

**Source Testing of Fugitive and Vented Emissions from  
Hydraulic Fracturing Operations and Wastewater Ponds  
Used in Crude Oil and Natural Gas Operations in  
California**

**Rev 1.0**

**Report prepared for the California Air Resources Board  
for IFB No. 12-414**

**Sage Environmental Consulting LP**

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## **Disclaimer**

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## TABLE OF CONTENTS

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|   |           |
|---|-----------|
| <b>1. Executive Summary .....</b>   | <b>1</b>  |
| <b>2. Background .....</b>  | <b>3</b>  |
| <b>3. Materials and Methods .....</b>   | <b>4</b>  |
| <b>4. Sampling Design Considerations and Modifications.....</b>                       | <b>7</b>  |
| <b>5. Results and Discussion.....</b>   | <b>10</b> |
| <b>6. Summary and Conclusions .....</b>   | <b>12</b> |
| <b>7. Recommendations.....</b>  | <b>13</b> |
| <b>8. References .....</b>  | <b>14</b> |
| <b>9. List of Inventions Reported and Publications Produced .....</b>                 | <b>15</b> |
| <b>10. Definitions and Acronyms.....</b>  | <b>16</b> |
| <b>Appendix A: Test Plan and QA/QC protocols .....</b>                                | <b>17</b> |
| <b>Appendix B: Composition of Hydraulic Fracturing Fluid Injected into Well .....</b> | <b>41</b> |
| <b>Appendix C: Wastewater Pond Testing .....</b>                                      | <b>45</b> |



# 1. Executive Summary

**Background.** The purpose of this study was to characterize sources of greenhouse gas (GHG), volatile organic compound (VOC), and toxic air contaminant (TAC) emissions from various types of oil and/or gas well stimulation and well working operations, and related activities, in California. This research is important for the quantification of emission inventories and for the development of Assembly Bill 32 (AB 32) emission reduction regulations.

**Methods.** To analyze the impacts of hydraulic fracturing and other well stimulation treatments, a draft test plan was developed with ARB and shared with industry representatives prior to field testing. The test plan included a variety of measurement techniques both to assess their suitability as well as to provide the project team with flexibility. These techniques included:

- Optical gas imaging (OGI) to detect emissions otherwise invisible to the human eye;
- A Hi Flow Sampler for direct volumetric leak rate measurements;
- A Flux Chamber to measure emissions from wastewater enclosures; *and*
- The procedures described in ARB’s draft document “Flash Emissions of Greenhouse Gases and Other Compounds from Crude Oil and Natural Separator and Tank Systems” ([http://www.arb.ca.gov/cc/oil-gas/flash\\_test\\_procedure\\_apr24.pdf](http://www.arb.ca.gov/cc/oil-gas/flash_test_procedure_apr24.pdf)) to quantify emissions from flowback fluids.

**Results.** Although this study intended to characterize emissions from approximately 40 well sites and from a variety of stimulation techniques, several factors, but primarily an inability to gain adequate site access due to scheduling and other issues, limited testing to two (2) hydraulically fractured wells, both situated on the same oil reservoir. This reduction in scope limited the project’s results. For instance, the study was unable to determine the possible effect on overall emissions from chemical additives within the hydraulic fracturing fluid. Further testing and analysis is warranted to establish more accurate emissions profile from WST operations.

However, the study did identify “well circulation” as a previously unidentified source of uncontrolled emissions associated with the hydraulic fracturing process. Emissions during well circulation, a process used to clear a well of excess sand using a circulation tank, were easily identified with the optical gas imaging camera, although quantifying them will require further testing. Flash test data were also too limited to draw conclusions.

In addition, samples were collected at three wastewater pond systems located near hydraulic fracturing operations. While no hydraulic fracturing chemicals were detected in the wastewater, non-methane hydrocarbon and TAC emissions were observed at significant levels. Given the small sample size and high degree of variability observed in the results, it is difficult to draw conclusions or extrapolations. Further testing and analysis is warranted.

**Conclusions.** An insufficient number of hydraulically fractured well sites were available for testing. Consequently, the results of this emissions study are inconclusive and the information cannot be used to determine the level of emissions from WST operations at this time. However, additional sources of potential emissions were identified including circulation tanks and wastewater ponds. Further testing and analysis is warranted to establish more accurate emissions profile from WST operations.



## 2. Background

The California Global Warming Solutions Act of 2006, also known as Assembly Bill 32 (AB 32), establishes a comprehensive program of regulatory and market mechanisms to achieve real, quantifiable, cost-effective reductions of greenhouse gases (GHG) (Health and Safety Code §38500 et seq.). AB 32 charges the California Air Resources Board (ARB) as the agency responsible for monitoring and reducing GHG emissions to 1990 levels by 2020 and requires ARB to indicate how emissions reductions will be achieved from significant GHG sources via regulation, market mechanisms, and other actions.

The ARB contracted Sage Environmental LP (Sage) to perform emission testing at hydraulically fractured, acid fractured, and acid matrix stimulated well sites at various locations in different underground reservoirs throughout California. Sage worked with ARB to identify viable source testing locations. Due to the uncertainties involved in identifying appropriate testing locations and in obtaining permissions from the operators to conduct such testing, a minimum number of sites to be inspected and tested could not be guaranteed. A test plan was drafted using a variety of test procedures to evaluate the contributory effect of well stimulation treatments to methane (CH<sub>4</sub>), carbon dioxide (CO<sub>2</sub>), hydrogen sulfide (H<sub>2</sub>S), volatile organic compound (VOC), and toxic air contaminant (TAC) emissions. The specific goal of this study was to gain an improved understanding about fugitive gaseous emissions associated with well stimulation activities.

- Hydraulic fracturing is a process of injecting water, chemicals, and proppants (also known as fracturing fluid) at high pressures into an oil or natural gas reservoir in order to enhance well production. Typically, multiple zones are hydraulically fractured in a well in order to expand the production surface area. These zones, separated by bridge plugs, allow the hydraulic fracturing process to occur without affecting other zones. Fracturing fluids typically include gels, friction reducers, crosslinkers, breakers, and surfactants similar to household cosmetics and cleaning products<sup>1</sup>. The proppants (e.g., silica sand) help to keep the fracture open after injection.

Acid Matrix stimulation is accomplished by injecting different types of acids into a well to dissolve and/or disperse materials near the wellbore in sandstones to create new, unimpaired flow channels between the wellbore and a carbonate formation.

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<sup>1</sup> [http://www.glossary.oilfield.slb.com/en/Terms/f/fracturing\\_fluid.aspx](http://www.glossary.oilfield.slb.com/en/Terms/f/fracturing_fluid.aspx)<sup>2</sup> ARB Flash Test Procedure [http://www.arb.ca.gov/cc/oil-gas/flash\\_test\\_procedure\\_apr24.pdf](http://www.arb.ca.gov/cc/oil-gas/flash_test_procedure_apr24.pdf).

### 3. Materials and Methods

To assess the emission impacts of well stimulation treatments, several different emission detection and emission characterization approaches were used to quantify and evaluate the three phases of operation in well stimulation activities (well completion, well start-up, and well production).

#### Emission Detection

Optical gas imaging (OGI) was employed to identify major emission points during the project. OGI uses infrared (IR) technology that allows for efficient detection of emissions from multiple sources. For this study a GasFinderIR™ and GF-320 models were used to detect emissions associated with well stimulation activities within a spectral range of 3.2-3.4 μm, which includes methane. Compounds with spectral absorption either below or above these ranges exponentially decrease in detectability as the absorption spectrum moves away from the range.

#### Emission Characterization

To characterize vessel flashing emissions, the procedures outlined in ARB's Flash Test Procedure, *"Flash Emissions of Greenhouse Gases and Other Compounds from Crude Oil and Natural Gas Separator and Tank Systems"* were followed. This procedure is specifically designed to collect pressurized liquid samples from crude oil, condensate, or produced water vessels to estimate vessel flash emissions. Collected samples were subsequently analyzed for GHGs, VOCs, and TACs. This test procedure was also used to predict the Gas to Water Ratio (GWR) and Gas to Oil Ratio (GOR) in flowback fluid samples.

The Hi-Flow Sampler™ (Hi-Flow) was used to characterize fugitive emissions from well-site component leaks. The Hi-Flow is a battery-powered, intrinsically safe instrument designed to determine volumetric emission rates of methane from leaking components. In the majority of cases, samples are taken at a sufficiently high flow rate to ensure a complete leak measurement. If the volumetric leak rate exceeds the Hi-Flow sampling rate, then other techniques, such as the timed filling of a large bag are used to determine leak rate volume.

Evacuated Summa™ canisters (nominally 30 mm Hg vacuum) were used to collect emission samples either from the flux chamber (described in the following paragraph), from the Hi-Flow, or simply as a grab sample. A flow regulator is typically used to control the canister fill rate. The completed canister sample was delivered to an analytical laboratory together with chain-of-custody documentation for analysis according to a specified analytical method.

The USEPA flux chamber sampling approach as described in EPA document #EPA/600/8-86/008 February 1986, Measurement of Gaseous Emission Rates from Land Surfaces Using an Emission Isolation Flux Chamber, was used to assess the emissions from wastewater treatment processes and other open-air systems. Fluid handling and treatment processes that vent to the

atmosphere were measured by interfacing the flux chamber to the emission source, directly measuring the air emissions, and prorating the air emissions to the process surface area and production rate.

Depending on the sampling method used, one or more of the following analytical methods was used to characterize the collected sample:

- Gas-to-Oil Ratio (GOR) Measurement and Gas-to-Water Ratio (GWR) Measurement by ARB's Flash Test Procedure;
- Methane (CH<sub>4</sub>) concentration by ASTM Method D1946;
- Carbon Dioxide (CO<sub>2</sub>) concentration by ASTM Method D1946;
- Hydrogen Sulfide (H<sub>2</sub>S) by USEPA Method TO-15, USEPA Method TO-16, ASTM D1945M, ASTM D-5504, or ASTM-D-6228;
- Volatile Organic Compounds (VOCs) by USEPA Method TO-15 (GC/MS or GC/FID), EPA Method 8260, or EPA Method 8270; *and*
- Specialty Compounds (BTEX & TIC List) by USEPA Method TO-15 (GC/MS or GC/FID)

In some cases, it was necessary to have the sampler provide a Tentatively Identified Compound (or TIC) List of uncommon compounds to guide the laboratories in the sample analysis.

### **Initial Sampling Design**

*Baseline Phase.* The purpose of baseline testing was to gather emission information about a well prior to a well stimulation treatment. Flash and wastewater samples were to be collected for laboratory evaluation and screening and measurement of fugitive emissions was to be performed. The results would then be used to determine emissions from the flowback and post-flowback phases.

*Flowback Phase.* The flowback phase occurs after a well stimulation treatment, and it was anticipated that this would be the phase in which the majority of testing would occur. Testing was to include real-time measurements of the flow back fluid gaseous emissions, tank headspace and gas composition, and the scanning and testing of fugitive or vented leak sources.

*Post-Flowback Phase.* The post-flow back phase testing was intended to determine the duration and completeness of the flow back phase. Accordingly it was planned that testing would be an extension of the flow back phase, continuing until concentrations of compounds observed in the oil or wastewater stream approached those recorded during the baseline phase testing.

A complete discussion of the initial test plan including QA/QC protocols can be found in Appendix A.

## 4. Sampling Design Considerations and Modifications

### Sampling Design Considerations and Issues

The results of the initial test design provided the best possibility of isolating emission impacts specific to hydraulic fracturing operations. However, based on discussions with site operators it was determined that the test design was not appropriate and was consequently adjusted to characterize emissions associated with well completion, well start-up, and well production.

First, baseline measurements were contingent on measurements of an existing well prior to and after a well stimulation treatment. However, discussions with operators in the filed indicated well stimulation usually only occurs for new wells and rarely for existing wells. As such, before-and-after measurements at existing wells were not feasible and baseline measurements were not collected.

After the well stimulation treatment is complete, circulation is used to remove excess sand from the wellbore. Discussions with operators indicated circulation as a potential uncontrolled emission source of gases and other VOCs dissolved or entrained in the circulation fluid.

Additionally, the initial test plan was designed for well production sites containing at least one well, separating equipment, and storage tanks. Operations like these are not common in the areas where testing occurred. Due to the sophisticated operating network of wells, isolating hydraulic fracturing emissions proved impossible when dozens to hundreds of wells are simultaneously feeding into the same production system. Consequently, the testing was modified to focus on operations and production at the well.

The original test plan envisaged testing and re-testing at multiple well sites in order to gather statistically significant data of known accuracy.

However, of the approximately forty (40) well sites that could possibly have been tested in ideal circumstances under the budget provided, only two (2) sites with hydraulic fracturing operations were available to be scanned for fugitive leaks by OGI, only two (2) gravel packing operations were available to be scanned for fugitive leaks by OGI, preliminary High-Flow sampling could be conducted on only one (1) circulation tank, and preliminary testing for emissions could be conducted on only four (4) circulation tanks and three (3) flowback events. The shortfall in the number of sites tested was due to an inability to schedule access to sites. There were difficulties including a low level of WST events during the contract timeframe, uncertainty in timing and execution of WST events, and general difficulty scheduling with operators for events that did occur.

The sample size did not conform to the original sampling strategy and was not statistically significant. Therefore, the resulting data collected is not likely to be representative of WST

operations and as a result is insufficient to accurately characterize emissions from well stimulation operations. Therefore, additional monitoring and testing is necessary to accurately determine the level of emissions from WST operations.

### **Sampled Activities and Modified Sampling Design**

While sampling was limited due to considerations discussed above, the well stimulation and production activities and corresponding sampling are discussed here. A summary of the sampling is shown in Table 1.

*Hydraulic Fracturing.* Site operator safety precautions and procedures were taken in areas with potential exposure to significant pressure systems. In designated areas, which generally included all the hydraulic fracturing piping and equipment, the study team was unable to get near to the equipment for testing. However, during hydraulic fracturing, the project team used optical gas imaging equipment to identify emissions at safe distances. The survey distances varied fifty feet or more as defined by the site operators or contractors. In total, the project observed two hydraulic fracturing operations.

Currently the Division of Oil, Gas, and Geothermal Resources (DOGGR) regulates these well stimulation activities under Senate Bill 4 (SB4). Characteristics of the fracturing fluid for each well, including injected compounds and their concentrations, were obtained from DOGGR.

*Well Flowback/Post Flowback.* Flowback is the process of allowing fluids to flow after a well stimulation treatment. In total, flowback from three wells was tested during both start-up and production phases. For these wells, sample collection occurred from a well tester. Operators use well testers to understand the characteristics of the underground reservoir as well as the well production capabilities. The well-tester used for this study was a three-phase (oil, water, gas) separator. Samples from the water and oil discharge lines were collected and analyzed using ARB's Flash Test Procedure<sup>2</sup>. The collected samples for this phase occurred approximately within the first hour of operation and approximately 24 hours later. In addition, testing occurred two weeks after well start-up to determine if the well production rate increased or decreased.

Fugitive emission sources including the wellhead and associated equipment were also screened with optical gas imaging equipment.

*Circulation Tanks.* Prior to flowback, the well undergoes circulation to remove sand from the wellbore. Often the circulation tanks are open to the atmosphere and may contain oil residues and hydraulic fracturing residuals. The study conducted testing on four circulation operations. During the circulation process, OGI identified emissions from the circulation tank and samples were taken. The pulled samples were collected from the inlet and outlet from three of the four

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<sup>2</sup> ARB Flash Test Procedure [http://www.arb.ca.gov/cc/oil-gas/flash\\_test\\_procedure\\_apr24.pdf](http://www.arb.ca.gov/cc/oil-gas/flash_test_procedure_apr24.pdf).

tanks. For one tank, only an inlet sample was collected. The ARB Flash Test Procedure was used to analyze GOR, GWR, GHG, VOC, and TAC for each sample.

*Gravel Packing.* Two gravel-packing activities were scanned for fugitive leaks by OGI. Gravel packing is used to prevent production of formation sand. Formation sand is produced from the breakdown of formations where the wells are located and commonly occurs in formations of sandstone, limestone, and similar rock types. Gravel-packing acts to stabilize the formation to maintain well productivity.

*Wastewater Pond Testing.* The handling and treatment of wastewater is a process that can be affected by well stimulation treatments, and was therefore included in this study as a possible indication of the differences between the baseline and post flow back phases. Wastewater streams typically include produced water (water that comes up with the oil) and may include other fluids from oil processing (e.g. hydraulic fracturing fluids, etc.).

Active wastewater disposal could not be identified or monitored; therefore, an adjacent set of three wastewater pond systems were tested in an effort to measure the post-flowback phase for chemicals injected as part of the hydraulic fracturing activities observed.

Testing was conducted using the Emission Isolation Flux Chamber at three wastewater pond systems located near the hydraulic fracturing operations that were evaluated and included the collection of eighteen (18) Flux Chamber air samples and twelve (12) Flux Chamber liquid samples. In addition, sixteen (16) liquid phase grab samples were also collected. Since the retention time of the wastewater in the pond systems was estimated to be between 15 to 30 days, the resulting emissions were expected to include known hydraulic fracturing chemicals from the adjacent operations.

**Table 1. Sampling Matrix**

| Activity                                  |                | Location    | Number of Samples (n)   | Measurement Method                            |
|---|----------------|-------------|---|---|
| Hydraulic Fracturing                      | 2 wells        | SJV         | n=1 per well  | OGI   |
| Circulation Tanks (for HF activity above) | 4 tanks        | SJV         | n=2 per tank <sup>3</sup>   | OGI, Flash Testing and High Flow <sup>4</sup> |
| Flowback                                  | 3 wells        | SJV         | n=3 per well (1 <sup>st</sup> hr, 24 hrs, 2 weeks)                              | OGI, Flash Testing <sup>5</sup>               |
| Gravel Packing                            | 2 wells        | South Coast | n=1 per well  | OGI   |
| Wastewater Pond Systems                   | 3 pond systems | SJV         | n=18 flux chamber, air<br>n=12 flux chamber, liquid<br>n=16 liquid grab samples | Flux Chamber/<br>Summa Canister               |

<sup>3</sup> Samples taken from inlet and outlet of each tank for three of the four tanks sampled. For one tank only inlet sampled.

<sup>4</sup> High Flow measurements made for only one tank.

<sup>5</sup> Sampled obtained from well tester with 3-phase separator (water, oil, gas).

## 5. Results and Discussion

**OGI Screening-Hydraulic Fracturing and Gravel Packing.** Two hydraulic fracturing and two gravel packing operations were screened for emissions with the infrared camera. No emissions were detected at the hydraulic fracturing or gravel packing operations. It is thought that the lack of detected emissions is due principally to the pressurization of all surface components. Since leaking components would present serious safety problems, the injection equipment is routinely monitored and checked for leakage by the operators.

As mentioned previously, operators are required to report the compounds and their concentrations injected into wells to DOGGR. The typical constituents are listed in Appendix B by weight percent. However, safety issues did not allow for direct sampling of the hydraulic fracturing fluid. Thus, no data are available to quantify specific hydraulic fracturing compound emissions from this activity.

**Flowback/Post-Flowback Phases.** The flowback phase of three wells was sampled during the well startup period in an effort to measure emissions from flowback fluid gases. However, since the flowback fluids were pumped from an underground reservoir and sent to the facility's separation and tank system, they were not readily accessible for testing, so a portable separator was used. However, the limited number of samples and the variability of the observed results led to data from which it was too uncertain to draw conclusions or extrapolations.

**Circulation Tanks.** During the circulation process, uncontrolled emissions were identified from the circulation tanks using OGI. Two methods were employed to quantify circulation process emissions: High Flow and liquid flash samples. Note for quantifying circulation tank emissions, both of these methods were highly experimental and appropriate quantification could not be conducted given the limited sample size.

The measurements from the Hi-Flow Sampler were unsuccessful due to the presence of numerous openings at the top of the circulation tank from which emissions could possibly escape. As such no results are available from Hi-Flow sampling.

Liquid flash samples were gathered from the inlet and outlet of the circulation tanks. For one tank only an inlet sample was taken. Preliminary data collected identifies circulation tanks as a potential emissions source but additional sampling is required to accurately quantify these emissions. In addition, it is important to understand that emissions from these operations and other related oil and gas operations can vary widely depending on the composition of the fractured zone and flowback constituents, as well as the volume of water circulated due to the depth of the well.



**Wastewater Pond Testing.** The results of the wastewater pond testing indicated that:

- No hydraulic fracturing chemicals were detected in the water. This indicates that the pond systems tested either
  - a) do not receive hydraulic fracturing fluids, or
  - b) did not receive hydraulic fracturing fluids during the past 15-30 days (retention time of the pond systems).
- Non-methane hydrocarbon and TAC emissions were observed at high levels, however, a high degree of variability in sample sets was also observed.
- Non-methane hydrocarbon emissions from the main ponds exceeded those from the inlets by more than an order of magnitude. Further testing is recommended to either confirm or correct this initial conclusion.

The results indicate that the VOC, GHG, and TAC emissions observed from the pond systems were not related to the fracturing fluid. Additional evaluation of the sources of wastewater in the pond systems is needed to determine the sources of observed emissions from the pond systems. Additionally, emissions data from the small sample size (n=3) is too uncertain to draw conclusions or extrapolations.

## 6. Summary and Conclusions

The purpose of this study was to quantify GHG, VOC, and TAC emissions from different types of well stimulation treatments in various locations throughout California, as well as to determine whether the chemicals used in the hydraulic fracturing process could increase the percent of GHG, VOC and TAC compounds in those emissions. The study focused on multiple phases in the hydraulic fracturing process and provided several test methodologies for detecting and quantifying their emissions. The study identified circulation tanks in the well completion process as the only uncontrolled source of emissions in the limited number of hydraulic fracturing operations observed. Additional testing is necessary to obtain verifiable data and provide a quantification of circulation tank emissions.

Overall, the results of this study are inconclusive. Additional testing at well stimulation sites is needed to verify and expand upon the current results and to further evaluate the different characteristics of well stimulation treatments throughout California.

## 7. Recommendations

As a general and broad statement, more data are necessary to reach conclusive results on the effects of well stimulation activities on air emissions.

Likewise, to improve the study results for the circulation tank emissions, more sampling is required, complemented perhaps with an estimate of the GHG, VOC and TAC concentrations entrapped in the tank water and solids. Alternatively, it may be possible to quantify vented tank emissions by closing off all tank openings to measure the resulting headspace gases or by building a hood sampler or by flux chamber testing. Western States Petroleum Association (WSPA) had recently conducted a study to measure the Methane and VOC emissions from circulation tanks. The source test involved enclosing the circulation tanks such that the emissions are routed through a vent and measured<sup>6</sup>. ARB is currently requiring operators to conduct ambient monitoring tests for WST wells to obtain additional data and information including TACs.

Further testing is recommended to understand the emissions from wastewater ponds. ARB has plans to conduct additional testing on ponds.

Further, to assess the impacts of added well stimulation chemicals on the overall GHG, VOC and TAC profile, additional testing is necessary to have a more developed baseline. During development of the test plan, the concept was to test wells before and after a well stimulation treatment to measure differences in the emission profiles. However, Sage was not able to identify any existing wells that were already in production and subsequently stimulated.

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<sup>6</sup> [WSPA Recirculation Tank Emissions Testing, October 2015](#)

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The State of California, Assembly Bill 32, <http://www.arb.ca.gov/cc/ab32/ab32.htm>

## 9. List of Inventions Reported and Publications Produced

Currently, there are no publications or pending publications produced from this study. There were also no inventions produced as a result of this study.

## 10. Definitions and Acronyms

| Acronym              | Definition   |
|----------------------|--|
| GHG                  | Green House Gas in terms of this study means methane and carbon dioxide.   |
| Acid Matrix          | A treatment conducted at pressures lower than the applied pressure necessary to fracture the underground geologic formation.   |
| Gravel Pack          | A sand-control method used to prevent production of formation sand.  |
| Hydraulic Fracturing | A treatment that, in whole or in part, includes the pressurized injection of hydraulic fracturing fluid into an underground geologic formation in order to fracture the formation, thereby causing or enhancing the production of oil or gas from a well.  |
| Fracturing Fluid     | One or more base fluids mixed with physical and chemical additives for hydraulic fracturing.   |
| Proppant             | Materials inserted or injected into the underground geologic formation that are intended to prevent fractures from closing.  |
| EPA                  | United States Environmental Protection Agency  |
| DOGGR                | Division of Oil, Gas & Geothermal Resources  |
| ARB                  | California Environmental Protection Agency Air Resources Board   |
| VOC                  | Volatile Organic Compound and uses the US EPA definition   |
| TAC                  | Toxic Air Contaminant [As listed at <a href="http://www.arb.ca.gov/toxics/quickref.htm">http://www.arb.ca.gov/toxics/quickref.htm</a> Substances identified as Toxic Air Contaminants by the Air Resources Board, pursuant to the provisions of AB 1807 and AB 2728 (includes all Hazardous Air Pollutants listed in the Federal Clean Air Act Amendments of 1990).] |
| TIC                  | Tentatively Identified Compound  |
| GOR                  | Gas to Oil Ratio   |
| GWR                  | Gas to Water Ratio   |
| CH4                  | Methane  |
| CO2                  | Carbon Dioxide   |
| H2S                  | Hydrogen Sulfide   |
| GC/MS                | Gas Chromatograph/Mass Spectrometry  |
| GC/FID               | Gas Chromatograph/Flame Ionization Detector  |
| BTEX                 | Benzene, Toluene, Ethyl benzene, and Xylenes   |

## **Appendix A: Test Plan and QA/QC protocols**





# California Air Resources Board

## **Test Plan for Emission Quantification of Various Sources from Hydraulic Fracturing and Other Well Stimulation Activities from Crude Oil and Natural Gas Operations in California, U.S.A. Sage Proposal No. 1344-01-01 ARB IFB No. 12-414**

**TEST PLAN, Revision 3**

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## TABLE OF CONTENTS

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|  |           |
|--|-----------|
| <b>SECTION 1 Project Introduction .....</b>  | <b>22</b> |
| <b>SECTION 2 Scope of Work.....</b>  | <b>23</b> |
| <b>SECTION 3 Project Test Plan .....</b>   | <b>24</b> |
| 3.1 TASK 1: Develop a Test Plan .....  | 24        |
| 3.2 TASK 2: Conduct Tests.....   | 26        |
| 3.2.1 Task 2.1 Flow-back Phase .....   | 27        |
| 3.2.2 Task 2.2 Post-Flow-back Phase.....   | 27        |
| 3.3 TASK 3: Analyze Test Results & Develop Emission Estimates.....   | 27        |
| 3.4 TASK 4: Reporting.....   | 27        |
| <b>SECTION 4 Sampling Strategy .....</b>   | <b>28</b> |
| <b>SECTION 5 Quality Control &amp; Quality Assurance.....</b>  | <b>34</b> |
| 5.1 Quality Control Actions.....   | 34        |
| 5.1.1 ARB Flash Emissions Test Procedure .....   | 34        |
| 5.1.2 Flux Chamber .....   | 35        |
| 5.1.3 HiFlow Sampler Calibration .....   | 36        |
| 5.1.4 TVA Calibration and Drift Checks.....  | 36        |
| 5.1.5 Summa Canister or Vacuum Canister Sample Collection QC<br>Procedures for Flux Chamber and Grab Samples ..... | 36        |
| 5.1.6 Analytical QC Procedures.....  | 37        |
| 5.1.7 Method Blank.....  | 37        |
| 5.1.8 Equipment Malfunctions .....   | 39        |
| 5.1.9 Point Source Test Plan .....   | 39        |
| <b>SECTION 6 Project Safety.....</b>   | <b>40</b> |

**LIST OF TABLES**

Table 1 Example Summary of Testing Schedule for Characterizing Generic Fracking or Other Well Stimulation Activity ..... 28

**LIST OF FIGURES**

Figure 1 Cylinder sampling being conducted on a liquid separator..... 29  
Figure 2 Cylinder sampling being conducted on an oil and natural gas separator. .... 29  
Figure 3 Flux testing conducted at a wastewater treatment plant. Air emissions are performed even on processes with advective flow. .... 30  
Figure 4 Flux chamber testing conducted on an oil/water separator unit process at a TSDf. The purpose of the photo is to show how the flux chamber can be used to access industrial tank emissions..... 31  
Figure 5 Hi Flow measurement of a leak interface from a valve at a natural gas well pad. .... 32  
Figure 6 Hi Flow measurement of a pressure relief device from a natural gas well pad storage tank. .... 32  
Figure 7 Preparation for Hi Flow measurements on a thief hatch with summa canister collection on a natural gas well pad storage tank. .... 33

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## SECTION 1

### Project Introduction

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The California Air Resources Board (ARB) is conducting a project to investigate the air quality emissions associated with well hydraulic fracturing (commonly known as “fracking”) and other well stimulation activities within the State of California. ARB has contracted Sage Environmental Consulting, LP (Sage) to assist with a source level air emission quantification project of well fracturing activities in selected locations across California. The project is strictly pointed at understanding fugitive gaseous emissions that affect air quality and explicitly excludes emissions associated with mobile source combustion, hazardous waste, naturally occurring radioactive material, and particulate matter. On a most applicable case by case basis, the following methods and technologies will characterize the fugitive emissions: emission screening, infrared imaging, direct emission measurements, and fluid sampling. This document provides test plan guidance for the outlined methods to characterize emissions from fracking and other well stimulation activities.

Fracking and other well stimulation operations generally include: pressure injecting a water-based fluid into the well-head, recovering the fluids from the well head, and treatment of the resulting fluids. Presumably, most, if not all, fluids injected return to the surface in an operational activity referred to as “flow-back” where the returning fluids are typically routed to a temporary frack tank or oil/water separator. Crude oil and produced water under pressure are known to flash greenhouse gases and organic compounds when exposed to pressure drops (commonly known as “flashing”) which occurs when the fluids are separated (oil and water) in the oil/water separator unit(s). The flow-back fluids will be co-mingled with the produced water and oil. Therefore, fugitive emissions from equipment, tanks, residual liquid, and disposal operations require testing before, during, and after fracking or other well stimulation activity to determine the emissions due to both normal operations and well stimulation operations.

The proposed testing methods provide a means for measuring fugitive emissions without any, or minimal, impact on normal operations.

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## SECTION 2

### Scope of Work

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The project scope of work is to conduct source testing of gaseous emissions from hydraulic fracturing and other well stimulation activities (like well acidizing, perforating, etc.) within the upstream crude oil and natural gas production sector in California for the purpose of characterizing activity-based emissions. Fugitive emission characterization for three phases of well work activities is developed in this test plan:

- Baseline Phase;
- Flow-back Phase; and
- Post-Flow-back Phase

The baseline phase is required to characterize emissions and collect information about the current well site and tank system prior to hydraulic fracturing or other well stimulation activities. The baseline effort will allow the project team to develop an essential standard of measure to assess impacts of operations during and post flow-back operations. If possible, additional emission data will be gathered from operations prior to or during well work such as removing the wellhead or the well casing or tubing but only if such activities occur during the planned field portion of the test. The testing team will not request the well operator to conduct the activity strictly for testing purposes.

During the flow-back phase, the project will characterize flow-back fluids and gases to determine the volume, estimated duration, and composition of gases that are produced from the well stimulation activity. The absolute objective is to quantify emissions from fluids while they are in flow-back. This testing will be conducted after the fluids are injected into the reservoir and while they flow back to the surface.

The post flow-back phase will conclude the sampling effort. This phase focuses specifically on addressing the question of how long after hydraulic fracturing or other well stimulation activities are completed the fugitive emissions take to return to baseline levels. In this phase, the project team will likely make multiple site visits to answer this question.

To successfully complete the three phases of the project outlined above, the following four tasks along with the agreed upon schedule will be utilized:

- TASK 1: Develop a Test Plan
  - To be completed within sixty (60) days of Contract start date (August 15, 2013).
- TASK 2: Conduct Tests
  - To be completed within ten (10) months of completion of Task 1.
- TASK 3: Analyze Test Results and Develop Emission Estimates
  - To be complete within sixty (60) days of completion of Task 2.
- TASK 4: Final Report
  - To be complete at least thirty (30) days prior to the end of contract period.

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## SECTION 3

### Project Test Plan

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The test plan herein will describe the technical approaches and quality controls to be performed. It shall be noted, while other emissions are present for any given site the project's purpose is to gather data specific to fugitive emissions which evolve from liquids and flow-back fluids. Emissions associated with mobile source combustion, hazardous waste, naturally occurring radioactive material, and particulate matter will not be considered for testing.

#### 3.1 TASK 1: Develop a Test Plan

Sage and ARB have worked together to develop this project test plan for the purpose of quantifying air emissions from fracking and other well stimulation activities. The plan will serve as the project blueprint wherein the testing schedule, frequency, and testing type to be conducted will be established, as well as contingency plans in the event unforeseen situations occur. The plan development is a coordinated and evolving effort between Sage and ARB which may require changes to the testing phases, targeted pollutants and testing methodology. All revisions to the test plan will be authorized prior to field implementation and will be made in consideration of the remaining scope, timing, and budget.

The ARB will coordinate a review of this test plan with its stakeholders, including trade associations, oil and gas companies, local air pollution districts, and technical community representatives for feedback on this plan. The review process is aimed at ensuring the technical aspects of this plan are sound.

As part of the testing plan development and prior to commencing testing, a pilot study will be conducted to evaluate a fracking operation and well activity variation, testing method parameters and feasibility, safety and logistics. Safety will be of the upmost priority for the study. Measurements will not be taken where there is a safety hazard present which will put any person in a dangerous situation without proper administrative and engineering controls. The pilot study will likely include a fracking operation in the Central Valley, intended to represent a 'common' hydraulic fracturing operation. The pilot study will obtain data for a complete operation (start to finish) that is representative of a 'common' fracking practices. The source testing and operational information gathered will strategically guide future aspects of study.

The proposed methods to be utilized for the project, as appropriate, are summarized below and detailed appendices.

- ARB Flash Emissions Test Procedure, "[Flash Emissions of Greenhouse Gases and Other Compounds from Crude Oil and Natural Gas Separator and Tank Systems](#)," which is a procedure used to acquire liquid samples of flowback fluid, crude oil, condensate, or produced water while minimizing gaseous emission losses. This procedure provides characteristic data of the pressurized fluid and is subsequently used to estimate the

characteristics of potential flashed gas emissions. The project team will attempt to take fluid samplings at all of the field assessments: baseline, flow-back, and post flow-back from different vessels to be identified in the field at each facility.

- The USEPA flux chamber sampling approach will be used to assess the emissions from wastewater treatment processes and other open air systems as observed and deemed appropriate in the field. Fluid handling and treatment processes that are vented to the atmosphere will be measured by interfacing the flux chamber to the emission source, directly measuring the air emissions, and prorating the air emissions to the process metric. Fugitive air emissions from these vented but not treated sources will be measured using this approach.
- Infrared imaging (IR camera) will be used to initially identify all major emission points during the project. Today's infrared technology will allow for efficient detection of emission points from common and uncommon sources. The IR camera(s) commercially available today are able to "see" emission within the following spectral range 3-5  $\mu\text{m}$  and 3.2-3.4  $\mu\text{m}$  for the GasFinderIR™ and GF-320 models, respectively. Compounds with spectral absorption either below or above these ranges exponentially decrease detectability as the absorption spectrum moves away from the range.
- Direct measurements will be obtained using the Hi-Flow Sampler™ (Hi-Flow) as appropriate. The sampler is a portable, intrinsically safe instrument designed to determine the rate of gas leakage as methane from components in natural gas service. A component's leak rate is measured by sampling at a high enough flowrate to ensure that all of the gas emitted from the component will be captured. An assortment of hose-end attachments are available to provide a means of capturing all the gas that is being emitted. In addition to the sampler, calibrated bags can be used to determine the emission rate of a specific source. The bags come in many different sizes but the application is the same: seal the bag around source and time the rate to fill the known volume.
- Evacuated Summa canisters (nominally -29 mm Hg in vacuum) will be used to collect fugitive emission gas samples from either the flux chamber or as a grab sample. A flow regulator maintains control of the sampling, keeping a minimum of a few in. Hg. of vacuum, except for the flux chamber which does not require a vacuum to be maintained. Gas compositions will be obtained from these samples through the various analytical methods referenced.
- Toxic vapor analyzer (TVA) is a portable hydrocarbon monitor with a screening range extending from 0.5 ppmv to 50,000 ppmv. The analyzer uses a flame ionization detector (FID) to sample and measure gases. Concentrations in ppmv can be read on both the hand held probe and on the instrument side pack. The response of the TVA to different hydrocarbons is determined by the response characteristics of the FID and by the gas species used to calibrate the instrument. The unit is factory calibrated with methane. Since methane is the largest constituent of natural gas, continued methane-calibration of the TVA is appropriate for this project. Thus all concentrations detected by the TVA

will be reported as methane. Since the TVA is portable, operators can take measurements as close to the equipment as possible. However, we do anticipate that at some sites, using this technology may not be possible due to access limitations.

### **3.2 TASK 2: Conduct Tests**

The source level testing has three (3) phases: Baseline Phase, Flow-back Phase, and Post-Flow-back Phase. Each phase will be conducted according to the test plan agreed upon by Sage and ARB as both time and budget will allow, recognizing that each well site to be evaluated entails at least 3 separate site visits. Sage, in coordination with the operations managers and ARB, will schedule the tests at the select oil and natural gas locations.

It is understood that for some operations specific phase testing or approaches will not be possible. In applicable situations, a supplemental plan will be developed to address the differences with this test procedure.

Independent of the specific sampling methods utilized where samples are gathered for analysis, the following list of pollutant compounds shall be included:

- Gas-to-Oil Ratio (GOR) Measurement and Gas-to-Water Ratio (GWR) Measurement; ARB Flash Emissions Test Procedure
- Methane (CH<sub>4</sub>) by ASTM Method D1946
- Carbon Dioxide (CO<sub>2</sub>) by ASTM Method D1946
- Hydrogen Sulfide (H<sub>2</sub>S) USEPA Method-15, USEPA Method-16, ASTM D1945M, ASTM D-5504, or ASTM-D-6228
- Volatile Organic Compounds (VOCs) by USEPA Method TO-15 (GC/MS or GC/FID, EPA Method 8260, or EPA Method 8270
- Specialty Compounds (BTEX & TIC List) by USEPA Method TO-15 (GC/MS or GC/FID)

In some cases, it is necessary to have the facility operator provide a Tentatively Identified Compound (or TIC) List of uncommon compounds so they may be identified by a laboratory doing the gas analysis. In addition, to the required sampling compounds ethane and ethylene will be included in the results as well as a total hydrocarbon analysis.

Field crews are instructed to collect all of the target data that is feasible given site health and safety restrictions. Restricted sampling situations will be noted in the field log books. It is estimated the time between sample collection and analysis will exceed 24 hours; consequently, the project team will collect samples in containers capable of storing the sample contents beyond 24 hours.

Site specific test plans will be prepared prior to field testing that will summarize the specific objective of testing and identify sample locations.



### **3.2.1 Task 2.1 Flow-back Phase**

Testing during the Flow-back Phase will be conducted while flow-back fluid returns to the surface. During this stage, Sage will sample the flow-back fluids and measure fugitive gases to determine the volume and composition of emissions produced from the operation to later be compared with the baseline. Fluid volumes will be determined from operations data, if available, or by non-intrusive flow meters, should operations data not be available. Non-intrusive flow meters are placed on process piping and use ultrasonic wavelengths to determine the volumetric flow-rate. Constituent breakdowns of the process fluids will be characterized by sample analysis of the ARB Flash Emissions Test Procedure. Fugitive emissions may also be measured using tank headspace monitoring in addition to liquid flash sampling. Fugitive or vented emissions will be repeated using the same methods conducted in the baseline phase such as by using infrared camera imagery, or measured by flux chamber and/or Hi Flow sampling depending largely on site accessibility and safety. All information, emission testing, and sample analysis will follow standard quality control procedures and required Chain-of-Custody.

### **3.2.2 Task 2.2 Post-Flow-back Phase**

The Post-Flow-back Phase will be used to collect information on the duration of the flow-back phase and to verify that the flow-back phase has been completed. It is expected that post-flow-back testing will be a continuation of the flow-back phase testing. All information, emission testing, and sample analysis will follow standard quality control procedures and required Chain-of-Custody.

## **3.3 TASK 3: Analyze Test Results & Develop Emission Estimates**

Sage will analyze the test results and develop emission estimates for each fracking or other well stimulation operation characterized in Task 2. Emission estimates will be provided in an Excel workbook to include detailed explanations of all calculations.

## **3.4 TASK 4: Reporting**

Sage will prepare and submit for review by ARB an electronic copy of the Draft Report of testing results, emissions estimated from the test results, and any other specific findings and recommendations at least sixty (60) days prior to the end of the contract period.

Sage will address all ARB review comments and issue both in hard copy and electronic form (in PDF format and in Word 2010 or later) the Final Report within no more than thirty (30) days after receiving back review comments on the Draft Report from ARB.

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## SECTION 4

### Sampling Strategy

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***Note the following sampling strategy is tentative and subject to change based in initial site visits and pilot study execution.***

The overview of the sampling strategy includes the proposed pilot-scale characterization of a fracking or well stimulation operation followed by focused sampling efforts that are intended to collect the data set required by ARB. An example test schedule for an undefined operation is provided below. The purpose of this schedule is to identify possible sample collection points and sampling methods, and provide a platform for evaluating each operation. A table like this will be completed and used for directing field activities per site visit.

**Table 1**  
**Example Summary of Testing Schedule for Characterizing Generic Fracking or Other Well Stimulation Activity**

| SOURCE TESTING                            | SAMPLE COLLECTION           | SAMPLE COUNT | QC AND/OR COMMENT                                |
|---|-----------------------------|--------------|--|
| Flow-Back Fluid – Oil, Production Fluids  | Duplicate Cylinder Sampling | 2            | TBD- Duplicate samples to be analyzed as needed. |
| Flow-Back Fluid – Water & Water Emulsions | Duplicate Piston Sampling   | 2            | TBD- Duplicate samples to be analyzed as needed. |
| Oil Separator – Air                       | Flux Test                   | 1-to-3       | 5% Blank, 5% Replicate Sample                    |
| Water Separator – Air                     | Flux Test                   | 1-to-3       | 5% Blank, 5% Replicate Sample                    |
| Wastewater Treatment - Air                | Flux Test                   | 1-to-3       | 5% Blank, 5% Replicate Sample                    |
| Wastewater Lagoon - Air (if different)    | Flux Test                   | 1-to-3       | 5% Blank, 5% Replicate Sample                    |
| Wastewater Sample – Liquid                | VOA Vial Sample             | 2            | 5% Blank, 5% Replicate Sample                    |
| Fugitive Equipment                        | Hi Flow                     | 1            | 5% Replicate Sample                              |
| TOTAL                                     |                             | Variable     |  |

**Duplicate Cylinder Sampling** – The samples determine the characteristics of the fluid from the well. The samples must be taken from the pressurized primary vessel either in a separator and tank system using the sampling methods specified in this procedure. Typical sampling points are from pressurized Two-Phase or Three-Phase Separators or vessels used to measure Percent Water Cut (e.g., Automatic Well Tester).



**Figure 1**

**Cylinder sampling being conducted on a liquid separator.**



**Figure 2**

**Cylinder sampling being conducted on an oil and natural gas separator.**

**Flux Test Sampling** - The flux test will be used to measure emissions from sources that are open to atmosphere. For the oil and natural gas industry this could be conducted on oily water separators, open air flow-back tanks, wastewater treatment facilities where flow-back fluid is treated, open lagoons, etc.



**Figure 3**

**Flux testing conducted at a wastewater treatment plant. Air emissions are performed even on processes with advective flow.**



**Figure 4**

**Flux chamber testing conducted on an oil/water separator unit process at a TSDf. The purpose of the photo is to show how the flux chamber can be used to access industrial tank emissions.**

**VOA Vial Sampling** - The VOA Vial samples will be collect at designated locations of the water being injected and returned in the flow-back process to establish a water characteristic baseline. These samples can be collected easily from bleed valves on the associated equipment.

**Hi-Flow Sampling** – The sampler will be used to measure fugitive emissions from various types of equipment. This method can be used to measure emissions from valves, flanges and connectors, thief hatches, pressure relief devices, pumps, pneumatic devices, etc. For the oil and natural gas industry it is typically deployed when measuring the emissions from leak interfaces on storage tank and associated equipment.



**Figure 5**

**Hi Flow measurement of a leak interface from a valve at a natural gas well pad.**



**Figure 6**

**Hi Flow measurement of a pressure relief device from a natural gas well pad storage tank.**





**Figure 7**

**Preparation for Hi Flow measurements on a thief hatch with summa canister collection on a natural gas well pad storage tank.**

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## SECTION 5

# Quality Control & Quality Assurance

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The objective of this task is to ensure that all quality assurance/quality control (QA/QC) procedures are followed and all testing equipment is working properly. The following specifies the responsibilities of the QA/QC reviewer, and specifies the equipment calibration procedures to be employed by the point source sampling teams.

Mr. David Ranum will serve as Quality Control officer for the project. The responsibilities will include the following:

- Oversight of the survey program for conformance with this plan, any relevant standards and instructions;
- Checking identification and completeness of project documentation;
- Checking for appropriate use of forms, logs or formats;
- Ensuring that all equipment is properly referenced and calibrated;
- Checking that equipment meets specifications; and
- Random inspection of field activities to ensure they are being performed in accordance with the procedures listed in this project plan and that instrument calibration records are complete and indicate that instruments are in a state of control during use.

Correspondence will be communicated to the project manager on a routine and timely basis.

### 5.1 Quality Control Actions

The project teams as part of their daily work routines will perform the following quality control actions. The purpose of these actions are to maximize the capture of valid data and to assure that each day's data is comparable to any other day's data.

#### 5.1.1 ARB Flash Emissions Test Procedure

For the pressurized sampling the following practices shall be followed.

- Verify all connections and fittings are secured and all sampling valves are in the closed position. After verification collect samples.
- Verify all samples collected are sealed as required in the test plan.
- Collect samples in duplicate; analyze 5% or as needed.



### 5.1.2 Flux Chamber

The specific operating test plan for solid surfaces is given below.

- Select the exact test location and seal the chamber by using the bottom seal system. The chamber should be sealed along the base preventing air infiltration.
- Initiate the sweep gas flow rate using the diffuser-type inlet air system and set the rotometer at 5.0 liters per minute. Constant sweep gas flow rate is critical. Record time.
- Collect instrument background data (thermocouples, site description) and record data.
- Connect the purge pump. A total of 5.0 liters per minute is added to the chamber and the gas not sampled is exhausted out the pressure equalization port in the top of the chamber. The chamber is operated at near atmospheric pressure. Verify the system does not exceed an exhaust gas sample/purge rate of 2.5 liters per minute. This will prevent entraining of ambient air into the chamber and maintain an exhaust rate of at least 2.5 liters per minute out of the pressure equalization port.
- Verify the chamber is operating at an air flow rate of 5.0 liters per minute and record data every residence time (6 minutes) for four to five residence times or 24 to 30 minutes and record data.
- Interface the sample collection media (trap/evacuated canister or impinger and sampling pump) to the purged sample line and collect the gas sample at the method-specific sample collection rate and location. Sample collection is specified in the 48" exhaust duct of the flux chamber at six duct diameters downstream of the flux chamber and two duct diameters upstream of the stack exhaust. Verify the system does not exceed a collection rate of 2.5 liters per minute at any time. This will prevent unwanted dilution of chamber exhaust gas by ambient air. Keep sample collection to the minimum time interval while meeting target detection limits. Discontinue sample collection and repeat for each sample collection media until complete. Discontinue sample collection media.
- Label samples, record sample collection or real-time monitoring data on the data sheet.
- Store the sample media in the appropriate storage or shipping media (bags in plastic shipping crate, canisters in cardboard shipping container, trap catch and impinger catch in sealed glass sample bottles on ice).
- Document sample collection in field master log book.
- Discontinue the flux measurement, shut off the sweep air, remove chamber and secure equipment.

- Decontaminate the chamber where contact was made with the soil using a clean paper towel and water (if needed). Purge the sample lines with sweep gas (5 liters/minute) for 2 minutes.

### **5.1.3 HiFlow Sampler Calibration**

The HiFlow Sampler will be calibrated prior to use. For calibration of the sensors, a 2.5% methane standard will be used and a 100% methane standard will be used. Both gas standards will be equipped with Demand Flow Regulators to assure steady and consistent flow rates.

### **5.1.4 TVA Calibration and Drift Checks**

The TVA analyzers will be calibrated daily prior to field use with certified  $\pm 2\%$  accurate calibration gases equipped with demand-flow regulators. Both TVAs will also be performance tested (response time, precision, flow rate) at the start of the project and, if needed, every 3 months thereafter. Four gas standard concentrations will be used for the daily calibrations: 0, 500, 1,000, and 10,000 ppmv methane-in-air. Drift checks will be performed using the 500-ppmv standard, at mid-day and at end-of-day. Calibration and drift check acceptance criteria will be  $\pm 10\%$  of each calibration gas certified concentration. Any responses outside the acceptance criteria will require either re-calibration or trouble shooting and repair of the analyzer. A check of the 10:1 dilution probe will be performed with the high span gas each time prior to its use and the resulting dilution factor recorded.

### **5.1.5 Summa Canister or Vacuum Canister Sample Collection QC Procedures for Flux Chamber and Grab Samples**

To ensure that canisters contain sufficient volume and do not leak, the vacuum of each Summa Canister will be checked and documented prior to sampling. Canisters with a vacuum of  $< 27$  in. Hg. will not be used. A residual vacuum of 2 -10 in. Hg. will be left in the canister following sample collection, except when used for collect samples with the flux chamber where the samples are collected to 0 in. Hg. This value will be documented. Appropriate chain-of-custody procedures will be followed for all Summa Canister samples and each team member will be held accountable for following these procedures. This means keeping an accurate written record to track the possession, handling, and location of the canisters from collection through analysis. Canisters in possession of the point source sampling teams will be kept in a secure area with access restricted to authorized personnel only. The following chain-of-custody guidelines will be observed:

- Only persons associated with the project will be allowed to handle the canisters.
- Strict documentation of the transfer of canisters and data from person to person will be kept on chain-of-custody forms.
- Written canister documentation will always be legible and made with permanent ink.

- Canister serial numbers will be recorded on the chain of custody documentation.

Canisters will be identified by permanent serial number and with preformatted shipping tags will be used to document important canister information. A bound field logbook will be kept by each project team to document each canister sample collection event. The field logbook will contain the following information:

- Sample location;
- Time/date of sample collection;
- Total number and type of sample containers;
- Method of sample collection, and equipment used;
- Physical description of sample;
- Name of sampler(s);
- Related field screening results; and
- Any other pertinent observations.

Field blank samples will be collected by filling canisters with ultrahigh purity air. Blank samples will be collected at a frequency of 5%. Field duplicates are second samples collected in the field simultaneously or near-simultaneously with the primary sample at the same location. The results of the duplicate sample may be compared with the primary sample to provide information on consistency and reproducibility of field sampling procedures. Field duplicates will be collected at a 5% rate (i.e. 1 duplicate per 20 canister samples).

### **5.1.6 Analytical QC Procedures**

The following is a listing of the Analytical QC procedures that will be followed to ensure sample capture and analysis integrity. These procedures are typically used before field deployment of equipment and as part of sample analysis in the laboratory. While this information is highly technical, we have provided it so readers of this sampling plan can see that state of the art procedures will be applied to assure that the analysis of the sampled data is performed in keeping with full compliance of scientific integrity so the captured data can withstand all levels of scrutiny.

### **5.1.7 Method Blank**

This is a control sample prepared using a well-characterized blank matrix (e.g., UHP nitrogen) and using the same reagents used for the samples. As part of a QC batch, it accompanies the samples through all steps of the analytical procedure. The Method Blank is used to monitor the level of contamination introduced to a batch of samples as a result of processing in the laboratory. One Method Blank is processed with each preparation batch.

- **Canister Blank Check** – Before any canister is sent into the field for sampling, each canister is blank-checked using EPA Method TO-12. Source level canisters must have a total non-methane hydrocarbon concentration of less than 20ppbV-C to pass acceptance criteria.
- **Instrument System/Blank/Replicates** – An instrument blank or system blank may be analyzed as a diagnostic tool to check for contamination for 5% of the samples collected.
- **Laboratory Control Sample/Laboratory Control Sample Duplicate** – The laboratory control sample (LCS) and laboratory control sample duplicate (LCSD) are prepared using a well-characterized blank matrix (e.g., UHP nitrogen) that is spiked with known amounts of representative analytes. A LCS is processed with each preparation batch. As part of a QC batch, the LCS accompanies the samples through all steps of the analytical process. The LCS is used to monitor the accuracy of the analytical process independent of possible interference effects due to sample matrix. Ongoing monitoring of the LCS results provides evidence that the laboratory is performing the method within acceptable accuracy and precision guidelines. The LCS recovery for the representative analytes must be within established control limits.
- **Surrogates** – Surrogates are organic compounds which are similar in chemical composition and behavior in the analytical process, but which are not normally found in environmental samples. For example, compounds such as 2-bromo-1,1,1-trifluoroethane; fluorobenzene; toluene-d8; 1,4-dichlorobutane; and 4-bromofluorobenzene are the surrogates typically used for Modified Method TO-14A and Method TO-15. Surrogates are injected into the canister at the end of the cleaning process. Surrogate spike recoveries help to measure the effects of both the matrix and the analytical process on accuracy.
- **Internal Standards** – Internal standards are added to each analytical standard, blank, and sample. The acceptance criteria for each internal standard's area for every analysis must be  $\pm 50\%$  recovery of the internal standard area from the continuing calibration standard. The acceptance criteria for each internal standard's retention time in every analysis must be within  $\pm 20$  seconds of the internal standard retention time from the continuing calibration standard.
- **Instrument Performance Check** – Prior to analysis of samples and blanks, each gas chromatograph/mass spectrometer (GC/MS) system must pass instrument performance criteria. Hardware tuning is checked daily to establish that the system meets the standard mass spectral abundance criteria.
- **Initial Calibration** – An initial calibration curve (ICAL) containing a minimum of five concentration levels is analyzed to determine the linear working range of the system for each compound. The dynamic range is generally 0.2 ppbV to 10 ppbV for most analytes. The retention time (RT) shift for each of the internal standards at each

calibration level must be within  $\pm 20$  seconds of the mean retention time over the initial calibration range for each internal standard.

- **Calibration Curve Fits** – An average response factor (RF) and percent relative standard deviation (%RSD) are calculated for each target analyte. Method TO-15 has an allowance that up to two target analytes may have an  $RSD \leq 40\%$ . The average response factors derived from the initial calibration are used to quantitate results.
- **Initial Calibration Verification (ICV/ICB)** – The initial calibration verification (ICV) is a second source standard of analytes and is analyzed just after the initial calibration. For each analyte, a percent recovery (%R) is calculated using the average response factor.
- **Continuing Calibration Verification (CCV/CCB)** – Every 24 hours of operation, a mid-range continuing calibration verification (CCV) standard of analytes is analyzed to verify the ICAL average RF. The CCV is routinely analyzed at a concentration matching the midpoint of the ICAL. The percent difference (%D) of the CCV RF from the ICAL average RF is calculated for each compound. In general, %D must be within  $\pm 30\%$ , with exceptions for ethane, 1, 2, 4-trichlorobenzene, and hexachlorobutadiene ( $\pm 50\%$ ).

### 5.1.8 Equipment Malfunctions

If major point source test equipment, such as the IR camera, the HiFlow Sampler, TVA 1000B analyzer malfunctions and cannot be easily repaired, it will be returned to the vendor for an expedited repair. In the meantime, it will be replaced with rental equipment of the same make, manufacturer, and operational specifications.

### 5.1.9 Point Source Test Plan

Each point source team member will be required to thoroughly review this plan to ensure that the correct survey, sampling methodologies as sample handling chain of custody procedures are observed throughout the term of the study.

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## **SECTION 6**

### **Project Safety**

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Project safety is important for everyone and especially to the project team members. A Point Source Project Safety Plan will be drafted specific to this project. Each point source sampling team will be required:

- To keep with them a signed copy of the project safety plan;
- To hold daily safety toolbox meetings to review specific project hazards, either encountered or anticipated;
- To have an emergency first aid kit readily available; and
- To have all required PPE as specified in the project safety plan.

The designated project safety leader will be responsible for ensuring that the project safety plan is implemented and followed by all project team members.

## **Appendix B: Composition of Hydraulic Fracturing Fluid Injected into Well**





For well completion, the study only included hydraulic fracturing. The hydraulic fracturing fluid compositions used by the operators include those compounds listed in Table B-1 and Table B-2 (obtained from DOGGR). In total, there were seven hydraulic fracturing events included in this review.

**Table B-1: Hydraulic fracturing fluid composition for tested wells**

| Hydraulic Fracturing Fluid Constituents | Average        | Minimum | Maximum |
|---|----------------|---------|---------|
|   | Weight Percent |         |         |
| Water                                   | 75.3%          | 70.4%   | 83.7%   |
| Crystalline Silica (Quartz)             | 24.0%          | 15.6%   | 29.1%   |
| Other Constituents                      | 0.6%           | 0.3%    | 0.8%    |

The hydraulic fracturing well stimulation fluids comprise by weight 70 – 84% of water, 15 - 29% crystalline silica (sand), less than 1% other constituents. The other constituents reported included those listed in Table B-2.

**Table B-2: Other Constituents concentration by weight percent in hydraulic fracturing fluid injected into tested wells**

| Other Constituents   | Average        | Minimum | Maximum |
|--|----------------|---------|---------|
|  | Weight Percent |         |         |
| 1-Butoxy-2-Propanol  | 0.017%         | 0.016%  | 0.017%  |
| 2-Butoxy-1-Propanol  | 0.000%         | 0.000%  | 0.000%  |
| 2-Methyl-4-Isothiazolin-3-One  | 0.000%         | 0.000%  | 0.000%  |
| 5-Chloro-2-Methyl-4-Isothiazolin-3-One   | 0.000%         | 0.000%  | 0.000%  |
| Ammonium chloride  | 0.011%         | 0.008%  | 0.015%  |
| Ammonium Persulfate  | 0.006%         | 0.006%  | 0.007%  |
| Bentonite, benzyl(hydrogenated tallow alkyl) dimethylammonium stearate complex | 0.005%         | 0.001%  | 0.008%  |
| Crystalline Silica: Cristobalite   | 0.000%         | 0.000%  | 0.000%  |
| Crystalline silica: Quartz (SiO <sub>2</sub> )                                 | 0.017%         | 0.016%  | 0.017%  |
| Diatomaceous Earth, Calcined   | 0.014%         | 0.011%  | 0.016%  |
| Diethanolamine   | 0.007%         | 0.005%  | 0.008%  |
| Ethylene Glycol  | 0.036%         | 0.031%  | 0.039%  |
| Guar Gum   | 0.180%         | 0.123%  | 0.206%  |
| Hemicellulase enzyme   | 0.034%         | 0.005%  | 0.055%  |
| Hemicellulase Enzyme Concentrate   | 0.002%         | 0.001%  | 0.002%  |
| Isotridecanol, ethoxylated   | 0.017%         | 0.016%  | 0.017%  |
| Lactose  | 0.162%         | 0.139%  | 0.183%  |
| Magnesium Chloride   | 0.000%         | 0.000%  | 0.000%  |
| Magnesium Nitrate  | 0.000%         | 0.000%  | 0.000%  |
| Monoethanolamine borate  | 0.023%         | 0.020%  | 0.026%  |
| NITRILOTRIS (Methylene phosphonic acid)  | 0.005%         | 0.004%  | 0.005%  |

| Other Constituents                     | Average        | Minimum | Maximum |
|--|----------------|---------|---------|
|  | Weight Percent |         |         |
| Oxyalkylated Amine Quat                | 0.057%         | 0.053%  | 0.065%  |
| Paraffinic Petroleum Distillate        | 0.099%         | 0.094%  | 0.103%  |
| Petroleum Distillates                  | 0.099%         | 0.094%  | 0.103%  |
| Phosphonic Acid                        | 0.000%         | 0.000%  | 0.000%  |
| Polydimethyl diallyl ammonium chloride | 0.023%         | 0.017%  | 0.030%  |
| Silica gel                             | 0.001%         | 0.001%  | 0.002%  |
| Sodium bisulfate                       | 0.002%         | 0.002%  | 0.002%  |
| Sodium Chloride                        | 0.002%         | 0.000%  | 0.002%  |
| Sodium Hydroxide                       | 0.010%         | 0.002%  | 0.013%  |
| Sodium persulfate                      | 0.014%         | 0.012%  | 0.016%  |
| Sodium polyacrylate                    | 0.011%         | 0.009%  | 0.012%  |
| Sodium sulfate                         | 0.000%         | 0.000%  | 0.000%  |
| Sodium Tetraborate Decahydrate         | 0.036%         | 0.031%  | 0.039%  |
| Triethanolamine                        | 0.024%         | 0.018%  | 0.027%  |
| Water                                  | 0.110%         | 0.093%  | 0.124%  |

- a) VOC compounds above: 1-Butoxy-2-Propanol, 2-Butoxy-1-Propanol, 2-Methyl-4-Isothiazolin-3-One, 5-Chloro-2-Methyl-4-Isothiazolin-3-One, Bentonite, Diethanolamine, Methylene Glycol, ethoxylated Isotridecanol, Monoethanolamine borate, Methylene phosphonic acid, Paraffinic Petroleum Distillate, Petroleum Distillates, Polydimethyl diallyl ammonium chloride, Triethanolamine
- b) TAC compounds above: Diethanolamine, Ethylene Glycol
- c) Compounds identified by TO-15: Paraffinic petroleum distillates, Petroleum distillates. Note: TO-15 identifies TPH gasoline, assumed analogous to petroleum distillates.
- d) The water that is represented here is likely its contribution in the chemical total for a specific mixture and not part of the water contribution listed in Table B-1.

## **Appendix C: Wastewater Pond Testing**



## Introduction

As part of the post-flowback phase testing conducted during the larger well stimulation study, preliminary testing of wastewater was conducted at three wastewater pond systems in the same general vicinity where hydraulic fracturing operations were known to have occurred or were occurring. The testing was designed to measure compounds vaporizing off the surface of the liquid, as well as compounds found in the water that could subsequently vaporize into the surrounding air. The laboratory analyses included testing for all types of hydrocarbon compounds, including those known to have been used in the adjacent hydraulic fracturing operations.

## Test Methods

To perform the wastewater testing, the USEPA preferred direct measurement technology, Flux Chamber, was used in addition to the collection of liquid samples in accordance with the EPA 1664 and EPA 8260b test methods. The Flux Chamber provides reliable and representative measurements of species flux (mass emitted per time per surface area) from a source, without the influence of surrounding air concentration from other sources, and modeling is not needed in order to generate the emission rate from sources. The flux chamber was used in conformance with the EPA Users Guide. Flux chamber samples were analyzed per EPA Method TO-14/15 using Summa® canisters and gas chromatograph analysis of various hydrocarbons and hydrocarbon groups using multiple detectors. Carbon dioxide was analyzed from the flux chamber using ASTM D1945.

For the liquid phase analysis, EPA test method 1664 measured for total oil and EPA test method 8260b measured for speciated (individual) volatile organic compounds (VOC).

## Testing Results

The inlet of each pond and the main pond were tested individually, and the total non-methane hydrocarbon emissions were calculated as shown below in Table D-1. By testing both the inlets and the main ponds themselves, the results show that the emission rate of the main ponds exceeded the inlets by more than an order of magnitude. The most likely cause for this observation was that the inlet liquid was likely highly variable in terms of entrained hydrocarbon compounds, and that the inlet concentration was low on the day of testing. The likely retention time of the wastewater within the ponds was estimated to be between 15 to 30 days, so the concentrations measured from the main ponds could represent a long-term concentration average. It should be noted that the data from the inlet represents the operational conditions on the day of testing and the extrapolation of these results is not advisable.

The test results showed that although VOC, GHG, and TAC emissions were observed from the pond systems (Tables D-1, D-2, D-3, and D-4), there were no hydraulic fracturing fluids in the ponds. This indicates that the pond systems tested either

- a) do not receive hydraulic fracturing fluids, or
- b) did not receive hydraulic fracturing fluids during the past 15-30 days (retention time of the pond systems)

Additional evaluation of the sources of wastewater in the pond systems is needed to determine the sources of observed emissions from the pond systems. Additionally, emissions data from the small sample size (n=3) is too uncertain to draw conclusions or extrapolations.

**Table D-1 Total Non-Methane Hydrocarbon Emission Results**

| Pond System  | mg/min         |                  |                  | Ton per day |
|--------------|----------------|------------------|------------------|-------------|
|              | Inlet          | Main Pond        | Total            | Total       |
| 1            | 36,300         | 165,077          | 201,377          | 0.32        |
| 2            | 85,692         | 2,122,797        | 2,208,489        | 3.51        |
| 3            | 855            | 18,002           | 18,857           | 0.03        |
| <b>Total</b> | <b>122,847</b> | <b>2,305,875</b> | <b>2,428,723</b> | <b>3.86</b> |

Additional analyses were also performed to evaluate the various other emission compounds found in the wastewater. Table D-2 presents methane emissions, Table D-3 presents carbon dioxide emissions, and Table D-4 presents BTEX emissions from this testing.

**Table D-2 Total Methane Emission Results**

| Pond System  | mg/min        |                |                | Ton per day |
|--------------|---------------|----------------|----------------|-------------|
|              | Inlet         | Main Pond      | Total          | Total       |
| 1            | 17,981        | 279,884        | 297,865        | 0.47        |
| 2            | 2,173         | 53,964         | 56,137         | 0.09        |
| 3            | 10,526        | 82,426         | 92,951         | 0.15        |
| <b>Total</b> | <b>30,679</b> | <b>416,274</b> | <b>446,953</b> | <b>0.71</b> |

**Table D-3 Total Carbon Dioxide Emission Results**

| Pond System  | mg/min         |                  |                  | Ton per day  |
|--------------|----------------|------------------|------------------|--------------|
|              | Inlet          | Main Pond        | Total            | Total        |
| 1            | 587,383        | 5,635,719        | 6,223,102        | 9.88         |
| 2            | 59,331         | 2,290,915        | 2,350,246        | 3.73         |
| 3            | 44,311         | 1,104,951        | 1,149,262        | 1.82         |
| <b>Total</b> | <b>691,025</b> | <b>9,031,585</b> | <b>9,722,610</b> | <b>15.43</b> |

**Table D-4 Total BTEX Results**

| Pond System  | mg/min        |                |                | Ton per day |
|--------------|---------------|----------------|----------------|-------------|
|              | Inlet         | Main Pond      | Total          | Total       |
| 1            | 23,555        | 99,495         | 123,050        | 0.20        |
| 2            | 857           | 15,884         | 16,740         | 0.03        |
| 3            | 188           | 1,646          | 1,834          | 0.003       |
| <b>Total</b> | <b>24,600</b> | <b>117,025</b> | <b>141,624</b> | <b>0.22</b> |

## Summary and Conclusions

The test results showed that although VOC, GHG, and TAC emissions were observed from the pond systems (Tables D-1, D-2, D-3, and D-4), there were no hydraulic fracturing fluids in the ponds. This indicates that the pond systems tested either

- c) do not receive hydraulic fracturing fluids, or
- d) did not receive hydraulic fracturing fluids during the past 15-30 days (retention time of the pond systems)

This also indicates that any emissions observed from the ponds are not related to hydraulic fracturing operations. Additional evaluation of the sources of wastewater in the pond systems is needed to determine the sources of observed emissions from the pond systems. Additionally, emissions data from the small sample size (n=3) is too uncertain to draw conclusions or extrapolations.

In order to accurately quantify the post-flowback phase of hydraulic fracturing and other types of well stimulation treatments, additional testing of wastewater must be conducted as it is discharged from the WST operation and from the various types of well stimulation treatments. In order to accurately estimate emissions from wastewater discharged as part of oil and gas operations, it is also recommended that additional statistically significant testing be conducted from wastewater ponds in various locations representing WST operations from different fields. The testing procedures used as part of this study are recommended for either post-flowback phase or general types of wastewater discharge, and to provide accurate, repeatable measurements.