

1        **Volatile Organic Compound Emissions from the Oil and Natural Gas**  
2        **Industry in the Uinta Basin, Utah: Oil and Gas Well Pad Emissions**  
3        **Compared to Ambient Air Composition**

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17       UT.

1 ABSTRACT. Emissions of volatile organic compounds (VOCs) associated with oil and natural  
2 gas production in the Uinta Basin, Utah were measured at a ground site in Horse Pool and from a  
3 NOAA mobile laboratory with PTR-MS instruments. The VOC compositions in the vicinity of  
4 individual gas and oil wells and other point sources such as evaporation ponds, compressor  
5 stations and injection wells are compared to the measurements at Horse Pool. High mixing ratios  
6 of aromatics, alkanes, cycloalkanes and methanol were observed for extended periods of time  
7 and short-term spikes caused by local point sources. The mixing ratios during the time the  
8 mobile laboratory spent on the well pads were averaged. High mixing ratios were found close to  
9 all point sources, but gas well pads with collection and dehydration on the well pad, were clearly  
10 associated with higher mixing ratios than other wells. The comparison of the VOC composition  
11 of the emissions from the oil and natural gas well pads showed that gas well pads without  
12 dehydration on the well pad compared well with the majority of the data at Horse Pool and that  
13 oil well pads compared well with the rest of the ground site data. Oil well pads on average emit  
14 heavier compounds than gas well pads. The mobile laboratory measurements confirm the results  
15 from an emissions inventory: the main VOC source categories from individual point sources are  
16 dehydrators, oil and condensate tank flashing and pneumatic devices and pumps. Raw natural  
17 gas is emitted from the pneumatic devices and pumps and heavier VOC mixes from the tank  
18 flashings.

19

1 1. INTRODUCTION. Since the introduction of hydraulic fracturing and horizontal drilling, the  
2 extraction of shale gas, often called unconventional natural gas, has increased and comprised  
3 40% of total production of natural dry gas in 2012 in the United States (US Energy Information  
4 Administration, 2014). In the Uinta Basin in Utah, the production of oil and natural gas also has  
5 increased in recent years and currently about 8000 gas wells and 2000 oil wells are in operation  
6 and about 1000 wells are added each year (Utah Oil and Gas, 2014). Most of the oil wells are  
7 located in Duchesne County on the western side of the basin and the gas wells are in Uintah  
8 County on the eastern side. In addition, there are also about 1000 coal bed methane wells and  
9 conventional wells located in Carbon County south of Uintah County. This intense oil and  
10 natural gas extraction operation results in emissions of greenhouse gases (mostly methane),  
11 volatile organic compounds (VOCs) and nitrogen oxides (NO<sub>x</sub>) (Gilman et al., 2013; Howarth et  
12 al., 2011; Karion et al., 2013; Katzenstein et al., 2003; Kemball-Cook et al., 2010; Litovitz et al.,  
13 2013; Petron et al., 2012; Swarthout et al., 2013). Some of the VOCs emitted by oil and gas  
14 extraction are air toxics and can have direct health impacts for oil and gas workers and local  
15 residents (McKenzie et al., 2012). VOCs and NO<sub>x</sub> can produce ozone in the atmosphere, which is  
16 generally seen as a summertime issue. In the Uinta Basin, however, ozone formation leading to  
17 mixing ratios above the EPA National Ambient Air Quality Standard (NAAQS) has been  
18 frequently observed in the winter, when the ground was snow-covered and strong temperature  
19 inversions persisted for several days (Schnell et al., 2009). The identification of the emission  
20 sources of VOCs and NO<sub>x</sub> from oil and natural gas production in the Uinta Basin is key to  
21 understanding the processes leading to the formation of wintertime ozone.

22 While there were no ozone exceedances in the Uinta Basin in 2012 due to weaker temperature  
23 inversions and the absence of snow (Edwards et al., 2013), these conditions were very amenable

1 to study VOC emissions. Here we present measurements of VOCs using Proton-Transfer-  
2 Reaction Mass Spectrometry (PTR-MS) from UBWOS2012 (Uinta Basin Winter Ozone Study  
3 2012) in the Uinta Basin in February 2012 at a ground site in Horse Pool and onboard a mobile  
4 laboratory to characterize the VOC composition of the emissions from individual gas and oil  
5 well pads and other point sources such as evaporation ponds, compressor stations and injection  
6 wells. Recent studies using mobile platforms have focused on methane emissions from oil and  
7 gas activities in the Uinta Basin and elsewhere (Allen et al., 2013; Karion et al., 2013). In this  
8 publication we focus primarily on VOCs.

9

## 10 2. EXPERIMENTAL.

### 11 **Instrumentation**

12 The UBWOS2012 study included a ground site in Horse Pool, Utah and the National Oceanic  
13 and Atmospheric Administration Global Monitoring Division (NOAA GMD) Mobile  
14 Laboratory. The Horse Pool ground site was fully equipped with a large suite of gas phase and  
15 aerosol measurements and only the instruments used in this study are described here. VOC  
16 measurements were made using PTR-MS instruments: the NOAA PTR-MS, which is described  
17 in detail by de Gouw and Warneke (de Gouw and Warneke, 2007) and the newly-developed  
18 Karlsruhe Institute of Technology (KIT) ULW-PTR-MS (ultra-light weight PTR-MS). PTR-MS  
19 is an on-line mass spectrometric technique for measuring VOCs in the atmosphere. In PTR-MS,  
20  $\text{H}_3\text{O}^+$  ions are used to ionize the compounds of interest in a reaction chamber and the primary  
21 and product ions are detected by a quadrupole mass spectrometer (de Gouw and Warneke, 2007).  
22 The NOAA PTR-MS was deployed at the Horse Pool ground site for the duration of the study  
23 from January 15 to February 29 2012, while the KIT PTR-MS was used at the ground site for the



1 first three weeks for detailed comparisons, and onboard the mobile laboratory for the next three  
2 weeks. The two PTR-MS instruments had similar reaction chambers and mass spectrometers, but  
3 the KIT ULW-PTR-MS was optimized for instrument size and weight and was 130 lbs compared  
4 to the standard PTR-MS, which is about 250 lbs. At the time of the study, the KIT ULW-  
5 PTRMS had a somewhat lower sensitivity of around 100-200 cps/ppbv compared to about 500-  
6 1000 cps/ppbv of the NOAA PTR-MS. After the study, the sensitivity of the KIT ULW-PTR-MS  
7 has been improved by about a factor of three. Calibrations were performed at the Horse Pool  
8 ground site every other day using a calibration standard with 10 different VOCs including  
9 oxygenates, aromatics and other compounds, and the mobile organic carbon calibration system  
10 (MOCCS) (Veres et al., 2010) for formaldehyde. The measurements at the ground site are  
11 averaged to 1-minute data and the individual compounds on the mobile laboratory were  
12 measured for 0.5 seconds every 19 seconds. At the ground site the two instruments used the same  
13 inlet, the same calibration set-up and were located in the same trailer. The two instruments  
14 agreed for all reported VOCs within 10% (not shown here), which gives a good confidence for  
15 the comparison of the ground site data with the mobile laboratory data.

16 VOCs were also measured at Horse Pool using an on-line gas chromatograph-mass  
17 spectrometer (GC-MS). The GC-MS sampled air for 5 minutes every 30 minutes and measured,  
18 among others, speciated C<sub>2</sub>-C<sub>12</sub> alkanes, C<sub>5</sub>-C<sub>8</sub> cycloalkanes, C<sub>6</sub>-C<sub>9</sub> aromatics and methanol. The  
19 instrument is described in more detail elsewhere (Gilman et al., 2010; Gilman et al., 2013).

20 Methane was measured at Horse Pool using a 3-channel Picarro for CO<sub>2</sub>, CH<sub>4</sub> and water vapor  
21 (Peischl et al., 2012) and on the NOAA GMD mobile laboratory using a 4-channel Picarro for  
22 CO<sub>2</sub>, CO, CH<sub>4</sub> and water vapor.

1 A two-channel cavity ring-down spectrometer instrument NO<sub>x</sub>CaRD (Nitrogen Oxide Cavity  
2 Ring Down) was deployed in the mobile laboratory for the direct measurement of NO<sub>2</sub> by optical  
3 extinction at 405 nm, as described in Fuchs et al. (2009), and of either NO<sub>x</sub> (= NO<sub>2</sub> + NO) or O<sub>x</sub>  
4 (= NO<sub>2</sub> + O<sub>3</sub>) after chemical conversion to NO<sub>2</sub>. Simultaneous NO<sub>2</sub> and NO<sub>x</sub> or O<sub>x</sub> observations  
5 were made at a measurement frequency of 1 Hz. Calibrations, based on the absorption cross  
6 section of NO<sub>2</sub>, were performed periodically and used a commercial O<sub>3</sub> monitor to generate and  
7 measure a known O<sub>3</sub> concentration, which was then quantitatively converted to NO<sub>2</sub>. During the  
8 mobile laboratory drives, the NO<sub>x</sub>CaRDs precision was approximately 50 pptv (2σ, 1s), and the  
9 accuracy, based on consistency of the in-field calibrations, was ±3% for NO<sub>2</sub> and ±8% for either  
10 NO<sub>x</sub> or O<sub>x</sub>.

11

### 12 **PTR-MS VOC identification and inter-comparison**

13 PTR-MS uses H<sub>3</sub>O<sup>+</sup> ions to ionize VOCs of interest, which react fast with all compounds that  
14 have a higher proton affinity than that of water (de Gouw and Warneke, 2007). Among the  
15 compounds of interest for oil and gas emissions, this includes the aromatic compounds and  
16 methanol. Straight chain, branched and cyclic alkanes generally have a lower proton affinity than  
17 water. Those compounds, together with methane, make up more than 90% of the mass of crude  
18 oil and natural gas (Ryerson et al., 2011).

19 Even though cycloalkanes have a lower proton affinity than water, they react with H<sub>3</sub>O<sup>+</sup>, albeit  
20 at a slower rate of about 10% compared to most other VOCs. The most common pathway after  
21 reaction with H<sub>3</sub>O<sup>+</sup> is proton transfer accompanied by hydrogen abstraction, such that the main  
22 masses produced from cycloalkanes in PTR-MS are masses 69, 83, 97, 111, and 125. Alkenes  
23 are also detected at these masses, especially isoprene, which is detected at mass 69. At the Horse

1 Pool site only small amounts of alkenes were detected using GC-MS compared to alkanes and  
2 cycloalkanes and we therefore assume that the main contributors to those masses in the Uinta  
3 Basin are cycloalkanes. Using the fragmentation patterns determined by Yuan et al (2014) we  
4 conclude that mass 83 is mainly from methylcyclopentane, mass 97 from methylcyclohexane,  
5 mass 111 and mass 69 from the C2-cyclohexanes, and mass 125 from the C3-cyclohexanes.  
6 PTR-MS calibrations of methylcyclopentane, methylcyclohexane, and 1,2-dimethylcyclohexane  
7 were performed prior to and during the field study using the MOCCS system (Veres et al., 2010).  
8 Using the determined sensitivities and mass identifications, the cycloalkanes from the PTR-MS  
9 are compared to the GC-MS at Horse Pool and the results are shown in Figure 1. The two  
10 instruments agreed within the stated uncertainty of about 20% for both instruments, which gives  
11 some confidence for the use of the PTR-MS cycloalkane mass signals. The PTR-MS signals for  
12 all measured cycloalkanes are larger than the GC-MS, which might indicate small interferences  
13 from other compounds besides the ones used in the sum of the GC-MS signals in Figure 1. Here  
14 it should be mentioned that the cycloalkanes also react fast with  $O_2^+$ , which is about 1-5% of  
15  $H_3O^+$  in the PTR-MS, but the contributions from  $O_2^+$  reactions to the cycloalkane masses are  
16 likely small compared to  $H_3O^+$  (Yuan et al., 2014).

17 Small alkanes, on the other hand, do not react with  $H_3O^+$ , they only undergo charge transfer  
18 reactions with  $O_2^+$ , which results in many different fragment ions with various masses (Francis et  
19 al., 2007; Spanel and Smith, 1998; Yuan et al., 2014). Small alkanes are therefore not detected  
20 very selectively and only with a very low sensitivity with PTR-MS. During UBWOS2012 we  
21 monitored several of those alkane masses and in the following we will use masses 43, 57, 71, and  
22 85. Each of these masses have contributions from several alkanes, straight-chain and branched,  
23 such that none of the masses can be used quantitatively for individual compounds, but generally

1 the lighter the alkane is the smaller the resulting ions are (Francis et al., 2007). Calibrations for  
2 several alkanes were performed in the lab and the determined sensitivities were about 3% of  
3 other VOCs, which was used to convert alkane mass signals into approximate corresponding  
4 mixing ratios. These masses are also common fragments of other compounds such as alcohols  
5 and ketones (Warneke et al., 2003; Warneke et al., 1996). Using the VOC composition at Horse  
6 Pool measured by GC-MS during UBWOS2012, the signals from these other compounds are  
7 expected to be small compared to the signals resulting from the alkanes. The alkane masses will  
8 be used in this work only as indicators for the presence of small alkanes.

9

### 10 3. RESULTS AND DISCUSSION.

11

#### 12 **3.1. Mixing ratios at the ground site in the Uinta Basin**

13 A map of the Uinta Basin that indicates the locations of the oil and gas wells and several other  
14 point sources is shown in Figure 2. The Horse Pool ground site and the drive tracks used for this  
15 study with the Mobile Laboratory are shown as well. The Horse Pool ground site is at the  
16 northern edge of the gas field and surrounded by many gas wells and also a few oil wells to the  
17 north of the site as shown in the insert map in Figure 2. The whole Uintah Basin has only a few  
18 minor towns (several tens of kilometers away from Horse Pool) and the Bonanza power plant,  
19 but its emissions were generally lofted from the stack outside the mixed layer. The top panel of  
20 Figure 3 shows a time series benzene and toluene for one selected day and the other panels  
21 selected VOCs for the UBWOS2012 campaign. The mixing ratios observed at the site are  
22 characterized by high values for extended periods of time during stagnation events in the basin  
23 and by very high mixing ratios during short-term spikes caused by local point sources such as the

1 oil and gas wells shown in the inserted map in Figure 2. For example, benzene and toluene were  
2 over 3 ppbv from January 30 to February 2 before the basin cleaned out just after noon on  
3 February 2. In addition toluene spikes of well over 10 ppbv for 1-minute average data were  
4 frequently observed. Methanol, used as an anti-freeze and anti-coagulant in gas and oil wells,  
5 was almost an order of magnitude higher than the aromatics and mixing ratios of several  
6 hundreds of ppbv were detected in the spikes. The smallest mixing ratios were observed after a  
7 clean-out event on February 2, 2012 and mixing ratios dropped to typical wintertime continental  
8 background levels.

### 10 3.2. Typical mixing ratios downwind of point sources

11 To investigate the emissions from point sources in the Uinta Basin that are responsible for the  
12 elevated mixing ratios of VOCs observed at the Horse Pool ground site, the Mobile Laboratory  
13 was used to measure immediately downwind of individual facilities: (1) gas well pads with  
14 dehydration not on the well pad but consolidated at a central facility, (2) gas well pads with  
15 collection and dehydration on the well pad, (3) oil wells, (4) gas well pads near Rangely, CO, (5)  
16 a recently hydraulically re-fractured well with a flow-back pond, (6) a newly producing gas well  
17 and (7) other point sources including natural gas compressor stations, produced-water injection  
18 wells, condensate and oil tank batteries, evaporation ponds and water treatment plants.

19 A photograph of a typical gas well pad in the Uinta Basin is shown in Figure 4a together with  
20 an oil well pad in Figure 4c and typical mixing ratios downwind of such wells are shown in  
21 Figure 5 (gas well pad) and Figure 6 (oil well pad). The track of the Mobile Laboratory in close  
22 proximity downwind (indicated by the wind barbs) of the well pads are shown in Figures 5b-e  
23 and 6b-e and are color-coded by methane, methanol, toluene, and NO<sub>2</sub>, respectively. The

1 corresponding time series are shown in Figures 5a and 6a. Close to this particular gas well pad,  
2 over 10 ppmv of methane, 40 ppbv of toluene and 500 ppbv of methanol were detected (Figure  
3 5). These three compounds illustrate the elevated mixing ratios close to the well pad and also that  
4 different components of the gas well pad are responsible for different emissions. At most well  
5 pads, methane is highest downwind of the separator, but is also emitted from the wellhead.  
6 Toluene and other aromatics are highest downwind of the condensate and water tanks. Methanol  
7 is highest downwind of the methanol and condensate tanks, and NO<sub>2</sub> downwind of the  
8 compressor. This means that the handling of the gas causes emissions of natural gas and the  
9 processing of the gas emissions of the heavier compounds, so called fugitives. As a result the  
10 heavier VOCs are not well correlated with methane on the well pads.

11 At many oil well pads, such as the one shown in Figure 6, oil tanks were used, which were the  
12 main source for the aromatic compounds similar to the gas well condensate tanks. Methane  
13 comes from the wellhead, methanol from the wellhead and also the pump jack, and the NO<sub>2</sub>  
14 comes mainly from the generator and pump jack, which is typically driven by an internal-  
15 combustion engine (Figure 6). At the Horse Pool ground site all of these compounds were much  
16 better correlated, because there was enough time for mixing after the emission. In Figures 5 and  
17 6 it can be seen that in a few occasions the plume was not measured on some of the transects,  
18 which is a result of the variable wind speed and direction and also of incomplete mixing so close  
19 to the emission source.

20 During UBWOS2012 38 different gas well pads, 12 oil well pads, a newly producing well, a  
21 re-fractured well with a flow back pond, and 17 other point sources such as evaporation ponds,  
22 storage tanks and compressor stations were investigated in a similar way as described above. The  
23 mixing ratios of the measured VOCs were averaged during the time the Mobile Laboratory spent

1 in close proximity downwind, generally within 300 feet of the wells or the other emission  
2 sources in order to provide a means of comparison with the Horse Pool site measurements and  
3 aggregated emissions inventories. The results are shown in Figure 7. This average is somewhat  
4 influenced by the relative amount of background air encountered during the averaging time, but  
5 this does not influence the conclusions in this work. It should also be mentioned here that the  
6 measurements on the well pads were done during periods when no truck traffic was in the  
7 vicinity. The maximum observed mixing ratios close to the sources for selected VOCs and  
8 methane (shown in Figure 8) show similar trends as the averages, but also give an indication of  
9 how elevated mixing ratios close to the sources were. Figures 5, 6, 7 and 8 demonstrate that  
10 mixing ratios of aromatics and methanol near 1 ppmv and of methane of hundreds of ppmv were  
11 measured several times during the drives.

12 The data in Figure 7 are then normalized to 2 m/s wind speed (dividing the mixing ratio by the  
13 wind speed in m/s and multiplying by 2 m/s) to account for different dilutions at different wind  
14 speeds by using the average observed horizontal winds over the same time period. The  
15 windspeed-normalized results for only the gas and oil well pads are averaged and shown in  
16 Figure 9. Here it should be mentioned that we do not have any information about the vertical  
17 extent of the plumes from the gas wells and the other point sources, such that an estimate of  
18 emission rates is not possible and therefore only average mixing ratios close to the sources are  
19 discussed here.

20 Strongly elevated mixing ratios of the measured VOCs were found at almost all source  
21 locations, but very large differences even between similar point sources existed. The largest  
22 relative differences were observed between individual gas well pads. For example, average  
23 normalized toluene mixing ratios <10 ppbv were observed next to several gas wells, but in the

1 same gas field or formation two orders of magnitude larger mixing ratios of >100 ppbv were  
2 found next to other gas wells. The average mixing ratios close to investigated oil well pads in  
3 Duchesne County in Figure 9 generally show smaller mixing ratios than gas wells using  
4 dehydrators and similar gas wells without dehydrators in Uintah County. The Mobile Laboratory  
5 usually spent about 20-30 minutes close to each gas well pad and generally no variations on the  
6 order of the well-to-well variability were observed. This seems to indicate that the main reason  
7 for the different emissions is the different practices and as a result different equipment used for  
8 wells that have the dehydration on the well pad compared to wells with only the gas collection,  
9 where the dehydration is consolidated at a central facility. On the well pads with dehydration,  
10 glycol dehydrators that include a heater and a glycol regenerator are used. All of these  
11 components have VOC emissions and therefore this category has higher mixing ratios associated  
12 with them. Wells with only the gas collection on the well pad do not use this equipment at the  
13 well site, but have the dehydration and therefore the associated emissions at centralized facilities.  
14 Furthermore, the investigated wells using dehydrators on site generally had higher condensate  
15 production rates, which usually also lead to higher emissions and as shown in Figure 5, the  
16 emissions of the aromatic compounds mainly came from the condensate tanks. No clear  
17 correlations of the average mixing ratios next to gas well pads with well age or cumulative well  
18 production were found.

19 As a comparison, also shown in Figure 7, 8 and 9 are average mixing ratios close to gas wells  
20 in Rangely, Colorado, which is another part of the Uinta-Piceance Basin and located in the north-  
21 west corner of Colorado. About 20 miles separate the gas field in Rangely from the Uinta Basin,  
22 but the oil and gas exploration has a very different character. The gas field is much drier (less  
23 hydrocarbon liquids and more gas) and the density of wells is higher, which results in very



1 different practices for the natural gas extraction. In the Piceance Basin about the same amount of  
2 gas but only a little more than a quarter of oil is produced compared to the Uinta Basin. A photo  
3 of a typical gas well pad in Rangely, CO is also shown in Figure 4b. The gas is transported with  
4 pipelines to a central facility in Rangely similar to the Uinta Basin, but in Rangely underground  
5 and in Uinta above ground pipelines are used. Another difference is that in Rangely electric  
6 power is available at most wells. As a result, few wellhead compressors, combustion generators  
7 or condensate tanks are used in this particular area, which are significant emitters of VOCs and  
8 NO<sub>x</sub> in the Uinta Basin. As a result, mixing ratios observed close to all investigated gas wells  
9 were still elevated from ambient but generally lower than in the Uinta Basin.

10 Very large mixing ratios (e.g.: ppmv levels of aromatics) were found downwind of a re-  
11 fractured well pad with flow-back pond and a newly producing well. These are point sources that  
12 are less frequent than operating wells in the Uinta Basin. Emissions from these two sites were  
13 measured multiple times with the Mobile Laboratory.

14 The other point sources investigated shown in Figure 7 and 8 included condensate and oil tank  
15 batteries, produced water treatment plants, compressor stations, produced water evaporation  
16 ponds, and processing plants. We do not have enough measurements of the individual types of  
17 point sources to compare them in statistically meaningful ways to the oil or gas well pads, but  
18 mixing ratios close to those sources were generally in the same range as many of the gas well  
19 pads. Here it should be mentioned that the potentially largest sources (according to the WRAP  
20 inventory described below) of VOC and NO<sub>x</sub> in the Uinta Basin are the natural gas processing  
21 plants such as the Chapita Plant. These plants use stacks and their main emissions cannot be  
22 reliably measured from the ground with the Mobile Laboratory.

1 Methanol is used as an anti-freeze and anti-coagulant, injected into pipelines and down the  
2 wellbore and, as a result, very high mixing ratios, often over 100 ppbv, were observed at many of  
3 the oil and gas well pads and at many of the other point sources. Methanol was especially high  
4 near the evaporation ponds, because methanol partitions out with the water in the separator. High  
5 mixing ratios of methanol were also observed at the Horse Pool ground site, often in very short-  
6 term spikes, as high as 1.1 ppmv for the 1-minute average. As can be seen in Figures 5 and 6,  
7 methanol was emitted at the methanol tanks and the wellheads and was not well correlated with  
8 aromatics or methane close to the individual gas wells. Methanol was also one of the very few  
9 compounds that was not well correlated with the other hydrocarbons at Horse Pool (e.g.  $R^2=0.18$   
10 with benzene) due to the different processes emitting methanol at the well pads and the  
11 additional strong sources of methanol in the oil and gas region.

12

### 13 **3.3. VOC composition comparison of oil and gas well pad emissions**

14 Gas and oil wells are by far the most numerous point sources in the Uinta Basin and as such  
15 will be important emission sources of VOCs. Therefore we focus on the analysis of the VOC  
16 composition of gas and oil wells. Scatter plots of the measured VOCs versus benzene are used to  
17 compare the VOC composition emitted from oil and gas well pads to the ground site. The Horse  
18 Pool data are segregated into two classes based on their unique chemical composition. About 5%  
19 of the data exhibited a distinctly different chemical composition. For example, these samples  
20 were enhanced in  $C_4$ - $C_{11}$  n-alkanes relative to propane, but had a significantly lower ethane to  
21 propane ratio as measured by the GC-MS for the majority of the Horse Pool data. Wind sector  
22 analysis showed that these samples were almost exclusively from the northwest where two

1 nearby oil wells were located. The predominant wind direction at Horse Pool had a southern  
2 component where the vast majority of the gas wells in Uinta Basin are located. The 5-minute  
3 averaged data from the two sectors (now referred to as oil and gas well sectors) are shown in  
4 Figure 10 and are compared to the average mixing ratios close to oil and gas wells measured  
5 from the Mobile Laboratory (data from Figures 7, 8 and 9). The left panel shows methane and  
6 the aromatics and the right panel the cycloalkanes. The Horse Pool data show good correlations  
7 for all compounds with benzene ( $R^2 > 0.91$ ), especially for the gas well sector. Ratios with  
8 benzene were used instead of the lightest compound methane, because most VOCs measured by  
9 PTR-MS downwind of the gas and oil well pads did not correlate well enough with methane. The  
10 slopes of the larger aromatics and the cycloalkanes with benzene in the oil well sector are clearly  
11 different from the gas well sector and the difference increases with the molecular weight of the  
12 compound. The mobile laboratory measurements from the individual wells show comparable  
13 slopes and differences between oil and gas wells, but the large well-to-well differences result in a  
14 larger variability. In the top right panel the linear fits for the four categories are shown together  
15 with the data.

16 In order to compare the emission profile of VOCs measured in the Mobile Laboratory  
17 downwind of oil and gas wells to the emission profiles observed at Horse Pool, we compare  
18 enhancement ratios with benzene shown in Figure 11, where each data point represents one  
19 compound and is colored by compound class. Enhancement ratios are determined from the  
20 slopes of the linear fits (indicated for methylcyclopentane in Figure 10), for cycloalkanes and  
21 aromatics and also for the PTR-MS alkane masses with benzene. Figure 11a and 11b compare  
22 the enhancement ratios for the individual gas wells with or without dehydrators and oil wells  
23 with the measurements from the Horse Pool ground site. In the surroundings of Horse Pool wells

1 without dehydrators dominate and their enhancement ratios are in good agreement with Horse  
2 Pool data. The wells with dehydrators do not agree as well with the Horse Pool data: the  
3 enhancement ratios with benzene, which is the lightest aromatic, are below the 1:1 line, which  
4 means that the composition of wells without dehydrators (alkanes, cycloalkanes and aromatics)  
5 is a lighter mixture of VOCs than the wells with dehydrators; however wells with dehydrators  
6 had higher mixing ratios associated with them. The enhancement ratios for the oil wells and the  
7 oil well sector at Horse Pool agree well with each other as shown in Figure 11b.

8 Figure 11c and 11d compare the gas with oil well sectors at Horse Pool and the individual gas  
9 (with and without dehydrators) with oil well pads, respectively. The enhancement ratios with  
10 benzene for the oil well pads are clearly larger than the ones from the gas wells and the  
11 difference increases with the molecular weight of the compound. This shows that the VOC  
12 mixture emitted by oil well pads consists of heavier compounds compared to gas well pads,  
13 which is expected due to the heavier composition of the hydrocarbons extracted by oil well pads  
14 compared to gas well pads.

15

### 16 **3.4. VOC composition comparison with emission inventory**

17 The Uinta Basin emission inventory from the Western Regional Air Partnership (WRAP)  
18 provides an estimation of the criteria pollutant emissions for oil and gas exploration and  
19 production in the Uinta Basin for 2006 and projections for 2012 (available at:  
20 [http://www.wrapair.org/forums/ogwg/PhaseIII\\_Inventory.html](http://www.wrapair.org/forums/ogwg/PhaseIII_Inventory.html)). The emissions calculated in the  
21 WRAP inventory are based on the well counts, production data and extensive operator survey  
22 data related to the identified oil and gas source categories. Figure 12 shows the VOC and NO<sub>x</sub>  
23 emissions as estimated by the WRAP inventory by source category for Uintah County (mainly

1 gas wells), Duchesne County (mainly oil wells) and the whole Uinta Basin. In the inventory,  
2 about 89% of the VOC emissions are from dehydrators, condensate and oil tanks, pneumatic  
3 pumps and pneumatic devices and about 78% of the NO<sub>x</sub> emissions are from drilling rigs,  
4 compressor engines, artificial lift engines and heaters. We did not systematically sample the  
5 largest NO<sub>x</sub> sources with the Mobile Laboratory and do not present an analysis of the NO<sub>x</sub>  
6 inventory here. In the WRAP inventory, fugitive emissions from oil and gas pipelines from  
7 wellheads to the main compressor stations are not included, which are potentially a large source  
8 category.

9 The VOC composition of each inventory source category is based on a composite gas and  
10 liquid analysis (provided by the different operators in the Uinta Basin) and calculations specific  
11 for each source category. The gas and liquid composition is calculated from an average of  
12 samples collected throughout the basin, but varies by location. From the main source categories,  
13 pneumatic devices and pumps emit raw gas and therefore the VOCs composition is the same as  
14 the natural gas, whereas dehydrators and tank flashings emit less of the smaller hydrocarbons. In  
15 Figure 13 the VOC composition used in the inventory for coal bed methane (CBM),  
16 conventional gas and oil and condensate tank flashing is shown as ratios with methane. CBM is  
17 mainly emitted outside the study region further south in the Uinta Basin in Carbon County and is  
18 very light in VOC composition. The conventional gas shows the typical decrease of  
19 concentration with increasing molecular weight of the compound. The oil and condensate tank  
20 flashing emissions are depleted in smaller hydrocarbons such that the C7 and heavier compounds  
21 make up the largest emissions from oil tanks.

22 Figure 11 showed that Horse Pool gas and oil well sectors compared closely to the individual  
23 gas and oil well pads and therefore these data are used as a good proxy for individual wells. The

1 VOC emission ratios with methane from Horse Pool are compared to the VOC composition used  
2 in the WRAP inventory in Figure 13. The gas well pad measurements resemble most closely the  
3 conventional gas, but are heavier in composition and the oil well pad emissions are even heavier,  
4 where the difference with the conventional gas is largest for the aromatic compounds. The  
5 measurements from the oil and gas wells and at Horse Pool will therefore be a mixture of  
6 conventional gas (from the pneumatic devices and pumps and other venting sources) with tank  
7 flashing and dehydrators, similar to what the WRAP inventory shows.

8 Measurements of the individual wells shown in Figures 5 and 6 have demonstrated that VOCs  
9 are emitted with varying compositions from the different source categories. The measurements  
10 are qualitatively consistent with the WRAP inventory: (1) in the inventory the dehydrator, the  
11 tank flashing and the pneumatic devices are major VOC emission sources from the gas and oil  
12 well pads and we observe high mixing ratios of VOCs downwind of those sources (Figures 5 and  
13 6). (2) the inventory has emissions of heavier compounds from the oil and condensate tanks  
14 (Figure 13), which we also see in the measurements (Figures 5 and 6). (3) in the inventory the  
15 wellhead, dehydrator and pneumatic devices emit raw natural gas as described above and the  
16 measurements show high methane mixing ratios downwind of these well pad parts (Figures 5  
17 and 6).

18

#### 19 4. CONCLUSIONS

20 High mixing ratios of VOCs associated with emissions from oil and gas exploration and  
21 production operations (alkane, cycloalkanes, aromatics and methanol) were found in the Uinta  
22 Basin in winter 2012 at a ground site and using a mobile laboratory. Individual oil and gas well  
23 pads were investigated using the Mobile Laboratory and it was found that the separator,

1 dehydrator and pneumatic devices and pumps emit a light VOC mix similar to the natural gas  
2 composition, whereas the oil and condensate tanks emit heavier VOCs. High methanol  
3 concentrations were observed downwind of methanol tanks and condensate tanks. Other point  
4 sources such as a flow-back pond from a recently hydraulically re-fractured well and evaporation  
5 ponds were also found to be large VOC emission sources. Looking at the measured VOC  
6 composition and the WRAP emission inventory it seems that the main emission sources in the  
7 Uinta Basin are individual well pads, such that the observed VOC composition is a mixture of  
8 raw natural gas with oil and condensate tank flashing.

9 The results presented here were some of the first measurements using fast-response VOC  
10 instruments to look at individual gas and oil well pads and other point sources associated with oil  
11 and natural gas production, but future measurements on a mobile laboratory are needed to  
12 determine emission rates in addition to ambient mixing ratios. [For determining emission fluxes  
13 from well pads, techniques exist or are emerging such as tracer releases and remote geospatial  
14 Gaussian methods or detailed measurements of individual equipment parts on the well pad as  
15 shown by Allen et al. \(2013\) and should be used in future studies.](#) Furthermore, more detailed  
16 fast-response VOC composition measurements are needed to better characterize the VOC  
17 composition of the individual source categories and identify the most important emission  
18 categories.

19

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8



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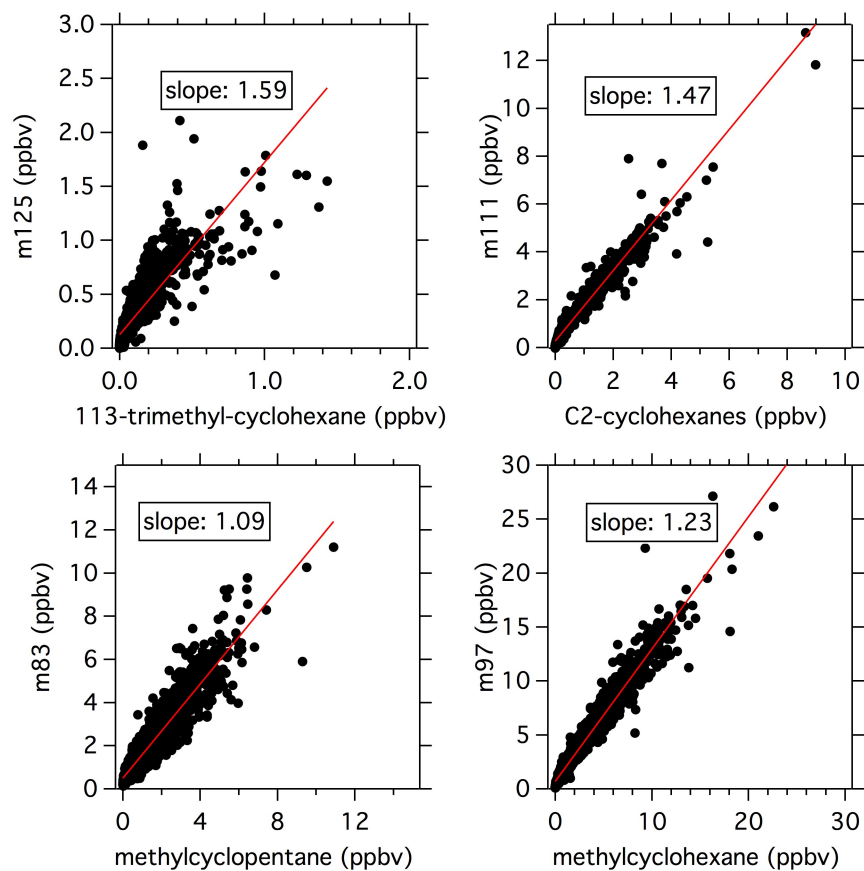
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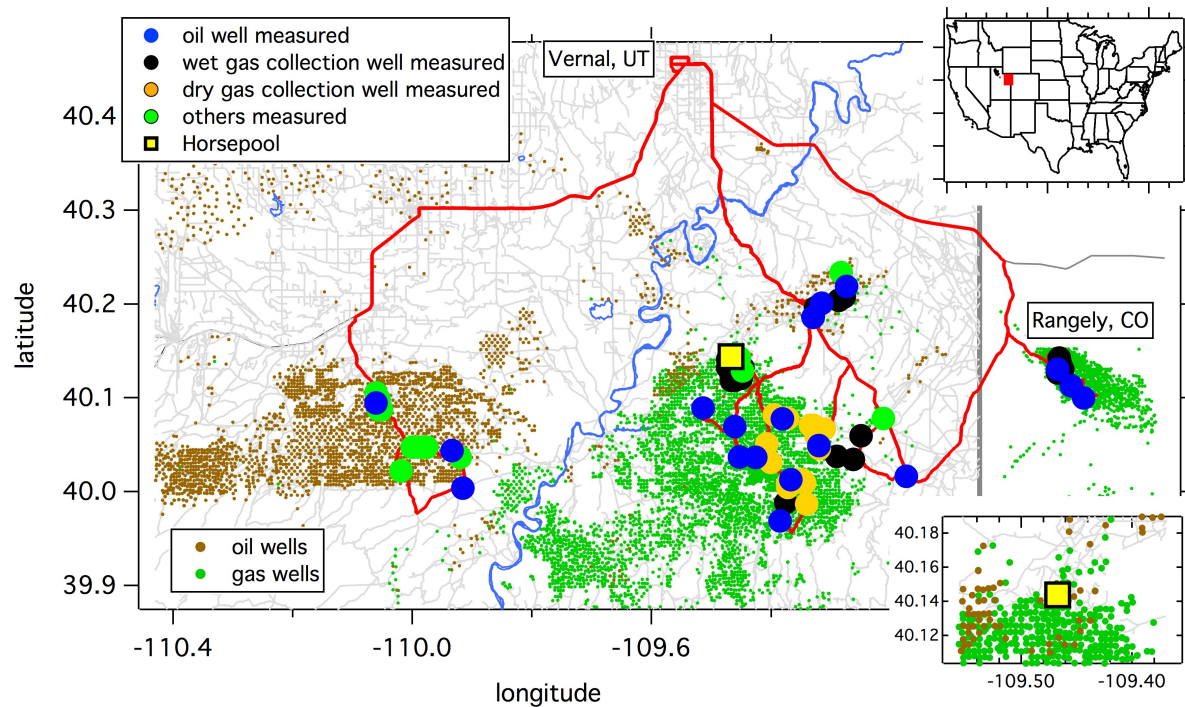
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1  
2 **Figure 1.** Inter-comparison of the masses measured by PTR-MS that are indicative of  
3 cycloalkanes with GC-MS cycloalkane mixing ratios at the Horse Pool site.

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2 **Figure 2.** A map of the Uinta Basin study area showing the locations of oil and gas wells and the

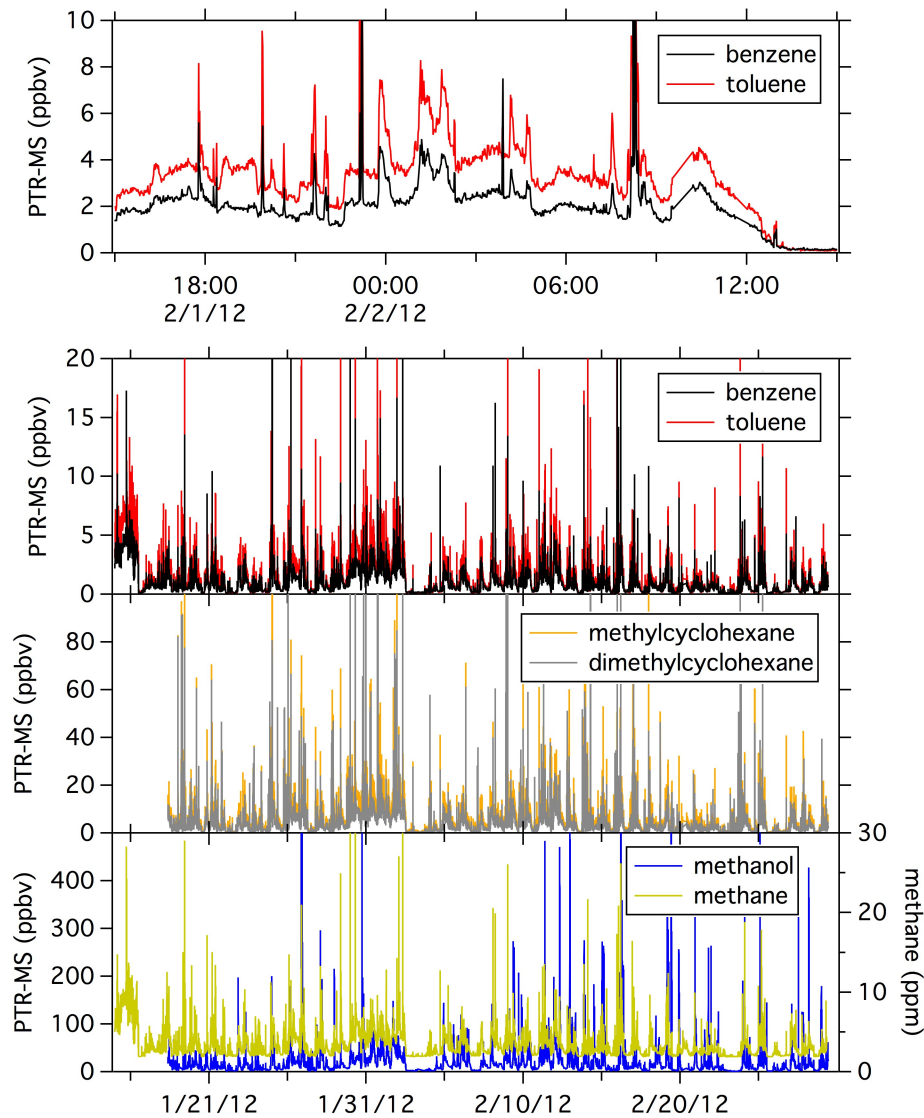
3 Horse Pool ground site. The route of the drives (red lines) is shown together with the locations of

4 the investigated point sources. The insert on the top shows the location of the Uintah Basin in the

5 United States and the bottom insert shows the immediate vicinity of the Horse Pool site, which is

6 surrounded by oil and gas wells.

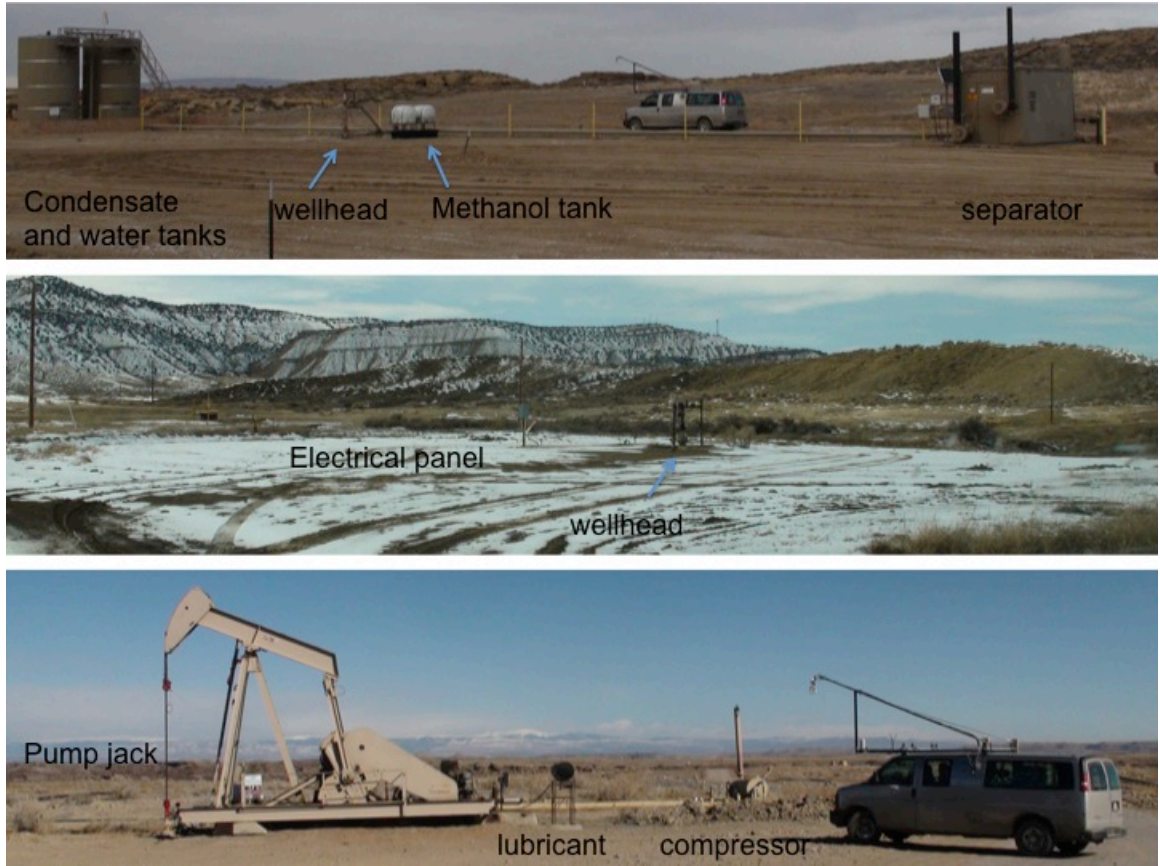
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2 **Figure 3.** The time series of benzene and toluene for one day and various VOCs measured by  
 3 PTR-MS and methane for the whole measurement period at the Horse Pool ground site during  
 4 the UBWOS2012 campaign. Maximum mixing ratios are off-scale.

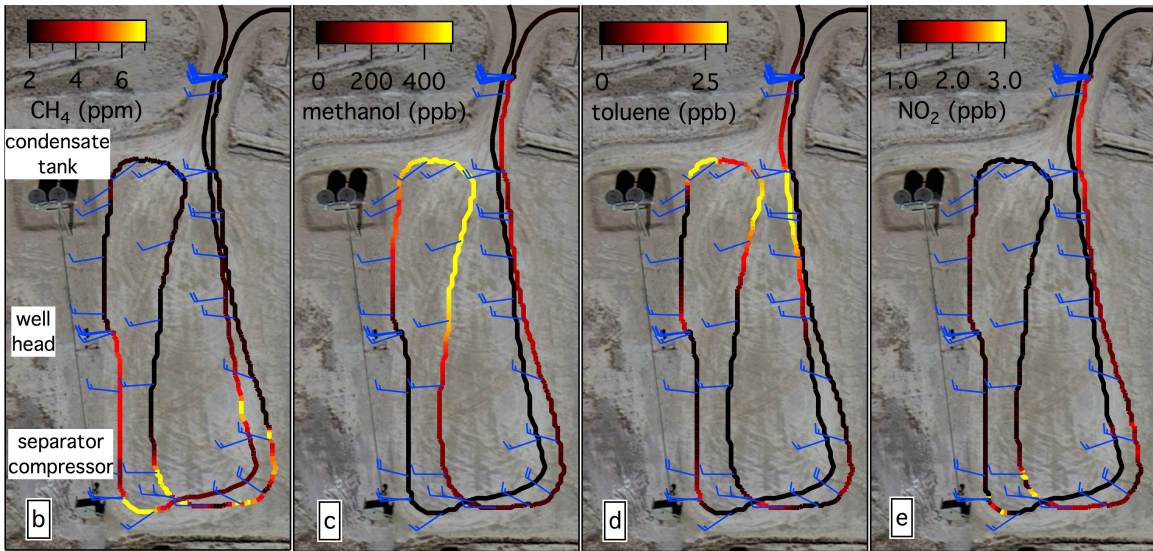
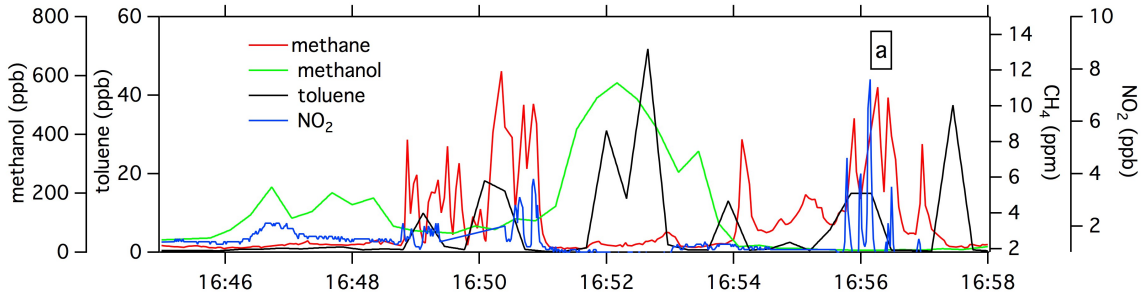
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**Figure 4.** Top: Picture of a typical natural gas well pad in the Uinta Basin. Middle: Picture of a typical natural gas well in Rangely, Colorado. Bottom: Picture of a typical oil well in the Uinta Basin.





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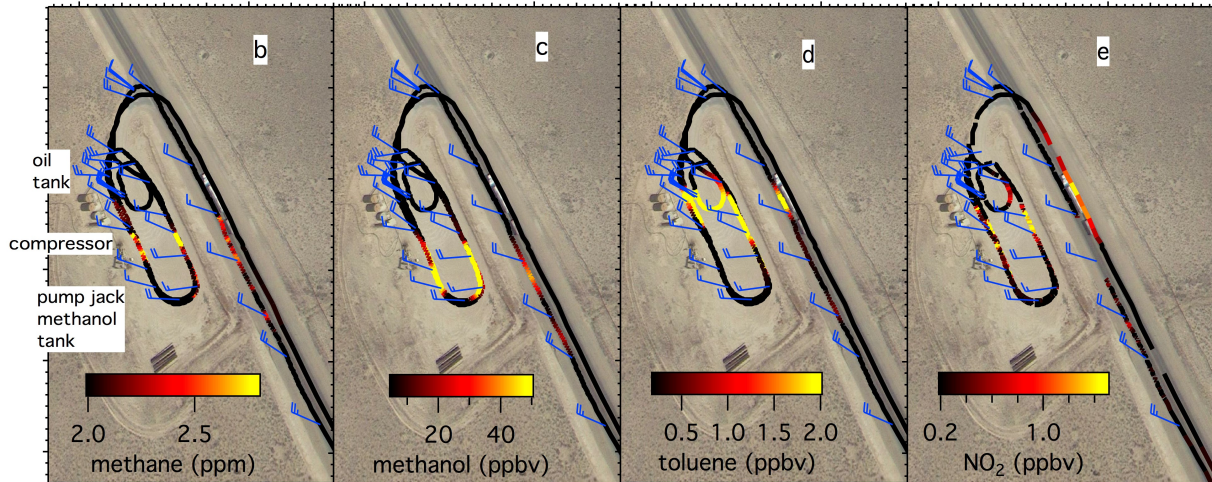
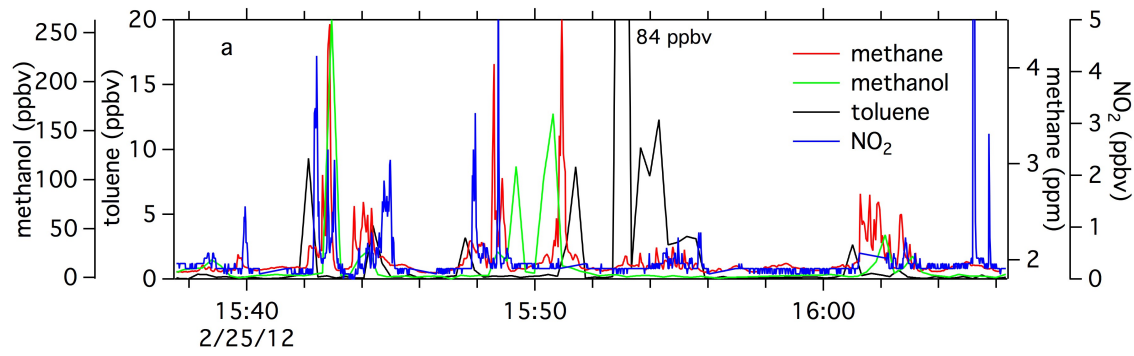
2 **Figure 5.** The drive track close to a gas well color coded by measured methane (b), methanol (c),

3 toluene (d) and (e) NO<sub>2</sub>. The wind barbs indicate the prevailing wind direction coming from left

4 to right in the image. The time series for this period is shown in (a).

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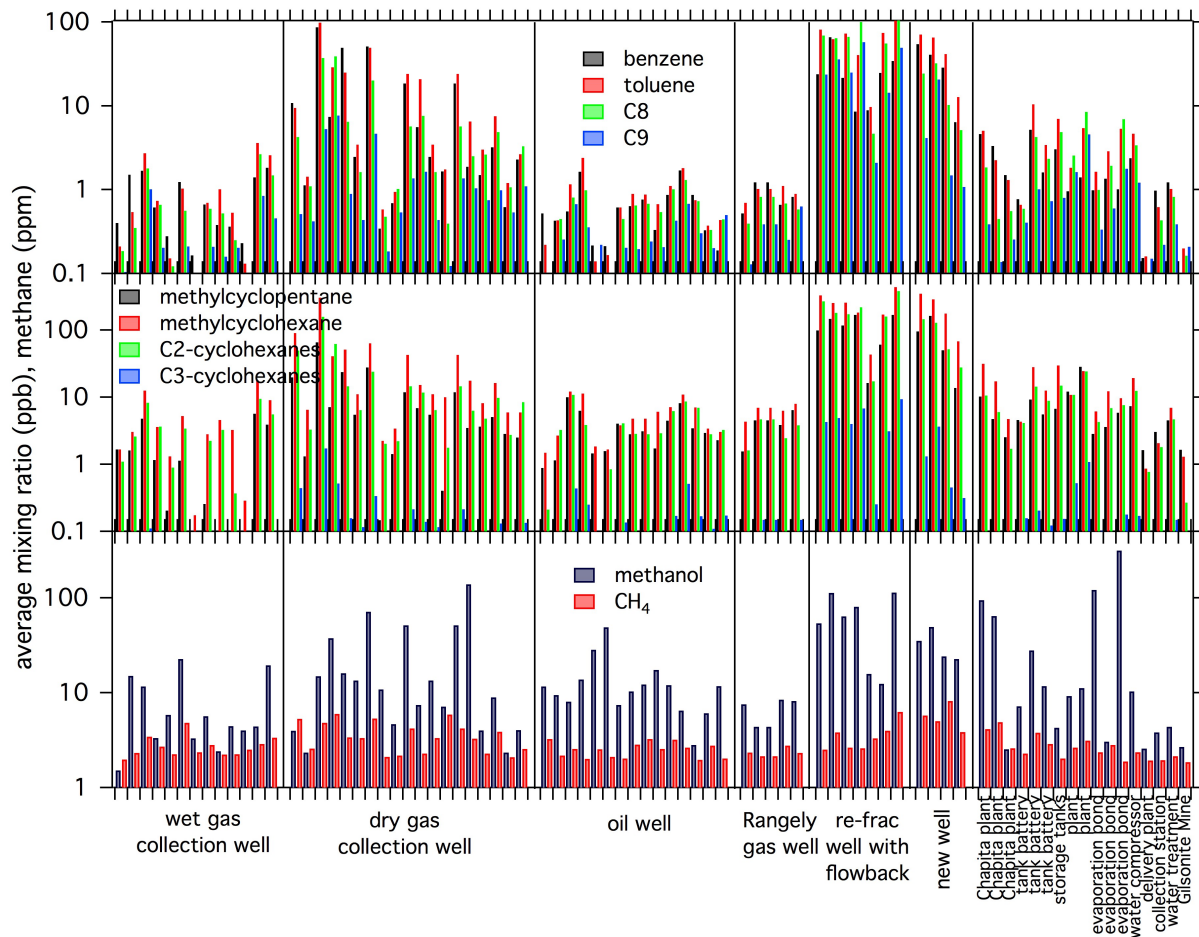




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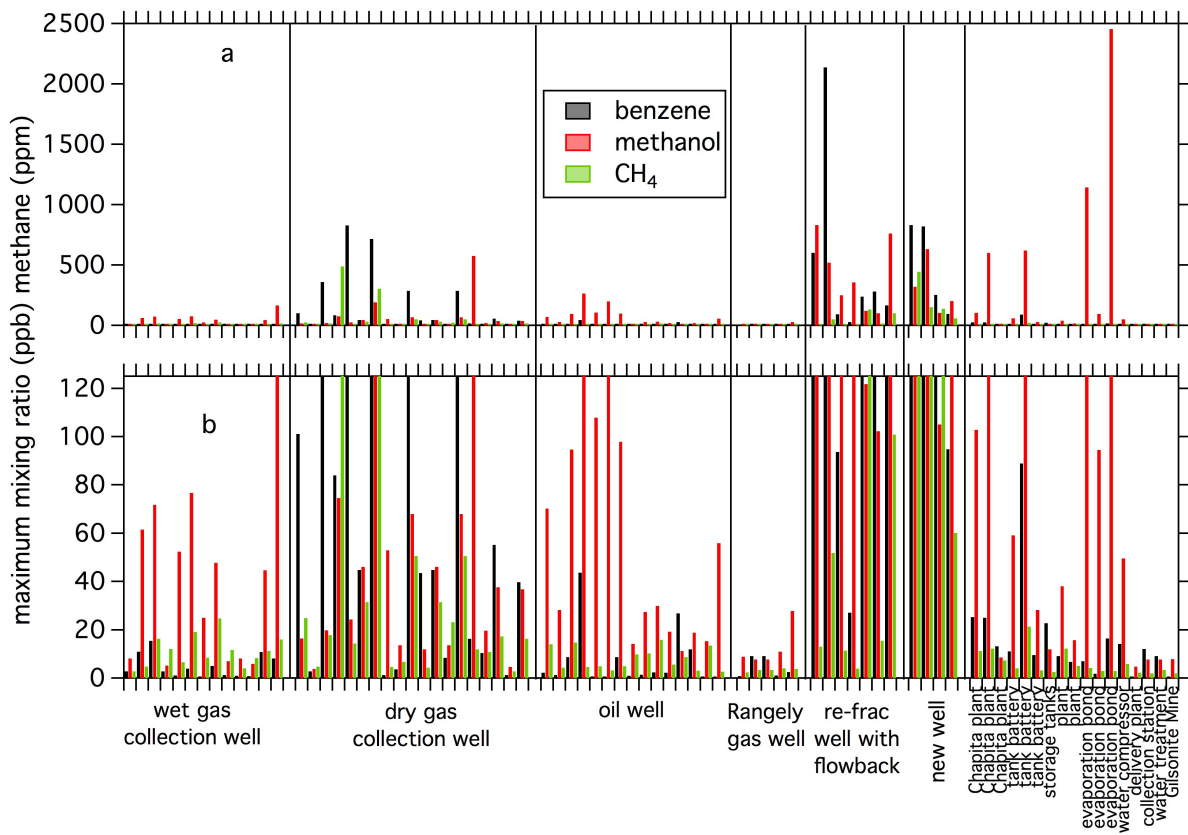
2 **Figure 6.** The drive track close to an oil well color coded with methane (b), methanol (c),  
 3 toluene (d) and (e) NO<sub>2</sub>. The wind barbs indicate the prevailing wind direction. The time series  
 4 for this period is shown in (a).

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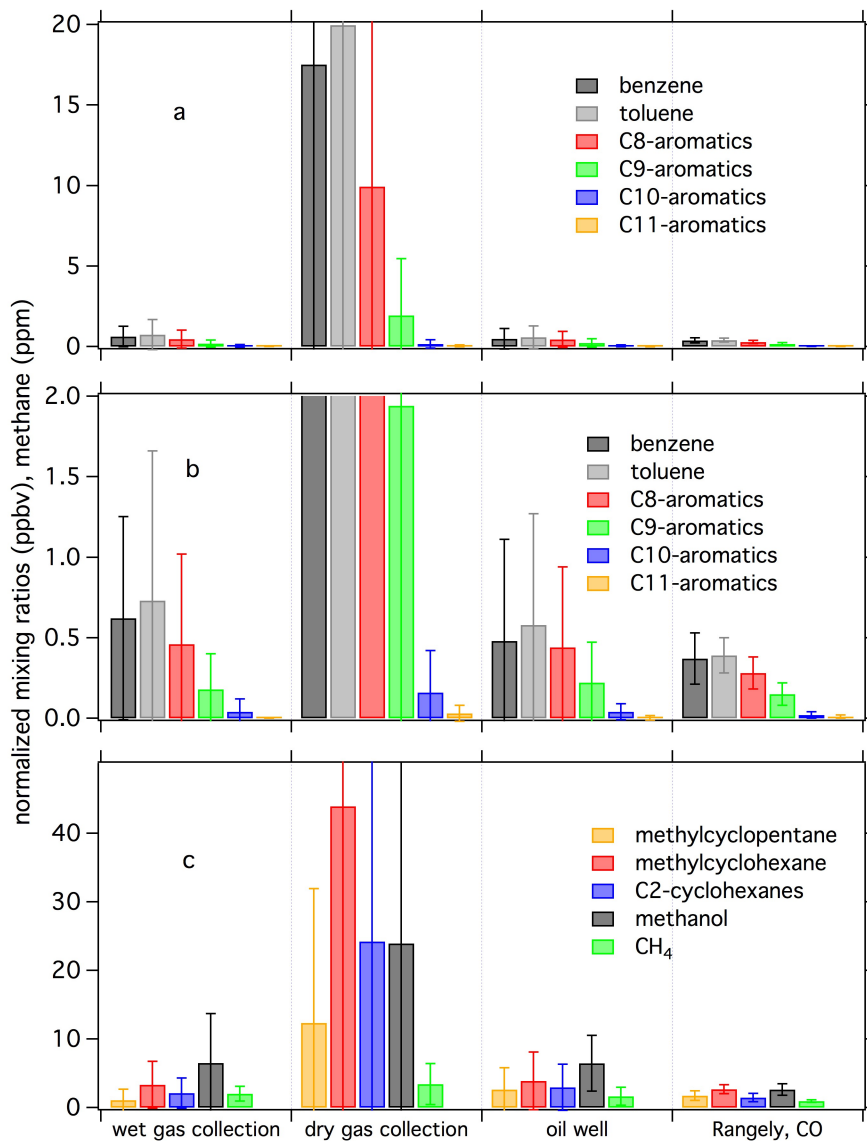
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 2 **Figure 7.** The average mixing ratios of various VOCs (aromatics, cycloalkanes, methanol and  
 3 methane) observed close to individual point sources in the Uinta Basin and in Rangely,  
 4 Colorado.

5  
 6



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 2 **Figure 8.** The maximum mixing ratio of benzene, methanol and methane observed close to the  
 3 investigated emission sources in the Uinta Basin and in Rangely, Colorado. (a) full scale and (b)  
 4 small scale.

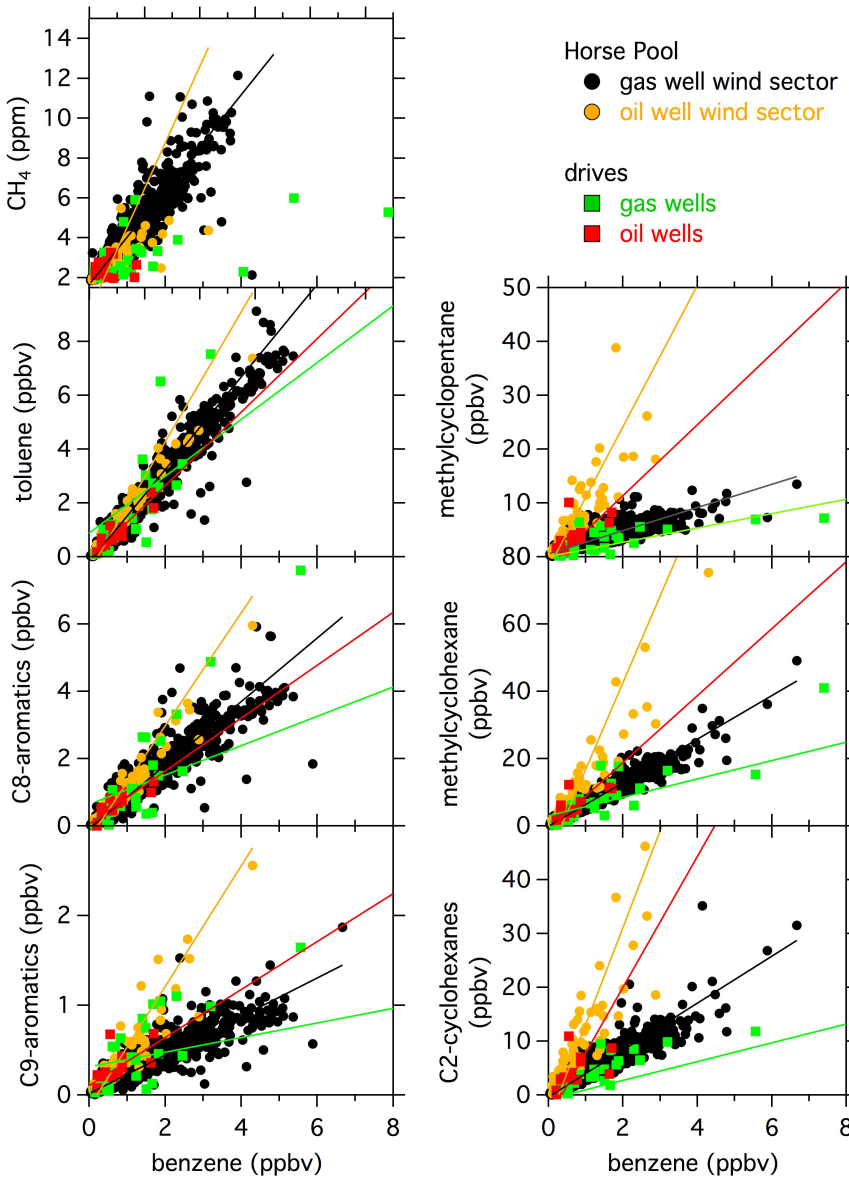
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2 **Figure 9.** The average mixing ratio of various VOCs (aromatics, cycloalkanes, methanol and  
 3 methane) close to emission sources in the Uintah basin are averaged for each category of point  
 4 sources. The error bars indicate the standard deviation. All average mixing ratios next to the  
 5 emission sources are normalized to an average 2 m/s wind speed.

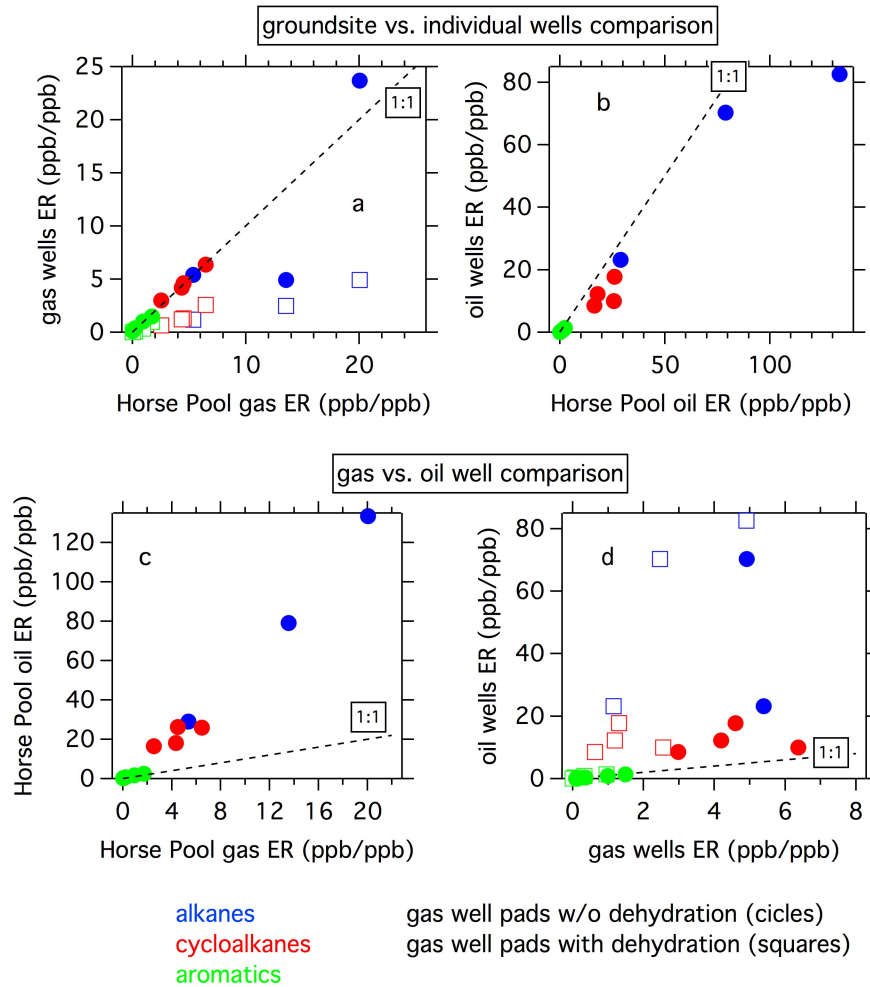
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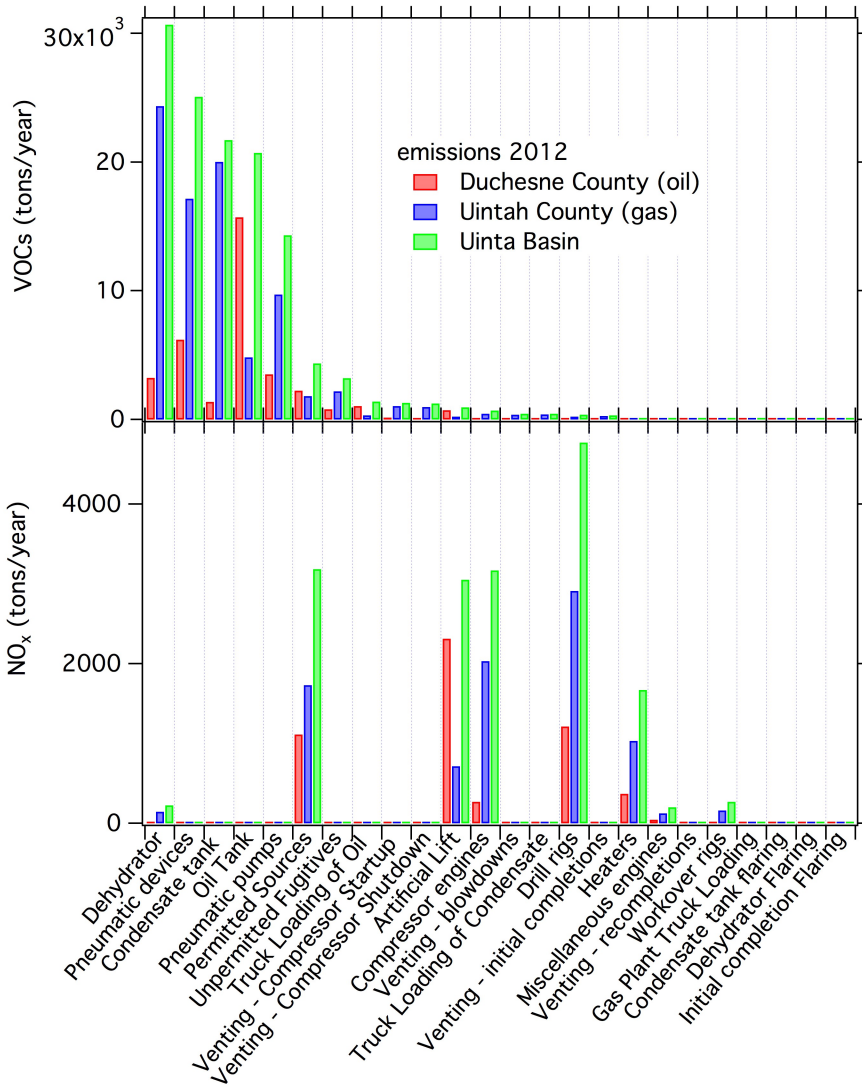
2 **Figure 10.** Scatter plots of various aromatics and cycloalkanes versus benzene for data from the  
 3 Horse Pool ground site separated into wind sectors that are dominated by either oil or gas wells  
 4 together with measurements from the mobile laboratory close to individual oil or gas well pads.

5



1  
 2 **Figure 11.** Enhancement ratios with benzene of aromatics (green), cycloalkanes (red) and  
 3 masses measured with the PTR-MS that are indicative of alkanes in arbitrary units (blue). (a) Gas  
 4 well pads without dehydration (circles) and gas well pads with dehydration (squares) compared  
 5 to the gas well sector from the Horse Pool ground site data, (b) oil well pads compared to the oil  
 6 well sector from the Horse Pool ground site data, (c) oil well sector compared to the gas well  
 7 sector for the Horse Pool ground site data, (d) oil well pads compared to gas well pads from the  
 8 Mobile Laboratory data.

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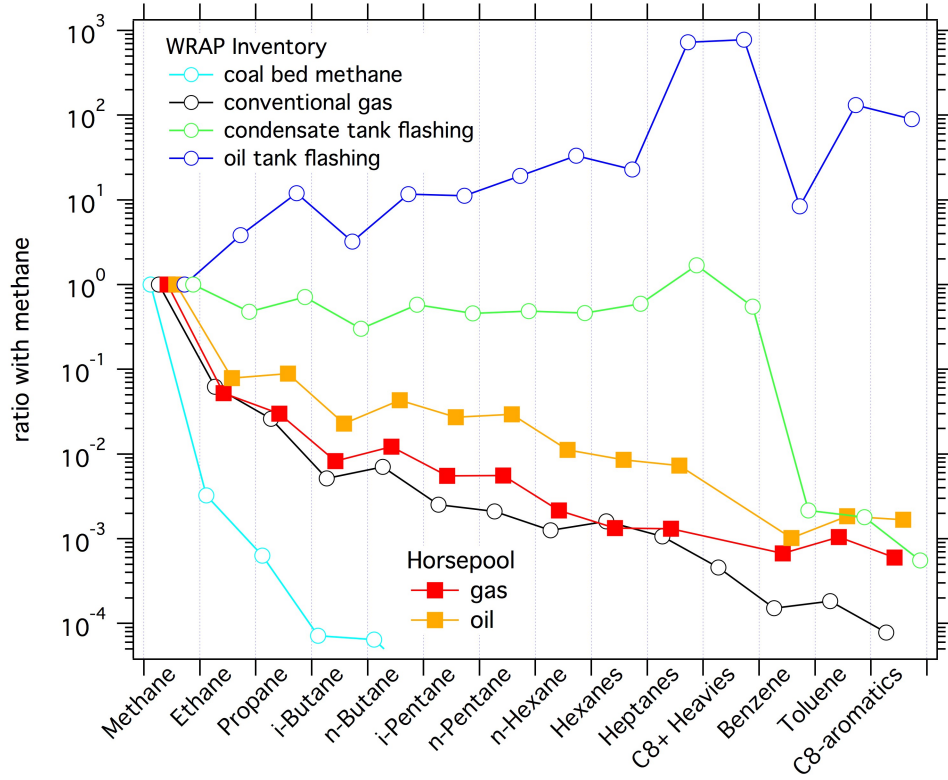


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2 **Figure 12.** Total emissions of VOCs and NO<sub>x</sub> as estimated from the Uinta Basin emission  
 3 inventory (WRAP inventory) by source category for Uintah and Duchesne Counties and the  
 4 Uinta Basin.

5





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2 **Figure 13.** Emission ratios of VOCs with methane from the Horsepool ground site compared to  
 3 the WRAP inventory VOC emission composition of the conventional gas, oil and condensate  
 4 tank flashing.

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