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Volatile organic compound emissions from the oil and natural gas industry in the Uinta Basin, Utah: point sources compared to ambient air composition

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Abstract

The emissions of volatile organic compounds (VOCs) associated with oil and natural gas production in the Uinta Basin, Utah were measured at a ground site in Horse Pool and from a NOAA mobile laboratory with PTR-MS instruments. The VOC compositions in the vicinity of individual gas and oil wells and other point sources such as evaporation ponds, compressor stations and injection wells are compared to the measurements at Horse Pool. High mixing ratios of aromatics, alkanes, cycloalkanes and methanol were observed for extended periods of time and short-term spikes caused by local point sources. The mixing ratios during the time the mobile laboratory spent on the well pads were averaged. High mixing ratios were found close to all point sources, but gas wells using dry-gas collection, which means dehydration happens at the well, were clearly associated with higher mixing ratios than other wells. Another large source was the flowback pond near a recently hydraulically re-fractured gas well. The comparison of the VOC composition of the emissions from the oil and natural gas wells showed that wet gas collection wells compared well with the majority of the data at Horse Pool and that oil wells compared well with the rest of the ground site data. Oil wells on average emit heavier compounds than gas wells. The mobile laboratory measurements confirm the results from an emissions inventory: the main VOC source categories from individual point sources are dehydrators, oil and condensate tank flashing and pneumatic devices and pumps. Raw natural gas is emitted from the pneumatic devices and pumps and heavier VOC mixes from the tank flashings.

1 Introduction

Since the introduction of hydraulic fracturing and horizontal drilling, the extraction of shale gas, often called unconventional natural gas, has increased and comprised 40 % of total production of natural dry gas in 2012 in the United States (US Energy Information Administration, 2014). In the Uinta Basin in Utah, the production of oil and natural gas also has increased in recent years and currently about 8000 gas wells and 2000 oil wells are in operation and about 1000 wells are added each year (Utah Oil and Gas, 2014). Most of the oil wells are located in Duchesne County on the western side of the basin and the gas wells are in Uintah County on the eastern side. In addition, there are also about 1000 coal bed methane wells and conventional wells located in Carbon County south of Uintah County. This intense oil and natural gas extraction operation results in emissions of greenhouse gases (mostly methane), volatile organic compounds (VOCs) and nitrogen oxides (NO_x) (Gilman et al., 2013; Howarth et al., 2011; Karion et al., 2013; Katzenstein et al., 2003; Kemball-Cook et al., 2010; Litovitz et al., 2013; Petron et al., 2012; Swarthout et al., 2013). Some of the VOCs emitted by oil and gas extraction are air toxics and can have direct health impacts for oil and gas workers and local residents (McKenzie et al., 2012). VOCs and NO_x can produce ozone in the atmosphere, which is generally seen as a summertime issue. In the Uinta Basin, however, ozone formation leading to mixing ratios above the EPA National Ambient Air Quality Standard (NAAQS) has been frequently observed in the winter, when the ground was snow-covered and strong temperature inversions persisted for several days (Schnell et al., 2009). The identification of the emission sources of VOCs and NO_x from oil and natural gas production in the Uinta Basin is key to understanding the processes leading to the formation of wintertime ozone.

In 2012 temperature inversions occurred, but the Uinta Basin was not snow covered and ozone formation was very small (Edwards et al., 2013). These conditions however were very amenable to study VOC emissions. Here we present measurements of VOCs using Proton-Transfer-Reaction Mass Spectrometry (PTR-MS) from UBWOS2012 (Uinta Basin Winter Ozone Study 2012) in the Uinta Basin in February 2012 at a ground site in Horse Pool and onboard a mobile laboratory to characterize the VOC composition of the emissions from individual gas and oil wells and other point sources such as evaporation ponds, compressor stations and injection wells. Recent studies using mobile platforms have focused on methane emissions from oil and gas activities in the Uinta Basin and elsewhere (Allen et al., 2013; Karion et al., 2013). In this publication we focus primarily on VOCs.

2 Experimental

2.1 Instrumentation

The UBWOS2012 study included a ground site in Horse Pool, Utah and the National Oceanic and Atmospheric Administration Global Monitoring Division (NOAA GMD) Mobile Laboratory. The Horse Pool ground site was fully equipped with a large suite of gas phase and aerosol measurements and only the instruments used in this study are described here. VOC measurements were made using PTR-MS instruments: the NOAA PTR-MS, which is described in detail by de Gouw and Warneke (de Gouw and Warneke, 2007) and the newly-developed Karlsruhe Institute of Technology (KIT) ULW-PTR-MS (ultra-light weight PTR-MS). PTR-MS is an on-line mass spectrometric technique for measuring VOCs in the atmosphere. In PTR-MS, H_3O^+ ions are used to ionize the compounds of interest in a reaction chamber and the primary and product ions are detected by a quadrupole mass spectrometer (de Gouw and Warneke, 2007). The NOAA PTR-MS was deployed at the Horse Pool ground site for the duration of the study from 15 January to 29 February 2012, while the KIT PTR-MS was used at the ground site for the first three weeks for detailed comparisons, and onboard the mobile laboratory for the next three weeks. The two PTR-MS instruments had similar reaction chambers and mass spectrometers, but the KIT ULW-PTR-MS was optimized for instrument size and weight and was 130 lbs compared to the standard PTR-MS, which is about 250 lbs. At the time of the study, the KIT ULW-PTRMS had a somewhat lower sensitivity of around 100–200 cps ppbv^{-1} compared to about 500–1000 cps ppbv^{-1} of the NOAA PTR-MS. After the study, the sensitivity of the KIT ULW-PTR-MS has been improved by about a factor of three. Calibrations were performed at the Horse Pool ground site every other day using a calibration standard with 10 different VOCs including oxygenates, aromatics and other compounds, and the mobile organic carbon calibration system (MOCCS) (Veres et al., 2010) for formaldehyde. The measurements at the ground site are averaged to 1 min data and the individual compounds on the mobile laboratory were measured for 0.5 s every 19 s. At the ground site the two instruments used the same inlet, the same calibration set-up and were located in the same trailer. The two instruments agreed for all reported VOCs within 10 % (not shown here), which gives a good confidence for the comparison of the ground site data with the mobile laboratory data.

VOCs were also measured at Horse Pool using an on-line gas chromatograph-mass spectrometer (GC-MS). The GC-MS sampled air for 5 min every 30 min and measured, among others, speciated C_2–C_{12} alkanes, C_5–C_8 cycloalkanes, C_6–C_9 aromatics and methanol. The instrument is described in more detail elsewhere (Gilman et al., 2010, 2013).

Methane was measured at Horse Pool using a 3-channel Picarro for CO_2, CH_4 and water vapor (Peischl et al., 2012) and on the NOAA GMD mobile laboratory using a 4-channel Picarro for CO_2, CO, CH_4 and water vapor.

A two-channel cavity ring-down spectrometer instrument NOxCaRD (Nitrogen Oxide Cavity Ring Down) was deployed in the mobile laboratory for the direct measurement of NO_2 by optical extinction at 405 nm, as described in Fuchs et al. (2009), and of either $NO_x (= NO_2 + NO)$ or $O_x (= NO_2 + O_3)$ after chemical conversion to NO_2. Simultaneous NO_2 and NO_x or O_x observations were made at a measurement frequency of 1 Hz. Calibrations, based on the absorption cross section of NO_2, were performed periodically and used a commercial O_3 monitor to generate and measure a known O_3 concentration, which was then quantitatively converted to NO_2. During the mobile laboratory drives, the NOxCaRDs precision was approximately 50 pptv (2σ, 1 s), and the accuracy, based on consistency of the in-field calibrations, was ±3 % for NO_2 and ±8 % for either NO_x or O_x.

2.2 PTR-MS VOC identification and inter-comparison

PTR-MS uses H_3O^+ ions to ionize VOCs of interest, which react fast with all compounds that have a higher proton affinity than that of water (de Gouw and Warneke, 2007). Among the compounds of interest for oil and gas emissions, this includes the aromatic compounds and methanol. Straight chain, branched and cyclic alkanes generally have a lower proton affinity than water. Those compounds, together with methane, make up more than 90 % of the mass of crude oil and natural gas (Ryerson et al., 2011).

Even though cycloalkanes have a lower proton affinity than water, they react with H_3O^+, albeit at a slower rate of about 10 % compared to most other VOCs. The most common pathway after reaction with H_3O^+ is proton transfer accompanied by hydrogen abstraction, such that the main masses produced from cycloalkanes in PTR-MS are masses 69, 83, 97, 111, and 125. Alkenes are also detected at these masses, especially isoprene, which is detected at mass 69. At the Horse Pool site only small amounts of alkenes were detected using GC-MS compared to alkanes and cycloalkanes and we therefore assume that the main contributors to those masses in the Uinta Basin are cycloalkanes. Using the fragmentation patterns determined by Yuan et al. (2014) we conclude that mass 83 is mainly from methylcyclopentane, mass 97 from methylcyclohexane, mass 111 and mass 69 from the C2-cyclohexanes, and mass 125 from the C3-cyclohexanes. PTR-MS calibrations of methylcyclopentane, methylcyclohexane, and 1,2-dimethylcyclohexane were performed prior to and during the field study using the MOCCS system (Veres et al., 2010). Using the determined sensitivities and mass identifications, the cycloalkanes from the PTR-MS are compared to the GC-MS at Horse Pool and the results are shown in Fig. 1. The two instruments agreed within the stated uncertainty of about 20 % for both instruments, which gives some confidence for the use of the PTR-MS cycloalkane mass signals. The PTR-MS signals for all measured cycloalkanes are larger than the GC-MS, which might indicate small interferences from other compounds besides the ones used in the sum of the GC-MS signals in Fig. 1.

Here it should be mentioned that the cycloalkanes also react fast with O_2^+, which is about 1–5 % of H_3O^+ in the PTR-MS, but the contributions from O_2^+ reactions to the cycloalkane masses are likely small compared to H_3O^+ (Yuan et al., 2014).

Small alkanes, on the other hand, do not react with H_3O^+, they only undergo charge transfer reactions with O_2^+, which results in many different fragment ions with various masses (Francis et al., 2007; Spanel and Smith, 1998; Yuan et al., 2014). Small alkanes are therefore not detected very selectively and only with a very low sensitivity with PTR-MS. During UBWOS2012 we monitored several of those alkane masses and in the following we will use masses 43, 57, 71, and 85. Each of these masses have contributions from several alkanes, straight-chain and branched, such that none of the masses can be used quantitatively for individual compounds, but generally the lighter the alkane is the smaller the resulting ions are (Francis et al., 2007). Calibrations for several alkanes were performed in the lab and the determined sensitivities were about 3 % of other VOCs, which was used to convert alkane mass signals into approximate corresponding mixing ratios. These masses are also common fragments of other compounds such as alcohols and ketones (Warneke et al., 2003, 1996). Using the VOC composition at Horse Pool measured by GC-MS during UBWOS2012, the signals from these other compounds are expected to be small compared to the signals resulting from the alkanes. The alkane masses will be used in this work only as indicators for the presence of small alkanes.

3 Results and discussion

3.1 Mixing ratios at the ground site in the Uinta Basin

A map of the Uinta Basin that indicates the locations of the oil and gas wells and several other point sources is shown in Fig. 2. The Horse Pool ground site and the drive tracks used for this study with the Mobile Laboratory are shown as well. The Horse Pool ground site is at the northern edge of the gas field and surrounded by

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many gas wells and also a few oil wells to the north of the site. The top panel of Fig. 3 shows a time series benzene and toluene for one selected day and the other panels selected VOCs for the UBWOS2012 campaign. The mixing ratios observed at the site are characterized by high values for extended periods of time during stagnation events in the basin and by very high mixing ratios during short-term spikes caused by local point sources. For example, benzene and toluene were over 3 ppbv from 30 January to 2 February before the basin cleaned out just after noon on 2 February. In addition toluene spikes of well over 10 ppbv for 1 min average data were frequently observed. Methanol, used as an anti-freeze and anti-coagulant in gas and oil wells, was almost an order of magnitude higher than the aromatics and mixing ratios of several hundreds of ppbv were detected in the spikes.

3.2 Typical mixing ratios downwind of point sources

To investigate the emissions from point sources in the Uinta Basin that are responsible for the elevated mixing ratios of VOCs observed at the Horse Pool ground site, the Mobile Laboratory was used to measure immediately downwind of individual facilities: (1) gas wells using wet-gas collection, which means dehydration happens at a central facility, (2) gas wells using dry-gas collection, which means dehydration happens at the well, (3) oil wells, (4) gas wells near Rangely, CO, (5) a recently hydraulically re-fractured well with a flow-back pond, (6) a newly producing gas well and (7) other point sources including natural gas compressor stations, produced-water injection wells, condensate and oil tank batteries, evaporation ponds and water treatment plants.

A photograph of a typical gas well in the Uinta Basin is shown in Fig. 4a together with an oil well in Fig. 4c and typical mixing ratios downwind of such wells are shown in Fig. 5 (gas well) and Fig. 6 (oil well). The track of the Mobile Laboratory in close proximity downwind (indicated by the wind barbs) of the wells are shown in Fig. 5b–e and 6b–e and are color-coded by methane, methanol, toluene, and NO_2, respectively. The corresponding time series are shown in Figs. 5a and 6a. Close to this particular gas well, over 10 ppmv of methane, 40 ppbv of toluene and 500 ppbv of methanol were detected (Fig. 5). These three compounds illustrate the elevated mixing ratios close to the well and also that different components of the gas well are responsible for different emissions. At most wells, methane is highest downwind of the separator, but is also emitted from the wellhead. Toluene and other aromatics are highest downwind of the condensate and water tanks. Methanol is highest downwind of the methanol and condensate tanks, and NO_2 downwind of the compressor.

At many oil wells, such as the one shown in Fig. 6, oil tanks were used, which were the main source for the aromatic compounds similar to the gas well condensate tanks. Methane comes from the wellhead, methanol from the wellhead and also the pump jack, and the NO_2 comes mainly from the generator and pump jack, which is typically driven by an internal-combustion engine (Fig. 6). At the Horse Pool ground site all of these compounds were much better correlated, because there was enough time for mixing after the emission.

During UBWOS2012 38 different gas wells, 12 oil wells, a newly producing well, a refractured well with a flow back pond, and 17 other point sources such as evaporation ponds, storage tanks and compressor stations were investigated in a similar way as described above. The mixing ratios of the measured VOCs were averaged during the time the Mobile Laboratory spent in close proximity downwind, generally within 300 feet of the wells or the other emission sources in order to provide a means of comparison with the Horse Pool site measurements and aggregated emissions inventories. The results are shown in Fig. 7. This average is somewhat influenced by the relative amount of background air encountered during the averaging time, but this does not influence the conclusions in this work. The maximum observed mixing ratios close to the sources for selected VOCs and methane (shown in Fig. 8) show similar trends as the averages, but also give an indication of how elevated mixing ratios close to the sources were. Figures 5–8 demonstrate that mixing ratios of aromatics and methanol near 1 ppmv and of methane of hundreds of ppmv were measured several times during the drives.

The data in Fig. 7 are then normalized to $2\,\mathrm{m\,s^{-1}}$ wind speed (dividing the mixing ratio by the wind speed in $\mathrm{m\ s^{-1}}$ and multiplying by $2\,\mathrm{m\,s^{-1}}$) to account for different dilutions at different wind speeds by using the average observed horizontal winds over the same time period. The windspeed-normalized results for only the gas and oil wells are averaged and shown in Fig. 9. Here it should be mentioned that we do not have any information about the vertical extent of the plumes from the gas wells and the other point sources, such that an estimate of emission rates is not possible and therefore only average mixing ratios close to the sources are discussed here.

Strongly elevated mixing ratios of the measured VOCs were found at almost all source locations, but very large differences even between similar point sources existed. The largest relative differences were observed between individual gas wells. For example, average normalized toluene mixing ratios < 10 ppbv were observed next to several gas wells, but in the same gas field or formation two orders of magnitude larger mixing ratios of > 100 ppbv were found next to other gas wells. The average mixing ratios close to investigated oil wells in Duchesne County in Fig. 9 generally show smaller mixing ratios than gas wells using dehydrators and similar gas wells without dehydrators in Uintah County. The Mobile Laboratory usually spent about 20–30 min close to each gas well and generally no variations on the order of the well-to-well variability were observed. This seems to indicate that the main reason for the different emissions is the different practices and as a result different equipment used for so-called wet and dry gas collection wells. The difference between these two types of wells is that the dehydration is done at the well site on a dry gas collection well and at a central facility on a wet gas collection well. Here wet or dry collection refers to the amount of water in the collection pipelines; the raw gas composition can be similar for both types of wells. This means that dry-gas collection wells require glycol dehydrators that include a heater and a glycol regenerator at the well site. All of these components have VOC emissions and therefore this category has higher mixing ratios associated with them. Wet-gas collection wells do not use this equipment at the well site, but have the dehydration and associated emissions at centralized compression stations. Furthermore, the investigated wells using dehydrators on site generally had higher condensate production rates, which usually also lead to higher emissions and as shown in Fig. 5, the emissions of the aromatic compounds mainly came from the condensate tanks. No clear correlations of the average mixing ratios next to gas wells with well age or cumulative well production were found.

As a comparison, also shown in Figs. 7–9 are average mixing ratios close to gas wells in Rangely, Colorado, which is another part of the Uinta-Piceance Basin and located in the north-west corner of Colorado. About 20 miles separate the gas field in Rangely from the Uinta Basin, but the oil and gas exploration has a very different character. The gas field is much drier (less hydrocarbon liquids and more gas) and the density of wells is higher, which results in very different practices for the natural gas extraction. In the Piceance Basin about the same amount of gas but only a little more than a quarter of oil is produced compared to the Uinta Basin. A photo of a typical gas well in Rangely, CO is also shown in Fig. 4b. The gas is transported with pipelines to a central facility in Rangely similar to the Uinta Basin, but in Rangely underground and in Uinta above ground pipelines are used. Another difference is that in Rangely electric power is available at most wells. As a result, few wellhead compressors, combustion generators or condensate tanks are used in this particular area, which are significant emitters of VOCs and NO_x in the Uinta Basin. As a result, mixing ratios observed close to all investigated gas wells were still elevated from ambient but generally lower than in the Uinta Basin.

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

The other point sources investigated shown in Figs. 7 and 8 included condensate and oil tank batteries, produced water treatment plants, compressor stations, produced water evaporation ponds, and processing plants. We do not have enough measurements of the individual types of point sources to compare them in statistically meaningful ways to the oil or gas wells, but mixing ratios close to those sources were generally in the same range as many of the gas wells. Here it should be mentioned that the potentially largest sources (according to the WRAP inventory described below) of VOC and NO_x in the Uinta Basin are the natural gas processing plants such as the Chapita Plant. These plants use stacks and their main emissions cannot be reliably measured from the ground with the Mobile Laboratory.

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

3.3 VOC composition comparison of oil and gas well emissions

Gas and oil wells are by far the most numerous point sources in the Uinta Basin and as such will be important emission sources of VOCs. Therefore we focus on the analysis of the VOC composition of gas and oil wells. Scatter plots of the measured VOCs vs. benzene are used to compare the VOC composition emitted from oil and gas wells to the ground site. The Horse Pool data are segregated into two classes based on their unique chemical composition. About 5 % of the data exhibited a distinctly different chemical composition. For example, these samples were enhanced in C_4–C_{11} n-alkanes relative to propane, but had a significantly lower ethane to propane ratio as measured by the GC-MS for the majority of the Horse Pool data. Wind sector analysis showed that these samples were almost exclusively from the northwest where two nearby oil wells were located. The predominant wind direction at Horse Pool had a southern component where the vast majority of the gas wells in Uinta Basin are located. The 5 mind averaged data from the two sectors (now referred to as oil and gas well sectors) are shown in Fig. 10 and are compared to the average mixing ratios close to oil and gas wells measured from the Mobile Laboratory (data from Figs. 7–9). The left panel shows methane and the aromatics and the right panel the cycloalkanes. The Horse Pool data show good correlations for all compounds with benzene, especially for the gas well sector. Ratios with benzene were used instead of the lightest compound methane, because most VOCs measured by PTR-MS downwind of the gas and oil wells did not correlate well enough with methane. The slopes of the larger aromatics and the cycloalkanes with benzene in the oil well sector are clearly different from the gas well sector and the difference increases with the molecular weight of the compound. The mobile laboratory measurements from the individual wells show comparable slopes and differences between oil and gas wells, but the large well-to-well differences result in a larger variability. In the top right panel the linear fits for the four categories are shown together with the data.

In order to compare the emission profile of VOCs measured in the Mobile Laboratory downwind of oil and gas wells to the emission profiles observed at Horse Pool, we compare enhancement ratios with benzene shown in Fig. 11, where each data point represents one compound and is colored by compound class. Enhancement ratios are determined from the slopes of the linear fits (indicated for methylcyclopentane in Fig. 10), for cycloalkanes and aromatics and also for the PTR-MS alkane masses with benzene. Figure 11a and b compare the enhancement ratios for the individual gas wells with or without dehydrators and oil wells with the measurements from the Horse Pool ground site. In the surroundings of Horse Pool wells without dehydrators dominate and their enhancement ratios are in good agreement with Horse Pool data. The wells with dehydrators do not agree as well with the Horse Pool data: the enhancement ratios with benzene, which is the lightest aromatic, are below the 1 : 1 line, which means that the composition of wells without dehydrators (alkanes, cycloalkanes and aromatics) is a lighter mixture of VOCs than the wells with dehydrators; however wells with dehydrators had higher mixing ratios associated with them. The enhancement ratios for the oil wells and the oil well sector at Horse Pool agree well with each other as shown in Fig. 11b.

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

3.4 VOC composition comparison with emission inventory

The Uinta Basin emission inventory from the Western Regional Air Partnership (WRAP) provides an estimation of the criteria pollutant emissions for oil and gas exploration and production in the Uinta Basin for 2006 and projections for 2012 (available at: http://www.wrapair.org/forums/ogwg/PhaseIII_Inventory.html). The emissions calculated in the WRAP inventory are based on the well counts, production data and extensive operator survey data related to the identified oil and gas source categories. Figure 12 shows the VOC and NO_x emissions as estimated by the WRAP inventory by source category for Uintah County (mainly gas wells), Duchesne County (mainly oil wells) and the whole Uinta Basin. In the inventory, about 89 % of the VOC emissions are from dehydrators, condensate and oil tanks, pneumatic pumps and pneumatic devices and about 78 % of the NO_x emissions are from drilling rigs, compressor engines, artificial lift engines and heaters. We did not systematically sample the largest NO_x sources with the Mobile Laboratory and do not present an analysis of the NO_x inventory here. In the WRAP inventory, fugitive emissions from oil and gas pipelines from wellheads to the main compressor stations are not included, which are potentially a large source category.

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

Figure 11 showed that Horse Pool gas and oil well sectors compared closely to the individual gas and oil wells and therefore these data are used as a good proxy for individual wells. The VOC emission ratios with methane from Horse Pool are compared to the VOC composition used in the WRAP inventory in Fig. 13. The gas well measurements resemble most closely the conventional gas, but are heavier in composition and the oil well emissions are even heavier, where the difference with the conventional gas is largest for the aromatic compounds. The measurements from the oil and gas wells and at Horse Pool will therefore be a mixture of conventional gas (from the pneumatic devices and pumps and other venting sources) with tank flashing and dehydrators, similar to what the WRAP inventory shows.

Measurements of the individual wells shown in Figs. 5 and 6 have demonstrated that VOCs are emitted with varying compositions from the different source categories. The measurements are broadly consistent with the WRAP inventory: (1) the inventory correctly identifies the dehydrator, the tank flashing and the pneumatic devices as major VOC emission sources from the gas and oil wells, (2) the oil and condensate tank emit heavier compounds and (3) the wellhead, dehydrator and pneumatic devices emit lighter compounds.

4 Conclusions

High mixing ratios of VOCs associated with emissions from oil and gas exploration and production operations (alkane, cycloalkanes, aromatics and methanol) were found in the Uinta Basin in winter 2012 at a ground site and using a mobile laboratory. Individual oil and gas wells were investigated using the Mobile Laboratory and it was found that the separator, dehydrator and pneumatic devices and pumps emit a light VOC mix similar to the natural gas composition, whereas the oil and condensate tanks emit heavier VOCs. High methanol concentrations were observed downwind of methanol tanks and condensate tanks. Other point sources such as a flow-back pond from a recently hydraulically re-fractured well and evaporation ponds were also found to be large VOC emission sources. Looking at the measured VOC composition and the WRAP emission inventory it seems that the main emission sources in the Uinta Basin are individual wells, such that the observed VOC composition is a mixture of raw natural gas with oil and condensate tank flashing.

The results presented here were some of the first measurements using fast-response VOC instruments to look at individual gas and oil wells and other point sources associated with oil and natural gas production, but future measurements on a mobile laboratory are needed to determine emission rates in addition to ambient mixing ratios. Furthermore, more detailed fast-response VOC composition measurements are needed to better characterize the VOC composition of the individual source categories and identify the most important emission categories.

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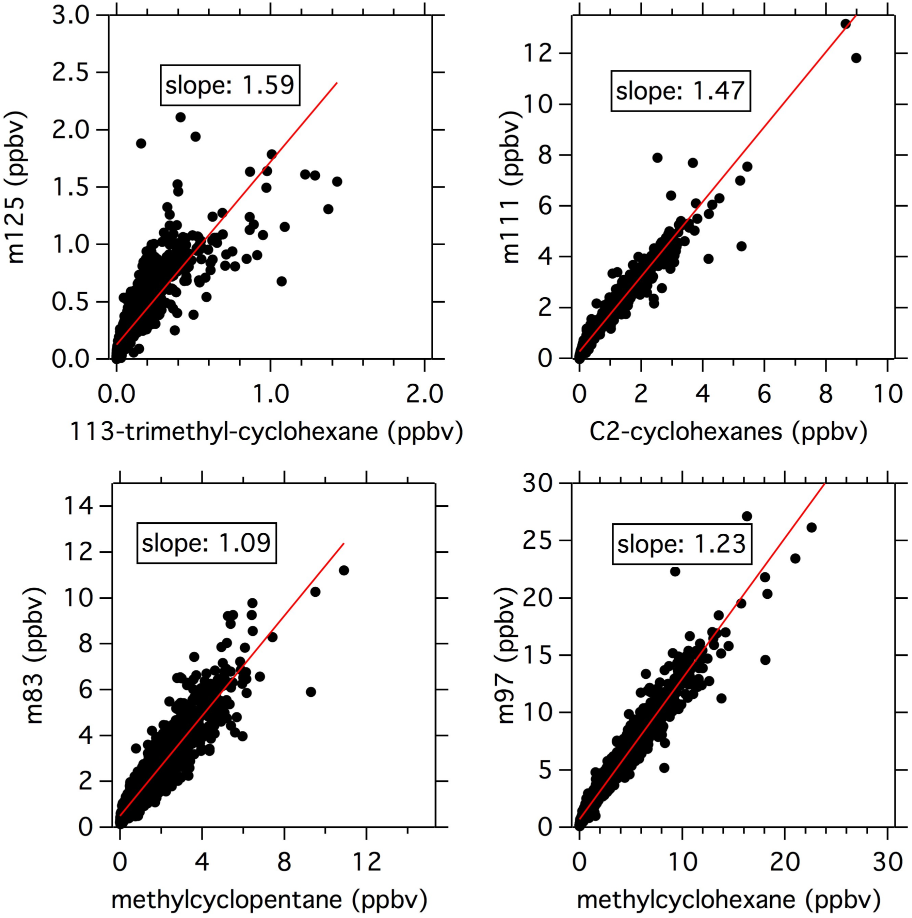

Fig. 1. Inter-comparison of the masses measured by PTR-MS that are indicative of cycloalkanes with GC-MS cycloalkane mixing ratios at the Horse Pool site.

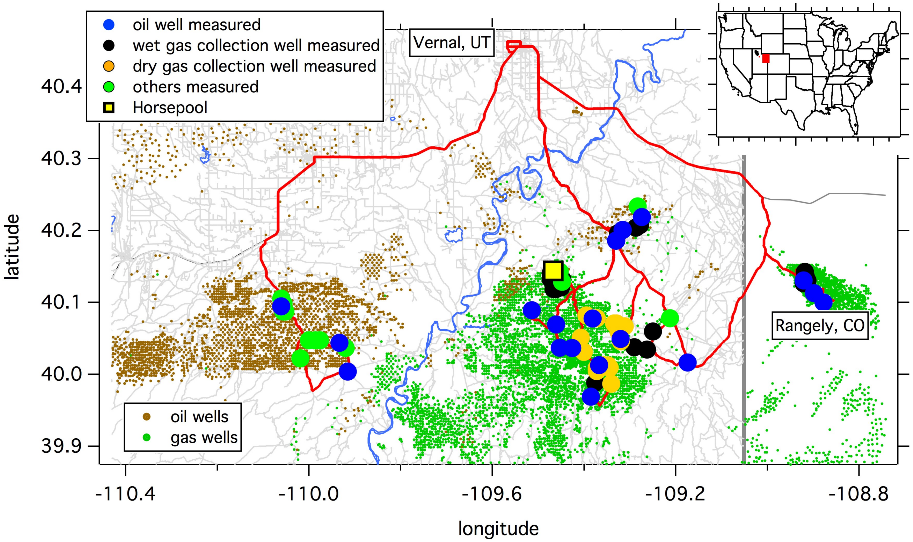

Fig. 2. A map of the Uinta Basin study area showing the locations of oil and gas wells and the Horse Pool ground site. The route of the drives (red lines) is shown together with the locations of the investigated point sources.

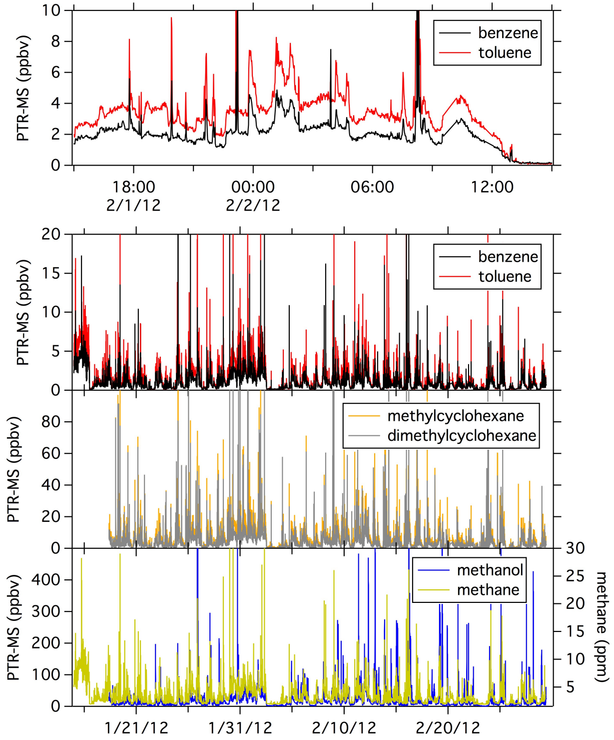

Fig. 3. The time series of benzene and toluene for one day and various VOCs measured by PTR-MS and methane for the whole measurement period at the Horse Pool ground site during the UBWOS2012 campaign. Maximum mixing ratios are off-scale.

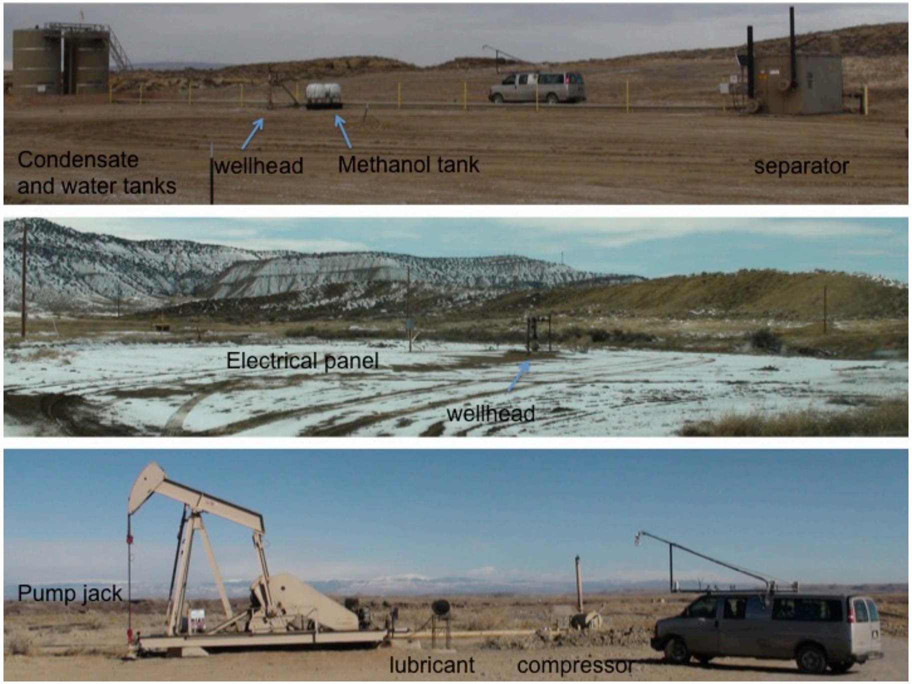

Fig. 4. Top: picture of a typical natural gas well in the Uinta Basin. Middle: picture of a typical natural gas well in Rangely, Colorado. Bottom: picture of a typical oil well in the Uinta Basin.

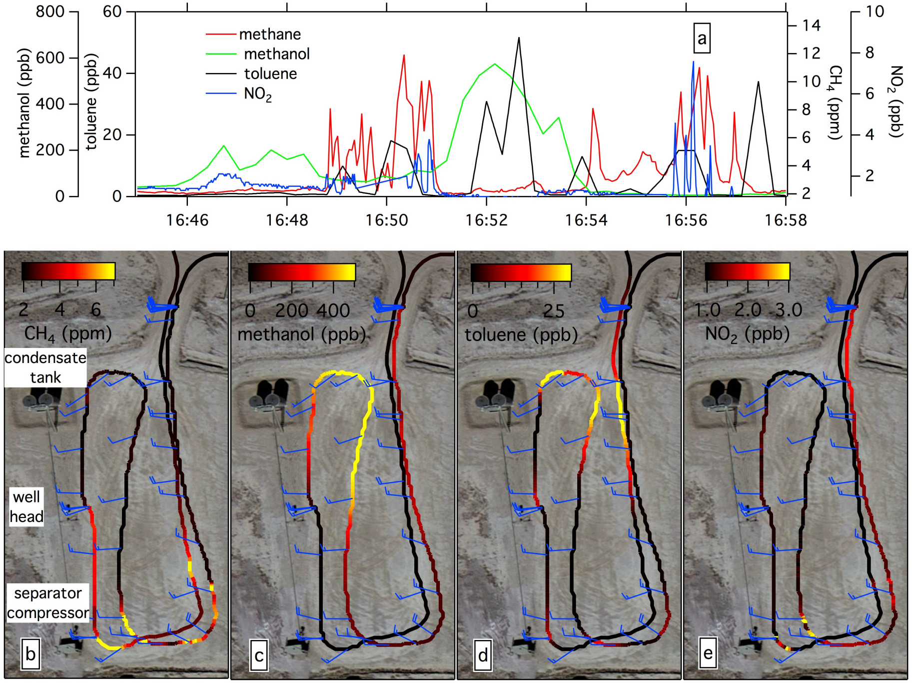

Fig. 5. The drive track close to a gas well color coded by measured methane **(b)**, methanol **(c)**, toluene **(d)** and **(e)** NO$_2$. The wind barbs indicate the prevailing wind direction coming from left to right in the image. The time series for this period is shown in **(a)**.

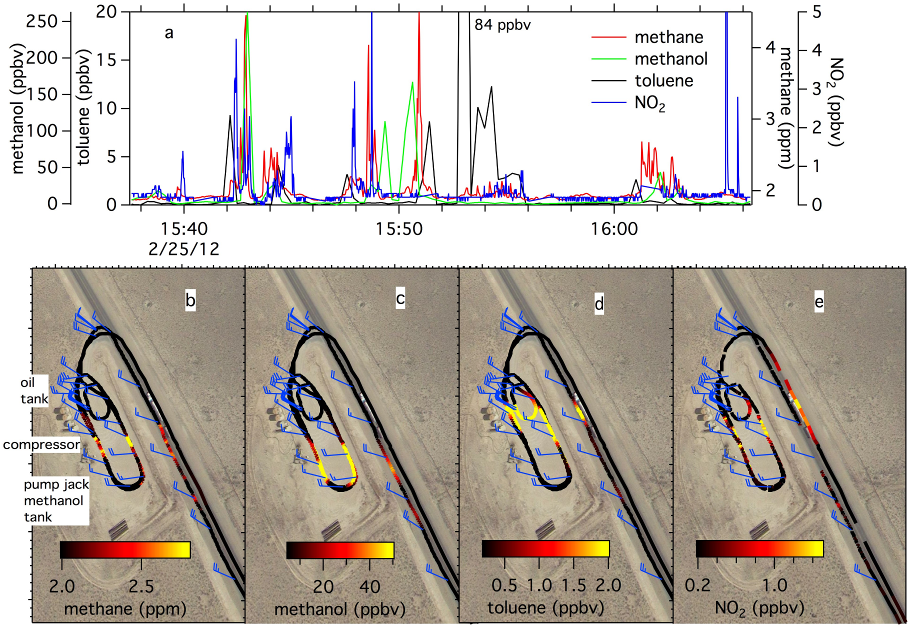

Fig. 6. The drive track close to an oil well color coded with methane **(b)**, methanol **(c)**, toluene **(d)** and **(e)** NO_2. The wind barbs indicate the prevailing wind direction. The time series for this period is shown in **(a)**.

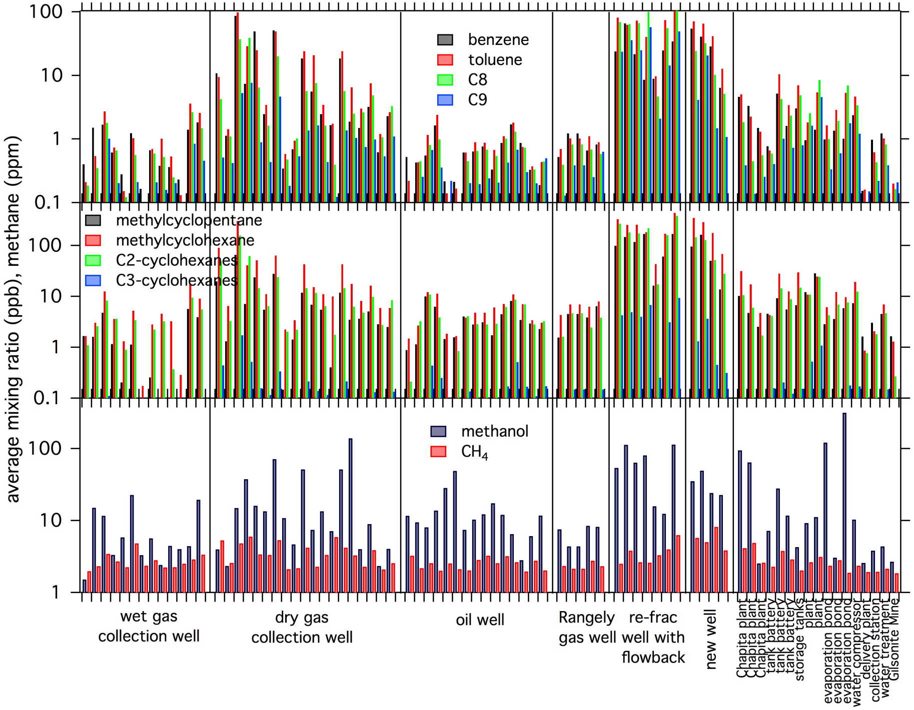

Fig. 7. The average mixing ratios of various VOCs (aromatics, cycloalkanes, methanol and methane) observed close to individual point sources in the Uinta Basin and in Rangely, Colorado.

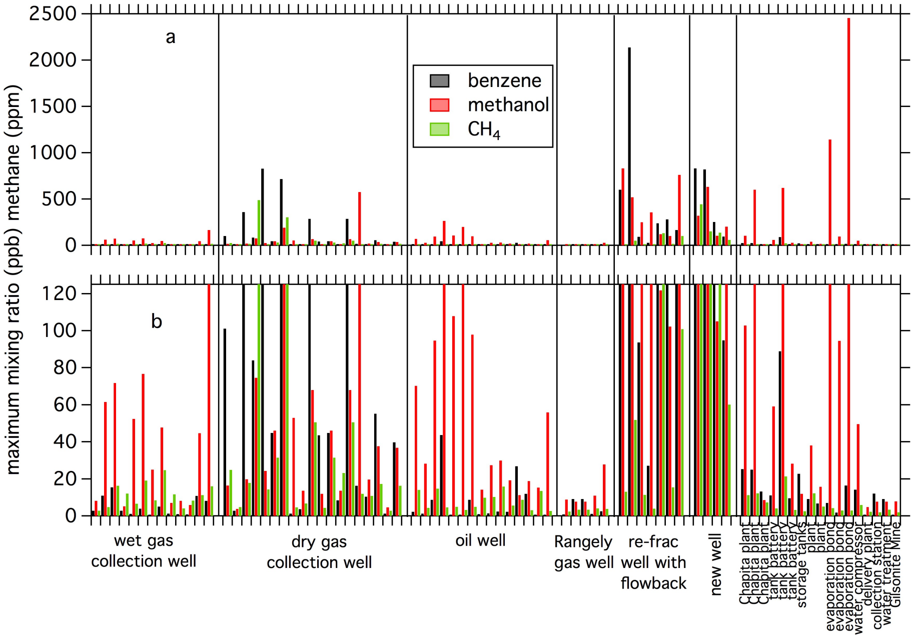

Fig. 8. The maximum mixing ratio of benzene, methanol and methane observed close to the investigated emission sources in the Uinta Basin and in Rangely, Colorado. **(a)** Full scale and **(b)** small scale.

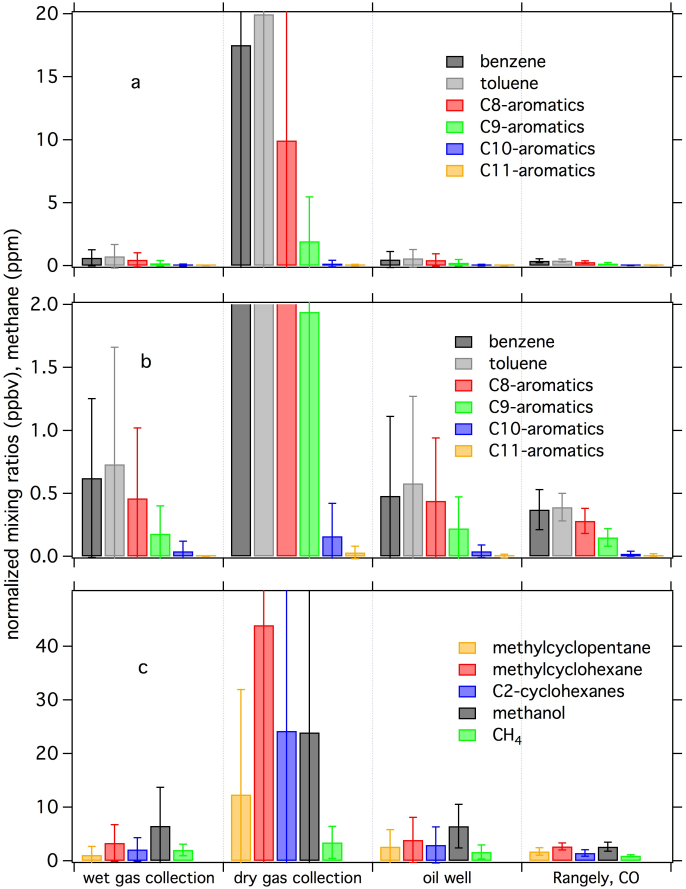

Fig. 9. The average mixing ratio of various VOCs (aromatics, cycloalkanes, methanol and methane) close to emission sources in the Uintah basin are averaged for each category of point sources. The error bars indicate the standard deviation. All average mixing ratios next to the emission sources are normalized to an average 2 m s^{-1} wind speed.

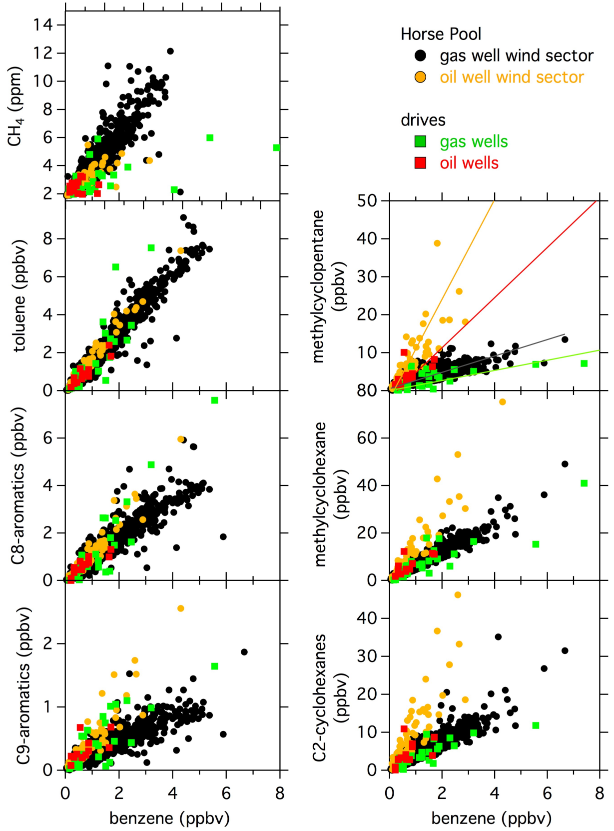

Fig. 10. Scatter plots of various aromatics and cycloalkanes vs. benzene for data from the Horse Pool ground site separated into wind sectors that are dominated by either oil or gas wells together with measurements from the mobile laboratory close to individual oil or gas wells.

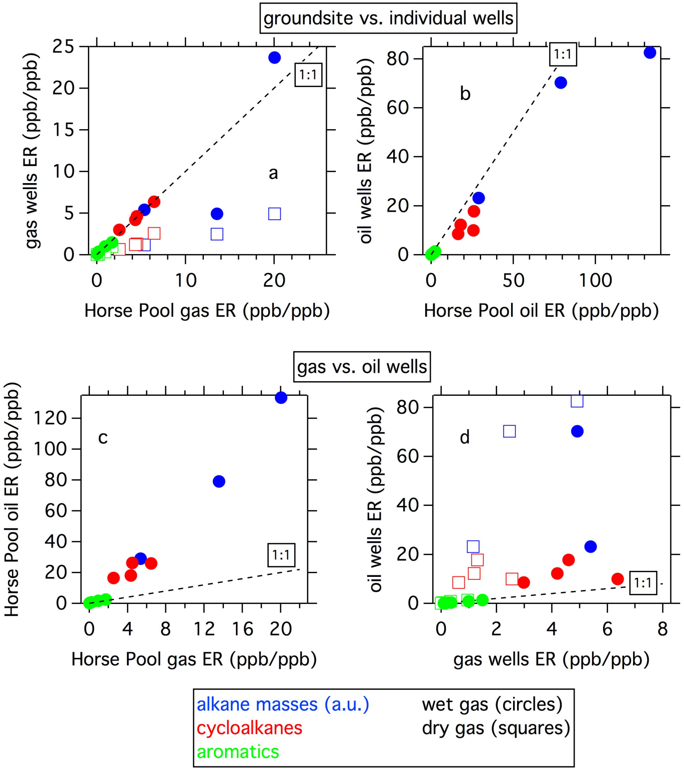

Fig. 11. Enhancement ratios with benzene of aromatics (green), cycloalkanes (red) and masses measured with the PTR-MS that are indicative of alkanes in arbitrary units (blue). **(a)** Wet (circles) and dry (squares) gas collection wells compared to the gas well sector from the Horse Pool ground site data, **(b)** oil wells compared to the oil well sector from the Horse Pool ground site data, **(c)** oil well sector compared to the gas well sector for the Horse Pool ground site data, **(d)** oil wells compared to gas wells from the Mobile Laboratory data.

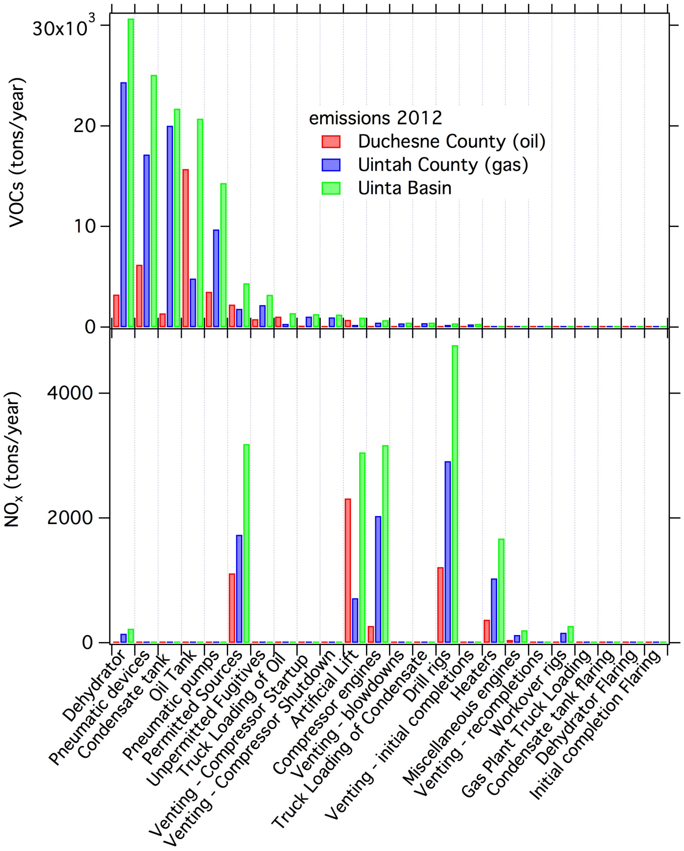

Fig. 12. Total emissions of VOCs and NO_x as estimated from the Uinta Basin emission inventory (WRAP inventory) by source category for Uintah and Duchesne Counties and the Uinta Basin.

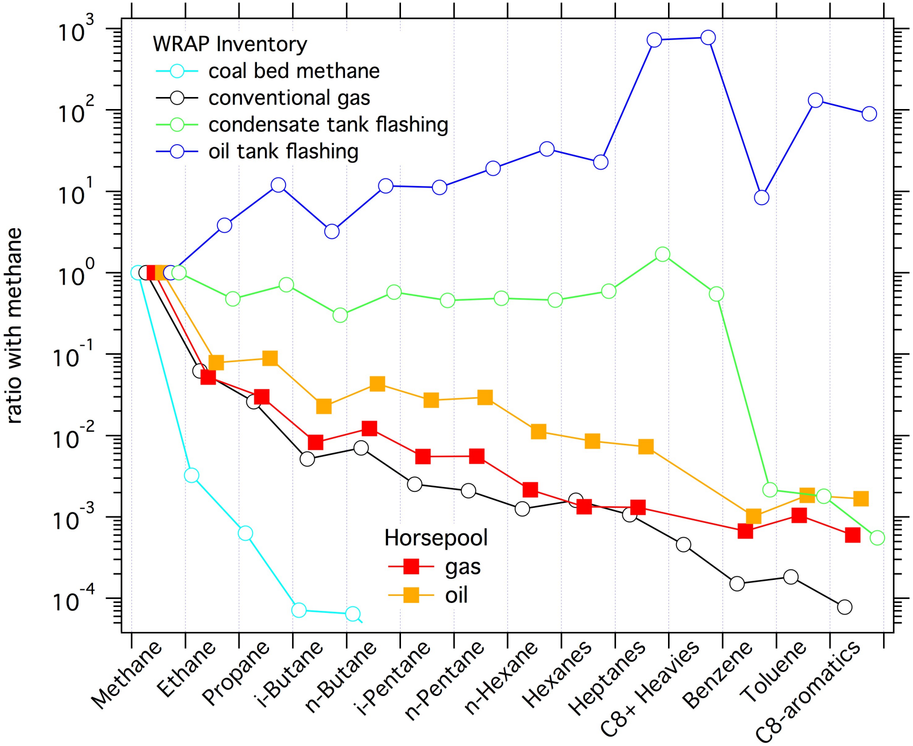

Fig. 13. Emission ratios of VOCs with methane from the Horsepool ground site compared to the WRAP inventory VOC emission composition of the conventional gas, oil and condensate tank flashing.