



Photochemical aging
of volatile organic
compounds

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Photochemical aging of volatile organic compounds associated with oil and natural gas extraction in the Uintah Basin, UT, during a wintertime ozone formation event

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Abstract

High concentrations of volatile organic compounds (VOCs) associated with oil and natural gas extraction were measured during a strong temperature inversion in winter of 2013 at a rural site in the Uintah Basin, Utah. During this period, photochemistry enhanced by the stagnant meteorological conditions and concentrated VOCs led to high ozone mixing ratios (150 ppbv). A simple analysis of aromatic VOCs measured by proton-transfer-reaction mass-spectrometry (PTR-MS) is used to estimate (1) VOC emission ratios (the ratio of two VOCs at the time of emission) relative to benzene, (2) aromatic VOC emission rates, and (3) ambient OH radical concentrations. These quantities are determined from a best fit to VOC:benzene ratios as a function of time. The main findings are that (1) emission ratios are consistent with contributions from both oil and gas producing wells, (2) the emission rate of methane ($27\text{--}57 \times 10^3 \text{ kg methane h}^{-1}$), extrapolated from the emission rate of benzene ($4.1 \pm 0.4 \times 10^5 \text{ molecules cm}^{-3} \text{ s}^{-1}$), agrees with an independent estimate of methane emissions from aircraft measurements in 2012, and (3) calculated daily OH concentrations are low, peaking at $1 \times 10^6 \text{ molecules cm}^{-3}$, and are consistent with Master Chemical Mechanism (MCM) modeling. The analysis is extended to photochemical production of oxygenated VOCs measured by PTRMS and is able to explain daytime variability of these species. It is not able to completely reproduce nighttime behavior, possibly due to surface deposition. Using results from this analysis, the carbon mass of secondary compounds expected to have formed by the sixth day of the stagnation event was calculated, then compared to the measured mass of primary and secondary compounds. Only 17% of the expected secondary carbon mass is accounted for by gas phase, aerosol, and snow organic carbon measurements. The disparity is likely due to substantial amounts of unquantified oxygenated products.

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1 Introduction

Natural gas, crude oil, and natural gas liquids are major fuel sources – accounting for 54 % of 2013 US domestic energy production – and extraction of these resources has been rising substantially since the mid 2000's (US Energy Information Administration, 2014). This activity is associated with a range of possible environmental issues. Emissions due to extraction can: increase atmospheric concentrations of methane, a greenhouse gas (Miller et al., 2013; Brandt et al., 2014); directly impact local air quality through release of air toxics (Moore et al., 2014; Adgate et al., 2014); and contribute to photochemical ozone formation (Schnell et al., 2009; Edwards et al., 2014; Carter and Seinfeld, 2012). Many scientific aspects of these processes are uncertain. Emissions budgets of methane and other VOCs are poorly constrained and frequently do not agree with inventory estimates (Brandt et al., 2014; Miller et al., 2013). Many variables can affect the composition of emissions, including well life-cycle stage, extraction techniques, whether the well is producing oil or gas, and diverse infrastructure/equipment components (Moore et al., 2014; Litovitz et al., 2013; Allen et al., 2013). Wintertime ozone events, while sharing some similarities with ozone formation typically seen in urban areas during the summer, occur in different meteorological and chemical conditions and have attracted several recent measurement and modeling investigations (Schnell et al., 2009; Kotamarthi and Holdridge, 2007; Carter and Seinfeld, 2012; Edwards et al., 2013, 2014).

The Uintah Basin, located in northeastern Utah, is a region of intense oil and natural gas extraction activity. Approximately 4000 active oil-producing and 6500 gas-producing wells are located in a 10 000 km² area, with an additional 1000 wells added each year (Utah Oil and Gas, 2014). In January and February of 2012–2014, a suite of chemical and meteorological instrumentation was deployed at Horse Pool, a remote site in the eastern part of the basin. Little active photochemistry was observed in 2012, but in 2013 ground snow cover was accompanied by several sustained periods of strong temperature inversion. Temperature inversions trap ozone precursors emitted by

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oil and natural gas activity (VOCs and NO_x) and ozone close to the surface. Increased actinic flux from reflective snow cover contributes to heightened ozone-producing photochemistry (Edwards, 2014). The gradual buildup of VOCs and ozone during a several day period of these conditions can lead to very high mixing ratios – in this case, up to 5 ppmC non-methane hydrocarbon and 150 ppb ozone. VOCs are a fundamental component of the photochemistry that occurred during these events, and so it is important to quantify (1) the rate at which VOCs are emitted from primary sources (“emission rate”), (2) the source composition of the VOC mixture (“emission ratios”), and (3) the degree of VOC oxidation.

In this paper, we analyze the photochemical aging of VOCs during an ozone formation period in 2013. We first examine primary, aromatic VOCs with a method that considers reaction with OH and constant primary emission. This analysis provides information on the emission rate and emission ratios of these VOCs, and the typical daily concentration of OH. We next investigate oxygenated VOCs with a method that includes production and loss via OH chemistry and loss to photolysis. This approach identifies oxygenated VOCs with substantial primary sources and suggests rates of carbonyl formation from photochemistry. Finally, we calculate the organic carbon mass balance of primary and product species. This defines overall VOC speciation and determines the fraction of product species measured with the Horse Pool instrumentation.

2 Methods

2.1 Measurement site and instrumentation

The Horse Pool site is located in the central eastern part of the Uintah Basin, approximately 30 km south of Vernal, Utah. Meteorological, gas, and particle-phase measurements were deployed concurrently at the site from 15 January–29 February 2012, 23 January–22 February 2013, and 15 January–13 February 2014. Data referenced in this paper are primarily from a proton-transfer-reaction mass-spectrometer (PTR-MS),

deployed in both 2012 and 2013, and a gas chromatograph with flame ionization detection (GC-FID), deployed in 2013. Measurements from 2014 are not discussed in this analysis.

PTR-MS uses chemical ionization with H_3O^+ ions to selectively detect VOCs (de Gouw and Warneke, 2007). The technique is particularly sensitive to aromatic and small oxygenated VOCs, but cannot detect small alkanes due to their low proton affinity. The instrument deployed at Horse Pool uses a quadrupole mass filter with unit mass resolution that scans through a set of selected ions every 38 s. Data are averaged to a 1 min time scale. Calibrated measurement accuracy is generally better than 20 %, with a precision of 10 %. The instrument is not able to distinguish between isomers; e.g. a measurement of C8 aromatics comprises the sum of ethylbenzene, o-, m-, and p-xylenes. Comparison with a high-resolution PTR- time-of-flight spectrometer operated by the University of Wyoming (Warneke et al., 2015) indicates negligible contribution from isobaric compounds (e.g., benzaldehyde).

The GC-FID deployed at Horse Pool resolves C2–C7 saturated and unsaturated hydrocarbons. Ambient air passes through water and carbon dioxide traps, then into a liquid nitrogen cryogenic VOC trap. VOCs are captured in the cryogenic trap for five minutes every half hour. After the five-minute sampling period, compounds are injected onto a 50 m $\text{Al}_2\text{O}_3/\text{KCl}$ PLOT column and analyzed using flame ionization detection. The accuracy and precision are dependent on compound and sample flow rate, but are generally < 20 and < 5 %, respectively. The instrument has been previously described in more detail by Kuster et al. (2004).

Other measurements used in this paper include gas-chromatography mass spectrometry (GC-MS) operated in 2012 (Gilman et al., 2010), methane cavity ring-down spectroscopy (CaRDS, Picarro) operated in 2013 (Crosson, 2008), organic aerosol via quartz filter collection/thermal desorption in 2013 (Bates et al., 2004), snow organic carbon using a Shimadzu TOC-VCSH instrument in 2013, and organic peroxy nitrate (PAN) species by chemical ionization mass spectrometry (Slusher et al., 2004). Further details on sampling methods and conditions, meteorological mea-

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surements, and calibrations are described in a summary report (Uintah Basin: 2013 Winter Ozone Study: Final Report; available at <http://www.deq.utah.gov/locations/U/uintahbasin/ozone/strategies/studies/UBOS-2013.htm>).

2.2 Data treatment

5 A stagnation event associated with high levels of ozone formation occurred from 29 January to 10 February 2013. A subset of this period, 31 January 2013 20:48 LT through 8 February 2013 05:29 LT, is analyzed here (Fig. 1). This period captures the majority of the ozone formation event, is characterized by a strong temperature inversion, and avoids periods of higher wind on 31 January and 8 February. Selecting these
10 meteorological conditions minimizes changes in VOC concentrations and ratios due to mixing into or out of the basin.

Primary hydrocarbons and oxygenated compounds investigated are listed in Table 1. The majority of analysis was applied to compounds measured by PTR-MS. The fast time resolution of this instrument (1 min) allows the separation of plumes of VOCs from nearby sources from the more regionally widespread, accumulated emissions in the basin. Additionally, restricting analyzed compounds to a single instrument helps eliminate instrumental variation. C6–C10 aromatic VOCs were selected for analysis because they have readily identifiable parent masses, they are sensitively detected by PTR-MS, and have a relatively wide range of reactivity with OH ($k_{\text{OH}} = 1.22 \times 10^{-12}$ to
15 $56 \times 10^{-12} \text{ s}^{-1}$). Additional compounds from the GC-FID data set were used to investigate the balance of primary and secondary species.

Concentrations of VOCs during an inversion event displayed rapid, diurnal, and multi-day variability (Fig. 2). Some of this variability is attributable to meteorology (such as changes in boundary layer height during the day, or temporary shifts in wind direction
25 bringing pollution from nearby sources), and some to chemistry, but the relative contributions can be difficult to separate. Analysis of ratios of VOCs provides a way to isolate the effects of chemistry from meteorology. This is a common and flexible approach: applications have included determining the photochemical age of urban emis-

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sions (Roberts et al., 1984; de Gouw et al., 2005), quantifying halogen chemistry in arctic air (Jobson et al., 1994), and identifying contributions from oil and natural gas operations to ambient pollution (Gilman et al., 2013).

Measurements of primary compounds by PTR-MS showed frequent 1–3 min duration episodes with very high mixing ratios, at least 50 % higher than short-term average concentration. These spikes signify interception of plumes of un-aged emissions and are not representative of the bulk air composition at the Horse Pool site. An hourly running median was applied to separate longer-term variability from transitory primary emissions (Fig. 2). For consistency, an hourly running median was also applied to oxygenated compounds. The ratio of each VOC to benzene was then determined. Benzene is a well-calibrated compound with few interferences on the PTR-MS; additionally, good agreement with other instrumentation (GC-FID and PTR-ToF) at the site affords a high level of confidence in this measurement (Warneke et al., 2015).

3 Results and discussion

3.1 Primary compounds

Primary compounds are defined as those species that are directly emitted and not formed by photochemistry. The rate of change with time of a single, primary VOC can be written as

$$\frac{d[\text{VOC}]}{dt} = P_{\text{VOC}} - k_{\text{VOC}}[\text{OH}][\text{VOC}] - \sum D_i[\text{VOC}] \quad (1)$$

where P_{VOC} is the emission rate of the VOC and k_{VOC} is the rate constant for the reaction of the VOC with OH. P_{VOC} is a volumetric input with units of molecule $\text{cm}^{-3} \text{s}^{-1}$ and describes how direct emission increases observed VOC concentrations. The only chemical loss term included is reaction with OH, the major oxidizing radical in this environment. Previous modeling has suggested that VOC reactions with other radicals,

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such Cl⁻, were negligible in comparison to reaction with OH (Edwards et al., 2014). D_i are rate constants for first-order loss processes; e.g. deposition, dilution, photolysis, etc. If two VOCs, “A” and “B”, behave according to Eq. (1), we can derive the rate of change of their ratio ($[A]/[B]$) as follows:

$$\text{ratio}(t) = \frac{[A](t)}{[B](t)} \quad (2a)$$

Using the partial derivatives of $\text{ratio}(t)$ with respect to $[A]$ and $[B]$, the rate of change of the ratio is:

$$\frac{d(\text{ratio})}{dt} = \frac{1}{[B]} \frac{d[A]}{dt} - \frac{[A]}{[B]^2} \frac{d[B]}{dt} \quad (2b)$$

Then, substituting Eq. (1) for dA/dt and dB/dt , we arrive at:

$$\frac{d(\text{ratio})}{dt} = \frac{P_B}{[B]} (ER - \text{ratio}) + (\text{ratio})[\text{OH}](k_B - k_A) + \sum (\text{ratio})(D_{iB} - D_{iA}) \quad (2c)$$

The primary emission rate (P_B), emission ratio (ER), and the concentration of OH are unknown. The emission ratio ($ER = P_A/P_B$) is the ratio of two VOCs in fresh emissions (time $t = 0$) and is a measure of source composition. We consistently used benzene as the denominator in the ratio, so that $[B] = [\text{benzene}]$, P_B is the emission rate of benzene, ER is the emission ratio of a VOC to benzene, and so on. Meteorological data and the measured ambient mixing ratio of benzene were used to determine the number density of benzene ($[B]$) as a function of time. These values were referenced directly when applying Eq. (2c).

Application of this analysis to VOCs measured by PTR-MS using Eq. (2c) includes the following assumptions.

1. For each first-order loss process, rate constants are nearly identical for aromatic compounds ($D_{iA} = D_{iB} = D_i$). These loss processes include mixing out of the

reduces to

$$\frac{d(\text{ratio})}{dt} = \frac{P_B}{[B]} (\text{ER} - \text{ratio}) \quad (3)$$

This method, using only night-time data, reduces the number of free variables. It completely separates primary emission from OH chemistry. Additionally, it allows the use of C9 and C10 aromatics measurements, as the OH rate constants for these groups are not well constrained.

The measured ratios of C7, C8, C9, and C10 aromatics to benzene were described using a best fit of Eq. (3) to the data. The free parameters in this fit are P_B and ER. A best fit was determined separately for each of the four aromatic ratios, providing four, similar, independent estimates of P_B (Fig. 3) and four emission ratios to benzene (Table 2). We evaluate the fit by comparing emission ratios to literature values and the composition of plumes from nearby sources, and, second, by comparing emission rate to an independent estimate.

The derived emission ratios from this analysis represent an averaged source composition of all point sources contributing VOCs to well-mixed air. In Fig. 4, the derived emission ratios are compared to three other measurements of source composition in the Uintah Basin: (1) Mobile laboratory measurements taken at individual wellpads in 2012 (Warneke et al., 2014), (2) ambient measurements taken at Horsepool in 2012 (Warneke et al., 2015), and (3) 2013 VOC enhancement ratios in spikes above a 1 h running median (discussed above). These spikes are likely plumes of fresh emissions from nearby wellpads. The fastest-reacting C10 aromatic (1,2,4-trimethylbenzene) had a peak daytime chemical lifetime against OH of about 30 min. Seven other wellpads were within 500 m of the Horsepool site; given average wind speed (1.6 m s^{-1}), this corresponds to a 5 min transport time – much shorter than the chemical lifetime of any of the analyzed aromatic species. All three measurements are separated into gas-producing and oil-producing well contributions; in mobile lab data, by type of wellpad sampled; in Horsepool data, by correlation with wind direction (Warneke et al., 2014).

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There is a clear distinction between oil and gas sources. The difference grows with carbon number; i.e. gas producing-wells emit a lighter mixture of VOCs. Emission ratios suggested by our analysis suggest significant contribution from both oil and gas sources. In addition to the oil/gas distinction, there is a large range of variability in source composition of aromatic species. This variability is difficult to represent in bulk emissions estimates and models. Together with supporting evidence from aircraft that emissions were reasonably well mixed across the basin (Oltmans et al., 2014), our analysis provides an independent measure of average emissions composition.

The average benzene emission rate was $4.1 \pm 0.4 \times 10^5$ molecules $\text{cm}^{-3} \text{s}^{-1}$. To evaluate this emission rate estimate, we compare to basin-wide methane emission measurements conducted by aircraft in 2012 (Karion et al., 2013). To our knowledge this is the only recent top-down emissions estimate for the Uintah Basin. Karion et al. determined that basin-wide methane emissions were $55 \pm 15 \times 10^3$ kg h^{-1} . To compare a volume-normalized estimate (molecules benzene $\text{cm}^{-3} \text{s}^{-1}$) to the whole-basin estimate (kg methane h^{-1}), we need (1) the emission ratio of methane to benzene and (2) the total volume of the polluted layer during the 2013 ozone episode.

A strong correlation between methane and benzene is apparent from ground site measurements at Horse Pool in 2012 and 2013 (Fig. 5). Aircraft flask samples taken in 2013 suggest that the methane : benzene ratio is independent of location in the basin – it was similar in both the eastern gas field and western oil field (Oltmans et al., 2014). The methane : benzene emission ratio was approximated from 2012 measurements and 2013 plumes ($\text{ER} = 1330 \pm 80$ ppbv ppbv^{-1}).

The polluted volume of the basin was determined from frequent ozonesonde measurements at a number of locations in the basin, as well as aircraft profiles. They showed well mixed ozone concentrations up 1600–1700 m a.s.l. (100–200 m a.g.l. at Horsepool), above which mixing ratios decreased sharply (Oltmans et al., 2014). Taking the terrain of the basin into account, we then integrate the volume of the basin from the surface to the mixing height. The uncertainty in the basin wide methane emis-

sion estimate is dominated by the uncertainty in this volume, and we report the values determined from minimum and maximum polluted layer altitude (1600–1700 m).

Using the methane : benzene ratio and the mixing volume of the basin, we derive an emission rate of $(14 - 39) \times 10^3$ kg methane h^{-1} . This is lower than the Karion et al. estimate, but of the same magnitude. An inspection of well locations in the basin shows that a significant fraction (40–50 %) of wells lie outside the polluted layer (Fig. 6). An aircraft flux measurement would have likely included contributions from these wells, whereas our analysis only included wells emitting inside the isolated polluted volume. A linear extrapolation based on the number of wells inside and outside the polluted volume suggests an emission rate of $(27 - 57) \times 10^3$ kg methane h^{-1} , which overlaps with the Karion et al. value. Although this estimate is considerably less precise than the aircraft flux measurement, it does confirm that the best-fit values of benzene emission rate are plausible.

3.1.2 Concentration of OH radical

The full time series (both day and night) was analyzed over the buildup period, using Eq. (2c). The primary emission term (P_B) and the emission ratio were fixed as determined from the night best fits. The only remaining free variable is the concentration of OH.

The calculation requires OH rate constant (k_{OH}) for the aromatics. Measurements of C8 aromatics in 2013 were not isomerically resolved by PTR-MS and represent the sum of ethylbenzene and o-, m-, and p-xylenes. Speciated measurements of C8 aromatics by GC-MS were made in 2012, when photochemical aging of VOCs was less active and the bulk air composition more closely resembled primary emissions. The 2012 GC-MS measurements were used to compute a weighted average OH rate constant for the C8 aromatics group. The OH rate constants for individual species in this group are within a factor of 2.1 of the mean. The groups C9 and C10 aromatics contain a much larger number of isomers, with a wider variance in OH rate constants. Not all these isomers

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were measured by GC-MS in 2012, and some of the OH rate constants are unknown. Therefore, the group average rate constant could not be constrained in the same way.

To parameterize the diurnal variation in OH, we constrained OH to be proportional to solar actinic flux. It is well established that [OH] is strongly linearly correlated with UV light intensity (Hard et al., 1986; Rohrer and Berresheim, 2006). A best fit and an average value of OH was computed separately for both toluene and C8 aromatics according to Eq. (3) (shown in Fig. 3). Results are included in Table 2. The average of these two values was used as the concentration of OH in further analysis.

Using this [OH], the k_{OH} for C9 and C10 aromatics were allowed to vary. Best fits for the C9 and C10 aromatics were calculated and are shown in Fig. 3. The group average rate constants (Table 2) are within the range of values known for isomers of C9 and C10 aromatics. For C9 aromatics, the group average rate constant was determined to be $16.9 \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$; known values range from 5.3 (n-propylbenzene) to $56.7 \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (1,3,5-trimethylbenzene) (Atkinson and Arey, 2003). For C10 aromatics, the group average rate constant was determined to be $24.2 \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$; known values range from 4.5 (t-butylbenzene) (Atkinson and Arey, 2003) to $55.5 \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (1,2,4,5-tetramethylbenzene) (Aschmann et al., 2013). The average rate constant constrains group composition, and could be useful in future investigations of photochemical processing.

Knowledge of typical daily OH concentrations is crucial to understand photochemical processing of VOCs and ozone production. OH was not measured directly in 2013, but our analysis provides an estimate of OH exposure that is constrained by solar actinic flux and VOC measurements. OH peaked daily at 1×10^6 ($\pm 21\%$) molecule cm^{-3} , which is low compared to urban areas affected by photochemical smog with typical OH concentrations between $(5 - 10) \times 10^6 \text{ molecule cm}^{-3}$ (Shirley et al., 2006). We compare to an independent estimate of [OH] in 2013 using the Master Chemical Mechanism v.3.2 (MCM) framework (Edwards et al., 2014). The MCM OH estimate is generated using more than 12 000 explicit reactions comprising degradation schemes for nearly all hydrocarbons measured at the Horse Pool site and has been applied previously to

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photochemistry in the Uintah Basin (Edwards et al., 2014, 2013). The agreement between our model and the MCM estimate in peak daytime concentration is within a factor of 1.7 overall and differs by only 2 % on 5 February 2013 (Fig. 7). The agreement is especially good considering that OH values in our analysis are constrained by measured photolysis rates and a single scaling factor, and so cannot generate the multi-day trend seen in the MCM calculation. This excellent agreement substantiates the chemistry described by the MCM model.

3.2 Oxygenated compounds

Oxygenated compounds may also have photochemical sources. For these species, the change in concentration with time is controlled by the production rate via photochemistry, loss to reaction with OH, and first-order loss processes such as mixing, photolysis and deposition. The rate of change can be written similarly to Eq. (1):

$$\frac{d[\text{VOC}]}{dt} = \text{Yield} \cdot k_{\text{precursors}} [\text{OH}][\text{precursors}] - k_{\text{VOC}} [\text{OH}][\text{VOC}] - D [\text{VOC}] \quad (4)$$

Here [precursors] is the sum concentration of all precursor species, Yield is the fraction of reactions with OH that form the product compound, and $k_{\text{precursors}}$ is the weighted average OH rate constant of precursor species. Again, D represents first-order loss processes. The oxygenated species considered here are formaldehyde, acetaldehyde, acetone, 2-butanone (MEK), formic acid, and methanol.

As with Eq. (2c), the rate of change of the ratio of a photochemically produced compound to benzene is:

$$\frac{d(\text{ratio})}{dt} = \text{Yield} \cdot k_{\text{precursors}} [\text{OH}] \cdot R_{P_B} - (\text{ratio}) \cdot \left([\text{OH}] (k_{\text{prod}} - k_B) + J + \frac{P_B}{[B]} \right) \quad (5a)$$

$$= \lambda_f \cdot [\text{OH}] - (\text{ratio}) \cdot \left([\text{OH}] (k_{\text{prod}} - k_B) + J + \frac{P_B}{[B]} \right) \quad (5b)$$

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R_{P_B} is the ambient ratio of precursor species to benzene, k_{prod} and k_B are the OH rate constants of the product species and benzene, and J is the photolysis rate constant of the product species. Here we again assume that other first-order processes, mixing and deposition, are not significantly different between the oxygenated VOCs and benzene. We also assume that the only source of these species is photochemistry; i.e. they are not emitted directly from primary sources. Primary emission of methanol and formaldehyde is considered separately later in the analysis (below). On the other hand, most of these compounds contain a carbonyl functional group, and photolysis rates could be significant. J was set proportional to solar actinic flux and scaled to photolysis constants from the literature (values and literature sources are given in Table 3).

As the relative amounts of precursor species and their product yields were unknown, yield, $k_{\text{precursors}}$, and R_{P_B} were bundled into a single free variable, λ_f (formation rate constant). The term R_{P_B} requires further discussion. The analysis of primary compounds (above) shows that the ratios of C7–C10 aromatics to benzene are highly variable and depend on photochemical exposure. R_{P_B} , the ratio of precursor species to benzene, should also change over time. However, in applying Eq. (5b), we have simplified analysis by treating R_{P_B} as approximately constant. By volume, the dominant VOCs measured at Horse Pool were C1–C5 alkanes. These compounds react more slowly with OH than C7–C10 aromatics. Reaction with OH has a proportionally smaller effect on their concentrations, and indeed, ratios of these compounds to benzene show less diurnal variability (Fig. 8a). Despite how slowly these compounds react with OH, the very large concentration of these compounds means that they account for most of the reactions between OH and VOCs, and are the most important precursor compounds (Fig. 8b). We can therefore use the simplifying approximation of constant precursor : benzene ratio.

Again, the analysis was first applied to night data only. During the night, Eq. (5b) reduces to:

$$\frac{d(\text{ratio})}{dt} = -(\text{ratio}) \left(\frac{P_B}{[B]} \right) \quad (6)$$

Using Eq. (6), a best fit was calculated for acetaldehyde, formic acid, acetone, MEK, methanol, and formaldehyde (Fig. 9), providing six values of the primary benzene emission rate (P_B) (Table 3).

The best fit functions to acetone, acetaldehyde, formic acid, and MEK for nighttime data only were able to predict a decreasing trend in the ratio of VOC : benzene, but did not replicate the strong decrease in ratio towards the end of the night. Primary emission of benzene during the night could only account for a portion of the decrease, signifying an additional oxygenate removal process not included in Eq. (6). A possible candidate is increased deposition of oxygenates. Including a free first-order deposition variable did not significantly affect model output, suggesting a complex process increasing in strength during the night. One possibility is deposition on ice crystals. Surfaces, including the sampling inlet, typically gained a thick coating of ice rime during the night, creating additional surface area available for deposition. This process would also affect polar oxygenated species much more than primary hydrocarbons, consistent with the additional decrease in oxygenates not observed with aromatics. Because this process affected our sampling inlet, it is possible that oxygenate behavior during early morning is an inlet artifact rather than a significant basin-wide process. We removed rime ice from the sampling inlet early each morning, and other surfaces were typically free of rime by mid-morning (snow cover remained during the day).

The values of benzene emission rate derived from night-only best fit to acetone, acetaldehyde, formic acid, and MEK were slightly higher than estimates from primary compounds: 5×10^5 as opposed to 4×10^5 molecule $\text{cm}^{-3} \text{s}^{-1}$. This is consistent with an undetermined additional removal process. In the absence of an appropriate loss term, a best fit using Eq. (6) would artificially increase the benzene emission rate to reproduce the stronger downwards trend in ratio.

The diurnal behaviors of methanol and formaldehyde differ significantly from other species. The ratios of methanol and formaldehyde to benzene do not increase steadily during the day and do not decrease at night. Additionally, the values of primary benzene emission rate determined from methanol and formaldehyde are at least a factor of two

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smaller than values determined from any other compound. A plausible explanation for this behavior is primary emission of these two compounds. Methanol is used by the oil and natural gas industry in a variety of applications in the basin (Lyman, 2014) and direct emissions of methanol associated with this use are very high as witnessed by hourly average mixing ratios in the basin, which can build up to more than 200 ppbv. Primary sources of formaldehyde are less clear. Incomplete combustion and emission from dehydrators, separators, compressors, flares, oil pumps and processing plants have been suggested as sources, but are not well quantified in the Uintah Basin. In accordance with our findings, Edwards et al. (2014) left the option open for primary emissions of formaldehyde due to the inability of the MCM model to reproduce the ambient mixing ratios.

To investigate primary emission of methanol and formaldehyde we modified Eq. (6) in several ways. First, we added a term representing primary emission of oxygenates and determined best-fit values of benzene emission rate and oxygenate:benzene emission ratio. χ^2 values decreased insignificantly (-5% , methanol) and slightly (-22% , formaldehyde) and calculated values of primary benzene emission rate were unreasonable (8×10^5 and 1×10^6 molecules $\text{cm}^{-3} \text{s}^{-1}$ from the methanol and formaldehyde analysis, respectively). Next, we fixed the primary benzene emission rate to the value determined from the primary compounds analysis and determined emission ratios for methanol and formaldehyde only. Emission ratios of formaldehyde:benzene and methanol:benzene were 1.01 and 10.3. These values are slightly less than the ambient ratios, consistent with accumulation from both photochemistry and primary emission. However, the best fit still did not capture the majority of measurement variability and may not be accurately characterizing physical processes affecting methanol or formaldehyde. For instance, an emission source poorly correlated with benzene would not be well represented by Eq. (6).

Because of possible complex deposition of oxygenated species during the night, and primary emission of methanol and formaldehyde, emission rates derived from the analysis of these oxygenates are less likely to be accurate than those derived from

analysis of primary species. We elected to exclude night data from further analysis, and retain the primary benzene emission rate (P_B) determined from the primary compounds model. The fit of Eq. (5b) was then calculated for acetone, MEK, acetaldehyde, and formic acid, using daytime data (Fig. 9), to determine values of the formation rate constant (λ_f) for each compound (Table 3).

The best-fit of daytime oxygenate ratios is better able to explain the measurements, with R^2 values of 0.4 to 0.8 (Table 3). Values of the formation rate constant (λ_f) are plausible. For instance, the best-fit value of λ_f for acetone is $8.72 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. The main precursors of acetone present in the Uintah Basin were iso-butane and propane. The weighted average rate constant for reaction of iso-butane and propane with OH is $1.3 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and the mol ratio of these compounds to benzene was approximately 70. Assuming that all propane-OH and iso-butane-OH reactions formed acetone, the calculated λ_f for acetone is $9.1 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, which is very close to the best-fit calculated value. The high R^2 values and reasonable λ_f suggest that Eq. (5b) captures the most important daytime processes affecting acetone, acetaldehyde, MEK, and formic acid.

4 Organic carbon budget

In this section, we categorize VOCs as either primary (directly emitted) or secondary (enhanced by oxidative chemistry), and quantify the total organic carbon mass in each category. Using two complementary mass balance approaches, we show that one would expect to see more oxygenated species than were measured. Both approaches rely on conservation of organic carbon mass: when a primary compound is oxidized, the total mass of organic carbon does not change. This is true regardless if the molecule's structure changes, if it fragments into several smaller molecules, if subsequent reactions form higher generation products, or if it moves into a different reservoir (e.g. aerosol or snowpack).

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First, carbon mass concentration is conserved. The total organic carbon mass of primary compounds lost to oxidation must be equal to the total organic carbon mass gained by secondary compounds. To quantify this mass, we use the loss rate of a primary compound to oxidation:

$$\left. \frac{d(\text{primary VOC})}{dt} \right|_{\text{chemical}} = -k_{\text{primary VOC}} [\text{OH}] [\text{primary VOC}] \quad (7)$$

The amount of organic carbon lost from all primary species measured by PTR-MS and GC-FID (compounds listed in Table 1) during the stagnation event can be found by integrating Eq. (7) for each individual primary VOC, then summing the results over all primary VOCs. For completeness, methane (from CaRDS) was also included. [OH] was set to the values calculated above (Table 2). OH rate constants for C8, C9, and C10 aromatics were taken from Table 2, and OH rate constants for all other species were taken from Atkinson and Arey, 2003.

Because total carbon mass is conserved, the total carbon mass lost from primary species is equal to the total carbon mass gained by all secondary species. This value, about $3.7 \times 10^{-10} \text{ g C cm}^{-3}$ on day 6 of the stagnation event, is the calculated or expected mass of secondary species. Measured secondary species, including methanol, formaldehyde, formic acid, acetone, acetaldehyde, MEK, PAN species (peroxyacrylic nitric anhydride (APAN), peroxyacetic nitric anhydride (PAN), and peroxypropionic nitric anhydride (PPN)), organic carbon in snow, and $\text{PM}_{2.5}$ organic aerosol, only sum to $0.64 \times 10^{-10} \text{ g C cm}^{-3}$.

This gap between the calculated (expected) mass of secondary species and the measured mass of secondary species is a factor of 5.8 (Fig. 10). Other measurement and modeling studies of the Uintah Basin suggest that unquantified secondary species are responsible for a large part of this gap: many additional oxygenated VOCs were detected, but not quantified, by PTR-time-of-flight (PTR-ToF) mass spectrometry (Warneke et al., 2015), and MCM modeling indicates that carbonyl groups formed from higher-weight species (e.g. aromatics) were not only abundant but major drivers of ozone formation.

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Oxidation of quantified secondary species to CO and CO₂, or loss to mixing out of the basin are alternate explanations that could account for some of the disparity. Using a second carbon mass balance technique, we show that unquantified secondary species are an important factor. The second technique compares oxidation rates: the oxidation loss rate of primary species must be equal to the photochemical formation rate of secondary species. Neither of these processes is affected by higher-generation oxidation reactions or loss to mixing or deposition. A disparity between the carbon mass loss rate to oxidation of primary species and the formation rate of measured secondary species means that there must be other, unquantified, secondary species forming. Therefore, comparing oxidation and formation rates provides a way to determine if the mass disparity between calculated and measured secondary species is at least partly due to unquantified compounds.

The total oxidation rate of primary species was determined by applying Eq. (7) to each measured primary species, then summing over all primary species. The formation rate of quantified secondary species was determined using Eq. (4). The first term in Eq. (4), Yield · k_{precursors} [OH][precursors], is the formation rate of a secondary VOC. To clarify, this is the rate at which a secondary VOC is produced by oxidation chemistry, not the rate of net increase in mass (net = formation – loss). As in Eq. (5b), this can be simplified to

$$\left. \frac{d(\text{secondary VOC})}{dt} \right|_{\text{formation}} = \lambda_f [\text{OH}] [\text{benzene}] \quad (8a)$$

$$\lambda_f = \text{Yield} \cdot k_{\text{precursors}} \cdot \frac{[\text{precursors}]}{[\text{benzene}]} \quad (8b)$$

λ_f is the formation rate constant, and was (above) determined for acetone, acetaldehyde, formic acid, and MEK. The oxidation rate of primary compounds is a factor of two higher than the formation rate of acetaldehyde, acetone, formic acid, and MEK (Fig. 11). This large disparity indicates a substantial presence of unquantified sec-

ondary species. The formation rate of these species is $3.2(\pm 1.2) \times 10^{-16} \text{ g C cm}^{-3} \text{ s}^{-1}$ on average or $60(\pm 23) \text{ ppbv C day}^{-1}$.

5 Conclusions

High concentrations of organic carbon species (up to 5 ppm nonmethane carbon) associated with oil and natural gas extraction were measured at a rural site in the Uintah Basin, Utah, during the winter of 2013. A relatively simple analysis was applied to measurements of aromatic species by PTRMS to explain variation in their ratios due to reaction with OH and primary emission. The analysis was extended to measurements of small oxygenated compounds by PTRMS, with the goal of explaining ratios of these compounds to benzene in terms of production and loss via OH chemistry, photolysis, and primary emission. Results of both analyses were used to develop a carbon mass budget, to determine the relative fractions of carbon in primary and secondary species.

The analysis of primary aromatic species provided plausible estimates of [OH], aromatic VOC emission ratios, and benzene emission rate. The daily peak of [OH] was low ($1 \times 10^6 \text{ molecule cm}^{-3}$), consistent with MCM modeling and highlighting the unusual oxidation chemistry occurring in this region. Emission ratios indicate source contributions from both oil and gas wells. Using measured correlation between benzene and methane, the benzene emission rate ($4.1 \pm 0.4 \times 10^5 \text{ molecule cm}^{-3} \text{ s}^{-1}$) was extrapolated to a basin-wide methane emission rate ($27 - 57 \times 10^3 \text{ kg methane h}^{-1}$) in order to compare with an independent top-down estimate from aircraft. Although the large uncertainties associated with the extrapolation of the benzene emission rate to a basin-wide methane emission rate preclude the use of our estimate as an assessment of regulatory inventories, the agreement with the 2012 aircraft methane flux value supports the plausibility of our analysis. Our analysis was not able to completely explain night time variability of small oxygenated VOCs, whose behavior may be affected by primary emission (methanol and formaldehyde) and deposition to ice surfaces. However, a best fit to day time data provided values of carbonyl formation rate consistent

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with expected formation rates from known precursors. The calculated carbon budget indicated that a large fraction of secondary carbon mass (83 %, or $3 \times 10^{-10} \text{ g C cm}^{-3}$) is unaccounted for. A comparison of measured carbonyl formation rates to primary compound oxidation rates indicated substantial presence of unquantified secondary species.

The analysis method outlined here is relatively simple, including just a few terms for basic chemistry and primary emission. It uses little computer processing power and references only measurements that can be made with standard VOC instrumentation. Despite its simplicity, this method is able to provide considerable information on VOC chemistry, including source composition and emission rates, the concentration of OH, and measurement thoroughness. Best-fit values are very reasonable and support findings from more complicated chemical models. A similar analysis could be applied to investigations of other regions where VOC pollutants are geographically or meteorologically contained, especially where detailed chemical measurements are unavailable or not possible.

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Table 1. Compounds analyzed.

PTR-MS	OH rate constant $10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Average mixing ratio ppbv (1σ)	
Primary compounds			
Benzene	1.22	3.30	(1.92)
Toluene	5.63	4.00	(2.76)
C8 aromatics	16.4 ^a	1.74	(1.36)
C9 aromatics	16.9 ^a	0.365	(0.271)
C10 aromatics	24.2 ^a	0.071	(0.055)
Oxygenated compounds			
Formaldehyde	9.37	3.71	(1.49)
Acetaldehyde	15.0	4.27	(2.39)
2-butanone (MEK)	1.22	2.81	(1.69)
Acetone	0.17	7.97	(4.69)
Formic acid	0.37 ^b	2.56	(1.43)
Methanol	0.94	44.9	(33.4)
GC-FID			
Primary compounds			
Ethane	0.248	300	(169)
Propane	1.09	140	(78.6)
n-butane	2.36	48.0	(26.9)
2-methylpropane	2.12	30.3	(17.1)
n-pentane	3.80	18.8	(10.5)
2-methylbutane	3.60	20.9	(11.8)
2,2-dimethylpropane	0.825	0.306	(0.181)
n-hexane	5.20	8.32	(4.65)
Sum of 2- and 3-methylpentane	5.20	6.62	(3.99)
2,2-dimethylbutane	2.23	0.467	(0.294)
Methylcyclopentane	6.90	3.65	(2.27)
n-heptane	6.76	4.00	(2.30)
Methylcyclohexane	9.64	6.74	(4.17)
Ethyne	0.88	0.796	(0.40)
Ethene	8.52	2.05	(1.06)
Propene	26.3	0.171	(0.0724)

^a Rate constants determined in this work.

^b Anglada, 2004.

All other OH rate constants from Atkinson and Arey (2003).

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Table 2. Primary compound results.

Compound	Emission ratio to benzene by mol	Benzene emission rate $10^5 \text{ molecule cm}^{-3} \text{ s}^{-1}$	[OH] avg. $10^5 \text{ molecule cm}^{-3}$	OH rate constant $10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	R^2 – full time series best fit
Toluene	1.5	4.5	2.66	5.63	0.242
C8 aromatics	0.82	4.1	1.86	16.4	0.421
C9 aromatics	0.18	3.9		16.9	0.614
C10 aromatics	0.042	3.8		24.2	0.273

Table 2 includes results from the night-data only best fit (emission ratios, benzene emission rate), and the full time series (including both day and night) best fit ([OH], k_{OH} , and R^2).

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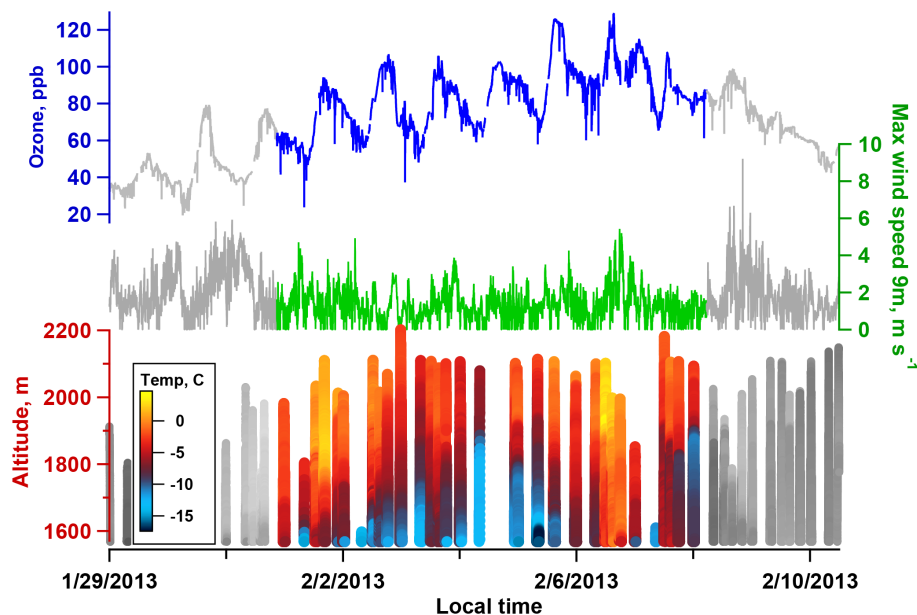


Figure 1. Ozone formation event and analysis period selection. The modeled period (colored) was selected to avoid high wind events on 31 January and 8 February (center) and include strong temperature inversions (bottom) to minimize mixing of VOCs in or out of the basin. Meteorological data courtesy of NOAA Physical Sciences Division. Temperature data from tethered balloon sonde operated by NOAA Global Monitoring Division.

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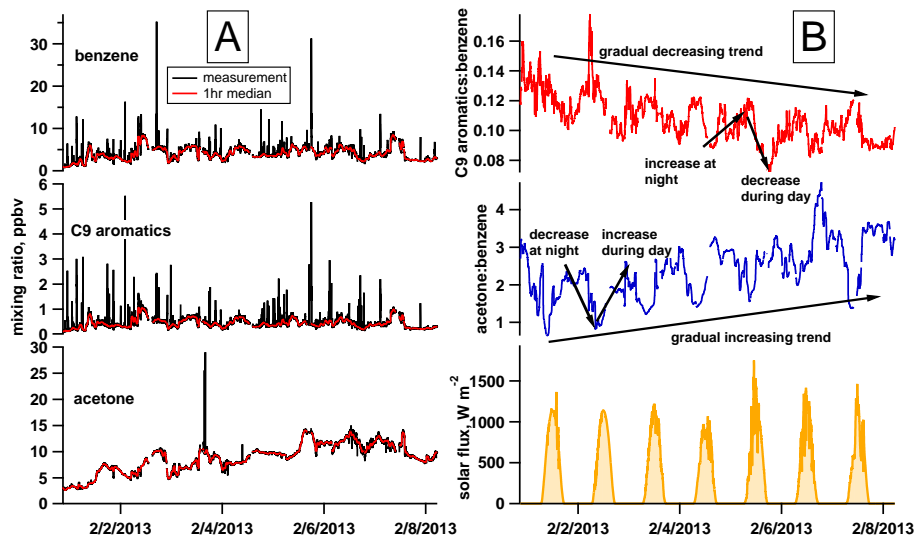


Figure 2. Description of trends in VOC concentrations and ratios. **(a)** Mixing ratios of benzene, C9 aromatics, and acetone (black), and a one hour running median to isolate spikes (red). **(b)** Ratios of C9 aromatics (top) and acetone (center) to benzene. Sunlight intensity is shown beneath. The spikes visible in panel **(a)** have been removed to isolate longer-term trends in VOC behavior (discussed in text).

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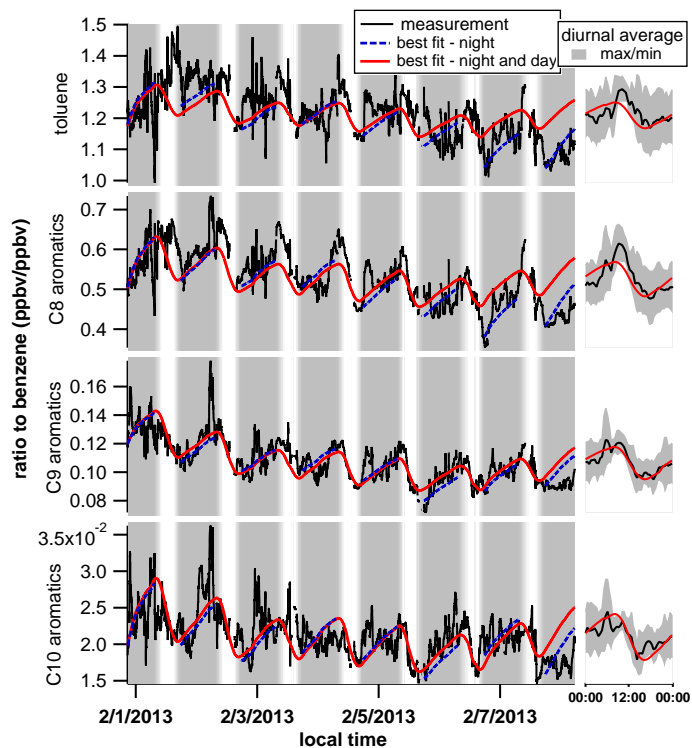


Figure 3. Aromatic compound ratios and best fit to night time data (blue) and both night and day data (red). The background is colored by sunlight intensity to distinguish day and night. For reproducibility, the initial ratio for each night was chosen from the 10th percentile of points during the first two hours of evening. In practice, best-fit parameters were largely insensitive to initial ratio, so long as the selected initial ratio was close to measurements during the early part of the night. A diurnal average is shown to the right.

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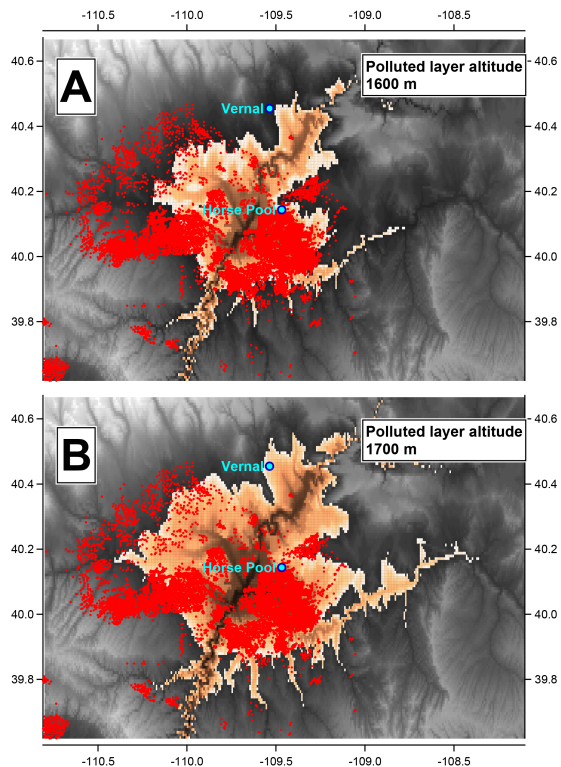


Figure 6. Topographical map of the Uintah Basin showing polluted region and well locations. Total relief is from 1398 to 3627 m a.s.l. The bright (tan) region shows the area of the polluted region assuming the polluted layer extends to 1600 (a) or 1700 m a.s.l. (b). Locations of producing oil and gas wells are marked in red.

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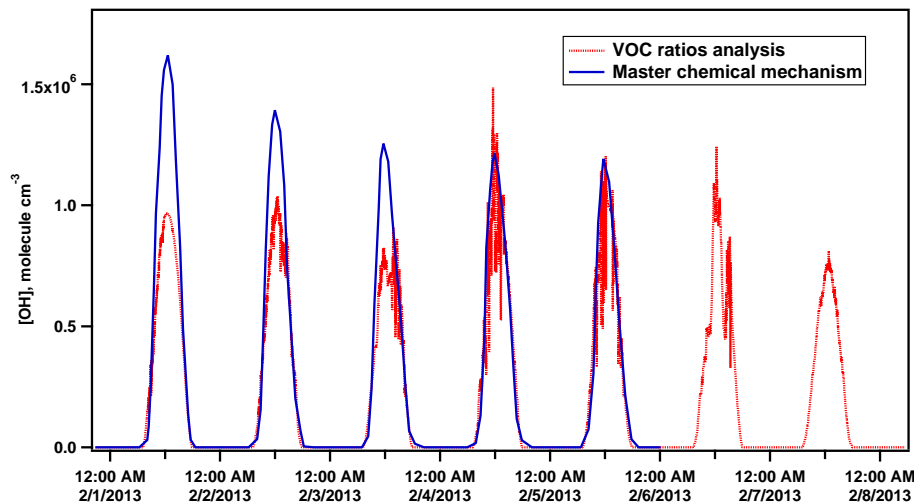


Figure 7. Comparison of OH with the Master Chemical Mechanism prediction. There is good agreement between the MCM OH and OH determined from our analysis.

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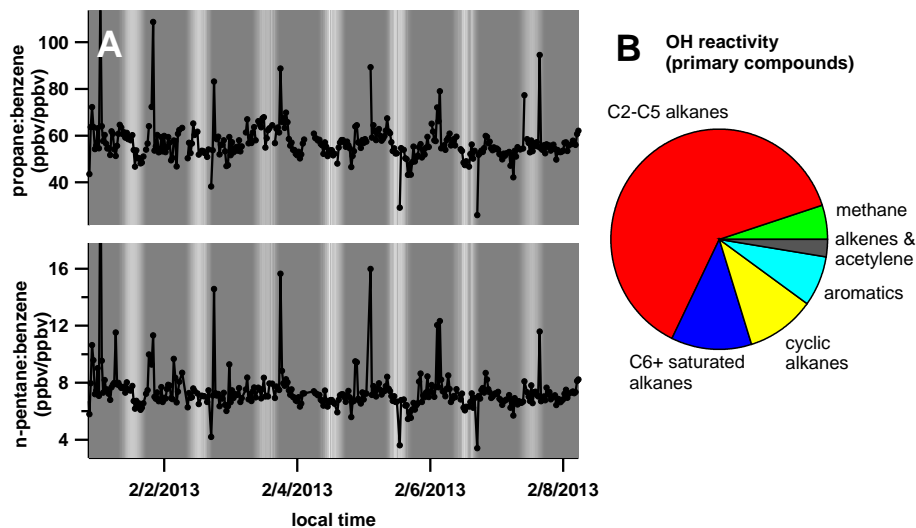


Figure 8. (a) Because of their slow reaction rates with OH, the ratios of C1–C5 alkanes to benzene did not have high diurnal variability and did not change substantially from beginning to end of the stagnation event (propane and n-pentane measured by GC-FID are shown as representatives). (b) However, because of their high mixing ratios, these species account for a large fraction (~ 70 %) of primary hydrocarbon-OH reactions.

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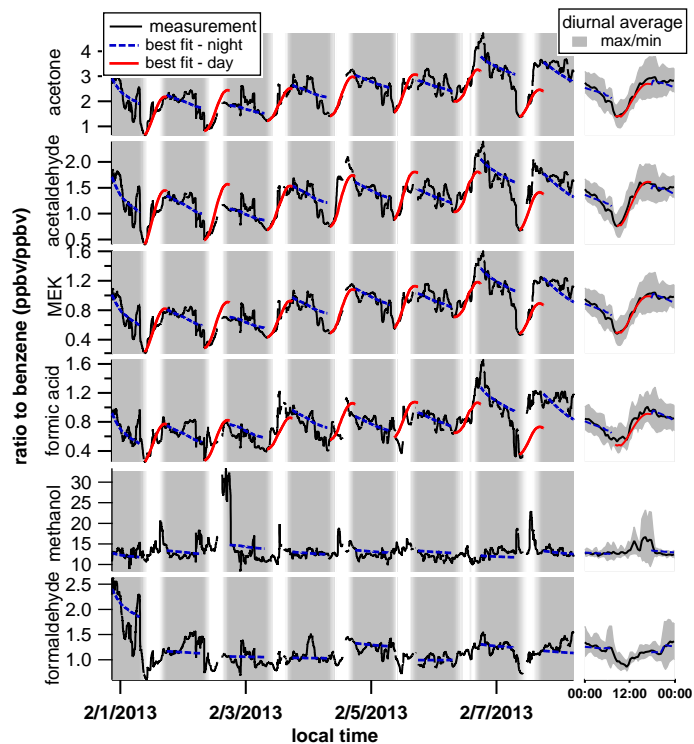


Figure 9. Analysis results for oxygenated compounds. Measured ratio is in black, night best fit in blue, and day best fit in red. The best fit is able to reproduce VOC trends during the day for acetone, MEK, acetaldehyde, and formic acid, but does not reproduce night time variability or trends in methanol and formaldehyde.

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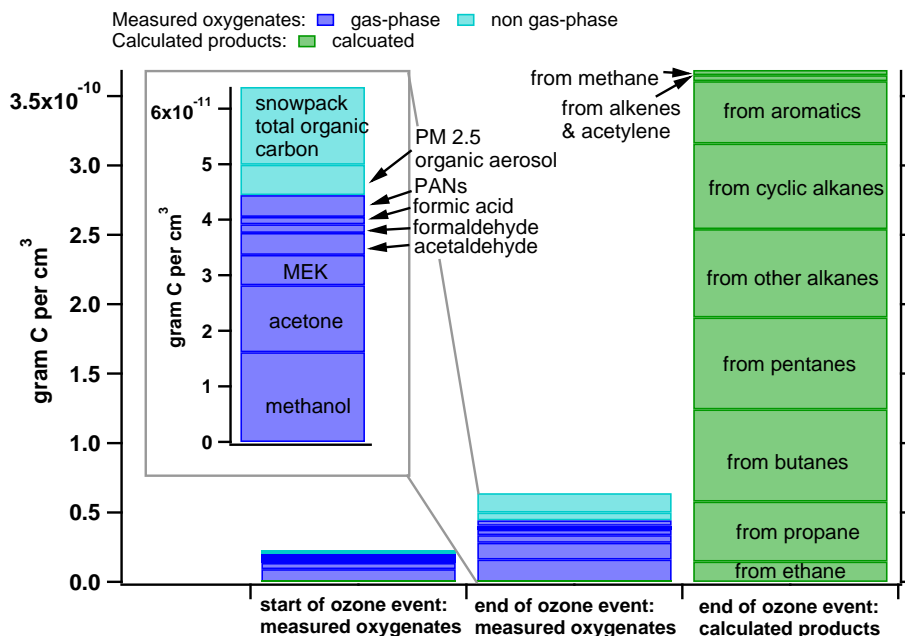


Figure 10. Organic carbon mass of oxygenated and secondary species. The leftmost two bars show the carbon mass of secondary species at the beginning (average of first 12 h) and end (average of last 12 h) of the ozone event; speciation is the same in both bars and is detailed in the inset. Although methanol and formaldehyde may have primary sources, they are included here in the “product compounds” category to show the maximum contribution of these species to measured products. The rightmost bar shows the calculated mass of secondary compounds at the end of the ozone event; within this bar, the contribution from each precursor is delineated.

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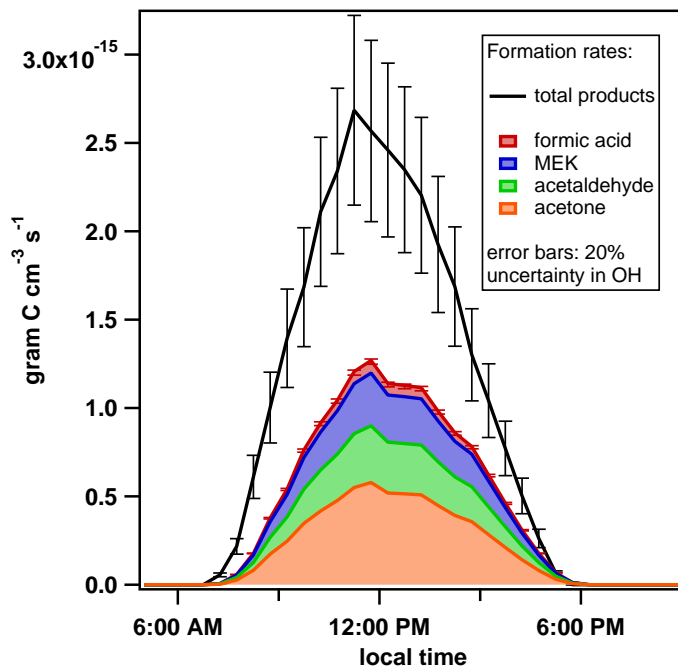


Figure 11. Comparison of total product formation rates (black) and measured carbonyl formation rates. There is a substantial gap that indicates the formation of other oxidation products.

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