Comparative Analysis
of
Air Monitoring Data Collected During Oil Field
Well Stimulation Treatments

Final Report

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"Prepared for the California Air Resources Board and the California Environmental Protection Agency."

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Abstract

This report provides a descriptive analysis of the results of air quality monitoring conducted during hydraulic fracturing (HyF), an acid fracturing treatment, and subsequent cleanout activities conducted as part of a well stimulation treatments (WST) in California. As part of this air monitoring study, measurements were also made at reference locations, including background locations on the oil field but away from WST activities and off-field (ambient) locations away from oil fields. Air quality analytes measured in this study include toxic air pollutants, greenhouse gasses, atmospheric gasses, and volatile organic compounds. Volatile hydrocarbons associated with crude oil and natural gas production and compounds associated with vehicle activity and refrigeration were found at the same concentration during hydraulic fracturing activity as were measured on the oil field in the absence of WST. The off-field reference locations had similar air quality as the on-field locations and a geospatial analysis suggests some off-field reference locations may be too close to oil fields. It was recommended that specific locations known to represent ambient air quality be selected for off-field monitoring locations. More data should be collected at both background (on-field) and ambient (off-field) monitoring sites to increase the reference sample size and enhance the certainty of statistical comparisons.

Executive Summary

Background

The objective of this report is to provide a descriptive analysis of the results of air monitoring conducted during a study of air pollutant emissions from hydraulic fracturing (HyF), an acid fracturing treatment, and subsequent "cleanout" activities conducted as part of well stimulation treatments (WST) in California. Oil field operators hired contractors to conduct air monitoring during hydraulic fracturing operations, acid treatments, and well cleanout activities that occur when a stimulated oil well is brought into production. As part of this air monitoring study, data was also collected at reference locations, both on and off of oil fields. In this report, the results of the air monitoring study are described and analysis was conducted to examine if there were statistical differences in measured air quality associated with different WST and cleanout activities and between oil fields and reference sites. This report is a companion report to an analysis that examines the public health implications of air emissions during well stimulation and cleanout.

Methods

As part of a joint program of the California Air Resources Board (CARB) and the former Department of Oil, Gas, and Geothermal Resources (DOGGR)[1], oil field operators hired contractors to conduct air monitoring following protocols described in "Air Sampling and Analysis Plan for Well Stimulation Treatment Operations" (California Air Resources Board, 2018). Under this plan, air quality was measured at eight locations in a 300 to 500 foot perimeter around wells as they were being stimulated and then an additional set of samples were collected around the perimeter of the well as they were being cleaned out after stimulation. In most cases, wind direction was measured during monitoring or regional weather station data were reported and it was possible to identify presumptive upwind and downwind monitoring locations.

In addition to collecting monitoring data at locations around the perimeter of the well, the CARB monitoring protocol specified the collection of "background" and "ambient" air quality measurements. Background samples were collected at locations intended to represent air quality on the oil field, but in areas away from WST activities. Ambient samples are intended to represent air quality away from an active oil and gas operation (California Air Resources Board, 2018). Background samples were collected for each simulation event, yielding a total of 25 independent background measurements. Ambient samples were collected less frequently and only 14 ambient measurements were made.

At each monitoring location, multiple analytes were measured, including toxic air pollutants, greenhouse gasses, atmospheric gasses, and volatile organic compounds. Approximately 150 analytes were measured and 64 were detected at least once (Table 3). Most of these analytes were detected infrequently. When an analyte is measured but not found (i.e. is reported as being less than the detection limit), it is referred to as being "left-censored" data. Having left-censored data and unequal sample sizes creates uncertainty when comparing activities and locations. In this report, analytes were placed into tiers based on how many less-than-detection measurements were reported, to identify the level of certainty associated with each analysis. Statistical analysis is less certain for more left-censored data.

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[1] DOGGR has been reorganized and is now the California Geologic Energy Management Division (CalGEM). For clarity, we are referring to DOGGR in this report, as it was the agency involved with this study.

Results

The most frequently detected air emissions were hydrocarbons found in natural gas (methane, iso-butane, and butane) and compounds associated with vehicle emissions (ethanol and formaldehyde). Other analytes found commonly include acetone and acetaldehyde, which are associated with internal combustion emissions; pentane, a volatile component of crude oil; and dichlorodifluoromethane, a refrigerant and global air pollutant. Other volatile hydrocarbons associated with crude oil (cyclohexane, hexane, and toluene) and another refrigerant (chloromethane) were found less than half of the time they were measured. The majority of analytes were found in less than one-third of the samples in which they were measured. Eight analytes were detected in only one sample (Table 3).

Comparisons were made between the air quality observed during WST and cleanout operations and air quality observed at background and ambient locations. Volatile hydrocarbons associated with crude oil and natural gas (methane, butane, iso-butane, pentane, hexane, toluene); compounds associated with vehicle activity (ethanol, formaldehyde, acetaldehyde, and acetone); and refrigerants (dichlorodifluoromethane, chloromethane) were found at the same concentration during hydraulic fracturing activity as were measured at background and ambient locations. Only cyclohexane was found in lower concentrations at ambient locations (representing off-field air quality) than at on-field locations.

Since the sample size for the background and ambient reference locations were much smaller than sample sizes associated with hydraulic fracturing and cleanout monitoring, comparisons were further made between upwind and downwind monitoring locations. Upwind locations were determined based on the predominant wind direction during HyF and cleanout. It is assumed that upwind locations were more representative of the background air quality on the oil field and the downwind location would be more likely to represent air emissions specifically from the WST operations. It was found that the concentration of the analytes were not different between the upwind and downwind locations, which confirms the previous analysis that WST emissions are indistinguishable from background oil field air quality.

Conclusions

Neither analysis shows a measurable increase in air pollutant concentrations within the nominal 500 foot monitoring perimeter in association with WST and cleanout. From this, it is concluded that hydraulic fracturing and cleanout have not been shown to measurably change air quality on on the measured oil fields. It was more surprising that air quality during WST operations and at oil fields background locations was the same as the air quality measured at the ambient reference locations, which are intended to represent off field air quality. In many cases, the ambient reference locations had similar or poorer air quality than the air quality observed during active oil field operations (i.e. WST and subsequent cleanout). A geospatial analysis of the ambient sampling locations (Figures 3 to 7) suggest that in at least some cases, ambient monitoring locations may not be truly representative of ambient air quality and some locations labeled as ambient may be more representative of on field air quality.

Based on the results of this study, it is recommended that specific locations known to represent ambient air quality be selected for ambient monitoring locations. More data should be collected at ambient and background reference monitoring sites to increase the reference sample size and enhance the certainty of statistical comparisons. Although not discussed in the executive summary, the study was complicated by the lack of standardization in the reporting of monitoring results.

Recommendations are made to standardize reporting of monitoring results, including requiring electronic reporting of analytical data, standardizing report formats and section headers, using API numbers, and limiting the number of WST included in a single report.

Introduction & Background

The objective of this report is to provide a summary and analysis of data provided to California Air Resources Board (CARB) by industry under requirements for air monitoring during well stimulation treatments (WST) and subsequent cleanout operations.

The need to increase oil and natural gas production in California has caused operators to utilize unconventional methods such as hydraulic fracturing to stimulate well production. The use of these unconventional methods may cause unknown effects to the environment and nearby populations. Therefore as the popularity of these unconventional methods increased so did the concern for safety of ecosystems and inhabitants of California. This prompted the legislature to set forth Senate Bill 4 (SB4).

Senate Bill 4 (SB4), which was signed into law on September 20, 2013 by Governor Brown, required the development of regulations for well stimulation treatment (WST) operations in California including hydraulic fracturing, acid fracturing, and matrix acidizing. In response to SB4 requirements, the California Council on Science and Technology (CCST) completed an independent scientific review of well stimulation (Long et al., 2015a; Long et al., 2015b). The CCST report noted that well stimulation is a potential source of air quality impacts in California and emissions could be concentrated near production wells. The CCST report recommended additional analysis be conducted to better understand toxic air emissions from oil field activities, including monitoring air quality during WST events and assessing potential public health effects of any emissions (Long et al., 2015a; Long et al., 2015b).

As part of the SB4 implementation effort, the California Air Resources Board (CARB) has entered into a formal agreement with Department of Oil, Gas, and Geothermal Resources (DOGGR) to review WST permit application materials and to provide comments and recommendations to DOGGR during its application review process. In some cases, CARB's comments included recommendations for DOGGR to require air sampling and analysis as a permit condition. CARB requested the permit condition for certain operations based on oil field, operator, proximity to sensitive receptors, and well stimulation fluid composition. DOGGR has implemented CARB recommendations and oil field operators have conducted air monitoring and submitted air monitoring reports to DOGGR. These reports to DOGGR are under review by CARB.

As part of the review of the air emission monitoring reports, CARB has contracted Stringfellow & Associates (S&A) to work with Physicians, Scientists, and Engineers for Healthy Energy (PSE) to evaluate WST air sample results and identify, to the extent possible, potential public health concerns of air pollutant concentrations measured during WST events.

The primary objective of this report is to organize and describe the results of the air monitoring reports in a format allowing further analysis by PSE concerning potential public health concerns of air pollutant concentrations measured during WST events. Additional objectives include determining if there are statistical differences in measured air quality between different types of oil field activities and between oil fields and reference sites. As documented in this report, S&A has compiled and conducted a descriptive analysis of the WST air monitoring data provided to

S&A by CARB. This report includes statistical analysis on data collected during WST that occurred from December 2016-December 2018.

Methods

Air monitoring data collection & reporting

WST air sampling was conducted by oil field operators following protocols described in CARB's "Air Sampling and Analysis Plan for Well Stimulation Treatment Operations" guidelines (California Air Resources Board, 2018). As part of this study, CARB provided to S&A several WST air sampling and analysis reports (Monitoring Reports), written by consultants (Consultants) for the oil field operators and owners (Producers). In most cases, the Monitoring Reports include tables and figures of analytical and weather station results. Some reports included appendices containing copies of laboratory reports and other detailed sources of information. The Monitoring Reports were provided in PDF or similar format. Data and analytical results were not consistently provided independently (electronically) of the reports and the data used in this study were extracted from report files by either CARB staff or S&A contractors, as described below.

Monitoring Reports were prepared by four different consultants working for five Producers (Table 1). Data were collected from WST on five fields (North Belridge, South Belridge, Buena Vista Nose, Elk Hills, and Lost Hills). Air quality analytical results were reported from five contract laboratories (ALS Salt Lake City; ALS Simi Valley; BC Laboratories; Eurofins; and TestAmerica) and from portable air monitoring equipment used on location by the Consultants.

Monitoring included air sampling during WST and cleanout operations, and for sampling conducted at off-field "ambient" reference locations and on-field "background" locations. In most cases, Consultants relied on nearby weather stations to provide wind data for the sample sites, but where these were not available the Consultants set up and recorded data from temporary weather stations.

Table 1. Matrix of association between wells, producers, consultants, data, and reports.

Well API	Report No.[b,c]	Producer	Consultant	Data provided	Monitoring report provided
030-62645[a] 030-60845	NA[d]	Company-1	Not known	Y	NA[d,g]
030-64286	NA[d]	Company-2	Not known	Y	NA[d,g]
030-54057	1	Company-3	Consultant-1	Y	Y
030-55914	1	Company-3	Consultant-1	Y	Y
030-55084	2	Company-1	Consultant-1	Y	Y
030-62399	3	Company-4	Consultant-2	Y	Y
030-62361	3	Company-4	Consultant-2	Y	Y
030-62398	3	Company-4	Consultant-2	Y	Y
030-55090[a] 030-55091	4	Company-1	Consultant-1	Y	Y
030-62130	5	Company-4	Consultant-2	Y[e]	Y
030-62132	5	Company-4	Consultant-2	Y[e]	Y
030-62142	5	Company-4	Consultant-2	Y[e]	Y
030-60081	6	Company-1	Consultant-1	Y	Y
030-60844	7	Company-1	Consultant-1	Y	Y
030-60841	8	Company-1	Consultant-1	Y	Y
030-63550	9	Company-1	Consultant-1	Y	Y
029-27186	10	Company-2	Consultant-3	Y	Y
030-59958	11	Company-5	Consultant-1	Y	Y
030-59872	11	Company-5	Consultant-1	Y	Y
030-60386	11	Company-5	Consultant-1	Y	Y
030-53804	12	Company-3	Consultant-1	Y	Y
030-63120	13	Company-2	Consultant-1	Y	Y
030-62169	14	Company-2	Consultant-1	Y	Y
030-63043	15	Company-2	Consultant-1	Y	Y
030-60471	16	Company-2	Consultant-3	Y	Y
030-62704	17	Company-2	Consultant-3	Y	Y
029-59550	18	Company-2	Consultant-4	NA[d,f]	Y
030-54264	19	Company-2	Consultant-4	NA[d,f]	Y

[a]Two stimulated wells were included in a single monitoring event, therefore only one API will be referenced here forward.
[b]Multiple wells may be included in one report as indicated by shared report numbers.
[c]Report number order assigned by S&A for tracking purposes, only.
[d]Not available
[e]Only monitored for greenhouse gasses.
[f]Severe weather contaminated sampling media and invalidated the data. Data was not used for this study.
[g]Retests of TO-13 in SIM mode, separate reports were not created.

Data compilation by CARB

CARB staff extracted chemical analytical data from the Monitoring Reports and entered the data manually into Excel spreadsheets. The data were entered into a template of all potential analytes measured in CARB studies (e.g. California Environmental Protection Agency Air Resources Board, 2010). However not all analytes were run by all the laboratories, so not all potential analytes were tested for all cases. Results from duplicate samples were included in the compiled data provided by CARB (CARB Excel File).

Data compilation by S&A

The analytical results from the CARB Excel File were aggregated and formatted for JMP statistical analysis software by S&A scientists and engineers. The analytical data were aggregated by well and all extraneous columns and rows were deleted. Data were stripped of all formulas and values were imported into JMP as calculated by CARB. Results from duplicate samples were included in the compiled data and were included as independent samples for most analysis included in this report. Data imported into JMP from the CARB Excel File were coded to include spatial information, temporal information, meteorological measurements, and other variables such as analytical laboratory using the Monitoring Reports and the CARB Excel File.

Meteorological measurements were taken from figures and tables of wind rose data included in the Monitoring Reports by S&A. Where available, the variables of mean wind speed (mean-speed), wind direction most frequently observed (peak direction), percent of observations where this wind direction was observed (peak frequency), percent of the time when calm conditions were observed (percent calm), and the definition of calm conditions were recorded from summary information, rather than estimated from figures. Wind data was compiled from 19 reports that included results for 30 wells (Table 1). Data were manually entered into Excel spreadsheets and then imported into JMP by S&A scientists.

Descriptive data for oil wells, stimulations, and air sample sites were taken from the CARB Excel File. The data extracted included the 8-digit API number, well name, oil field name, producer, month and year of observations, number of stages completed in well stimulation, approximate distance from the wellhead to the sample sites, stimulation type, and latitude/longitude of the sample site locations. For each WST observed, there were eight locations, labeled #1 – 8, where air samples were collected. During cleanout of the well following stimulation, the same eight locations were again used, but the samples were labeled #9 – 16, with the site for #9 corresponding to #1 and so forth. For some WST events, air samples were collected at corresponding sites to reflect ambient air quality conditions and at sites within the oil field to reflect background conditions.

Wind data, including predominant wind direction and peak speeds, were extracted from monitoring reports, as possible. Data were taken from tables when available or estimated from wind roses. Wind and other weather data provide in the monitoring reports were a mixture of data from measurements made with on-site stations, during monitoring, and data taken from regional California Irrigation Management Information System (CIMIS) weather stations.

Other supportive data were located from the Monitoring Reports and DOGGR database. PSE and CARB staff reviewed and corrected as necessary data compiled by S&A. The companies collecting the air samples and laboratories completing the analyses were determined by review of the Monitoring Reports. The dates of well stimulation and cleanout activities as well as ambient and background sampling were also determined from the Monitoring Reports. Oil well locations (latitude and longitude) were found using Well Finder on the DOGGR website. Geospatial analysis was conducted using JMP and Google Earth.

Calculation of distances & wind direction

The distances between the oil wells and sample sites were calculated using the Haversine equation (Sinnott, 1984):

$$d = 2r \sin^{-1} \left(\sqrt{\sin^2 \left(\frac{\varphi_2 - \varphi_1}{2} \right) + \cos \varphi_1 \cos \varphi_2 \sin^2 \left(\frac{\lambda_2 - \lambda_1}{2} \right)} \right)$$

where d is the distance between two points (km), r is the radius of the earth (km), φ_1 and λ_1 are the latitude and longitude of the first point (oil well), and φ_2 and λ_2 are the latitude and longitude of the second point (sample sites). The Haversine distance was calculated in Excel where the latitude and longitude were first converted from degrees to radians by multiplying by $\pi/180$. A value of 6,371 km was used for the earth's radius (Moritz, 1980). In calculating the Haversine distance for each sample site, it was apparent that some of the latitude and longitude values provided in the raw data file might be in error due to the large calculated distance between the oil wells and sample sites (for wells 030-60081, 030-60844, 030-60841, 030-55090/030-55091, and 030-55084). In these cases where there appeared to an error, the latitude and longitude values were taken directly from the field reports and the values were converted from degrees and minutes to degrees with a floating decimal place.

The bearing (θ) was calculated for each sample site, relative to the oil well location (Williams, 2011):

$$\theta = arctan2(\sin \lambda_2 - \lambda_1 \cos \varphi_2 , \cos \varphi_1 \sin \varphi_2 - \sin \varphi_1 \cos \varphi_2 \cos \lambda_2 - \lambda_1)$$

After the bearing was calculated, the cardinal direction was determined for each sample site relative to the oil well. Note that the bearing was calculated in Excel where the "MOD" function was used to account for the radial nature of the bearing. The "MOD" function returns the remainder after the angle (in degrees) is divided by 360.

The cardinal direction of the prevailing wind was used to determine which sample sites were upwind and which sample sites were downwind. The prevailing wind direction was first converted to degrees of the compass. Upwind sample sites were those where the bearing was ±90 degrees of the prevailing wind direction. Downwind sample sites were those where the bearing was not ±90 degrees of the prevailing wind direction. The formula was coded to accommodate prevailing wind in any direction. As an example, where the prevailing wind direction was north, upwind sites would

have a bearing of 0-90 degrees or a bearing of 270-360 degrees and downwind sites would have a bearing of 90-270 degrees.

Data analysis

Data were analyzed using JMP Statistical Software (SAS Institute Inc., Cary, NC). Significance was evaluated using a standard of 95% probability (alpha = 0.05). JMP software was used because it provides comprehensive tools for database management, statistical analyses, and data visualization.

Data sets that include large numbers of "less than detection limit" values are sometimes referred to as left-censored data. In other words, measurements in samples that are above the level of detection have a known distribution of concentration values, but the distribution of concentration values below the level of detection is unknown. There are a number of possible approaches to analyzing censored data, including substituting non-detect data with a value of zero (0) or a concentration equal to the detection limit, or some fraction of the detection limit (Helsel and Gilliom, 1986; Kayhanian et al., 2002). For robust determinations of parametric distributions and central tendency (e.g. means), missing data can also be estimated by statistical models (Gilliom and Helsel, 1986; Kayhanian et al., 2002; Shumway et al., 2002; Helsel, 2005; Helsel and Lee, 2006; Singh, 2006; Leith et al., 2010).

In this report, we substituted zero values for non-detected results and used non-parametric statistical methods to examine the data (Sokal and Rohlf, 1995; Hollander and Wolfe, 1999; Kayhanian et al., 2002; Zar, 2010). This approach has been used in previous studies and is a conservative and clear approach to examining and interpreting data in a regulatory context (e.g. Stringfellow, 2018). Non-parametric methods are preferable for censored data, since non-parametric analysis does not rely on a normal distribution of the data, however it has been shown that parametric methods are informative, even for the analysis of data that do not have a normal distribution (Gulati et al., 2014). Therefore, results from both parametric and non-parametric analysis are included throughout this report.

Structure of the air quality monitoring data

This report examines monitoring events associated with well stimulation treatments (WST) and associated cleanout activities between December 21, 2016 and September 28, 2018. The data used for this report include monitoring results from 23 stimulated wells, as identified by API number. In most cases, there were nine monitoring locations around the well and two monitoring events per treatment: one monitoring event taking place during the WST and a second monitoring event taking place during the cleanout activity that follows the WST and before the well is placed into production. Sampling during the WST and cleanout yielded up to 18 individual samples collected per well. In total, there were approximately 400 air quality monitoring samples collected during WST and cleanout activities that were included in this analysis.

In addition to collecting monitoring data around the perimeter of the well, the CARB monitoring protocol specified the collection of "background" samples, which are intended to represent air quality on the oil field in the absence of WST activities, and "ambient" samples, that are intended to represent air quality in the region, but away from an active oil and gas operation (California Air Resources Board, 2018). Background samples were collected for each simulation event, yielding a total of 25 independent background measurements. Although each WST has an associated ambient measurement, ambient samples were not collected in each individual case and only 14

ambient measurements were made. In some cases, a single ambient monitoring event was assigned to reference more than one well.

In most cases wind direction was measured using a portable meteorological station during monitoring and it was possible to identify presumptive upwind and downwind locations (see methods section). Upwind and downwind samples were analyzed separately, to determine if upwind samples were more like background samples and to prevent upwind samples from "diluting" the results of air monitoring occurring downwind of WST and cleanout operations. The proximity of the sampling locations other oil field activities and infrastructure was not reported.

Monitoring reports—prepared by consultants subcontracted by the producers and subsequently submitted to CARB—contained descriptions and analysis of data from individual or clusters of oil field operations, typically consisting of a WST, a cleanout, and data from associated ambient or background stations. In this report, data from multiple oil companies and operations were pooled for analysis. Pooling the data and information from multiple operators and operations allows a broader and more robust evaluation of the potential air quality impacts of WST and oil and gas operations. In addition, pooled data allows for comparison of results between producers, consultants, and analytical labs.

Analytes measured and detected

The CARB protocols include comprehensive requirements for chemical analysis as part of the WST monitoring program (California Air Resources Board, 2018). The protocol requires air monitoring samples to be analyzed by five analytical methods developed for air quality monitoring (Table 2). CARB created a comprehensive list of 193 analytes that may be included in these five analyses, including air pollutants or other atmospheric constituents (e.g. nitrogen, oxygen), however not every analyte is measured on each sample due to method variability from lab to lab. In this study, 167 analytes were measured and 101 of the measured analytes were not detected in any sample. The list of analytes that for which no detectable analytical results were reported is presented in Appendix A. The list of 64 analytes that for which measurable analytical results were reported is presented in Table 3. Only analytes for which there were measurable results reported are considered further in this report.

Table 2. Analytical methods used for monitoring air quality as part of the SB-4 air monitoring program.

ASTM D1945 Standard Test Method for Analysis of Natural Gas by Gas Chromatography
ASTM D1946 Standard Practice for Analysis of Reformed Gas by Gas Chromatography
EPA Air Method, Toxic Organics – 15 (TO-15): Determination of Volatile Organic Compounds (VOCs) in Air Collected in Specially-Prepared Canisters and Analyzed by Gas Chromatography/Mass Spectrometry (GC/MS) (EPA/625/R-96/010b)
EPA Compendium Method TO-11A: Determination of Formaldehyde in Ambient Air Using Adsorbent Cartridge Followed by High Performance Liquid Chromatography (HPLC) (EPA/625/R-96/010b)
EPA Method TO-13A: Determination of Polycyclic Aromatic Hydrocarbons (PAHs) in Ambient Air Using Gas Chromatography/Mass Spectrometry (GC/MS)
NIOSH Method 5523 Glycols

Table 3. Analytes detected in at least one sample collected as part of the SB-4 well stimulation treatment monitoring program (N=64).

1,1,1,-Trichloroethane	Chloroform
1,1,2,2-Tetrachloroethane	Chloromethane
1,1,2-Trichloro-1,2,2-Trifluoroethane	Cyclohexane
1,1,2-Trichloroethane	Dibromochloromethane
1,1-Dichloroethane	Dichlorodifluoromethane
1,1-Dichloroethene	Ethane
1,2,4-Trichlorobenzene	Ethanol
1,2,4-Trimethylbenzene	Ethylbenzene
1,2-Dichloro-1,1,2,2-Tetrafluoroethane	Formaldehyde
1,2-Dichloroethane	Heptane
1,3,5-Trimethylbenzene	Hexaldehyde
1,3-Butadiene	Hexane+
1,4-Dichlorobenzene	Hydrogen
2,2,4-Trimethylpentane	I-Butane
2,5-Dimethyl Benzaldehyde	m,p-Xylene
2-Butanone	Methane
2-Hexanone	Methylene Chloride
2-Methylnaphthalene	Naphthalene
4-Ethyltoluene	Nitrogen
4-Methyl-2-Pentanone	Nonane
Acetaldehyde	Octane
Acetone	o-Tolualdehyde
Benzaldehyde	Oxygen
Benzene	o-Xylene
Bis(2-Ethylhexyl)phthalate	Pentane
Butane	Propionaldehyde
Butyraldehyde	Styrene
C-1,2-Dichloroethene	Tetrachloroethene
Carbon Dioxide	Tetraethylene Glycol
Carbon Disulfide	Toluene
Carbon Tetrachloride	Trichloroethene
Chloroethane	Trichlorofluoromethane

Results

Summary of air quality measurements

Table 3 lists all of the analytes by name that were detected in any sample, including samples from background and ambient locations. From the CARB analyte list, 64 analytes identified by name had analytical results (Table 3), but in some cases an analyte was measured by more than one method or reported by more than one concentration unit, therefore there are 73 analyte-measurement-unit combinations (Table 4). These name-concentration unit combinations are used throughout the remainder of this report, including appendixes. It should be noted that in some cases the same data are reported in both mg/m^3 and ppm units.

The most frequently detected analytes were atmospheric oxygen and nitrogen (dioxygen and dinitrogen); hydrocarbons found in natural gas (methane, and butane); and formaldehyde (Tables 3 and 4). These most frequently detected analytes were found in over 90% of the samples for which they were tested. Ethanol and iso-Butane were detected in over 80% of the samples. Acetone, acetaldehyde, and dichlorodifluoromethane were found in over 60% of the samples tested.

The remaining analytes in Table 3 were detected in less than 50% of the samples for which they were measured and 46 of the analytes were found in less than one-third of the samples in which they were measured. Eight of these analytes in Table 3 were detected in only one sample: 1,1,2,2-tetrachloroethane; 1,1,2-trichloroethane; 1,1-dichloroethane; 1,1-dichloroethene; bis(2-ethylhexyl)phthalate; dibromochloromethane; ethane; and styrene.

Although there is not set rule, the more highly censored data, the less reliable the statistical comparisons. Figure 1 shows the distribution of frequency of detection (percent detected as a function of times analyzed) of all analytes that were detected at least once (Table 4). Analytes were placed in categories (Tiers) as: > 80% detected (Tier #1, N = 9); 50-79% detected (Tier #2, N = 6); 30% - 49% detected (Tier #3, N = 5); or < 30% detected (Tier #4, N=53). Tier assignments for individual compounds are shown in Table 4. The increasing Tier number indicated that less information is available and statistical comparisons become less reliable or robust.

In this report, results and interpretation are organized by "Tiers" to differentiate the level of certainty associated with each analysis. Although highly censored data limit the reliability of comparisons between activities, even compounds that are infrequently measured can indicate emissions that may have environmental or human health significance. All compounds that were detected (Table 3) are considered and evaluated in the companion public health analysis conducted by PSE.

The mean, median, 90% quantile value, and maximum observed value for all analytes is presented in Table 4. Maximum and 90% values can be important parameters in air monitoring, since some regulatory controls are based on exceedances of acceptable values and even one-time events can be serious public health or regulatory violations. Shonkoff and Hill (2020) evaluated concentrations of the detected compounds in a public health context considering non cancer and cancer risks. Table 4 contains results from all monitoring activities, including measurements from ambient and background monitoring locations. Table 4 includes the frequency of detection and concentrations at quantiles and maximum. Mean values are included for reference.

Table 4. Summary of results for all detected analytes, showing percent detected when analyzed (% Det.); statistical confidence Tier (Stat Tier) as described in text; mean and median concentration (conc.); the 90th quantile (90% value), indicating that 90% of the measurements were at or below this value; and the maximum value observed in any sample, including ambient samples. Sorted by frequency of detection.

Analyte (Units)	% Det.	Stat. Tier	Mean Conc.	Median Conc.	90% Value	Max Value
Butane (ppb v/v)	96.6	1	8.572	3.800	28.000	570.00
Ethanol (ppb v/v)	82.1	1	3.259	2.900	7.400	90.221
Formaldehyde (mg/m^3)	96.9	1	0.003	0.002	0.006	0.008
Formaldehyde (ppb)	94.0	1	2.228	1.970	5.129	6.587
I-Butane (ppb v/v)	80.0	1	2.525	1.178	7.970	190.00
Methane (% v/v)	93.4	1	0.000	0.000	0.001	0.009
Methane-ppmv (ppmv)	94.0	1	3.953	3.800	5.405	92.000
Nitrogen (% v/v)	95.3	1	73.138	77.000	79.000	85.000
Oxygen (% v/v)	100.0	1	18.121	19.000	22.000	32.000
Acetaldehyde (mg/m^3)	62.4	2	0.002	0.001	0.006	0.016
Acetaldehyde (ppb)	60.7	2	0.972	0.716	3.219	8.881
Acetone (mg/m^3)	69.8	2	0.002	0.002	0.007	0.017
Acetone TO-11 (ppb)	64.5	2	0.891	0.636	2.880	7.157
Dichlorodifluoromethane (ppb v/v)	62.5	2	0.302	0.410	0.575	0.650
Pentane (ppb v/v)	50.4	2	1.918	0.800	6.050	190.00
Acetone TO-15 (ppb v/v)	47.8	3	3.973	0.000	9.450	210.00
Chloromethane (ppb v/v)	31.8	3	0.244	0.000	0.975	1.800
Cyclohexane (ppb v/v)	39.2	3	0.448	0.000	2.100	16.000
Hexane+ (ppb v/v)	35.9	3	10.907	0.000	110.00	270.00
Toluene (ppb v/v)	33.1	3	0.278	0.000	1.100	8.300
1,1,1,-Trichloroethane (ppb v/v)	1.2	4	0.000	0.000	0.000	0.009
1,1,2,2-Tetrachloroethane (ppb v/v)	0.2	4	0.000	0.000	0.000	0.012
1,1,2-Trichloro-1,2,2-Trifluoroethane (ppb v/v)	7.0	4	0.004	0.000	0.059	0.124
1,1-Dichloroethane (ppb v/v)	0.2	4	0.000	0.000	0.000	0.003
1,1-Dichloroethene ppb v/v	0.2	4	0.000	0.000	0.000	0.017
1,1,2-Trichloroethane ppb v/v	0.2	4	0.001	0.000	0.000	0.460
1,2,4-Trichlorobenzene (ppb v/v)	0.5	4	0.002	0.000	0.000	0.900
1,2,4-Trimethylbenzene (ppb v/v)	10.5	4	0.016	0.000	0.076	1.400
1,2-Dichloro-1,1,2,2-Tetrafluoroethane (ppb v/v)	9.8	4	0.001	0.000	0.014	0.017
1,2-Dichloroethane (ppb v/v)	9.8	4	0.001	0.000	0.013	0.016
1,3,5-Trimethylbenzene (ppb v/v)	2.8	4	0.004	0.000	0.000	0.740
1,3-Butadiene (ppb v/v)	1.2	4	0.001	0.000	0.000	0.260

Analyte (Units)	% Det.	Stat. Tier	Mean Conc.	Median Conc.	90% Value	Max Value
1,4-Dichlorobenzene (ppb v/v)	6.5	4	0.000	0.000	0.003	0.007
2,2,4-Trimethylpentane (ppb v/v)	0.7	4	0.005	0.000	0.000	0.800
2,5-Dimethyl Benzaldehyde (mg/m^3)	4.3	4	0.000	0.000	0.000	0.001
2,5-Dimethyl Benzaldehyde (ppb)	4.4	4	0.004	0.000	0.000	0.115
2-Butanone (ppb v/v)	25.4	4	0.440	0.000	1.580	35.000
2-Hexanone (ppb v/v)	1.4	4	0.005	0.000	0.000	0.550
2-Methylnaphthalene (ug/m^3)	2.1	4	0.016	0.000	0.000	1.600
4-Ethyltoluene (ppb v/v)	10.7	4	0.022	0.000	0.090	1.000
4-Methyl-2-Pentanone (ppb v/v)	2.8	4	0.078	0.000	0.000	23.000
Benzaldehyde (mg/m^3)	13.3	4	0.000	0.000	0.001	0.004
Benzaldehyde (ppb)	13.6	4	0.024	0.000	0.127	0.885
Benzene (ppb v/v)	23.5	4	0.309	0.000	0.550	59.000
Bis(2-Ethylhexyl)phthalate (mg/m^3)	0.9	4	0.000	0.000	0.000	0.007
Butyraldehyde (mg/m^3)	4.3	4	0.000	0.000	0.000	0.002
Butyraldehyde (ppb)	4.4	4	0.009	0.000	0.000	0.593
C-1,2-Dichloroethene (ppb v/v)	1.2	4	0.002	0.000	0.000	0.560
Carbon Dioxide (% v/v)	19.0	4	0.009	0.000	0.045	0.410
Carbon Disulfide (ppb v/v)	9.1	4	0.296	0.000	1.650	54.000
Carbon Tetrachloride (ppb v/v)	14.9	4	0.009	0.000	0.066	0.071
Chloroethane (ppb v/v)	1.9	4	0.001	0.000	0.000	0.038
Chloroform (ppb v/v)	9.8	4	0.003	0.000	0.019	0.160
Dibromochloromethane (ppb v/v)	0.2	4	0.001	0.000	0.000	0.410
Ethane (% v/v)	0.2	4	0.000	0.000	0.000	0.001
Ethylbenzene (ppb v/v)	16.3	4	0.024	0.000	0.071	1.300
Heptane (ppb v/v)	20.0	4	0.172	0.000	1.100	5.000
Hexaldehyde (mg/m^3)	15.0	4	0.000	0.000	0.002	0.005
Hexaldehyde (ppb)	15.0	4	0.053	0.000	0.610	1.238
Hydrogen (% v/v)	1.1	4	0.000	0.000	0.000	0.036
m,p-Xylene (ppb v/v)	18.4	4	0.092	0.000	0.410	3.200
Methylene Chloride (ppb v/v)	13.8	4	0.132	0.000	0.389	18.712
Naphthalene (ppb v/v)	10.3	4	0.005	0.000	0.012	0.970
Nonane ppb v/v	1.0	4	0.020	0.000	0.000	2.700
Octane (ppb v/v)	6.8	4	0.058	0.000	0.540	1.884
o-Tolualdehyde (mg/m^3)	4.3	4	0.000	0.000	0.000	0.000
o-Tolualdehyde (ppb)	4.4	4	0.002	0.000	0.000	0.099
o-Xylene (ppb v/v)	16.8	4	0.027	0.000	0.086	1.100
Propionaldehyde (mg/m^3)	28.3	4	0.000	0.000	0.001	0.002
Propionaldehyde (ppb)	29.0	4	0.047	0.000	0.234	0.720
Styrene (ppb v/v)	0.2	4	0.001	0.000	0.000	0.510

Analyte (Units)	% Det.	Stat. Tier	Mean Conc.	Median Conc.	90% Value	Max Value
Tetrachloroethene (ppb v/v)	9.6	4	0.058	0.000	0.014	13.000
Tetraethylene Glycol (mg/m^3)	1.4	4	0.002	0.000	0.000	0.260
Trichloroethene (ppb v/v)	5.8	4	0.033	0.000	0.004	9.305
Trichlorofluoromethane (ppb v/v)	15.1	4	0.030	0.000	0.210	0.445

Distributions

Pct det

Quantiles

100.0%	maximum	100
99.5%		100
97.5%		97.369047619
90.0%		88.85824867
75.0%	quartile	34.498834499
50.0%	median	10.722610723
25.0%	quartile	3.5414585415
10.0%		0.8174562901
2.5%		0.2321488036
0.5%		0.2267573696
0.0%	minimum	0.2267573696

Summary Statistics

Mean	25.275875
Std Dev	30.741695
Std Err Mean	3.5980433
Upper 95% Mean	32.448443
Lower 95% Mean	18.103306
N	73

Figure 1. Distribution of frequency of detection (Pct det) of all analytes detected at least once. From this analysis, the following bins were developed: > 80% detected, 50-79% detected, 30% - 49% detected and < 30% detected. Analytes with low detection limits do not allow robust comparison between conditions, such as comparison between measurements made on oil fields and ambient locations.

Comparison of analytical results by oil field activity

Monitoring conducted under this program was conducted in association with four types of activities or conditions: 1) samples collected in the absence of any oil field activities (ambient samples); 2) samples collected on oil fields, but in areas away from hydraulic fracturing (HyF) and other WST activities (background samples); 3) samples collected during hydraulic fracturing and acid stimulation activities (WST samples); and 4) samples collected during well-cleanout activities that follow WST (cleanout samples). In the case of this analysis, the acid treatment was

excluded and all WST are HyF treatment and are referred to as such. Analytical results are compared between those activity conditions (i.e. activities) in this section.

Determining the significance of the difference between off-field ambient air quality, background oil field air quality, and emissions from WST and cleanout activities is hampered by two factors: 1) the inequality in the sample size (N) between data sets and 2) the large number of "non-detect" values reported for each analyte. When combined, ambient stations had on average 29 measurements made per analyte and background stations had 48 measurements, whereas the cleanout and WST monitoring events had an average of 245 and 244 measurements made per analyte, respectively.

The samples were "tiered" according to completeness of data, as described above, and a comparative analysis was made between oil field activities and background and ambient locations. The results for Tier-1 analytes is presented in Appendix B. Tier-1 analytes include oxygen (% v/v) and nitrogen (% v/v), which were not different between activities, which is expected since oxygen and nitrogen are major atmospheric gasses.

Methane, the major component of natural gas, is also an atmospheric gas, but could be expected to be at higher concentration during active well operation, such as a cleanout or a WST, than would be found during routine oil and gas operations (i.e. background stations) or off-field (ambient stations). The mean methane concentration does not differ between ambient, background, WST, or cleanout. Wilcoxon analysis indicates that there are significant differences between activities, with HyF showing higher concentrations than cleanout, but not the ambient or background measurements, which also exhibit higher methane concentrations than the cleanout (Appendix B). Butane concentration, another component of unrefined natural gas, did not differ between activities. However, iso-butane was found at higher concentrations in background measurements than in ambient, cleanout or HyF samples (Appendix B).

The other analytes that were detected frequently (i.e. included in Tier-1) are formaldehyde and ethanol. Formaldehyde is a combustion by-product and is found in engine exhaust (Guigard et al., 2015; Kim et al., 2018; Kumar et al., 2018). Ethanol was used during some of the WST HyF treatments (Table 5) and can be emitted by a variety of other sources, including vapors from vehicles using ethanol blended fuel (Kumar et al., 2018). Given the large concentrations of diesel truck and other equipment that occurs during a WST (Figure 2), it may be expected that combustion products and vapors associated with blended fuel handling may be found at higher concentrations than occur during reference activities.

The mean values for formaldehyde and ethanol do not differ between activities. However non-parametric (Wilcoxon) analysis shows that ethanol concentrations were higher in the HyF, ambient, and background samples than the cleanout. Similar results were found for formaldehyde, with the cleanout being lower than the ambient, background or HyF treatment, which were equal to each other (Appendix B).

Other combustion products, acetaldehyde and acetone, were found in the Tier-2 confidence category (Table 4 and Appendix C). Acetaldehyde and acetone were reported in two different units (mg/m^3 and ppb), as were many analytes (see Table 4). It was not determined which data were independent measurements and in which cases the same data was reported in more than one unit, however there is a difference in sample sizes between the units, suggesting some independence between the data sets (Appendix C). For acetaldehyde, no statistical difference was observed between activities, except for HyF being higher than the cleanout when data was reported in units

of ppb (Appendix C). In the case of acetone, a statistical difference was found independent of the reporting units, with acetone being higher in the HyF samples than the cleanout samples. In all cases, ambient, background, and HyF samples had statistically the same concentrations of acetone and acetaldehyde.

Pentane, a component of natural gas, was reported in one unit (ppb v/v). Although means did not differ between activities, non-parametric analysis showed that higher concentrations of pentane were found during cleanout and in background samples than in ambient samples, but HyF pentane concentrations were less than background and not significantly different from ambient measurements (Appendix C).

Dichlorodifluoromethane was detected and quantitated in 62% of the samples in which it was measured (Table 4). However, there was no statistical difference in dichlorodifluoromethane concentrations between activities when they were compared (Appendix C). Dichlorodifluoromethane is chlorofluorocarbon or halomethane that is commonly called Freon-12. Dichlorodifluoromethane is widely used as a refrigerant (Xiang et al., 2014) and its frequent detection (> 57%) in samples from all activities is disturbing due to its recognized impact on the environment, but not entirely unexpected given the known global emission of this compound (Xiang et al., 2014).

Tier-3 contains analytes which were detected between 30% - 49% of the times they were measured and statistical differences found in comparisons between activities using these data, shown in Appendix D, should be interpreted as indicative rather than conclusive. For example, the Tier-3 data set includes results for acetone as measured by the USEPA analytical method "Air Method, Toxic Organics – 15 (TO-15)" whereas data for acetone discussed above (Tier-2) were measured using USEPA "Compendium Method TO-11A" (Table 2). The TO-15 results for acetone are in agreement with the TO-11A data in that both sets of data indicate that HyF acetone concentrations are higher than cleanout. However, the TO-15 data suggests that HyF and cleanout acetone concentrations are less than found in the background or even the ambient (in the case of cleanout). As discussed above, there is not a hard rule as to when data is "too censored" for even parametric analysis, but the more censored the data, the less reliable the conclusion that can be drawn from the data. Where possible, detection limits should be lowered to collect more useful data.

Even though the Tier-3 data are censored, there is some interpretation that can be made concerning the results in Appendix D. Chloromethane, another chlorofluorocarbon used as a refrigerant, was found in many samples and the concentrations did not appear to be different between activities (Appendix D), suggesting chlorofluorocarbons are ubiquitous air pollutants in this region, but chloromethane is not reported to be used in WST and therefore can not be specifically related to emissions from WST. Cyclohexane, hexane, and toluene are hydrocarbons found in oil and can also be emissions from combustion (Kumar et al., 2018). Hexane and toluene concentrations were not found to be different between activities. However, cyclohexane was higher in HyF, cleanout, and background samples than ambient. Cyclohexane was also higher in cleanout samples than those associated with HyF treatment. Cyclohexane is a volatile, relatively stable hydrocarbon found in both oil and raw natural gas, so it is not unexpected that this hydrocarbon could be higher in samples taken on oil fields that in ambient samples. The Tier-3 data also supports a pattern observed with Tier-1 and Tier-2 data, that emission of volatile hydrocarbon associated raw natural gas appear to be less during a HyF treatment than during cleanout. This could be logical, since wells are tightly closed and pressurized during HyF treatment.

Tier-4 data is highly censored, having a less than 30% detection rate when analyzed (Appendix E). There were 54 compounds included in this fourth tier (Table 4) and comparative analysis between activities are not conclusive but can be examined in Appendix E. Most of the chlorinated or halogenated compounds that were detected were detected rarely and fell into the Tier-3 category. Although there is some indication some of the halogenated compounds were found at higher concentration during HyF activity than during cleanouts (e.g. 1,1,1-trichloroethane, Appendix E), there are compounding factors to be considered, including that some laboratories had a higher detection frequency for chlorinated compounds than other laboratories (Table 6).

The observed differences between laboratories for the same analysis (Table 6 and Appendix F) could be due to any number of reasons, including real differences in the samples from different WST, laboratory contamination, or variance in realized detection limits between laboratories. In the CARB protocol, the detection limit is specified detection limits for laboratory analysis are required to be less than one microgram per cubic meter (ug/m^3) for most analysis (California Air Resources Board, 2018). One compounding factor is that, in many cases the producers (or their contractors) used different analytical laboratories, with insufficient overlap between correlated variables to allow robust analysis of the independence of variables (i.e. producer, contractor, and laboratory are highly correlated). An analysis of the trip blank results and other QA/QC information could help resolve questions concerning false positives for chlorinated compounds, since chlorinated compounds are common analytical laboratory contaminates that may result in false positives. An analysis of method detection limit by analyte, method, and laboratory was not conducted as part of this study.

Table 5. Chemical constituents, with Chemical Abstracts Service Registry Number (CASRN), used in stimulation fluid formulations for the following wells where air sampling was completed: 029-27186, 030-53804, 030-54057, 030-55084, 030-55090, 030-55091, 030-55914, 030-60081, 030-60471, 030-60841, 030-60844, 030-62169, 030-62399, 030-62704, 030-63043, 030-63120, 030-63550. Fluid formulation records were located for 17 of the wells using data obtained from the Division of Oil, Gas, and Geothermal Resources (DOGGR) on June 14, 2019.

Chemical constituents	CASRN	Number of stimulations
Sodium chloride	7647-14-5	25
Water	7732-18-5	25
2,2 Dibromo-3-nitrilopropionamide	10222-01-2	24
2-Monobromo-3-nitrilopropionamide	1113-55-9	24
Crystalline silica, quartz	14808-60-7	24
Guar gum	9000-30-0	24
Sodium hydroxide	1310-73-2	24
Hemicellulase enzyme	9012-54-8	21
Lactose	63-42-3	21
Monoethanolamine borate	26038-87-9	21
Sodium persulfate	7775-27-1	21
Sodium sulfate	7757-82-6	21
Ammonium chloride	12125-02-9	19
Polydimethyl diallyl ammonium chloride	26062-79-3	18
Sodium bisulfite	7631-90-5	12
Laryl dimethyl hydroxysulfobetaine	13197-76-7	10
Sodium polyacrylate	9003-04-7	9
Methanol	67-56-1	7
Ethanol	64-17-5	6
Glutaraldehyde	111-30-8	6
Hexamethylenetetramine	100-97-0	6
Phenol / formaldehyde resin	9003-35-4	6
Phosphoric acid	7664-38-2	6
Potassium chloride	7447-40-7	6
Quaternary ammonium compounds, benzyl-C12-16-alkyldimethyl chlorides	68424-85-1	6
Castor oil, ethoxylated	61791-12-6	4
Isopropanol	67-63-0	4
Sorbitan, monohexadecanoate,poly(oxy-1,2-ethanediyl) derivs.	9005-66-7	4
Terpenes and Terpenoids, sweet orange-oil	68647-72-3	4
4-Methyl-1,3-dioxolan-2-one	108-32-7	3
Acrylic acid, butyl ester, polymer with ethenylbenzene and 2-propenamide	25037-33-6	3
Alcohols, C10-16, ethoxylated propoxylated	69227-22-1	3
Alcohols, C6-12, ethoxylated propoxylated	68937-66-6	3

Chemical constituents	CASRN	Number of stimulations
Aluminum oxide	1344-28-1	3
Aluminum silicate	1302-76-7	3
Ammonium acetate	631-61-8	3
Arsenic	7440-38-2	3
Chlorous acid, sodium salt	7758-19-2	3
Colbalt acetate	71-48-7	3
Hydrotreated light petroleum distillate	64742-47-8	3
Isotridecyl alcohol ethoxylates	9043-30-5	3
Potassium hydroxide	1310-58-3	3
Potassium metaborate	13709-94-9	3
Propylene glycol	57-55-6	3
Quaternary ammonium compounds, bis(hydrogenated tallow alkyl) dimethyl,salts with bentonite	68953-58-2	3
Sodium polyacrylate	9003-4-7	3
Sorbitan, monododecanoate, poly(oxy-1,2-ethanediyl) dervis	26266-58-0	3
Ulexite	1319-33-1	3
Polylactide resin	9051-89-2	2
1-Eicosene	567040	1
1-Hexadecene	629-73-2	1
1-Octadecene	112-88-9	1
1-Tetradecene	1120-36-1	1
2-Ethyl hexanol	104-76-7	1
Acetic acid	64-19-7	1
Alcohols, C14-C15, ethoxylated	68951-67-7	1
Alkenes, C >10 alpha-	64743-02-8	1
Amines, hydrogenated tallow alkyl, acetates	61790-59-8	1
Ammonium fluoride	12125-01-8	1
Benzoic acid	65-85-0	1
Citric acid	77-92-9	1
Copper dichloride	7447-39-4	1
Dodecylbenzene sulfonic acid	27176-87-0	1
Ethoxylated hexanol	68439-45-2	1
Ethylene glycol	107-21-1	1
Ethylene glycol monobutyl ether	111-76-2	1
Ethylene oxide	75-21-8	1
Hydrochloric acid	7647-01-0	1
Hydroxylamine hydrochloride	1304222	1
Mixture of dimer and trimer fatty acids of indefinite compostion derived from tall oil	61790-12-3	1
Poly(oxy-1,2-ethandiyl), a-(nonylphenyl)-w-hydroxy-	9016-45-9	1
Poly(oxy-1,2-ethanediyl), alpha-hexyl-omega-hydroxy	31726-34-8	1
Propargyl alcohol	107-19-7	1

Chemical constituents	CASRN	Number of stimulations
Reaction product of acetophenone, formaldehyde, thiourea and oleic acid in dimethyl formamide	68527-49-1	1
Silica, amorphous - fumed	7631-86-9	1
Sodium carbonate	497-19-8	1
Tricalcium phosphate	7758-87-4	1

Table 6. Comparison of analytical results between laboratories for chlorinated compounds, hydrocarbons, and other analytes non-chlorinated compounds. See Appendix H for a detailed analysis by laboratory.

Laboratory	Method Name	Chemical Category	Percent Detected
BC Laboratories	EPA TO-15	Halogenated	0.0
Eurofins	EPA TO-15	Halogenated	44.1
TestAmerica	EPA TO-15	Halogenated	5.0
TestAmerica	EPA TO-13A SIM	Hydrocarbon	2.2
BC Laboratories	EPA TO-15	Hydrocarbon	0.4
Eurofins	EPA TO-15	Hydrocarbon	71.7
TestAmerica	EPA TO-15	Hydrocarbon	8.4
Eurofins	ASTM D-1945/3588	Hydrocarbon-gas	66.7
Portable	ASTM D-1945/3588	Hydrocarbon-gas	58.1
Eurofins	EPA TO-15	Hydrocarbon-gas	100.0
TestAmerica	EPA TO-15	Hydrocarbon-gas	95.9
ALS Simi Valley	EPA TO-11A	Hydrocarbon-oxygenate	32.6
TestAmerica	EPA TO-11A	Hydrocarbon-oxygenate	32.8
TestAmerica	EPA TO-13A SIM	Hydrocarbon-oxygenate	0.9
BC Laboratories	EPA TO-15	Hydrocarbon-oxygenate	0.0
Eurofins	EPA TO-15	Hydrocarbon-oxygenate	42.9
TestAmerica	EPA TO-15	Hydrocarbon-oxygenate	20.6
ALS Salt Lake City	NIOSH 5523	Hydrocarbon-oxygenate	9.4
TestAmerica	NIOSH 5523	Hydrocarbon-oxygenate	0.0
BC Laboratories	EPA TO-15	Carbon disulfide	0.0
Eurofins	EPA TO-15	Carbon disulfide	4.7
TestAmerica	EPA TO-15	Carbon disulfide	10.4
Eurofins	ASTM D-1945/3588	Atmospheric	75.0
Portable	ASTM D-1945/3588	Atmospheric	50.3

Figure 2. Hydraulic fracturing and other well stimulation treatments (WST) require the use of trucks, pumps, and other equipment that can produce air emissions. Shown is one of the hydraulic fracturing treatment in the Central Valley of California photographed by Google Earth. Red mixing and pump trucks can be seen next to rectangular and circular water, sand, and chemical storage and blending tanks. Pump-jacks, located at adjacent wells, and white pickup trucks are ubiquitous features on oil fields in California.

Comparison of air quality at ambient, background, upwind, and downwind locations

In many cases, monitoring reports included results from a local weather station that was operated in conjunction with air monitoring. Using the weather data from the monitoring reports, the predominant wind direction during the monitoring event could be determined (see methods section). Using predominant wind direction, sampling locations associated with WST and cleanout were designated as either upwind or downwind, as described in the methods.

In this section, comparisons are made between ambient, background, upwind, and downwind locations. Since the air quality associated with WST and the cleanout activities were similar (see discussion above), samples from WST and cleanout activities are pooled for this analysis.

In the previous analysis of air quality by activity, it is possible that by including upwind samples with downwind samples we may be "diluting" the actual effects of WST, since upwind samples may be more representative of background air quality on the oil field than emissions from trucks and equipment that are used in WST (Figure 2). Analysis by wind direction also helps address statistical issues associated with the disparity in sample sizes between WST and reference conditions. In this analysis, upwind is considered a reference location, in addition to the background and ambient locations, and upwind and downwind samples sizes are approximately equal.

The results for the Tier-1 analytes, including formaldehyde, butanes, methane, and ethanol are presented in Appendix G. Methane and iso-butane were found to be significantly lower at upwind and downwind locations than ambient locations. Methane was also found to be lower at downwind than background. Upwind and background methane concentrations did not differ. Formaldehyde and ethanol were not found to be statistically different at any location (Appendix G). For the Tier-2 compounds (Table 4), only pentane was found to be higher at both upwind and downwind samples than background locations (Appendix H). The results of this analysis by location were consistent with the results by activity, reported above. Upwind and downwind concentrations did not differ for any analyte in the Tier-1, Tier-2 or Tier-3, or Tier-4 categories (see Appendix G, H, I and J respectively).

The results of the analysis by location are consistent with the analysis by activity in the previous section. Neither analysis shows a measurable increase in air pollutant concentrations in association with WST and cleanout. In many cases, the reference locations had similar or poorer air quality than the air quality measured during active oil field operations (i.e. WST and subsequent cleanout).

Analysis of ambient and background station locations

In many cases, the ambient and background locations had concentrations of analytes as high or higher than those measured during WST activities or cleanouts. For example, samples collected at ambient stations, which are intended to represent air quality independent of influences from oil fields, had as high or higher concentrations of formaldehyde and ethanol as samples collected on the oil fields (Appendix B). In order to examine this result further a preliminary geospatial analysis was conducted to examine the location of the ambient and background monitoring stations.

Figure 3 presents an overview of the location of the wells that were stimulated and the associated background and ambient stations. Figures 4, 5, 6, and 7 present expanded views of the locations in a North to South direction. In some cases, ambient stations are clearly off of the oil fields (Figure 4), but in other cases ambient stations appear to be located on oil fields or approximate to oil fields (Figures 5 and 6). An ambient station was placed next to a roadway (Figure 7). Background sampling locations appear to be in close proximity to stimulated wells, including located between stimulated wells (Figure 4).

This preliminary analysis suggests that some of the background stations are located within 300 feet of the stimulated well and some of the ambient stations are located within 400 feet of the monitored well. It was not determined how close ambient and background stations were located to other wells ancillary infrastructure. In some cases, there may be temporal spacing between background measurements and treatments, but a systematic analysis was not conducted for the temporal variable.

The observation that the concentration of air pollutants is frequently higher at ambient and background stations than during times of active treatment, suggests that the criteria or method being used for siting background and ambient stations should be evaluated. It may be necessary to choose specific ambient monitoring locations known to represent ambient conditions. There may also be opportunities to compare data from this study with data collected by CARB or other agencies in other locations throughout the region.
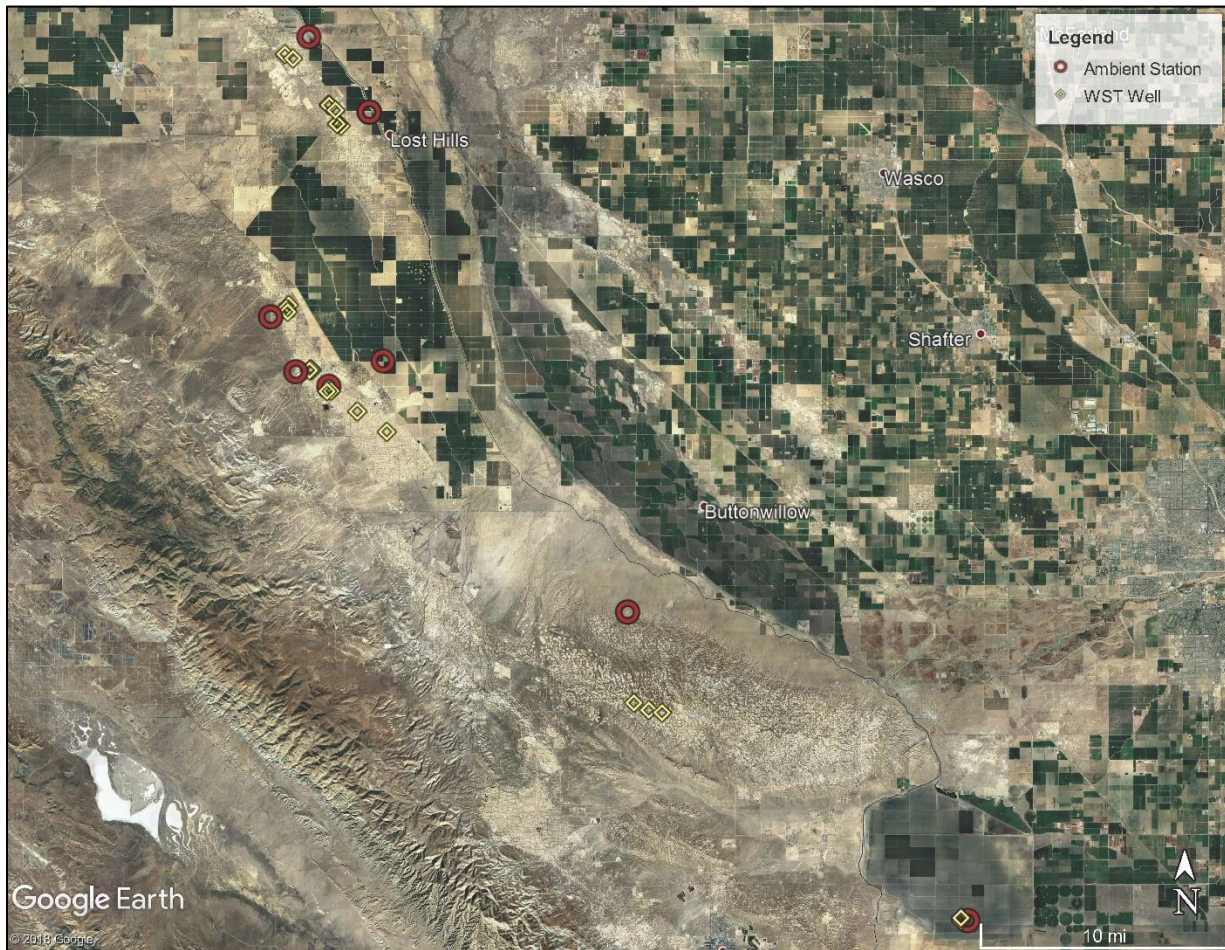

Figure 3. Overview map of all ambient monitoring locations and stimulated wells included in monitoring program. At this scale, more than one ambient station location may be represented by a single circle.
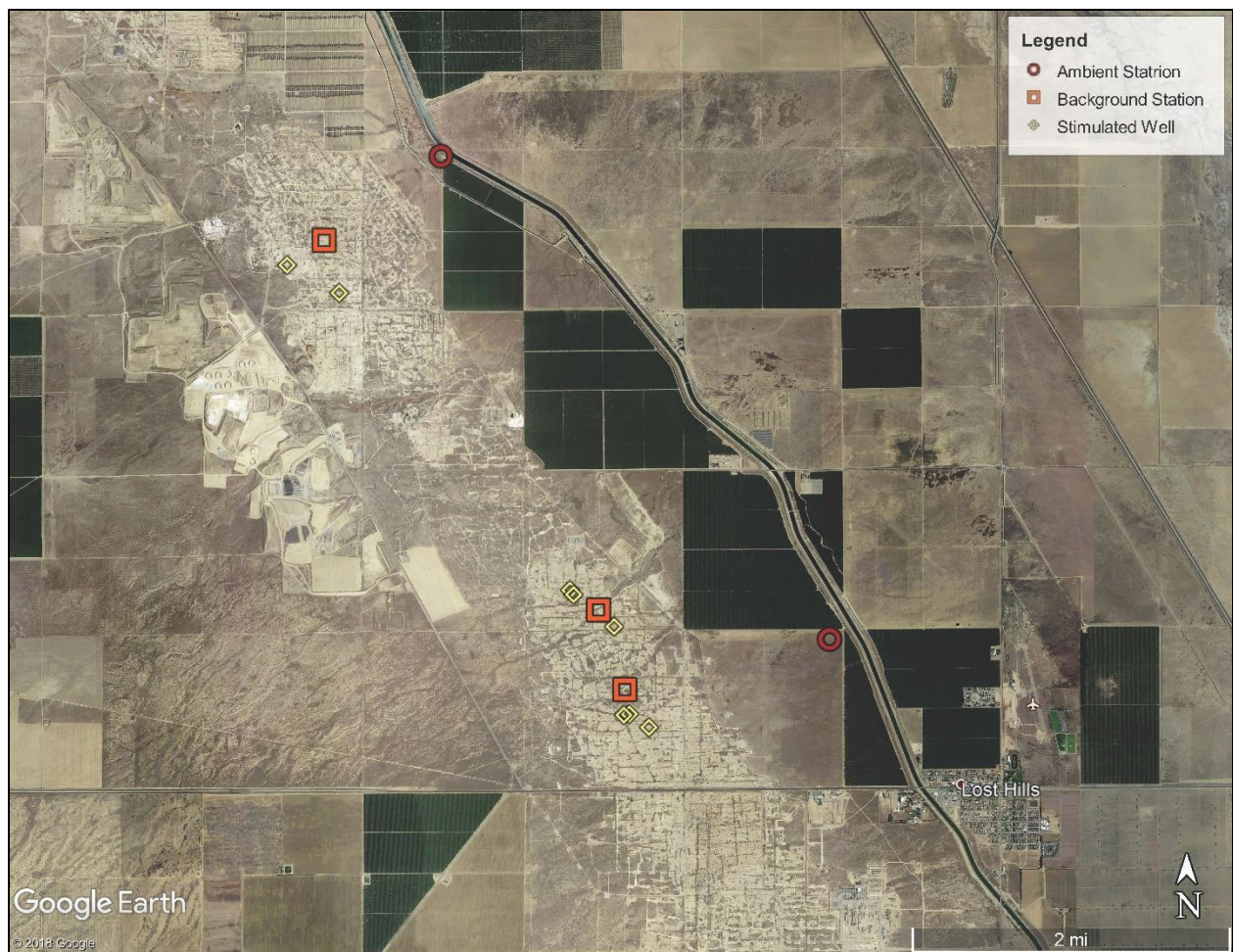
Figure 4. North area: location of ambient and background monitoring locations in relation to the stimulated wells included in monitoring program. At this scale, background and ambient markers may over lap and more than one station location may be represented by a single marker.
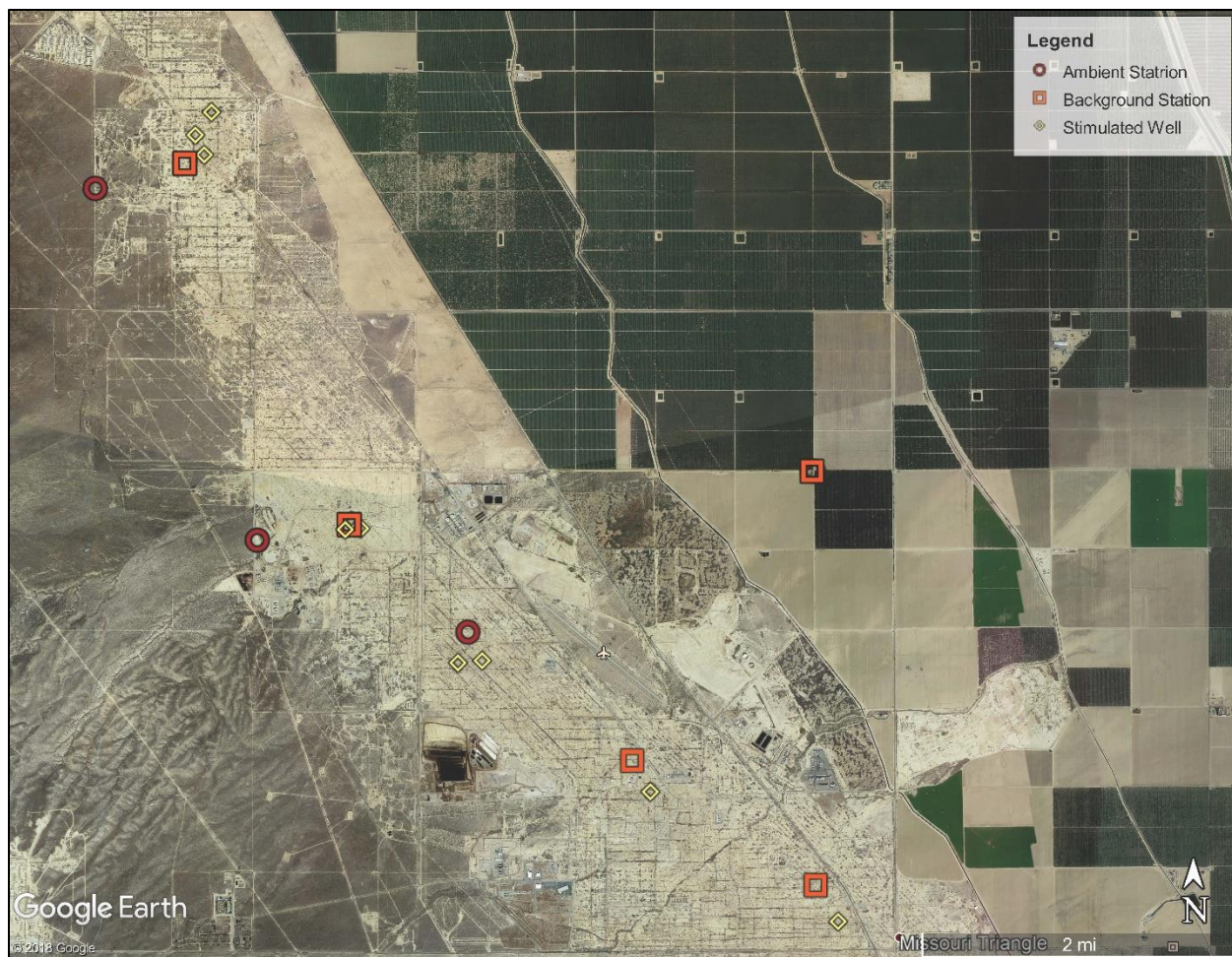
Figure 5. Mid-North area: location of ambient and background monitoring locations in relation to the stimulated wells included in monitoring program. Note overlap of ambient and background station in agricultural area. At this scale, background and ambient markers may over lap and more than one station location may be represented by a single marker.

Figure 6. Mid-South area: location of ambient and background monitoring sites in relation to the stimulated wells included in monitoring program. At this scale, background and ambient markers may over lap and more than one station location may be represented by a single marker.
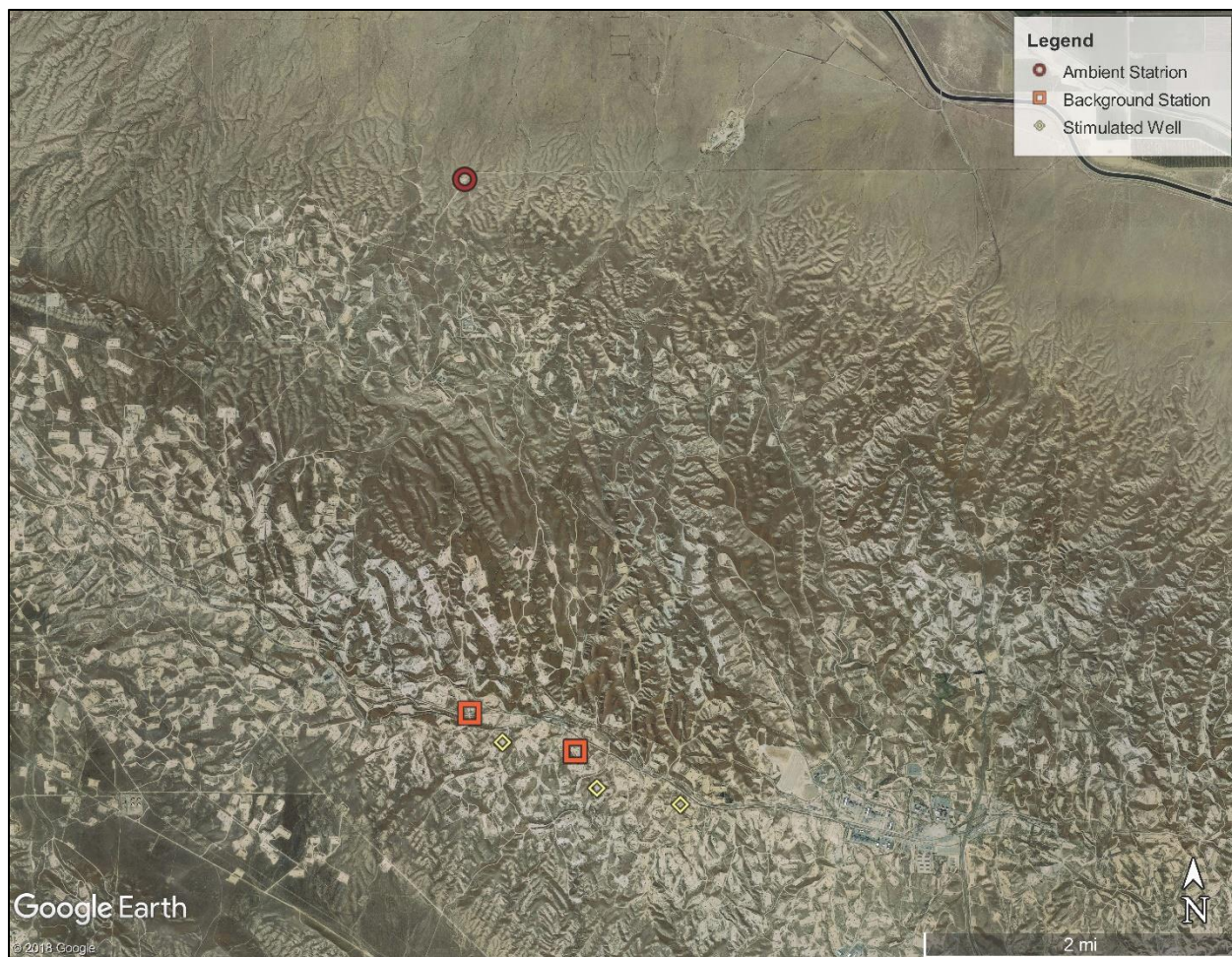
Figure 7. South area: location of ambient and background monitoring sites in relation to the stimulated wells included in monitoring program. At this scale, background and ambient markers may over lap and more than one station location may be represented by a single marker.

Analysis of QA/QC data.

The CARB protocol requires both matrix spikes and trip blanks as part of the QA/QC for the sampling protocol. Results for trip blanks were not included in the data package.

Data from some samples labeled "matrix spike" were included in the data provided to S&A by CARB. Two stimulated wells had results from samples labeled matrix spike: API 030-55084 and API 030-60081. Information concerning those matrix spikes were found in the monitoring reports

Conclusions

In addition to the atmospheric gasses, the most frequently detected analytes were hydrocarbons associated with raw natural gas (methane, butane, iso-butane, and pentane) and volatile compounds

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associated with general oil extraction and internal combustion engine emissions (formaldehyde, ethanol, acetone, and acetaldehyde). One halogenated hydrocarbon, dichlorodifluoromethane, was found frequently and other halogenated hydrocarbon were found occasionally (Table 4). Dichlorodifluoromethane is a refrigerant and is known to be a common air contaminant (Xiang et al., 2014). Most of the other halogenated hydrocarbons were reported by one operator and contractor, which may or may not indicate that the associated contract analytical laboratory had a contamination problem (Appendix F). Chlorinated solvents, chlorine based oxidants, and other halogenated compounds were not reported to be used during WST at these wells (Table 5). Polyvinyl chloride may be used in shape charges used to perforate well casings during WST (Elbeih et al., 2018), but it is not known is chlorinated breakdown products are produced.

In many cases, the analytical results were left-censored and a tiered approach was taken to assign confidence to the comparisons made between off-field reference stations (ambient), on-field reference stations (background), and treatments (WST and cleanout). Overall, air quality was not poorer during WST than during cleanout or in comparison the reference conditions. For several analytes, background and ambient concentrations were statistically greater at reference stations than during active treatments.

Although a tiered approach was used to organize comparative analysis, it should be considered that even contaminants measured infrequently or in only one location could have important informational value. It is possible that measured compounds are found heterogeneously geographically and were only emitted by some operations. It is also likely that many of these analytes (e.g., BTEX) are found in sampling near certain types of ancillary infrastructure (e.g., condensate tanks) that could be in the vicinity of some WST and not others. Detailed information about nearby infrastructure or other proximate operations were not provided in the sampling reports.

There was a large difference in the number of samples taken at the reference stations and during the WST and associated cleanout, so an analysis was conducted comparing analytical results from upwind locations to downwind locations. No differences were found between upwind and downwind locations, indicating that the measurable emissions during the WST and cleanout were not higher than the background conditions on the oil field.

An analysis was conducted examining the location of ambient and background monitoring in relation to the stimulated well and the oil fields in general. Ambient sites in particular serve as the "control" measurements for comparison to air monitoring during the well "treatment." From this analysis, it was not clear what criteria were used to select ambient locations, as several stations designated as ambient were located either on or near oil fields. Background monitoring locations were on-field, but in some cases background station were located within a few hundred feet of the well or wells undergoing treatment. The locations of the reference sites may help explain why reference locations could have poorer air quality than observed during WST.

Recommendations

Ambient reference monitoring sites should be specified. CARB has established criteria for selection of locations for ambient monitoring. However, each operator selects the final ambient monitoring locations independently and in some cases may have placed ambient sites in proximity to oil field or oil field associated activities. CARB should consider identifying one or more specific locations where operators should collect ambient samples. This location should be an area with

public access or with arranged access for consultants to conduct sampling. Locations such as parks, state owned property, or a specific public access area away from major traffic (i.e. open field or lot, remote intersection in farming area) should be considered for ambient sampling locations. Having more samples collected from a single site chosen to represent ambient conditions would increase the value of the reference data by insuring the data truly represent ambient conditions.

More data should be collected at ambient and background reference monitoring sites. More data should be collected at reference sites with the objective of achieving more equal sample population size (N) as measurements made during WST activities. Equal sample sizes will enhance the certainty of statistical comparisons. For on-field (background) samples, information on proximity to on-field activities other than WST, such as drilling and oil-water separation facilities, should be noted. For both ambient and background monitoring, a specific effort should be made to collect more reference data for comparison with WST activities. Other sources of ambient air quality information, such as data collected by local air districts, could also be useful for increasing the sample size for reference data.

Reporting of monitoring analytical data should be standardized. Standardization should include requirements for electronic reporting of analytical data. Extraction of data from PDF files is both time consuming and inherently prone to error. Electronic data will reduce error and streamline oversight. Monitoring reports should include appendix of the laboratory reports containing the analytical data.

Reporting of wind and other weather data should be standardized. Standardization should include requirements for electronic reporting of weather station data. Direct comparison among different companies was particularly challenging when they used different formats for wind rose, different units, different data collection time range and frequencies. As possible, the contractor should clearly designate the predominant wind direction and assign upwind and downwind designations to monitoring samples.

Report formats and section headers should be standardized. Different consultants used different reporting formats and report sections, so there was little consistence between consultants concerning what information was reported and where in the report specific information (e.g. weather data, geographic information) could be found. Standardization of report section headers, having requirements for types of data to be included, and specifying the reporting units would assist CARB and DOGGR staff in determining if appropriate monitoring was conducted and if all reporting of primary and ancillary information was complete.

Reports should use API number and limit the number of wells or WST included in one report. In many cases, the on-field well name was used on the report cover and in tables and figures, but the API number of the well was not and it was difficult to establish which wells were included in which reports. The number of WST included per report varied and in some cases it was difficult to relate information in the reports to the data (which was reported by API number). Requiring the use of API numbers in the report and limiting the maximum number of WST in one report should be considered. Having only one well or one WST per report is recommended.

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Glossary of Terms, Abbreviations, and Symbols

% v/v	percent as a volume fraction
Amb	Ambient sample site, off the oil field
API	American Petroleum Institute
Bkg	Background sample site, on the oil field, but away from hydraulic fracturing activities
CARB	California Air Resources Board
CASRN	Chemical Abstracts Service Registry Number
CCST	California Council on Science and Technology
CIMIS	California Irrigation Management Information System
CO	Clean out (of a well)
DOGGR	Department of Oil, Gas, and Geothermal Resources
HyF	Hydraulic fracturing
JMP	Statistical software from SAS Institute Inc. (Cary, NC)
mg/m^3	milligram per meter cubed
N	Sample size
Pct det	Frequency of detection as a percent of the number of times an analytes was measured
ppb	parts per billion
ppb v/v	parts per billion as a volume fraction
PSE	Physicians, Scientists, and Engineers for Healthy Energy
S&A	Stringfellow & Associates
SB4	Senate Bill 4
WST	Well stimulation treatment

Appendix A - J