3.4 Source identification using PMF analysis

Analyses were carried out to explore the sensitivity of possible solutions for factor signatures of emission sources contributing to BSR site samples, for two, three, and four factors. Of these, the three-factor solution performs optimally, because it yields factors that are associated with likely emissions sources, is numerically stable using bootstrapping, and gives 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 solutions converge and are stable over multiple runs, and bootstrapping in each of 400 runs reproduces 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 predicted with  $R^2 < 0.88$ . 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 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 t) are from “natural gas leakage”, from source categories coded as tanks,

dehydration units, pneumatic pumps, and fugitives (WDEQ, 2014a). Of the estimated ~ 70 t of BTEX emissions for the winter 2011 inventory, ~ 50 t are assigned to dehydration units, and ~ 10 t 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.

Figure 5 illustrates the average contribution of each PMF factor to the total derived mixing ratio for each compound across the entire monitoring period. The average percentage contributions of each factor to the measured mass of total NMHC in the period October 2010 to March 2011 are ~ 10, ~ 50, and ~ 40 % respectively, for factor 1 (combustion/traffic), factor 2 (fugitive natural gas), and factor 3 (fugitive condensate). However for the 14 speciated NMHC used for Fig. 6, (ethane, propane, *n*-butane, *i*-butane, *n*-pentane, *i*-pentane, 2-methylpentane, 3-methylpentane, *n*-hexane, benzene, toluene, ethylbenzene, *m* + *p*-xylene, and *o*-xylene) this weighting is 25 %, 60 %, and 15 %, respectively. Factor 3 weighting declines as some speciated NMHC, e, g, nonane, that are more prevalent within this factor, are excluded. Figure 6 compares factor profiles with emission source profiles for the 14 NMHC that characterize both PMF factors and are reported as individual rather than grouped compounds within emission profiles. We have chosen identifier names for the factors based on the similarity of factor profiles to emission source profiles. They are designated as “combustion/traffic” (factor 1), “fugitive natural gas” (factor 2) and “fugitive condensate” (factor 3).

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<sub>x</sub> (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 O<sub>3</sub> production, as discussed

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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 2009/10. 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  $\sim 14$  times the average mass value. The compositional profiles for natural gas is 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 ( $\leq C_5$ ) hydrocarbons. Measurements carried out at 190 natural 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 natural gas. The gas profiles are very similar to factor 2. However factor 2 has slightly elevated contributions from BTEX and



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that the contaminated water feed to the facility contains BTEX between 28 000 and 80 000  $\mu\text{g L}^{-1}$ , gasoline organics in the range of 88 000 to 420 000  $\mu\text{g L}^{-1}$ , and diesel organics that range from 77 to 1100  $\mu\text{g L}^{-1}$ . 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 (US BLM, 2014).

An “in vs. out” calculation of emissions is not possible due to a lack of process information. The WDEQ inventory estimates (footprint of 0.08  $\text{mile}^2$ ; 0.21  $\text{km}^2$ ) emissions for the 2011 calendar year from the facility as  $\sim 49\text{ t}$  of VOC and  $\sim 21\text{ t}$  of BTEX, of which  $\sim 18\text{ t}$  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  $\sim 15 : 1$ , rather than  $\sim 1 : 1$  as implied by inventory data. Additionally, fence line mixing ratios up to 991.5 ppbv of toluene and 911.1 ppbv of xylene isomers were measured suggesting significant emissions. An inventory derived emission rate of  $20\text{ t year}^{-1}$  of BTEX corresponds to an emission intensity of  $\sim 250\text{ t mile}^{-2}$  ( $\sim 95\text{ t km}^{-2}$ ). This value compares to a general intensity for the Pinedale Anticline (footprint of 312  $\text{mile}^2$ ; 808  $\text{km}^2$ ) of  $\sim 1\text{ t mile}^{-2}$  ( $\sim 0.39\text{ t km}^{-2}$ ) when emissions from dehydration ( $258\text{ t year}^{-1}$ ), pneumatics ( $30\text{ t year}^{-1}$ ) and fugitives ( $73\text{ t year}^{-1}$ ) from the 2045 operating wells in 2011 are combined. Factor 3 could equally well be labeled water treatment facility as fugitive condensate. While the facility is an important point source of VOC and BTEX, the magnitude of emissions is uncertain. Overall, this data suggests that water treatment operations may have a significant influence on ambient VOC composition and on  $\text{O}_3$  formation.

### 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 3× and 10× 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). 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 ratios of light hydrocarbons are relatively constant, ambient mixing ratios showed considerable variability, reflecting the local influence of 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 485.1 and 11.3 ppbv, respectively, were observed. Similarly, measurements ~ 300 m downwind of flow back

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operations at Mesa South Loop (Table S2) showed fugitive natural gas and condensate signatures with ethane and toluene up to 179.4 and 201.6 ppbv, respectively.

During 2011/12 twelve surveys of 24 h or three-day duration were performed at the 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 the dominance of alkanes to the total speciated NMHC mass (C<sub>2</sub> to C<sub>8</sub>) 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 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). Inventory data for the winter of 2011 estimates that over 80 % of Pinedale Anticline BTEX production emissions are from dehydration units. Since dehydration emission sources are widely dispersed throughout the Pinedale 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 are 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 2011 as zero for BTEX (WDEQ, 2014a). While the underlying causes of elevated BTEX on the Pinedale Mesa are uncertain, the influence of a water treatment facility in the Boulder Crest area is evident. Omission of water treatment and completions in inventories could be a significant oversight.

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

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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 t of VOC and 99 % of the 68 t 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 O<sub>3</sub> formation

O<sub>3</sub> episodes at both Boulder sites are associated with high total NMHC mixing ratios. Despite being located only 5 km apart, peak O<sub>3</sub> differences of > 50 ppbv were evident on both 1 and 2 March 2011 (Fig. 3). These episode days are the least impacted by factor 3 at BSR. The BLDR site is located 7.5 km from the water treatment facility at a heading of 190° (Fig. 1). It is possible that BLDR was impacted by emissions from the facility on these days. The large differences in maximum O<sub>3</sub> mixing ratio at the two sites together with the observed hour by hour variations, indicates the localized nature of O<sub>3</sub> production and transport and the difficulties of modeling O<sub>3</sub> 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).

Figure 10 shows time series plots of the total OH reactivity of each PMF factor with the NO<sub>x</sub> and O<sub>3</sub> mixing ratios, for four representative O<sub>3</sub> 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  $k_{\text{OH}}$  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<sup>-1</sup>) for 2 March 2011, 0–20 (s<sup>-1</sup>) for 5 and 15 March 2011 and 0–40 (s<sup>-1</sup>) for 18 February 2011. Spiking of OH reactivity in Fig. 10 is most prevalent for factor 3. Individual rate coefficient ( $k_{\text{OH}}$ ) values are listed in Table S9. Figure S8 shows similar plots for all episode days.

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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  $\sim 2\%$  and  $\sim 5\%$  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  $k_{\text{OH}}$  values. Factor 3 reactivity contributions are 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  $\text{O}_3$  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  $\text{O}_3$  formation cannot be directly correlated with OH reactivity and that NMHC species are mixed into the air parcels after  $\text{O}_3$  has been formed.

On 18 February,  $\text{NO}_x$  levels are somewhat higher than usual so that accumulated  $\text{O}_3$  is reduced before and after sunrise. A secondary spike in  $\text{O}_3$  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 2 March 2011, when  $\text{O}_3$  peaks some 50 ppbv higher at BLDR than at BSR, as noted in Fig. 3. Again, as on 18 February 2011, an increase in  $m + p$ -xylene late in the day, from 0.5 to 5.1 ppbv, coincides with an observed  $\text{O}_3$  increase in early evening. The influence of two peak reactivity contributions from factor 3 on 5 March 2011 occur when  $m + p$ -xylene mixing ratios increase from 1.0 to 7.8 ppbv at 12:00 MST and then, after declining, increase from 3.0 to 16.0 ppbv at 15:00 MST. On 15 March 2011 factor 3 spikes and there is an associated increase of  $m + p$ -xylene from 0.4 to 12.3 ppbv at 13:00 MST. Each of these elevated factor 3 contributions coincide with a measured spike in  $\text{O}_3$ .

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In summary, the time series plots in Fig. 10 (and Fig. S8) demonstrate that factor 3 emission sources releasing condensate range NMHC can have a significant effect on O<sub>3</sub> 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 O<sub>3</sub> 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 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 18:00MST time periods, one on 20 February when both O<sub>3</sub> and factor 3 contributions were low, and one on 18 February, during the O<sub>3</sub> episode illustrated in Fig. 10. The listed values also lead to the conclusion that neither CO nor CH<sub>4</sub> are important contributors to OH reactivity during O<sub>3</sub> episodes.

Wintertime O<sub>3</sub> episodes in the UGRB and the Uintah Basin share many important common characteristics (Oltmans et al., 2014). Episodic O<sub>3</sub> production in both basins is associated with high NMHC levels and moderate NO<sub>x</sub>. A key difference is that unlike the Uintah basin, O<sub>3</sub> in the UGRB can be spatially highly variable with large gradients over small distances. In the UGRB, our results show that 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).

## 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 a significant reduction in ambient total NMHC mixing ratios

resulted in a lack of O<sub>3</sub> episodes. During 2011, numerous localized O<sub>3</sub> episodes were evident in the Boulder area of the UGRB, sometimes with significant gradients in O<sub>3</sub> mixing ratios over relatively short distances.

Total NMHC mixing ratios are dominated by compounds associated with fugitive emissions of natural gas and condensate. C<sub>2</sub> to C<sub>4</sub> alkanes and C<sub>7</sub> to C<sub>8</sub> 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 sources profiles, in particular, for sources related to O & NG activities. In addition to fugitive natural gas, factor 2 includes emissions from 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.

Surveys of speciated NMHC within the UGRB reveal fugitive emission of natural gas to be the dominant source of both methane and C<sub>2</sub> to C<sub>4</sub> 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 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.

**The Supplement related to this article is available online at doi:10.5194/acpd-14-24943-2014-supplement.**

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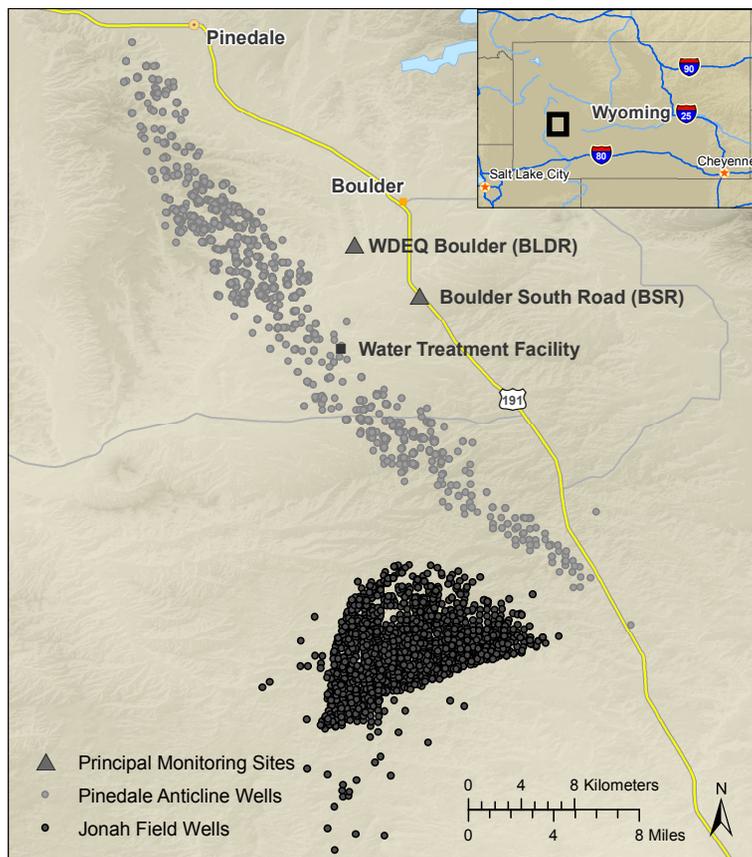
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**Table 1.** Speciated NMHC measured with the Perkin Elmer Ozone Precursor Analyzer.

Alkane	Alkene (& Alkyne)	Aromatic
ethane	ethene (ethylene)	benzene
propane	propene (propylene)	toluene
butane ( <i>n</i> -butane)	trans-but-2-ene ( <i>t</i> -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 ( <i>t</i> -2-pentene)	1,2,4-trimethylbenzene*
2-methylpentane ( <i>i</i> -hexane)	cis-pent-2-ene ( <i>c</i> -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.



**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.

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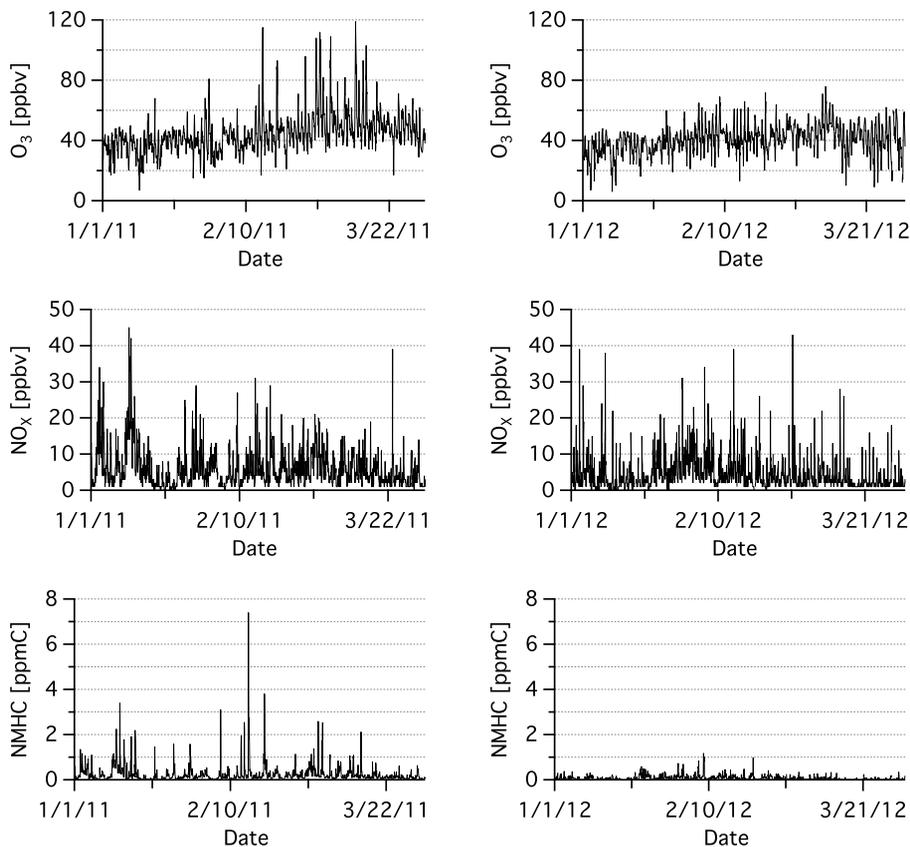
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**Figure 2.** Time series of O<sub>3</sub>, NO<sub>x</sub> and NMHC at Boulder South Road (BSR) for the period January through March during 2011 and 2012.

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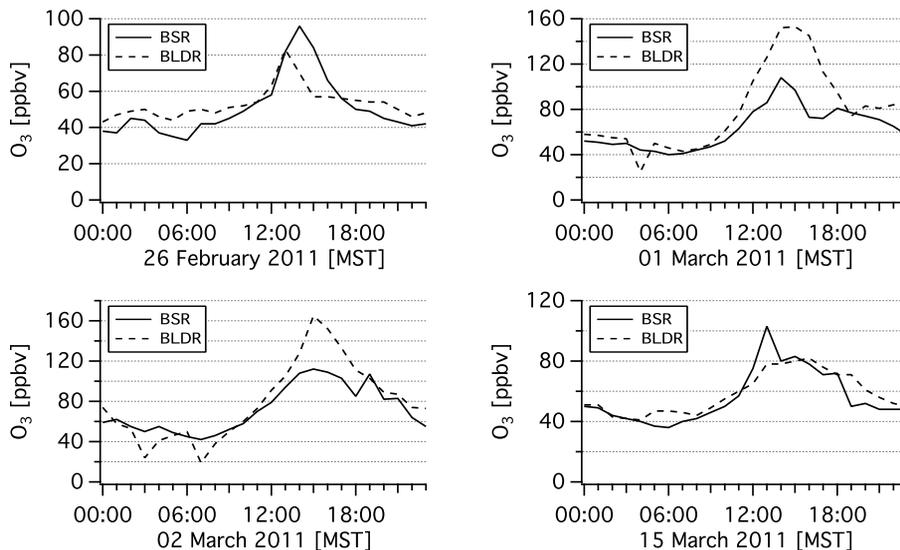
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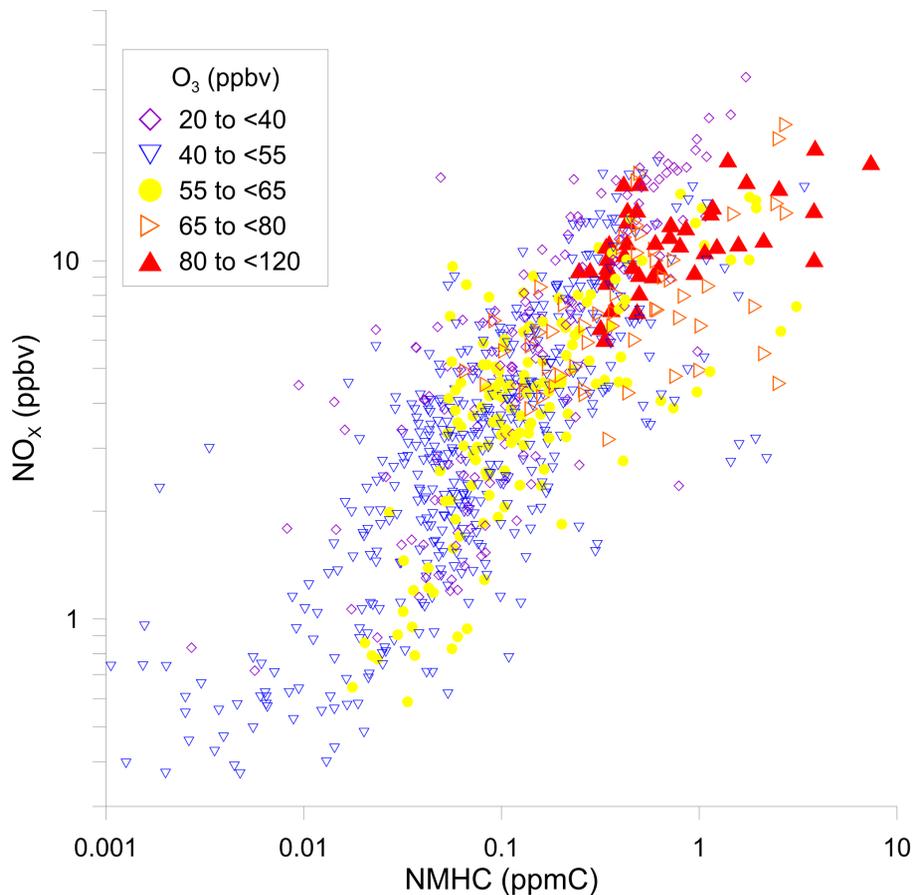
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**Figure 3.** O<sub>3</sub> mixing ratios during 4 episodes at Boulder sites February to March 2011.

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**Figure 4.** O<sub>3</sub>, NMHC and NO<sub>x</sub> during daytime (11:00 to 20:00 MST) for the period January to March 2011 at Boulder South Road (BSR).

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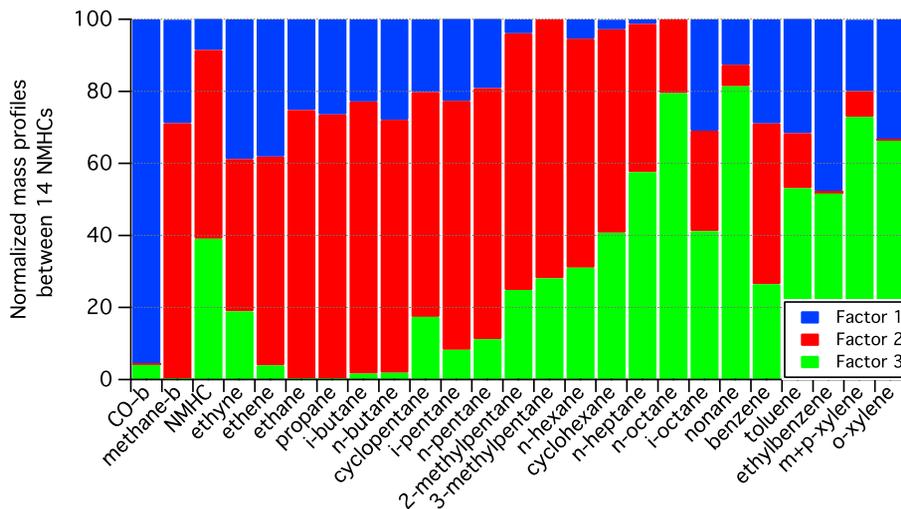
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**Figure 5.** Percentage contribution of PMF factors to the average mixing ratio of each analyzed pollutant from the whole sampling period at Boulder South Road (BSR).

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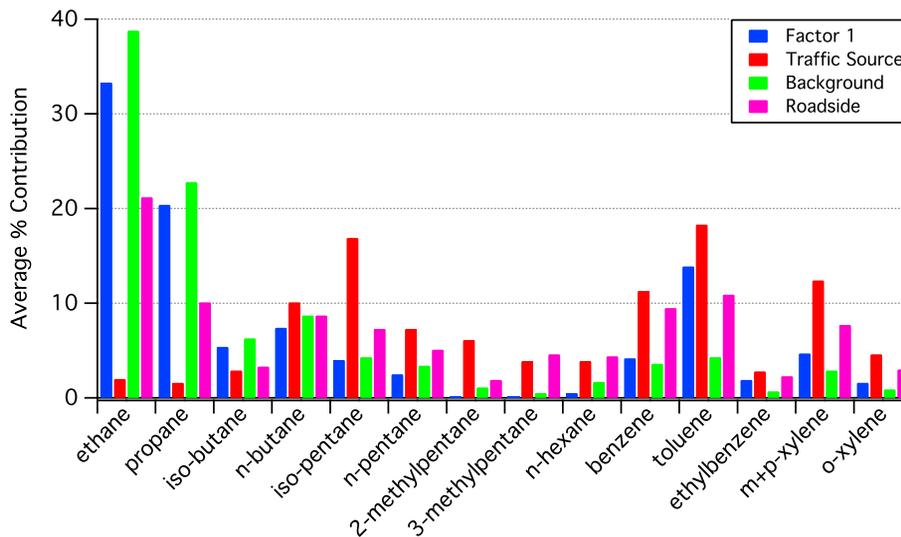
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**Figure 6a.** Comparison of factor 1 with emission source profiles as percentage contribution by mass for selected NMHC.

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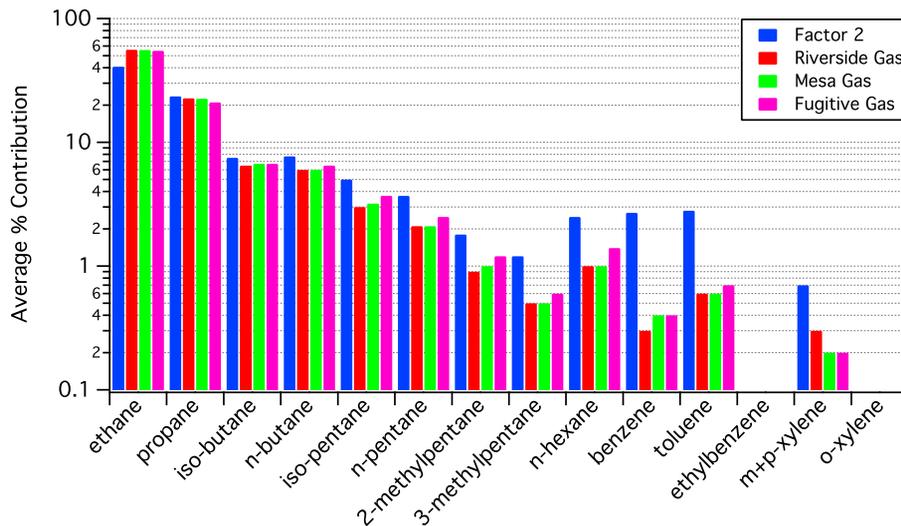
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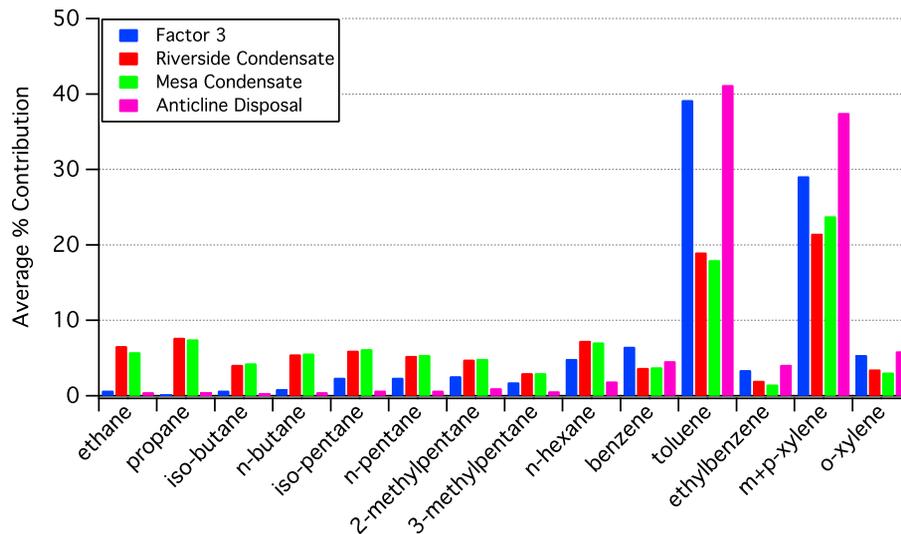
**Figure 6b.** Comparison of factor 2 with emission source profiles as percentage contribution by mass for selected NMHC.

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

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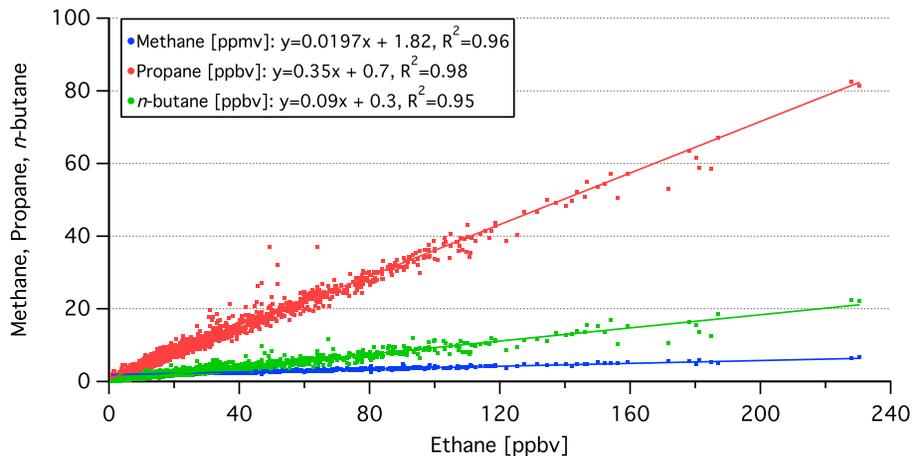
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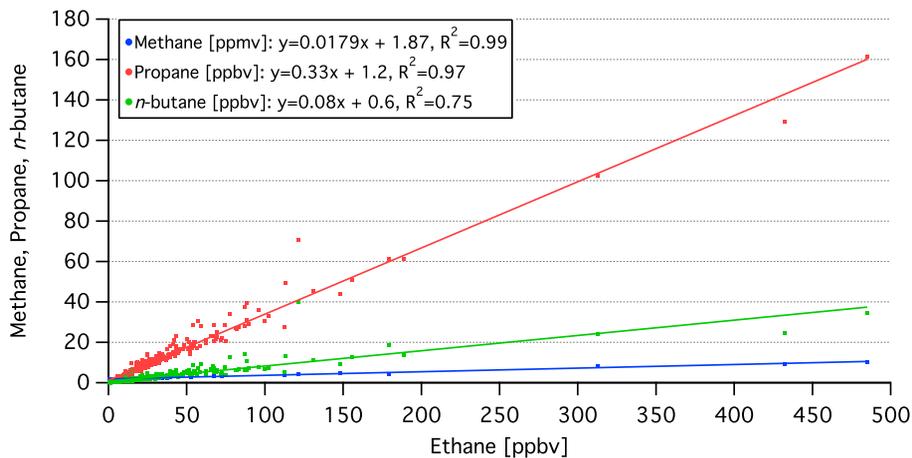
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**Figure 7.** Correlation of methane, propane and *n*-butane with ethane at Boulder South Road (BSR) from 2010 to 2011.

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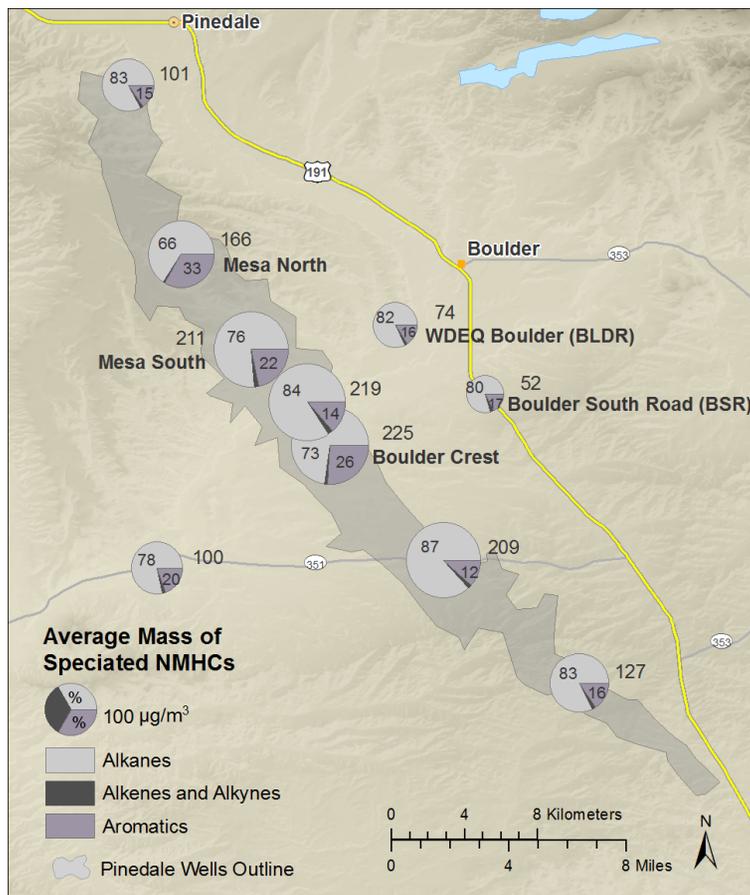
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**Figure 8.** Correlation of methane, propane and *n*-butane with ethane for locations within and around the Pinedale Anticline during 2010–2013 surveys.

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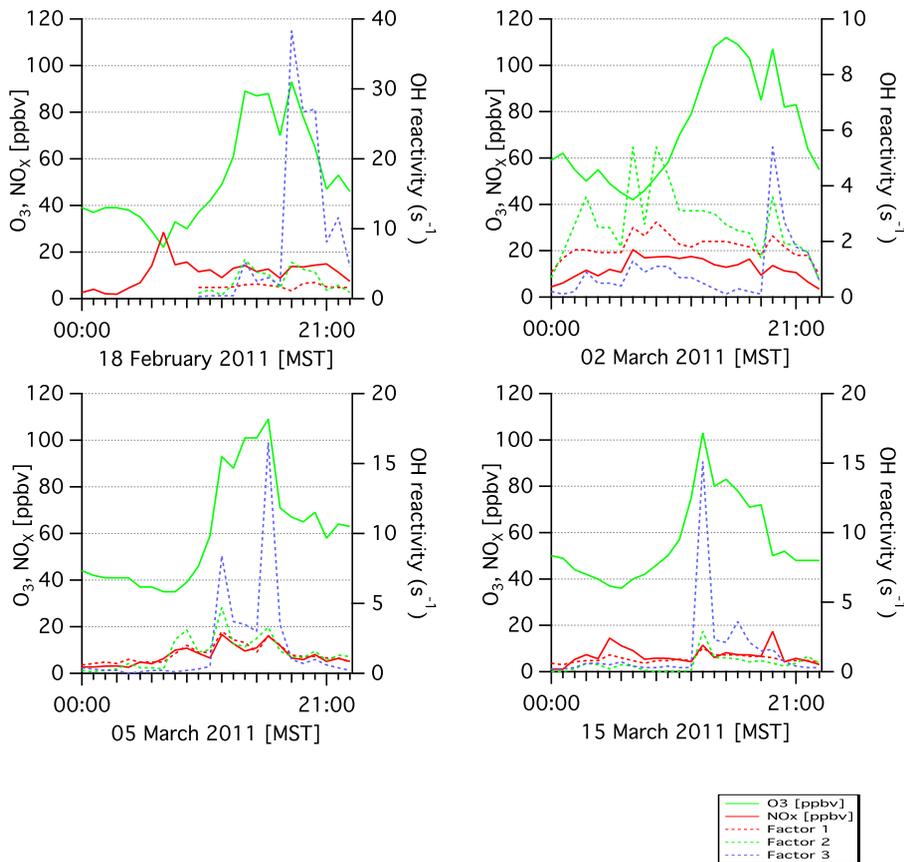
**Figure 9.** NMHC class distributions for 2011–2012 surveys at 10 sites within and around the Pinedale Anticline.

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**Figure 10.** Relationship of PMF factor OH reactivity, NO<sub>x</sub> and O<sub>3</sub> during selected episodes at Boulder South Road (BSR).

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