

**COMPOSITION OF VOLATILE ORGANIC COMPOUND
EMISSIONS FROM OIL AND GAS WELLS IN THE UINTA BASIN**

STATEMENT OF WORK AND BUDGET

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2. Introduction

Regulatory agencies, industry, and academic researchers have worked for the past nine years to better understand organic compound emission rates and composition from a number of types of oil and gas facilities and equipment in the Uinta Basin. These efforts have included top-down estimates of whole-basin emissions (Ahmadov et al., 2015; Foster et al., 2017; Karion et al., 2013), various facility-level and equipment-level emissions measurement campaigns (Lyman, 2015; Lyman and Mansfield, 2018; Lyman et al., 2018; Lyman et al., 2017; Mansfield et al., 2018; Robertson et al., 2017; Tran et al., 2017; Warneke et al., 2014), intercomparisons of modeled and measured emissions (Ahmadov et al., 2015; Edwards et al., 2014; Mansfield, 2014; Matichuk et al., 2017; Tran et al., 2014) and emissions inventory efforts (Lyman et al., 2013; Stoeckenius, 2015; UDAQ, 2018). These efforts have filled in knowledge gaps and allowed industry and regulators to develop emissions reduction strategies that are based on sound scientific information.

The Utah Division of Air Quality (UDAQ) is leading a new effort to improve estimates of the speciation of organic compound emissions from Uinta Basin oil and gas wells. This effort will entail collection and analysis of pressurized gas and liquid samples from oil and gas well separators, as well as data processing and analysis. Utah State University (USU) will work with UDAQ in this effort in the following ways:

1. Collect pressurized liquid samples from ten oil and gas wells and analyze the concentrations of a suite of carbonyl compounds in flash gas (i.e., gas emitted when liquid petroleum samples are depressurized) emitted from those samples.
2. Receive, process, and distribute organic compound composition data from commercial laboratories.
3. Use composition data to develop speciation profiles that can be used in air quality modeling.
4. Coordinate this project with direct organic compound emissions measurements that will be carried out with separate funding from UDAQ (as part of the ULEnd program) and the Utah Legislature, and conduct a comparison of results from the two studies, as well as other relevant available datasets.

The following sections provide detailed information about how USU will complete these tasks, as well as the project's schedule, deliverables, and budget.

3. Carbonyl Speciation in Flash Gas

We will collect pressurized liquid samples from ten wells and analyze the gas evolved from the samples for concentrations of a suite of carbonyls. This is a preliminary effort to determine whether carbonyls exist in flashed gas in measureable quantities. Additional work would be needed to comprehensively characterize the carbonyl composition of flashed gas at Uinta Basin oil and gas wells.

3.1. Field Sample Collection

We will collect fifteen pressurized liquid samples from separators at ten oil and gas wells (one from each well, as well as five additional quality control samples from one well). Then ten wells will be a subset of the 70 wells from which raw gas and pressurized liquid samples will be collected for analysis by a

commercial laboratory. We will collect samples with a floating piston cylinder according to GPA 2174. We will coordinate with the commercial laboratory and collect our liquid samples at the same times and locations at which they collect other samples. We will also use the same sampling ports and lines.

3.2. Laboratory Sample Processing

We will analyze pressurized liquid samples following PS Memo 17-01 from the Colorado Department of Public Health and Environment, *Flash Gas Liberation Analysis Method for Pressurized Liquid Hydrocarbon Samples* (CDPHE, 2017). This method will involve the following steps:

1. We will use a custom-built heating apparatus to heat the sample cylinder to the temperature of the well-site separator at the time of sample collection.
2. We will pressurize the sample cylinder to the pressure of the well-site separator at the time of sample collection by connecting a regulated, pressurized inert gas source to the inert gas side of the cylinder.
3. We will connect the liquid sample side of the cylinder to tubing that leads to a sealed PFA Teflon flask. A manual needle valve will allow us to control the flow of liquid into the flask.
4. The flask will connect via another tube to a DNPH cartridge followed by a totalizing mass flow controller. The DNPH cartridge will retain carbonyls from the gas sample, and the mass flow controller will regulate and record gas flow.
5. We will install an analog pressure gauge on the flask to ensure that its pressure stays within a safe range.
6. We will mix the liquid sample and then slowly open the needle valve to allow sampled liquid to slowly transfer into the flask and depressurize. The evolved gas will pass from the flask, through the DNPH cartridge, through the mass flow controller, and to exhaust.
7. After all the flash gas has exhausted, we will record the total volume of gas exhausted and analyze the DNPH cartridges for carbonyl content. We will not determine the carbonyl content in the liquid portion of the sample.

3.3. Analysis of DNPH Cartridges by High Performance Liquid Chromatography

We will use BPE-DNPH sorbent cartridges following Uchiyama et al. (2009), which is similar to EPA Method TO-11A. The first portion of each cartridge will be packed with BPE-coated silica, which captures ozone and reduces sampling artifacts. The second portion of the cartridge will be packed with DNPH-coated silica. Carbonyls react with and are retained on these cartridges by DNPH. Non-carbonyl organics pass through the cartridges and are exhausted. We will keep DNPH cartridges refrigerated or on ice, except when installed for sampling.

We will analyze cartridges within 14 days of sampling. To prepare samples for analysis, we will flush cartridges with a 5 mL solution of 75% acetonitrile and 25% dimethyl sulfoxide to release DNPH-carbonyls into solution. The solution will be collected into 5 mL volumetric flasks, and we will bring the flasks to a volume of 5ml using 0.5-1 mL of the acetonitrile/dimethyl sulfoxide solution. Finally, we will pipette a 1 mL aliquot from the 5 mL flask into a 1.5 mL autosampler vial for analysis by High Performance Liquid Chromatography (HPLC).

We will analyze samples using a Hewlett Packard series 1050 HPLC analyzer with a Restek Ultra AQ C18 column and a diode array detector. We will use a mixture of acetonitrile and water as the eluent. We will prepare standards by diluting commercially available carbonyl-DNPH standards.

Samples will be analyzed for the following compounds:

- Formaldehyde
- Acetaldehyde
- Acrolein
- Acetone
- Propionaldehyde
- Crotonaldehyde
- Butyraldehyde/methacrolein/2-butanone (eluted together)
- Benzaldehyde
- Valeraldehyde
- Toluualdehyde
- Hexaldehyde

3.4. Quality Assurance

3.4.1. Sample Integrity

We will check sample cylinders for gas leaks before and just after sample collection using a Restek inert gas electronic leak detector. We will also record the sample pressure after the sample has cooled to room temperature, and check that the pressure has not changed at the time of analysis.

3.4.2. Analytical Precision

We will calibrate the HPLC on each analysis day with a five-point calibration curve. We will run an additional standard at the beginning and end of each analysis batch to check for retention time drift or other errors.

We will conduct a detection limit study by analyzing a diluted calibration standard with concentrations near the detection limit at least five times. The detection limit of each analyzed carbonyl compound will be calculated as three times the standard deviation of the concentration.

3.4.3. Blank Checks

We will analyze a laboratory blank DNPH cartridge for each batch of samples analyzed. Laboratory blank cartridges will be processed and analyzed just like normal samples, but will not sample emitted gas. We will not analyze less than three laboratory blanks.

3.4.4. Matrix Spikes

We will add a known mass of several of the carbonyls measured to the sample gas stream as three replicate samples are emitting flashed gas to determine the ability of the method to quantitatively

recover carbonyls. Carbonyls will be diluted from commercially-available stock standards, diluted in methanol, and injected with a syringe via an injection port just downstream of the liquids collection flask.

3.4.5. *Replicates*

We will collect and analyze three replicate samples at one well site to determine method stability.

4. Data Processing, Storage and Distribution

4.1. Data and Metadata Handling and Storage

We will make field and laboratory notes using paper log sheets or a Microsoft Word-based logbook. At the end of each work day, we will digitize all notes and upload them to a secure, cloud-based, electronic log book. The electronic log will record the date and time of upload and the person that executed the upload. It will also keep all versions of every entry in perpetuity.

At the conclusion of each field sampling or laboratory analysis day, we will upload all collected electronic data to a cloud-based server, and we will back up the server monthly with local removable hard drives.

We will retain all collected data for at least five years.

4.2. Data Processing

The commercial laboratory that collects and analyzes liquid and gas samples for organic compound composition will send us their analytical results. We will combine these data with our carbonyl analysis data to prepare a single organic compound composition dataset.

4.3. Data Confidentiality

Study data will be considered protected research data, which means they are protected against public release under GRAMA. We will execute non-disclosure agreements with operators if requested.

4.4. Data Distribution

We will send data to the individual companies at whose wells the samples were collected. We will also provide an anonymized data set to UDAQ. If some samples are collected on wells within Indian Country, we will send the data for those wells to the Ute Indian Tribe Air Quality Program. UDAQ may then request those data from the Ute Indian Tribe. We will make data available to all parties via password-protected download from Box.com. At the conclusion of the study, when the final report is released, we will prepare an anonymized final dataset, and we will post the dataset for free public access at USU's Digital Commons (<http://digitalcommons.usu.edu>). Table 1 provides a data distribution summary.

Table 1. Information about data distribution, including recipients, distribution method, and distribution schedule.

Data Recipient	Data Type	Distribution Method	Schedule
Well Owners	Company-specific	Password-protected download	As soon as available
Ute Indian Tribe	Anonymized dataset	Password-protected download	As soon as available
UDAQ	Anonymized dataset	Password-protected download	As soon as available
Public	Anonymized dataset	USU Digital Commons	At study conclusion

5. Development of Speciation Profiles

Organic compound composition profiles will be processed into Carbon Bond Version 6 (CB6) species in the digestible format for the SMOKE emission model and photochemical models (e.g. CAMx). The eleven carbonyl compounds analyzed by USU will be grouped into three CB6 species readable for SMOKE and CAMx models: i) formaldehyde (FORM), ii) acetaldehyde (ALD2) and iii) and higher aldehydes (ALDX). The composition of each measured compound (both hydrocarbons and carbonyls) will be converted to weight % (or split factor) for the model-ready speciation profiles. We will develop speciation profiles that are specific to producing formations and to different types of equipment at oil and gas wells, and we will compare these profiles to other available datasets (see next section). Finally, we will use the results of this study to update the EPA SPECIATE_V4.5 database (EPA, 2018).

6. Coordination and Comparison with Related Projects

6.1. Coordination with the ULenEmissions Measurement Project

We were funded by UDAQ in 2017 to participate in the ULenE infrared camera lending program. As part of the ULenE project, UDAQ purchased software developed by Providence Photonics that processes data collected by infrared leak detection cameras and produces estimates of emission rates from cameras' data output. UDAQ provided us with funds to compare leak rates estimated by the Providence Photonics software against leak rates measured with our custom-built high flow emissions measurement system. In addition to UDAQ funding, we have a small amount of funding we have made available from the Utah Legislature to increase the number of wells we can visit for the ULenE emissions measurement project. The ULenE statement of work can be downloaded here:

<https://usu.box.com/s/xlofwnjj6neftq9iyppxlkruxyiuofv>. The project will involve the following at each oil and gas well visited:

1. We will use the ULenE infrared camera to detect organic compound emissions from equipment at the well.

2. We will use the Providence Photonics software to estimate the emission rate from all detected emission sources at the well, unless the sources are in a location or have characteristics that make use of the Providence Photonics software inadvisable.
3. We will use our high flow sampling system to quantify the emission rate from all detected emission sources at the well, unless those sources are in a location or have characteristics that make use of the high flow system inadvisable.
4. We will compare the emission values from the two approaches to determine the effectiveness of the Providence Photonics method under different conditions and source types.

6.1.1. ULeD Emissions Measurement Locations

To maximize the value of the ULeD emissions measurement study and this study, we will conduct the ULeD emissions measurements at the same 70 wells at which liquid and gas samples will be collected for this study. We will not conduct the ULeD emissions measurement study until the 70 wells for the composition study have been selected.

6.1.2. Compounds Measured for the ULeD Project

The ULeD emissions measurement study will provide speciated emission measurements from the 70 wells sampled in this study. Emission sources measured will likely include pneumatic controllers, leaks in valves and fittings, tanks, glycol dehydrators, etc. A list of all compounds measured in both studies is included in Table 2.

Table 2. List of compounds measured as part of the organic compound composition study and the ULeD emissions study.

Compound	Compound Class	Analyzed for Composition Study	Analyzed for ULeD Emissions Study
Methane	Hydrocarbon	Yes	Yes
Ethane	Hydrocarbon	Yes, as C2	Yes
Ethane	Hydrocarbon	Yes, as C2	Yes
Ethylene	Hydrocarbon	Yes, as C2	Yes
Propane	Hydrocarbon	Yes, as C3	Yes
Propylene	Hydrocarbon	Yes, as C3	Yes
Isobutane	Hydrocarbon	Yes, as C4	Yes
n-Butane	Hydrocarbon	Yes, as C4	Yes
Acetylene	Hydrocarbon	Yes, as C2	Yes
Trans-2-butene	Hydrocarbon	Yes, as C4	Yes
1-Butene	Hydrocarbon	Yes, as C4	Yes
Cis-2-butene	Hydrocarbon	Yes, as C4	Yes
Isopentane	Hydrocarbon	Yes, as C5	Yes
N-Pentane	Hydrocarbon	Yes, as C5	Yes
Trans-2-pentene	Hydrocarbon	Yes, as C5	Yes
1-Pentene	Hydrocarbon	Yes, as C5	Yes
Cis-2-pentene	Hydrocarbon	Yes, as C5	Yes

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Compound	Compound Class	Analyzed for Composition Study	Analyzed for ULeND Emissions Study
2,2-Dimethylbutane	Hydrocarbon	Yes, as C6	Yes
Cyclopentane	Hydrocarbon	Yes, as C5	Yes
2,3-Dimethylbutane	Hydrocarbon	Yes, as C6	Yes
2-Methylpentane	Hydrocarbon	Yes, as C6	Yes
3-Methylpentane	Hydrocarbon	Yes, as C6	Yes
Isoprene	Hydrocarbon	Yes, as C5	Yes
1-Hexene	Hydrocarbon	Yes, as C6	Yes
n-Hexane	Hydrocarbon	Yes, as C6	Yes
Methylcyclopentane	Hydrocarbon	Yes, as C6	Yes
2,4-Dimethylpentane	Hydrocarbon	Yes, as C7	Yes
Benzene	Hydrocarbon	Yes	Yes
Cyclohexane	Hydrocarbon	Yes, as C6	Yes
2-Methylhexane	Hydrocarbon	Yes, as C7	Yes
2,3-Dimethylpentane	Hydrocarbon	Yes, as C7	Yes
3-Methylhexane	Hydrocarbon	Yes, as C7	Yes
2,2,4-Trimethylpentane	Hydrocarbon	Yes, as C8	Yes
n-Heptane	Hydrocarbon	Yes, as C7	Yes
Methylcyclohexane	Hydrocarbon	Yes, as C7	Yes
2,3,4-Trimethylpentane	Hydrocarbon	Yes, as C8	Yes
Toluene	Hydrocarbon	Yes	Yes
2-Methylheptane	Hydrocarbon	Yes, as C8	Yes
3-Methylheptane	Hydrocarbon	Yes, as C8	Yes
n-Octane	Hydrocarbon	Yes, as C8	Yes
Ethylbenzene	Hydrocarbon	Yes	Yes
m/p-Xylene	Hydrocarbon	Yes	Yes
Styrene	Hydrocarbon	Yes, as C8	Yes
o-Xylene	Hydrocarbon	Yes	Yes
n-Nonane	Hydrocarbon	Yes, as C9	Yes
Isopropylbenzene	Hydrocarbon	Yes, as C9	Yes
n-Propylbenzene	Hydrocarbon	Yes, as C9	Yes
1-Ethyl-3-methylbenzene	Hydrocarbon	Yes, as C9	Yes
1-Ethyl-4-methylbenzene	Hydrocarbon	Yes, as C9	Yes
1,3,5-Trimethylbenzene	Hydrocarbon	Yes, as C9	Yes
1-Ethyl-2-methylbenzene	Hydrocarbon	Yes, as C9	Yes
1,2,4-Trimethylbenzene	Hydrocarbon	Yes, as C9	Yes
n-Decane	Hydrocarbon	Yes, as C10	Yes
1,2,3-Trimethylbenzene	Hydrocarbon	Yes, as C9	Yes
1,3-Diethylbenzene	Hydrocarbon	Yes, as C10	Yes

Compound	Compound Class	Analyzed for Composition Study	Analyzed for ULeud Emissions Study
1,4-Diethylbenzene	Hydrocarbon	Yes, as C10	Yes
n-Undecane	Hydrocarbon	No	Yes
Methanol	Alcohol	No	Yes
Ethanol	Alcohol	No	Yes
Isopropanol	Alcohol	No	Yes
Formaldehyde	Carbonyl	Yes, for 10 samples	Yes
Acetaldehyde	Carbonyl	Yes, for 10 samples	Yes
Acrolein	Carbonyl	Yes, for 10 samples	Yes
Acetone	Carbonyl	Yes, for 10 samples	Yes
Propionaldehyde	Carbonyl	Yes, for 10 samples	Yes
Crotonaldehyde	Carbonyl	Yes, for 10 samples	Yes
Butyraldehyde	Carbonyl	Yes, for 10 samples	Yes
Methacrolein	Carbonyl	Yes, for 10 samples	Yes
2-Butanone	Carbonyl	Yes, for 10 samples	Yes
Benzaldehyde	Carbonyl	Yes, for 10 samples	Yes
Valeraldehyde	Carbonyl	Yes, for 10 samples	Yes
Tolualdehyde	Carbonyl	Yes, for 10 samples	Yes
Hexaldehyde	Carbonyl	Yes, for 10 samples	Yes

6.2. Comparison of Speciation Profiles from this Study with ULeud and Other Available Datasets

We compare the organic compound speciation profiles developed for this study against other available datasets. These will include the following:

6.2.1. Uinta Basin-specific Profiles Developed for the WRAP-III Emissions Inventory

EPA SPECIATE Version 4.5 (EPA, 2018) includes four organic compound speciation profiles from the WRAP-III emissions inventory developed specifically for the Uintah Basin (UNT01,02,03 and 04). These profiles have served as Uinta basin-wide weighted average composite profiles. They were created by averaging gas profiles obtained from GC/MS analysis of produced and flash gas from a few samples collected at coal bed and non-coal bed methane wells, oil tanks and condensate tanks provided by oil and gas companies (Hsu et al., 2016). Thus, they are not fully representative of actual emissions from oil and gas wells in the Uintah Basin. Moreover, these profiles did not include measurements of carbonyls, which are more photochemically reactive than hydrocarbons.

We will compare the speciation of organic compounds in the WRAP-III profiles against those developed for this study.

6.2.2. Emissions Measurements Collected by USU in 2015 and for ULeND in 2018

With funding from UDAQ, we collected carbonyl emissions measurements from liquid storage tanks, glycol dehydrators, raw gas sources, and pump jack engines during winter 2015 (Lyman, 2015), and we used those data to modify SPECIATE speciation profiles. Since we only measured carbonyls in the 2015 study, we used hydrocarbon composition data collected during field campaigns in Texas (Hendler et al., 2009; Viswanath and Van Sandt, 1989) to make assumptions about hydrocarbon split factors in the speciation profiles.

We will compare the speciation profiles developed for this study against the carbonyl emissions data collected in 2015 and the emissions data collected for the ULeND project. If appropriate, we will modify the speciation profiles from this study based on this comparison.

7. Deliverables

This project will result in the deliverables shown in Table 3. Since the dates of field sample collection are not yet known with certainty, due dates are shown relative to the date composition data become available from USU’s laboratory and the commercial laboratory.

Table 3. Project deliverables and due dates.

Deliverable	Due Date
Final organic compound composition dataset	60 days after carbonyl analysis is completed and other composition data are received from commercial laboratory
Speciation profile dataset	90 days after final datasets are complete
Quarterly reports	90, 180, and 270 days after the project begins
Draft final report	60 days after completion of speciation profile dataset
Final Report	60 days after release of draft report

7.1. Collaborative Report Preparation

7.1.1. Collaboration with UDAQ

We will complete quarterly reports according to a protocol that will be provided by UDAQ. We will work collaboratively with UDAQ on the final report, and the report will contain information about the tasks described herein, as well as related work completed by UDAQ.

7.1.2. Solicitation of Comments on Draft Final Report

After we complete the draft final report in concert with UDAQ, we will distribute the report to representatives of UDAQ, the Ute Indian Tribe, the U.S. Environmental Protection Agency, interested oil and gas companies and associations, and perhaps others. We will invite these parties to review the report and provide comments prior to its release. We will give all parties 30 days to provide comments.

We will consider all the comments received and make changes to the report as appropriate prior to its final release.

8. Schedule

Table 4 shows a Gantt chart for the project. The project will last one year after field sample collection begins. The Gantt chart is shown relative to the start of field sample collection.

Table 4. Gantt chart showing project schedule

	Q1	Q2	Q3	Q4
TASKS				
Field sample collection, lab analysis				
ULend emissions measurements				
Data processing and distribution				
Data comparison				
Speciation profile development				
Report preparation				
DELIVERABLES				
Composition dataset				
Speciation profile dataset				
Quarterly Progress Reports				
Final Report				

9. Budget

A budget for this project appears in Table 5. The budget includes the following:

- Salary costs for work by project scientists and technicians. A total of 386 hours of labor are included. Fringe benefits are calculated at 46% of salary costs. Overtime may be charged for nonexempt employees for the field portion of this project.
- Travel costs for miles traveled to collect field samples. Costs are calculated at \$0.86 per mile. Three days of travel are included at 130 miles per day.
- Costs for materials and supplies are included. These include:
 - Rental of floating piston sampling cylinders (\$2,100)
 - Consumable and maintenance costs for DNPH cartridge analysis (\$1,384)
 - Materials for flash gas sampling (\$1,420)
- Indirect costs have been included at the rate of 10% of direct costs.

Table 5. Project budget, separated by expense category.

Description	Cost
Salaries	\$15,262
Benefits	\$7,097
Travel	\$335
Materials	\$4,904
Indirect Costs	\$2,760
Total	\$30,358

Table 6 provides a breakdown of costs for each of the two main project tasks.

Table 6. Budget for the project, divided by task.

Task Description	Cost
Collection and analysis of carbonyl flash gas samples	\$11,196
Data processing and distribution	\$1,521
Development of speciation profiles	\$5,303
Coordination and comparison with other projects and datasets	\$4,933
Analysis and reporting	\$7,405
Total	\$30,358

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