RESEARCH ARTICLE

Air quality measurements in the western Eagle Ford Shale

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The Eagle Ford Shale in southern Texas remains one of the most productive oil and gas regions in the US. Like the Permian Basin and Bakken Shale, ubiquitous natural gas flaring serves as an uncertain source of trace gas emissions within the Eagle Ford. A lack of ambient air quality data, especially in the western shale, impedes a thorough understanding of trace gas emissions within the shale and the subsequent local/regional air quality impacts. Meteorological and trace gas instrumentation was deployed to Shape Ranch in southwestern Dimmit County, near the US/Mexico border, from April to November of 2015. Mixing ratios of CO, NO\textsubscript{x}, O\textsubscript{3}, and VOCs did not exceed ambient air quality standards and were generally lower than mixing ratios measured in US cities, with the exception of alkanes. A non-negative matrix factorization demonstrated the dominance of oil and gas-sector emission sources in local trace gas variability, with combustion processes and transport of continental air also present. An analysis of NO\textsubscript{x}/CO and NO\textsubscript{x}/CO\textsubscript{2} ratios during periods of O\textsubscript{3} titration, identified by the ambient NO\textsubscript{x}/O\textsubscript{3} ratio, suggested that combustion and biospheric sources contributed to emissions of NO\textsubscript{x}, CO, and CO\textsubscript{2}. In-plume NO\textsubscript{x}/CO\textsubscript{2} ratios indicated relatively low-temperature combustion sources, with median NO\textsubscript{x}/CO\textsubscript{2} ratios close to that expected for natural gas flaring (0.54 ppb/ppm), and much lower than emission ratios for internal combustion engines (>10 ppb/ppm). However, the NO\textsubscript{x}/CO\textsubscript{2} ratio within these plumes exhibited a large variability, spanning more than an order of magnitude. Future research should focus on improving flaring emission factors and flaring volume estimates such that their air quality impacts can be better understood.

Keywords: Petroleum; Air quality; Oil and Gas; Emissions; Flaring; Eagle Ford Shale

1. Introduction

The Eagle Ford Shale (EFS) in south-central Texas has become one of the most productive shale plays in the United States – second in oil production and fifth in natural gas production among US shale plays in 2017 (U.S. Energy Information Administration, 2018a, 2018b). Like other shale oil and gas plays and conventional fossil fuel sources, production of oil and gas in the EFS has potential impacts on both the climate and local/regional air quality (Pacsi et al., 2015; Parrish et al., 2017; Peischl et al., 2018; Roest and Schade, 2017; Schade and Roest, 2015, 2016, 2018). Emissions of criteria air pollutants (CAPs), hazardous air pollutants (HAPs), and other pollutant precursors have been studied in active oil and gas producing regions across the US. Elevated mixing ratios of volatile organic compounds (VOCs) – important ozone (O\textsubscript{3}) and particulate matter (PM) precursors – have been found in several active oil and gas producing regions, including the Colorado Front Range (Gilman et al., 2013), the Marcellus Shale (Swarthout et al., 2015), the Permian Basin (Koss et al., 2017), and the EFS (Schade and Roest, 2018, 2016), among others. Nitrogen oxides (NO\textsubscript{x}) – also important O\textsubscript{3} and PM precursors and respiratory irritants (Chauhan et al., 1998) – have also been observed in high abundance in several regions, such as the Bakken Shale in North Dakota (Prenni et al., 2016).

The proximity of the EFS to the city of San Antonio has raised air quality concerns as the city’s O\textsubscript{3} design values – the three-year average of the fourth-highest annual daily maximum 8 hour average mixing ratio (U.S. Code of Federal Regulations, 2015) – have been above the EPA’s 8-hour O\textsubscript{3} National Ambient Air Quality Standard (NAAQS) for several years. However, due to the large uncertainties in emissions from oil and gas and the sparsity of ambient air quality measurements, knowledge of the local and regional air quality impacts of the EFS remains limited. Furthermore, as the EFS rapidly developed in rural Texas, a limited pipeline network led to widespread flaring to destroy gas that would otherwise be emitted into the atmosphere. Flaring is used principally to destroy excess natural gas produced at oil wells, called “associated gas.”
The EFS, along with the Bakken Shale and the Permian Basin, has been identified in satellite imagery as a region with a high density of observed flares (Elvidge et al., 2015, Fig. S1) and coincident increases in NO$_x$ abundances have been detected using satellite data (Majid et al., 2017). This increased use of flaring introduces a particularly indeterminate emission source since flaring volumes are under-reported in Texas (Wilardy and Schade, 2019) and flaring emission factors are highly uncertain (Strosher, 2000; Torres et al., 2012; U.S. Environmental Protection Agency, 2016). Because flaring may have significant air quality impacts on a local- to regional-scale (Olague, 2012), flaring emissions need to be properly quantified before overall air quality impacts can be accurately assessed.

To better understand the air quality impacts of unconventional oil and gas development, increased monitoring and data analyses are needed to identify and characterize emission sources. Here, we present an assessment of ambient air quality measurements on Shape Ranch – a working bison ranch in southwestern Dimmit County in the western EFS. This site, which is far removed from urban emissions, may represent ambient air quality in the more rural regions of the EFS where no other ambient air quality data exist. This assessment provides information about the exposure to pollution of rural communities in the EFS, and the airmass composition that may be advected into major urban areas, such as San Antonio. Emission source types were identified using a non-negative matrix factorization, and NO$_x$/CO$_2$ ratios were used to identify and characterize low temperature combustion plumes.

2. Measurements

2.1. Site location and environment
An air-conditioned trailer was placed on Shape Ranch – a large, working bison ranch near the southwestern corner of Dimmit County in southern Texas. The trailer was parked south of an olive tree grove adjacent to a house construction site toward the northeast. This location provided access to reliable line power and would provide the homeowners with information about their exposure to pollution near their new home. An air conditioner on the trailer’s roof cooled the inside, which housed all trace gas instrumentation, a Campbell Scientific CR1000 data logger, and a Dell Precision T3400 PC. Trace gas instrumentation included a NO/NO$_x$ analyzer, a Gas-Filter-Correlation (GFC) CO analyzer, an NDIR CO$_2$/H$_2$O analyzer, a UV-absorption O$_3$ analyzer, and a dual-channel gas chromatograph (GC) with FIDs (SRI model 8610). Specifications for these instruments are shown in Tables S1 and S2.

Meteorological instrumentation from Campbell Scientific included a temperature and relative humidity sensor, a tri-cup anemometer, a barometer, a pyranometer, and a tipping-bucket rain gauge, all installed on a beam 3 m agl extending from the rear of the trailer toward the east. Air sampling was performed at the end of the beam through a single ¼” ID PFA Teflon line with PTFE inlet filter using the air quality monitors’ internal pumps and splitting gas paths inside the trailer while reducing PFA tubing diameters. Meteorology and trace gas mixing ratios, except for the hydrocarbon measurements, were recorded by the CR1000 data logger as 10 s averages.

The NO$_x$ analyzer was set up to output mixing ratios expressed as a 20 s moving average. Zero and span calibrations (104 ppb NO in N$_2$, prepared in July 2010 by Scott-Marrin, CA) were performed during each site visit – approximately once every ten days. Interference from nitric acid (HNO$_3$) was avoided via using a nylon membrane as the instrument’s inlet filter. For data analyses using the 10 s averages, the NO$_x$ data were shifted forward by 50 s to account for the instrument’s response time relative to the O$_3$ and CO$_2$ measurements. The CO analyzer was also set up to record 20 s moving averages and it as well was zeroed and calibrated during each site visit (547 ppb CO in zero air, prepared in July 2011 by Scott-Marrin, CA). However, the measurements from this instrument are more temperature sensitive, and thus, automated internal zeroing was performed once every 6 h to counteract electronic drift. The O$_3$ analyzer was operated with a recent factory calibration and was regularly zero checked using an O$_3$ scrubber. CO$_2$ was measured using a single channel NDIR instrument (LI-840, Licor Inc.) calibrated using a 454 ppm CO$_2$ standard (prepared in August 2014 by Scott-Marrin, CA), while water vapor measurements relied on a factory calibration.

The gas chromatograph was set up to perform half-hourly hydrocarbon measurements to maximize temporal resolution, at the expense of measuring more compounds. Samples were collected at 100 mL min$^{-1}$ onto
two-stage activated carbon adsorption micro-traps, one containing Carbotrap B with Carbotrap X backup for C$_2$ and higher hydrocarbons, and one containing Carbotrap X and Carboxen 1000 to trap short-chain hydrocarbons. The former sample, injected into a 60 m, wide-bore MTX-624 column, was collected directly from ambient air before injection. The latter sample, injected into a 30 m, wide-bore PLOT-Alumina column, was first dried through a Nafion dryer (except for a period from 7–28 August when a Drierite desiccant tower was used instead); the flow then passed through an Ascarite II CO$_2$ scrubber with additional potassium perchlorate to remove any leftover moisture. Both samples were thermally desorbed directly into two wide-bore 5 m retention gaps ahead of the chromatographic columns, similar to Park et al. (2010, Table S2). Sampling time was twenty minutes for both samples, from 8 to 28 min into each 30 min period. Thermal desorption at 200°C occurred for 2 min at the beginning of each run, after which the traps cooled down with a fan to approximately room temperature before the next sample period. A ppm-level internal standard of 2,2-dimethybutane (prepared in March 2015 by Scott-Marrin, CA) was diluted into the main sampling line to quantify observed hydrocarbon peaks in the chromatograms. Other standard gases, including mixes of normal alkanes, branched alkanes, alkenes, methyl ethyl ketone (MEK), benzene, toluene, ethylbenzene, and xylenes (collectively referred to as BTEX) were injected into the main sampling line inlet using a syringe during selected site visits. An automated zero-air run was performed once every 15 hours to monitor for contamination. A mixture of hydrogen gas and zero air produced onsite using hydrogen and zero air generators was used for the FIDs, as well as carrier gas (H$_2$). The chromatography data were re-analyzed offline using SRI PeakSimple Software (SRI Instruments, Version 3.88, 2010). Additional information regarding the quantification of VOCs is available in the supplement (Text S1).

The non-hydrocarbon trace gas and meteorological data were reduced to 30 min resolution to align with the hydrocarbon measurements. This was performed by finding the median measurement for each variable in 15 min periods and then averaging the medians for the two 15 min periods to create each 30 min data point. The exceptions were rainfall, which was totaled for each 30 min period, and wind speed and direction, for which a resultant mean (vector averaging) was used. Medians were chosen to remove artificial instantaneous spikes in the measurements. Once 30 min data were obtained, regular invalid measurements (e.g. automated zeroes) were flagged for removal and other invalid measurements (e.g. contamination, bad readings related to power issues, irregular zeroes and calibrations) were flagged and removed manually. For certain analyses discussed below, the original 10 s resolution data were used. In these instances, quality control was performed for the relevant subset of data.

3. Analysis methods

3.1. Source identification using non-negative matrix factorization

A number of emission source types were expected to contribute to observed trace gas variability on Shape Ranch. In addition to emissions from local and regional oil and gas activities, possible emission sources included vegetation, soils, livestock and agriculture, distant urban sources, biomass burning, and local and regional automotive traffic. However, it should be noted that most of regional vehicle emissions came from traffic associated with the oil and gas industry, as traffic counts on the nearby FM 186 increased by more than a factor of 10 as the shale was developed between 2010 and 2015 (Texas Department of Transportation, 2018). Some emissions sources, including, e.g., biogenic emissions and evaporative hydrocarbon emissions, are strongly dependent on temperature (Guenther et al., 2012; Rubin et al., 2006), with biogenic and soil emissions also depending on soil moisture availability (Guenther et al., 2012; Vinken et al., 2014). Varying wind directions brought different air masses towards Shape Ranch: air over the Gulf of Mexico to the southeast is relatively clean (Gilman et al., 2009), while continental air masses, with emissions from distant urban centers such as San Antonio, are located to the east and to the north; westerly winds were very rare during the field campaign, as discussed in section 4.1.1. Emissions from biomass burning were assumed to have a negligible impact on trace gas variability due to the lack of detected fires during the field campaign (Andela et al., 2019).

Several methods are available to identify source types contributing to observed trace gas variability. Traditional matrix factorization techniques have been employed, such as singular value decomposition (SVD) and positive matrix factorization (PMF). The latter, which was originally developed by Paatero and Tapper (1994), is a preferred source apportionment method often used by the US EPA (Reff et al., 2007). Several new PMF variations have been developed and are referred to as non-negative matrix factorization (NMF), a name that was popularized by Lee and Seung (1999). NMF models have been developed for a variety of applications, including image decomposition (Lee and Seung, 1999), metagenomic analysis (Brunet et al., 2004), and atmospheric pollutant source attribution (e.g. Thiem et al., 2012). The NMF models work as follows:

1. A number of factors is prescribed by the user. This choice must be made carefully to allow for a sufficiently informative number of factors, though too many factors will cause results that cannot be physically explained, explain a negligible fraction of the total variability in the dataset, or are unstable.

2. Two matrices are initialized: the first is the contribution of individual variables (trace gases in the case of Shape Ranch) within each factor ($W$), and the second is the expression of each factor during every time step in the database ($H$), such that the matrix multiplication of $W$ and $H$ are an approximation of the observed dataset $V = WH + e$, where $e$ is the residual error. The initialization of $W$ and $H$ may be based on other matrix factorization methods, such as non-negative SVD; it may also be randomly generated based on the observed distributions of variables; or it may be prescribed by the user. For random initializations, the NMF model should be run several times to identify the best solution based...
on the large number of possible starting points.

3. The initial guess is improved upon to reduce the error between the observed dataset and the modeled dataset — i.e., the matrix multiplication of the variables within each factor by the expression of each factor over time. There are a number of algorithms to reduce this error.

The least-squares NMF (LS-NMF) algorithm (Wang et al., 2006) was chosen because this method allows for the resulting factors to be weighted by uncertainties in the observed dataset, such that highly-uncertain variables have less of an influence on the solution than highly certain variables.

The NMF package (Gaujoux and Seoighe, 2010) in the R programming language (R Core Team, 2018) was used to perform a source apportionment of the Shape Ranch dataset. This package includes several initialization methods and error-reducing algorithms. Both the SVD and random-seed initializations were tested with the LS-NMF algorithm. The SVD has the advantage of performing a high-quality initial guess, resulting in relatively small errors between the observed and modeled datasets and a low computational cost. Meanwhile, the random-seed initialization, while relatively slow due to the large number of runs needed, may result in a lower residual error if one of the random initializations converges towards a true solution.

Data were prepared in a manner following Guha et al. (2015). Observations that were missing hydrocarbon measurements — e.g., during zero runs — were removed. Ethylbenzenes and xylenes were summed for the NMF due to periodic misidentifications associated with the near-coelution of ethylbenzene and m/p-xylene. The limit of detection (LOD) for each trace gas species was assumed to be the minimum non-missing measurement in the timeline. Missing CO and CO\textsubscript{2} values were linearly interpolated. There were no missing O\textsubscript{3} data during the NMF analysis period. VOC and NO\textsubscript{X} mixing ratios below the LOD were replaced with random values between zero and 0.5 \times LOD. The top 1% of mixing ratios for each species were considered to be extreme. These values were scaled downward to equal the 99th percentile of the distribution of mixing ratios in an NMF run to limit the influence of episodic plumes on the overall source attribution. The background mixing ratio for each species, assumed to be the minimum mixing ratio in the timeline, was subtracted to remove the background but a value of e\textsuperscript{-3} was added back in to avoid mixing ratios of zero in the NMF model. Uncertainties were quantified based on instrument precision and accuracy and mixing ratio, as shown in Table 1, with absolute uncertainties converted to relative uncertainties using the mixing ratio time series for the associated species. Lastly, the mixing ratios for each species were normalized such that the maximum mixing ratio was equal to one for each species.

The US EPA has developed a VOC emission factor database for anthropogenic sources known as SPECIATE (U.S. Environmental Protection Agency, 2015a). The source factors from the NMF model were compared to the SPECIATE sources to identify source categories that may be associated with the NMF factors. The comparison was performed by calculating the dot product of normalized emission factors, following eq. 5 from Kota et al. (2014):

\[
\theta = \frac{\sum_{i=1}^{n} f_s^i}{\sqrt{\sum_{i=1}^{n} f_i^2 \sum_{i=1}^{n} s_i^2}},
\]

where \(f_i\) and \(s_i\) are the NMF and SPECIATE scores for VOC \(i\) for an arbitrary paring of emission factors from the NMF model output and SPECIATE database. A value of \(\theta = 1\) implies a perfect match between the NMF and SPECIATE factors whereas \(\theta = 0\) would result from factors that have no overlapping species.

Table 1: Assumed uncertainties for the LS-NMF dataset. DOI: https://doi.org/10.1525/elementa.414.t1

| Species | Precision | Accuracy | Measurement uncertainty\(^{(a)}\) |
|---------|-----------|----------|----------------------------------|
| CO      | ±20 ppb\(^{(b)}\) | ±2%\(^{(b)}\) | [CO] \times 2% + 20 ppb          |
| CO\textsubscript{2} | ±1 ppm\(^{(b)}\) | ±1.5%\(^{(b)}\) | [CO\textsubscript{2}] \times 1.5% + 1 ppm |
| O\textsubscript{3} | ±1.5 ppb\(^{(b)}\) | ±1.5 ppb\(^{(b)}\) | 3 ppb                           |
| NO\textsubscript{X} | ±0.2 ppb\(^{(b)}\) | ±5%\(^{(b)}\) | [NO\textsubscript{X}] \times 5% + 0.2 ppb |
| VOCs    | ±1.8%\(^{(c)}\) | ±8%\(^{(d)}\) | 2 \times LOD for mixing ratios < LOD\(^{(d)}\) |

\(^{(a)}\) Total uncertainty is assumed to be the sum of precision and accuracy, except for VOCs.
\(^{(b)}\) From instrument operation manual.
\(^{(c)}\) Accuracy of standard gas used for calibration.
\(^{(d)}\) NO\textsubscript{X} was not included in the NMF analysis due to an instrument failure during a period of complete VOC data. Nonetheless, the uncertainty in the NO\textsubscript{X} data is quantified in this table.
\(^{(e)}\) Variability (2\(\sigma\)) of the internal standard measurements.
\(^{(f)}\) Conservative estimate of 5% accuracy for each of two flow meters and 2% accuracy for standard gas concentration, added in quadrature.
\(^{(g)}\) From Guha et al. (2015).
3.2. Plume identification using trace gas ratios

3.2.1. General plume identification

Plumes from combustion sources were identified within the 30 min dataset using a combination of NO, CO, and O3 mixing ratios. The background levels for NO, CO, and O3 were assumed to be moving 10\textsuperscript{th} percentiles over a moving 12 h window. The ratio of NO/O3 serves as a sensitive indicator of combustion plumes, particularly at night, as O3 is rapidly titrated by NO emissions from combustion sources to form NO\textsubscript{2}. During the nighttime, NO\textsubscript{2} is not photolyzed and the NO/O3 ratio remains elevated as the plume is transported downwind. However, during the daytime, NO\textsubscript{2} is photolyzed and O3 increases again further downwind from the emission source. Therefore, this method does not capture plumes from distant combustion sources during the daytime. It may also fail to capture plumes that occur in a high background O3 environment, as the NO/O3 ratio may remain low even within a plume. NO3/O3 thresholds of 0.25 and 1 were both used to test the sensitivity of plume detections to the selected NO3/O3 ratio. Mixing ratios of selected VOCs within plumes were assessed for their relationships with one another and with CO2 and NO\textsubscript{3}. Alkanes and benzene were chosen due to their presence in emissions from combustion sources and their persistent signals above the LOD. Trace gas ratios within plumes were measured as the slope of a standard major axis (SMA) regression from – also known as a reduced major axis regression – which has been identified as a useful regression method for air quality data as the uncertainty in both variables is accounted for (Ayers, 2001).

3.2.2. In-plume ratios of carbon dioxide and nitrogen oxides

The high temporal resolution of the original 10 s data provided more insight into the plumes identified using the NO3/O3 ratio. However, due to the poor precision of the 10 s CO data, the NO3/CO ratio was excessively noisy. Therefore, only the NO3/CO ratio was analyzed in more detail. A NO3/CO ratio of 0.25 was used to filter 30 min data. Consecutive 30 min periods with NO3/O3 greater than 0.25 were assumed to be one continuous combustion plume event. For each of these events, 30 min was added before and after the time period to include pre- and post-plume observations. This expanded time period was then used to analyze the corresponding 10 s data. The moving 10\textsuperscript{th} percentile from the 30 min dataset was linearly interpolated to a 10 s resolution to represent the background mixing ratios, which were then subtracted from the 10 s time series to obtain trace gas enhancements. For each plume event, the 10 s NO3/CO3 enhancement ratios were assessed using the slope of an SMA regression when ambient NO3/O3 exceeded 0.25.

4. Results

A brief discussion of air quality and meteorological observations is presented, followed by the results of the source attribution using non-negative matrix factorization. Next, combustion plumes are identified and characterized using trace gas correlations.

4.1. Ambient air quality at Shape Ranch

4.1.1. Meteorology

The observed meteorology at Shape Ranch in 2015 is compared to climatological means (1981–2010) at Carrizo Springs (Arguez et al., 2010) in Table S3. Temperatures and precipitation were near average from April through June. July and August, however, were hot and dry, with average daily maximum temperatures over 38°C and less than 1 mm of rain in July, followed by no rain in August. Below-average rain was observed in September and near-normal rain amounts in October and November. These months continued to be warmer than average, with daily mean temperatures and daily minimum temperatures exceeding the respective average temperatures by more than 3°C in both October and November. Winds were predominantly southeasterly – especially in the summer, while occasional cold fronts in the spring and fall brought northwesterly winds (Fig. S2). Wind speeds reached a daily minimum prior to sunrise before increasing during the day and peaking in the late evening and early overnight hours (Fig. S3). However, the late evening and overnight hours also had a relatively high frequency of calm observations, suggesting that the late-evening peak in wind speeds is not always present. While southeasterly winds remained prevalent throughout the diurnal cycle, easterly winds were frequently observed during the afternoon and evening hours.

4.1.2. Carbon dioxide

Figure S4 shows the diurnal cycle of CO\textsubscript{2} mixing ratios at Shape Ranch, with low CO\textsubscript{2} during the daytime and elevated CO\textsubscript{2} during the night. Several measurements during the early morning hours exceeded 500 ppm, with peak CO\textsubscript{2} mixing ratios reaching 567 ppm. Most of these elevated CO\textsubscript{2} mixing ratios measured at Shape Ranch occurred within two weeks of a precipitation pulse (3+ mm per hour, Hao et al., 2010), suggesting that high CO\textsubscript{2} events were generally associated with nighttime emissions due to enhanced ecosystem respiration as a result of increased soil moisture from recent rainfall, in addition to other local CO\textsubscript{2} sources (e.g. combustion, Fig. S5).

4.1.3. Carbon monoxide

Carbon monoxide levels at Shape Ranch were low, with a median mixing ratio of 97 ppb. This mixing ratio is lower than past observations in urban (Fig. S6, Baker et al., 2008) and at remote continental locations (Chin et al., 1994). Low CO mixing ratios compared to other remote areas are sensible considering the observed decreasing trend in CO in recent decades (Worden et al., 2013), since the measurements in Chin et al. (1994) were made in the late 1980’s and early 1990’s. The diurnal cycle of CO showed higher medians during the daytime as compared to overnight. However, the highest observations (above 200 ppb) often occurred during the late evening and overnight hours. These observations were likely associated with combustion plumes in a stable nighttime boundary layer.
4.1.4. Nitrogen oxides

Similar to CO, NO\textsubscript{x} levels were also low at Shape Ranch, with median mixing ratios of 0.1 ppb for NO and 1.7 ppb for NO\textsubscript{x}, compared to a median NO\textsubscript{x} mixing ratio of 2.0 ppb in Karnes City (AQS code 482551070, Texas Commission on Environmental Quality, 2020) in the center of the EFS (Fig. S6). During the nighttime, total NO\textsubscript{x} was elevated while NO remained low as any emissions will react with O\textsubscript{3} to produce NO\textsubscript{2} (Fig. S7). Increased NO and NO\textsubscript{x} mixing ratios during the early morning hours may represent emissions from local traffic. While background NO remained low through the evening, several outliers above 4 ppb with concurrently elevated NO/NO\textsubscript{x} ratios serve as evidence of NO plumes from nearby combustion sources. Additionally, several high nocturnal NO\textsubscript{x} observations, including the highest NO observations, were made shortly after minor rainfall events (3 mm), suggesting that some high-NO\textsubscript{x} events were associated with higher local NO emissions from wetted soil (Williams et al., 1992).

4.1.5. Volatile organic compounds

Several sources impact ambient VOC mixing ratios at Shape Ranch – notably evaporative emissions of hydrocarbons and emissions from combustion sources. Figure 1 shows the log-normal distributions of several hydrocarbons compared to past median observations in 28 US cities (Baker et al., 2008). The median mixing ratios for propane, butanes, pentanes, n-hexane, n-heptane, and

![Figure 1: Comparison of VOCs at Shape Ranch and US cities. A boxplot comparison of VOC mixing ratios at Shape Ranch vs 28 US cities (Baker et al., 2008). Note that the y-axis is each panel is log-normal. Alkanes trended higher at Shape Ranch than in the 28 cities study while alkenes and BTEX trended lower. DOI: https://doi.org/10.1525/elementa.414.f1]
n-octane were all higher than the median of the 28 US cities study. The ratio of isopentane to n-pentane of 1.14 (95% CI of 1.13 – 1.15, $R = 0.98$) was close to that observed for the pentane enhancement over the central EFS (Roest and Schade, 2017) and is much lower than in most urban areas. The high alkane levels and the isopentane to pentane ratio suggest that evaporative emissions from oil and gas industry sources dominate the observed alkane mixing ratios (Gilman et al., 2013). Mixing ratios of alkenes and BTEX species at Shape Ranch were generally lower than in the 28 cities (Figure 1), which was expected since internal combustion sources contribute to higher mixing ratios of these species in urban areas. The benzene to toluene ratio in the 28 cities study was 0.22 (0.17 – 0.29, $R = 0.72$, Figure 2) which is indicative of fresh automotive emissions combined with evaporative emissions of toluene (Baker et al., 2008). The ratio of 1.17 (1.15 – 1.19, $R = 0.93$) at Shape Ranch serves as evidence of a higher benzene to toluene ratio from local emission sources. This is confirmed by the retention of this ratio during high VOC episodes, which often result from an accumulation of local emissions in the boundary layer. However, there are observations of benzene, toluene, and o-xylene at Shape Ranch that are higher than all the median observations in the 28 cities study. Figure S8 shows that the alkanes and BTEX species were elevated at night, so high mixing ratios were likely associated with accumulation of local and regional emissions in a shallower nocturnal boundary layer. However, propene and isoprene were both elevated during the day. Isoprene is known to be emitted from certain green plants during the day, and the higher propene during the day may be indicative of similar, local emissions during daytime (Goldstein et al., 1996).

4.1.6. Ozone
During the entire field campaign, the maximum daily 8-hour average $O_3$ mixing ratio exceeded the current EPA standard (U.S. Environmental Protection Agency, 2015b) on only one day (1 August 2015). The fourth-highest maximum daily 8-h average $O_3$ mixing ratio – the three-year average of which is used to compare against the EPA’s standard (U.S. Code of Federal Regulations, 2015) – was 65 ppb, 5 ppb below the standard. The maximum daily 8-h average was generally higher than the nearby city of Laredo (Fig. S6, AQS code 484790016, Texas Commission on Environmental Quality, 2020), possibly due to $O_3$ titration in the urban air mass. The $O_3$ mixing ratios at Shape Ranch followed a typical diurnal pattern with high mixing ratios during the daytime, followed by decreasing mixing ratios throughout the night, reaching a minimum in the early morning hours as $O_3$ is titrated by local NO emissions.

4.2. Emission sources impacting Shape Ranch
4.2.1. Non-negative matrix factorization
A source attribution was performed for the Shape Ranch dataset for a period from 13:00 LST 4 September to 9:30 LST 5 October 2015, when most trace gas instruments functioned without interruption except for calibrations. However, due to an instrument failure, NOx data are missing after 15 September and have therefore not been included in the NMF source attribution. During this time, temperatures were characteristically warm with only one

![Figure 2: Benzene and toluene ratios at Shape Ranch and US cities.](https://doi.org/10.1525/elementa.414.f2)
day of observed precipitation, and winds were generally from the SE to ESE.

Several LS-NMF runs were performed with varying numbers of factors and seeding methods. The performances of LS-NMF runs with two to seven factors were first evaluated against LS-NMF runs with randomized data. Runs with three, four, and five factors performed better as compared to two, six, or seven factor runs. The three-factor run was selected over the four- and five-factor runs based on the physical interpretation of the factors and the stability of the three-factor run, as measured by a bootstrap with replacement analysis (Norris et al., 2008). Each factor of the three-factor run was replicated with at least 96% accuracy after resampling the data 1,000 times, while the four- and five-factor runs had factors that were replicated with as little as 11% and 8% accuracy, respectively. The random seed and non-negative SVD seed produced similar factors but with a slightly larger residual error for the non-negative SVD seed than for the random seed (Fig. S9). The SVD seed was chosen for presentation here due to its much lower computational cost.

Figures 3–5 show the results from the non-negative SVD-seed three-factor LS-NMF. The dominant factor (top panels of Figures 3–5) features most of the measured trace gases, except for \( \text{O}_3 \), propene, and isoprene (Figure 3). This factor appears when winds were from the easterly direction, with many outliers indicating episodic periods of high hydrocarbon abundances (Figure 4). This factor followed a diurnal pattern that is largely dictated by boundary layer dynamics, with surface emissions

![Figure 3: Species scores in factors from the LS-NMF model.](https://doi.org/10.1525/elementa.414.f3)
accumulating in a shallow nocturnal boundary layer before being mixed into a deeper layer during daytime (Figure 5). This factor most closely matched gasoline exhaust, gasoline headspace vapor, and oil field sources, including natural gas wells and condensate tanks, as listed in the EPA SPECIATE database. Hence, this factor was attributed to general oil field emissions. It explained 53% of the variability in the data set.

The second factor (middle panels of Figures 3–5) was dominated by CO and O₃ (Figure 3). The dominant hydrocarbon in this factor was isoprene, though several relatively long-lived alkanes had high scores as well. This factor had the highest scores when winds were from the northeast sector, indicating a continental air mass origin (Figure 4). The factor features a diurnal cycle that peaked in the afternoon and slowly declined overnight, with a minimum near sunrise (Figure 5). There were no reasonable matches in the SPECIATE database because the dominant hydrocarbon – isoprene – is generally biogenic while the SPECIATE database consists only of anthropogenic sources. Due to the diurnal cycle and continental origin, we attributed this ‘source’ to transport of regional O₃ and isoprene during the daytime, with distant urban sources explaining elevated CO levels due to direct emissions and hydrocarbon oxidation. This factor explained 28% of the data set’s variability.

The third factor (bottom panels of Figures 3–5) features propene as the dominant component, with CO₂, O₃, and some long-chain hydrocarbons also present (Figure 3). This factor was highest when winds were from...
the southeast sector (Figure 4). There was no apparent diurnal cycle in the median scores for this factor, though the upper quartile showed elevated scores during the overnight and morning hours and slightly lower scores during the afternoon hours (Figure 5). This factor matched gasoline exhaust in the EPA SPECIATE database, and we attribute it to combustion sources including engine exhaust and flaring. It explained 18% of the data set’s variability.

4.2.2.General plume identification using trace gas enhancement ratios
Initially, a $\text{NO}_x/\text{O}_3$ threshold of 0.25 was used to identify times of substantial $\text{O}_3$ reductions by NO based on ambient mixing ratios. There were 749 thirty-min periods when $\text{NO}_x/\text{O}_3$ exceeded 0.25. These periods showed a strong diurnal dependence with increasing frequency after sunset, peaking during the early morning near 06:00 LST. Of the 749 periods, only one occurred between 11:00-17:00 LST. This is likely due to higher ambient $\text{O}_3$ mixing ratios during daylight hours, and efficient mixing in a turbulent daytime boundary layer reducing the number of defined plumes that reach the measurement site. The correlation between benzene and toluene when $\text{NO}_x/\text{O}_3 > 0.25$ was strong ($R = 0.86$) with a benzene/toluene slope of 1.23 (1.13 – 1.33). Most of these observations exceeded the median benzene and toluene observations during the field campaign, suggesting that this method does generally capture air masses with elevated mixing ratios of trace gases associated with combustion.

Figure 4: LS-NMF factor expression vs. hour of day. Boxplots of the derived diurnal cycle of the factors. Boxplots show medians (thick horizontal bar), interquartile ranges (lower and upper ends of rectangle), estimated 95% confidence limits (lower and upper whiskers), and associated outliers (open circles). DOI: https://doi.org/10.1525/elementa.414.f5
A weak correlation between CO₂ and NOₓ was observed ($R = 0.11$), with a NOₓ/CO₂ slope of 0.15 ppb/ppm (0.14 – 0.16). However, there were distinct clusters of data points with high CO₂ and low NOₓ, low CO₂ and high NOₓ, high CO₂ and high NOₓ, and high CO₂ and high NOₓ. While high NOₓ episodes were likely associated with combustion plumes and possibly episodic high soil NO emissions, high CO₂ events can also be associated with respiration, especially during wet periods (Fig. S5, Meyers, 2001). There was also a weak relationship between NOₓ and CO when NOₓ/O₃ > 0.25 ($R = 0.16$). The slope of NOₓ/CO in that case was 0.17 (0.15–0.18). A higher NOₓ/O₃ threshold of 1 was subsequently used to isolate plumes with increased ozone titration. This threshold identified 103 30 min observations, with a similar diurnal pattern as the observations when NOₓ/O₃ exceeded 0.25. Benzene and toluene showed a slightly weaker but still highly significant relationship ($R = 0.81$). In contrast, the relationship between CO₂ and NOₓ remained very weak ($R = 0.06$) and statistically insignificant, with a wide range of NOₓ/CO₂ ratios. The CO to NOₓ relationship was stronger ($R = 0.18$) with a slope of 0.18 (0.15 – 0.22), though the observations still exhibited a wide range of NOₓ/CO ratios. The weak correlations between NOₓ and both CO and CO₂ suggest that a general threshold NOₓ/O₃ ratio for 30 min data and assumed background mixing ratios equal to a moving 10th percentile provides limited insight into the nature of specific combustion sources types affecting the air quality at Shape Ranch. Instead, it is likely that a variety of sources, including both high- and low-temperature combustion sources and biogenic emissions of NO and CO₂, contributed to the observed enhancements above background.

4.2.3. VOCs within combustion plumes

Enhancements of several VOCs were also tested. Figure 6 shows correlations of n-butane with n-hexane and benzene within plumes (NOₓ/O₃ > 0.25), one hour before and after plumes (referred to as plume shoulders), and other non-plume observations. Correlations of n-hexane and n-butane did not show any statistically significant differences between in-plume and out-of-plume observations. The n-butane to benzene ratio was significantly lower within plumes than out of plumes, possibly indicating benzene emissions from combustion, though the range of ratios was still large. This difference in ratios was not statistically significant when a plume definition of NOₓ/O₃ > 1 was used. The sum of C₃–C₅ alkanes were also compared to CO₂ and NOₓ within plumes and out of plumes (NOₓ/O₃ > 0.25, Fig. S10). While non-plume observations showed a positive correlation between alkanes with both NOₓ and CO₂, alkanes were not enhanced within plumes while both NOₓ and CO₂ increased. This indicates that combustion plumes were not distinct sources of alkane emission on oil and gas well pads.

An episode with frequent plume detections was examined for evidence of VOC emissions from flaring. There were 62 individual 30 min observations when NOₓ/O₃ exceeded 0.25 from 10 September through 13 September 2015 (>30% of the period), separated into nine continuous events. Supporting Figure S11 shows the same correlations as Figure 6 for the four-day period, with in-plume, plume shoulder, and non-plume observations assessed separately. Like the general plume assessment shown in Figure 6, the ratios of n-butane and n-hexane were similar for all three scenarios and the correlations were poorly constrained. However, the n-butane/benzene ratio was reduced within combustion plumes compared to other observations, with the highest benzene mixing ratios occurring during plume passages. Likewise, supporting Figure S12 shows the same correlations as supporting Figure S10 for the four-day period, with lower

![Figure 6: VOC ratios in and out of combustion plumes.](https://doi.org/10.1525/elementa.414.f6)
alkane/NO\textsubscript{x} and alkane/CO\textsubscript{2} ratios in combustion plumes. While the correlations were weak, the highest NO\textsubscript{x} \textendash CO\textsubscript{2} and alkane mixing ratios occurred in plumes. This four-day period with frequent combustion plume detections demonstrates that while there is evidence of elevated VOC mixing ratios in combustion plumes, the co-location of other VOC emission sources on well pads and the poorly constrained VOC ratios with other trace gases means that VOC emission factors cannot be assessed with confidence for the observed plumes.

4.2.4. Carbon dioxide and nitrogen oxide ratios within plumes
While the NO\textsubscript{x}/O\textsubscript{2} ratios within the 30 min dataset provided limited insight into the general NO\textsubscript{x}/CO and NO\textsubscript{x}/CO\textsubscript{2} emission ratios within combustion plumes, it did succeed in identifying apparent plumes. A total of 176 plume events, defined as consecutive 30 min NO\textsubscript{x}/O\textsubscript{2} ratios exceeding 0.25, were identified. These plumes were further analyzed using 10 s data, which allowed for a more robust statistical analysis of trace gas mixing ratios within plumes. Many of the identified events had statistically insignificant relationships between NO\textsubscript{x} and CO\textsubscript{2} enhancements (large uncertainty in the slope) or a low correlation coefficient. Furthermore, events with significant rainfall (>3 mm, Hao et al., 2010) observed in the previous three days were discarded to minimize the influence of nitrification and ecosystem respiration on elevated NO\textsubscript{x} and CO\textsubscript{2} mixing ratios, respectively. Lastly, events prior to the end of May were discarded as the recording precision of the NO\textsubscript{x} instrument data was too low during the early portion of the field campaign.

The correlation coefficient and uncertainty of the NO\textsubscript{x}/CO\textsubscript{2} SMA slope, which we interpreted as the average NO\textsubscript{x}/CO\textsubscript{2} emission ratio for the detected plumes, were used to analyze subsets of plumes. Three thresholds for the correlation coefficients were used (0.25, 0.50, and 0.75) and two thresholds for the certainty of the slope were used (±5% and ±10%). A summary of the identified plumes is shown in Table 2. Out of the 176 identified plume events, 34 met the least-restrictive criteria of R > 0.25 and a slope uncertainty of less than ±10%, while only three plumes met the most restrictive criteria of R > 0.75 and a slope uncertainty of less than ±5%. Figure 7 shows the slope (ppb NO\textsubscript{x}/ppm CO\textsubscript{2}) and the R value for each of these events, with black points showing plumes with slope uncertainties less than ±5% and red points showing slope uncertainties between ±5 – 10%. Emission ratios of NO\textsubscript{x}/CO\textsubscript{2} were generally lower for plumes with slope uncertainties less than ±5%. Only one plume with a slope uncertainty less than ±5% had a NO\textsubscript{x}/CO\textsubscript{2} ratio greater than the flaring emission ratio of 0.54 ppb/ppm based on AP-42 emission factors. Meanwhile, several plumes with higher slope uncertainties had higher NO\textsubscript{x}/CO\textsubscript{2} ratios, with one plume exceeding a NO\textsubscript{x}/CO\textsubscript{2} ratio of 4. Still, this ratio is more than a factor of two lower than the expected emission ratios for controlled diesel engines (NO\textsubscript{x}/CO\textsubscript{2} = 11.0 ppm/ppb) and more than a factor of five lower than large, uncontrolled diesel engines (NO\textsubscript{x}/CO\textsubscript{2} = 25.7, U.S. Energy Information Administration, 2016; U.S. Environmental Protection Agency, 2016).

An example of a plume event with a high correlation coefficient is presented in Figure 8 and is circled in grey in Figure 7. For this event on the evening of 24 July 2015, the observed NO\textsubscript{x}/CO\textsubscript{2} enhancement ratio of 1.95 was within a factor of four of the ratio of AP-42 emission factors for flares. The high correlation coefficient of the NO\textsubscript{x}/CO\textsubscript{2} relationship (R = 0.91) suggests that this event was likely a plume from a low-temperature combustion source, such as a flare, although with an apparently higher temperature than the EPA and EIA emission factors for flares suggest, as higher temperature combustion produces more NO\textsubscript{x} (Flagan and Seinfeld, 1988; Zeldovich, 1992).

An example for a combustion event that met the least restrictive criteria (R > 0.25, slope uncertainty < ±10%) is shown in Fig. S13. On 17 July 2015, a prolonged episode of NO\textsubscript{x}/CO\textsubscript{2} exceeding 0.25 occurred from approximately 05:00 to 07:00 LST. Most of this time period featured NO\textsubscript{x}/O\textsubscript{2} < 0.5, except for two distinct NO\textsubscript{x} plumes when NO\textsubscript{x}/O\textsubscript{2} approached 3. During these plumes, NO\textsubscript{x} increased by several ppb while CO\textsubscript{2} varied by less than 1 ppm. Though the overall NO\textsubscript{x}/CO\textsubscript{2} ratio showed a relationship (R = 0.47, slope = 0.94), the two distinct NO\textsubscript{x} plumes appeared as a cluster of data points with a much higher NO\textsubscript{x}/CO\textsubscript{2} ratio. These two narrow plumes may have been associated with a high-temperature combustion source, such as vehicle exhaust. This demonstrates that the method of screening for plumes using the NO\textsubscript{x}/O\textsubscript{2} ratio during episodes of O\textsubscript{2} titration is not perfect, and there exists a potential to mischaracterize the apparent NO\textsubscript{x}/CO\textsubscript{2} emission ratio.

### Table 2: A summary of plumes identified using varying thresholds for the correlation coefficient and the uncertainty of the NO\textsubscript{x}/CO\textsubscript{2} slope. DOI: [https://doi.org/10.1525/elements.414.12](https://doi.org/10.1525/elements.414.12)

| Correlation coefficient | Slope uncertainty | Number of identified plumes | NO\textsubscript{x}/CO\textsubscript{2} ratios |
|-------------------------|-------------------|-----------------------------|---------------------------------------------|
| R > 0.25                | <±10%             | 34                          | 0.81 0.51 0.10 4.77                         |
| R > 0.50                |                   | 18                          | 0.85 0.45                                  |
| R > 0.75                |                   | 7                           | 1.47 0.92                                  |
| R > 0.25                | <±5%              | 14                          | 0.35 0.36 0.10 0.90                         |
| R > 0.50                |                   | 11                          | 0.33 0.27                                  |
| R > 0.75                |                   | 3                           | 0.48 0.46                                  |
Figure 7: NO\textsubscript{x} to CO\textsubscript{2} enhancement ratios within combustion plumes. The slope and \( R \) values for \( \Delta \text{NO}_x/\Delta \text{CO}_2 \) for each of the 34 combustion events with meaningful relationships (\( R > 0.25, R > 0.50, \) or \( R > 0.75 \)), low uncertainty in the slope (\( \leq 5\% \) or \( \leq 10\% \)), and without significant rainfall (\( > 3 \text{ mm} \), Hao et al., 2010) during the previous three days. Plumes with a lower slope uncertainty tended to have lower \( \text{NO}_x/\text{CO}_2 \) ratios, though plumes with strong correlation coefficients (\( R > 0.75 \)) had \( \text{NO}_x/\text{CO}_2 \) ratios that spanned more than an order of magnitude. One data point identified with a grey circle is used as a case study in Fig. 8. The \( \text{NO}_x/\text{CO}_2 \) emission factor ratio for flares (0.54) is indicated with a vertical dotted line (U.S. Environmental Protection Agency, 2016). DOI: https://doi.org/10.1525/elementa.414.f7

Figure 8: NO\textsubscript{x} and CO\textsubscript{2} enhancements for a plume on 24 July 2015. (Top panel) Time series of CO\textsubscript{2} and NO\textsubscript{x} measurements above background (black and blue lines, left axis), and NO\textsubscript{x}/O\textsubscript{3} ratio (red, right axis) used to identify combustion plumes. The data points in the bottom panel correspond to the NO\textsubscript{x} and CO\textsubscript{2} enhancements above background when NO\textsubscript{x}/O\textsubscript{3} exceeded 0.25. DOI: https://doi.org/10.1525/elementa.414.f8
when a low threshold for the correlation is used. A second example of an apparent high-temperature combustion plume appeared on the morning of 10 September 2015, when several very narrow, distinct plumes occurred between 07:00 and 07:30 LST (Fig. S14). A marginally elevated NO$_2$/O$_3$ ratio during the preceding hours resulted in a negative correlation, with the distinct plumes appearing as outliers in the bottom panel of Fig. S14. Due to the very brief duration of these plumes, and the high NO$_2$/CO$_2$ ratio of the associated data points, it is likely that a nearby high-temperature combustion source, such as truck or generator exhaust, was responsible for those plumes. Overall, the combustion events that met the set correlation and slope uncertainty criteria imply that low-temperature combustion sources with low NO$_2$/CO$_2$ emission ratios dominated combustion plumes observed at Shape Ranch. The highest observed ratio of 4.77 was more than a factor of two lower than the expected emission ratios for diesel engines. Most of the other plumes had NO$_2$/CO$_2$ ratios lower than 2, implying that low-temperature combustion sources were mostly responsible for the observed plumes at Shape Ranch. Regardless of the chosen correlation coefficient threshold, the median NO$_2$/CO$_2$ ratios were between 0.27 and 0.92 ppb/ppm—all within a factor of two of the ratio of 0.54 derived from the emission factors for flaring (U.S. Environmental Protection Agency, 2016). A more conservative correlation threshold of $R > 0.75$ resulted in generally higher NO$_2$/CO$_2$ ratios; though with fewer data points, the statistical measures of these slopes become less defensible.

Overall, these results imply that (i) low-temperature combustion sources were generally responsible for the observed plume events, which are assumed to be dominated by flares, but they have widely varying emission factors, and (ii) a combination of other sources of NO and CO, including biogenic sources and high-temperature combustion, as well as atmospheric transport and chemistry, may interfere with the detection of distinct plumes from distant combustion sources.

5. Conclusions
Uncertainties in emission estimates of both VOCs and NOx from the shale industry prevent an accurate estimate of the regional air quality impacts associated with oil and gas production in the area. This is especially true in areas with widespread flaring, which has poorly quantified emissions due to uncertain emission factors. Ambient air quality was studied on Shape Ranch in the sparsely populated western portion of the EFS. Transport of continental air was associated with CO, O$_3$, isoprene, and short-chain, longer lived alkanes. High alkane abundances indicated regional oil and natural gas production as a dominant emission source, which was confirmed by a non-negative matrix factorization analysis. Combustion was also identified as a local emission source, though mixing ratios of associated aromatics, alkenes, CO, and NO were generally low.

Flaring was identified as a significant source of NO and benzene emissions, similar to our previous work (Schade and Roest, 2018). Analyzed NO$_2$/CO$_2$ ratios during episodes of high NO$_2$/O$_3$ suggest that low-temperature combustion is very often responsible for plumes identified at Shape Ranch. While flaring is the most likely source for many of these events, the NO$_2$/CO$_2$ ratio exhibited variability spanning more than an order of magnitude, suggesting that these low-temperature combustion sources have widely varying emission factors and/or other sources of NO and CO interfere to introduce larger variability than would otherwise be expected. Regardless of the NO$_2$/CO$_2$ correlation and slope uncertainty thresholds used to identify combustion plumes, the observed median NO$_2$/CO$_2$ ratio in these plumes was within a factor of two of the expected ratio calculated from the EPA AP-42 flaring NO$_2$ emissions factor.

Determining the relevant emissions from flares can be improved by studying emission factors associated with these relatively small diffusion flares in the field. Closely monitoring and reporting flaring activity data could improve inventories, which in turn would more accurately reflect real-world flaring and its impacts in liquid-rich shale plays such as the EFS, the Permian, and the Bakken shale.

Data accessibility statement
Data tables (.csv) and code (R scripts) are available through the Texas Data Repository (https://doi.org/10.18738/T8/ISKZOC). Ancillary data sources have been included in the bibliography.

Supplemental file
The Supplemental file for this article can be found as follows:

- Supplemental material. Figures S1–14. Tables S1–3. Text S1. References. DOI: https://doi.org/10.1525/elementa.414.s1

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Competing interests
The authors have no competing interests to declare.

Author contributions
- Contributed to conception and design: GWS designed the field study.
- Contributed to acquisition of data: GSR and GWS contributed to data acquisition and quality control.
- Contributed to analysis and interpretation of data: GSR and GWS contributed to the general air quality analysis and non-negative matrix factorization. GSR performed the analysis of trace gas ratios within combustion plumes.
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