



PROPOSAL

MEASUREMENT OF CARBONYL EMISSIONS FROM NON-COMBUSTION OIL AND GAS SOURCES IN THE UINTAH BASIN

Submitted to:

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1. Background

Investigations of inversion episodes in the Uintah Basin have shown that formaldehyde and other carbonyls are key precursors to wintertime ozone formation. Three principal categories of carbonyl sources exist in the Basin. These include combustion-related primary emissions, non-combustion primary emissions, and secondary formation in the atmosphere from photochemical reactions involving organic compounds. Combustion-related emissions of formaldehyde are relatively well characterized, and EPA emission factors for formaldehyde are available for some oil and gas-related combustion processes, though emission factors for other carbonyls are less readily available. Photochemical production of carbonyls from organic compounds is represented in the chemical mechanisms utilized by regional-scale air quality models such as CAMx and CMAQ. These chemical mechanisms are imperfect, and more work is needed to improve them, but a basic computational framework for estimating atmospheric production of carbonyls exists.

Non-combustion primary emissions of carbonyls from oil and gas processes are completely uncharacterized, however. No measurements of non-combustion carbonyl emissions have ever been collected in the Uintah Basin or elsewhere. Analyses of ambient air in the Basin have indicated that non-combustion emissions of carbonyls from oil and gas-related sources may be an important component of total emissions. These analyses also suggest that formaldehyde emissions from non-combustion sources in oil and gas-producing areas are connected with methanol emissions in some cases. Methanol is used as a deicer and solvent in oil and gas operations, and it is likely that some methanol degrades to formaldehyde during use, although it is not clear where in the oil and gas production stream this occurs. Measurements of carbonyl concentrations in methanol and produced water have shown higher concentrations in older methanol, downstream of oil and gas processing equipment, and in produced water relative to methanol. Aldehydes are routinely used as a component of hydraulic fracturing fluid. Carbonyls could also be produced in high-temperature and/or high-pressure oil and gas processes, such as well-site separation, glycol dehydration, or gas purification.

Still, very little is known about non-combustion sources of carbonyls in oil and gas fields. We will begin the task of developing an emissions inventory for formaldehyde and other carbonyls in the Uintah Basin by collecting emissions measurements from some likely non-combustion formaldehyde sources. This work will not allow us to fully characterize emissions from these sources. Instead, it will allow us to determine whether these sources are important contributors to wintertime ozone production. A second, larger phase of study would be required to generate enough data to allow addition of non-combustion carbonyl sources to an emissions inventory.

2. Purpose

Ozone concentrations almost twice the EPA standard of 75 ppb have been measured in the Uintah Basin. Stringent emissions controls may be required to bring the Basin into compliance with EPA standards. Because carbonyls have emerged as a key contributor to wintertime ozone formation in the Basin, control of carbonyl emissions may be more economical and effective than control of volatile organic compounds in general. To give one example, methanol alternatives exist, are economically feasible, and are less likely to degrade to formaldehyde. Replacement of methanol with alternative deicing products could reduce non-combustion formaldehyde emissions. This study will provide information that helps determine whether non-combustion carbonyl emission controls would be useful for reducing ozone concentrations in the Basin.

3. Related Projects

We currently participate in a number of research efforts that are related to this work. These projects are listed below, along with a short description of how they related to the formaldehyde emissions measurement work.

3.1. Emissions of methane and nonmethane hydrocarbons from soils near well pads

A wealth of recent studies have shown that current emission inventories for oil and gas operations are inadequate. Our group is working to close gaps in those inventories, especially by measuring emissions from uncharacterized or poorly characterized sources. We have funding from the Bureau of Land Management and the Research Partnership to Secure Energy for America (RPSEA; a contractor for the Department of Energy) to measure emissions of methane and nonmethane hydrocarbons from soils in oil and gas fields, especially well pads. These measurements will allow quantification of the source strength of natural hydrocarbon seepage and subsurface oil and gas infrastructure leaks, which are currently not included in emission inventories. These projects are related to carbonyl emission measurements in that both efforts will improve emission inventories, allowing for better photochemical model representation of air quality in the Uintah Basin and better decisions about remediation strategies.

3.2. Emissions of methane, nonmethane hydrocarbons, and alcohols from produced water and land farms

We recently received funding from the RPSEA and the Department of Energy to measure emissions of methane, nonmethane hydrocarbons, and alcohols from produced water impoundments and land farms. This project seeks to characterize current emissions and determine whether various waste treatment processes would be effective at reducing emissions. We will work with RPSEA to add carbonyl emissions measurements from produced water to this project. As with the soil emissions work, this project will also improve current emission inventories, modeling efforts, and decision-making.

3.3. Air quality modeling and emissions inventory development for the Uintah Basin

Our group is engaged in several projects to develop emissions inventories and photochemical models for air quality in Utah and the Uintah Basin. These projects are supported by industry, the State of Utah, and Federal Agencies. Our modeling and inventory efforts are impaired by incomplete emissions information. The current formaldehyde emissions measurement project will allow us to improve emissions inventories. When possible, we will incorporate the results of this and other emissions work into our models.

3.4. Measurement of air chemistry and meteorology around the Uintah Basin

We receive funding from the Uintah Impact Mitigation Special Service District and the Ute Indian Tribe to measure ozone, ozone precursors, particulate matter, and meteorology at several sites around the Uintah Basin. These measurements allow us to track the spatial and temporal behavior of these parameters, providing information against which to verify models and by which the effectiveness of mitigation strategies can be shown. We are working to add routine ambient air carbonyl measurements at a few of our ambient air measurement sites in the coming year. These measurements would allow us to determine the spatial distribution of carbonyls around the Uintah Basin, validating and supporting the carbonyl emissions measurements to be carried out for this project.

4. Plan of Work

4.1. Engaging companies for participation

We hope to involve several oil and gas exploration and production companies actively in this project. We need active participation from companies to gain direct access to oil and gas production equipment. We are working with the Western Energy Alliance to coordinate our effort to reach out to and engage companies in this work. We will also work with the Ute Indian Tribe and the Bureau of Land management to reach out to and engage companies. We plan to sign non-disclosure agreements with companies that work with us on this project to keep their involvement confidential and protect their interests.

4.2. Literature review

Very little information exists about non-combustion emissions of carbonyls from oil and gas operations. Some information exists about combustion-related emissions of carbonyls, but information for combustion-related emissions is not fully incorporated in current emission inventories. We will compile all available information about primary carbonyl emissions from the oil and gas industry, whether from peer-reviewed publications, reports, current emission inventories, industry websites, or interviews with experts. This information will be included in our Final Report.

4.3. Measurement of emissions from oil and gas well-site equipment

4.3.1. Source types

It is not yet known which oil and gas equipment or processes are important non-combustion sources of carbonyls to the atmosphere. Possibilities include:

- Methanol use (due to possible degradation of methanol to formaldehyde)
- Three-phase separators
- Glycol dehydrators
- Well site storage tanks (crude oil, condensate, and produced water)
- Produced water impoundments
- Hydraulic fracturing processes, especially flowback
- Distillation and other heating processes

We will measure emissions from most of these sources. We will not measure emissions from produced water impoundments, since we plan to use our current Department of Energy funding for this. We may not be able to measure emissions from distillation and heating processes because these are often embedded within larger oil and gas facilities such as compressor stations or gas plants, and isolating these emissions from other sources may be impossible without direct access to the facilities.

4.3.2. Carbonyl emissions measurements

Carbonyls will be collected with BPE-DNPH sorbent cartridges following Uchiyama et al., *Analytical Chemistry* 81, 6552-6557, 2009. The first portion of the cartridge is packed with BPE-coated silica, which captures ozone and eliminate sampling artifacts. The second portion of the cartridge is packed with DNPH-coated silica. Carbonyls react with and are retained on the cartridge by DNPH. Battery-powered sample pumps connected to cartridges with nylon tubing will pull air through the cartridges, and these pumps will also regulate flow. PTFE filters upstream of the BPE-DNPH cartridges will exclude particulate

matter from samples. Sampling components will be stored in airtight containers before and after field deployment. Hand warmers will be packed around cartridges to keep them warm during sampling and ensure adequate collection of formaldehyde. After collection, carbonyls will be extracted from cartridges with a solution of acetonitrile and dimethyl sulfoxide and analyzed by HPLC with UV absorption detection, following EPA Method 0100 (<http://www.epa.gov/osw/hazard/testmethods/sw846/pdfs/0100.pdf>).

We will use two different methods to measure carbonyl emissions:

4.3.2.1. Emissions measurements: Bag sampling

Bag sampling involves enclosing the component to be tested (e.g., a leaky fitting, a separator pressure relief valve, a solar-powered methanol pump, etc.) in a Teflon bag. Carbonyl concentrations are measured inside and outside of the bag with BPE-DNPH sorbent cartridges. A sample pump powered by a generator provides flow through the bag. The flow through the bag must be higher than the flow of gas from the component to be tested, so that all of the gas emitted from the component passes through the bag. The bag is sealed around the component to be tested with rubber bands and/or adhesive tape (a perfect seal is not needed). Battery-powered pumps pull air through the BPE-DNPH cartridges inside and outside the bag for 1-3 hours. The difference in concentration inside and outside the bag is multiplied by the flow rate through the bag to determine the emission rate.

4.3.2.2. Emissions measurements: Plume characterization/inverse modeling

We will also measure emissions from potential sources via plume characterization/inverse modeling. This involves collecting measurements of carbonyls upwind and downwind of an emission source, and collecting meteorological data (wind speed and direction, temperature, humidity, pressure, and solar radiation). After collection, the meteorological data and the site's physical characteristics are used to build a plume dispersion computer model of emissions from the potential source. Finally, the measured concentrations of carbonyls are used to adjust the dispersion model's emission rate until the modeled emission plume best matches the measured air concentrations. This method works best with constant, steady wind speed and direction. It will not work well during inversion events, possibly necessitating sample collection at the beginning and end of the winter season. Figure 1 shows a schematic of a measurement site.

Carbonyl sampling apparatuses will be mounted at 2-3 meters above ground level on tripods. We will deploy one carbonyl sampler upwind of each site, and 5-6 samplers downwind of each site to adequately characterize the emission plume. Samples will be collected over 1-3 hours.

We will use AERMOD, a commercially-available, EPA-approved modeling platform (http://www.epa.gov/scram001/7thconf/aermod/aermod_mfd.pdf), for plume dispersion modeling. Figure 2 shows a simulated emission plume from a produced water pond, derived using AERMOD.

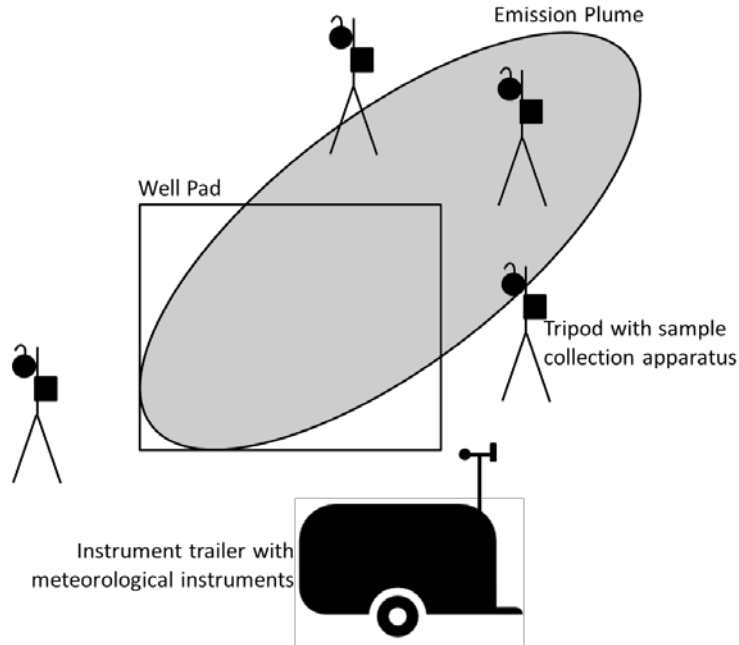


Figure 1. Conceptual diagram of measurement of emissions from a well site.

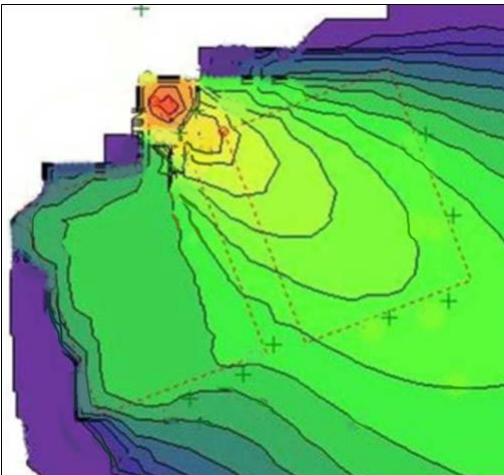


Figure 2. AERMOD visualization of emissions from a produced water evaporation facility.

4.3.3. Number of measurements collected

The number of emissions measurements collected will depend on the level of cooperation we receive from operators. Bag sample measurements are simpler, more direct, cheaper, require less time, and provide emission measurements from individual components, rather than from an entire well pad or facility. However, they require direct contact with equipment, which necessitates a greater level of cooperation from companies. We will collect bag sample measurements when direct contact with equipment is feasible and permitted. Otherwise, we will conduct plume characterization/inverse modeling measurements. The exact sampling locations and number of location will need to be determined after consultation with industry. The budget for this project contains enough funding for 18 plume characterization measurement periods and 25 bag sampling measurement periods.

4.3.4. QA/QC

We will collect 10 field blanks over the course of the study. Field blank BPE-DNPH cartridges will be handled and analyzed exactly the same as other cartridges, but they will be collected immediately after being connected to sampling apparatuses in the field.

We will analyze a laboratory blank during each laboratory analysis period. Laboratory blank cartridges will be analyzed just like samples, but will not be taken to the field.

10 matrix spikes will be collected over the course of the study. We will use a VICI Dynacal acetaldehyde permeation tube with a VICI portable permeation oven to generate a known concentration of gaseous acetaldehyde. This air stream will be diluted with air scrubbed with Purafil SP Media. A BPE-DNPH cartridge will sample this air stream in field conditions and then be analyzed normally in the laboratory.

Polyethylene gloves will be worn at all times while handling sample cartridges to minimize the possibility of sample contamination.

Before each sampling period, each sample apparatus will be checked for leaks by plugging the sample inlet with a gloved hand and ensuring that the flow rate drops to zero. Flow rates indicated on flow controllers and sampling pumps will be checked against a NIST traceable standard every two months.

Calibration standards will be created from commercially-available, pre-prepared, pre-derivitized carbonyl standards.

4.4. Report and final dataset preparation

We will analyze data as they are collected, and will provide DAQ with an update of our progress throughout the study period upon request. We will supply raw data, lab and field notes, analyses, operating procedures, etc., upon request. We will deliver a short interim report of study progress and preliminary results to DAQ in January 2015, and we will deliver a final report, along with a final dataset, at the end of the project. The final report will contain a literature review, a description of methods used, a description of project results, and recommendations for next steps. The final dataset will include all final emissions data. Depending on agreements formed with companies, the final dataset may not include exact locations of emissions measurements, but it will include site characteristics, source types, and sampling dates.

4.5. Participation in DAQ communication strategy

We will work with DAQ to publicize the benefits of this research project to the public and the Utah Legislature. We will prepare summary slides, presentations, and travel to meetings as needed for this effort.

5. Deliverables

<u>Due Date</u>	<u>Deliverable</u>
15 January 2015	Interim report
15 July 2015	Final report
15 July 2015	Final dataset
As requested	Raw data, operating procedures, project updates

5. Schedule and Deliverables

This project will last for 12 months. A schedule for project tasks and deliverables appears in Table 1.

	2014					2015						
	Aug	Sep	Oct	Nov	Dec	Jan	Feb	Mar	Apr	May	Jun	Jul
Contact companies	■	■										
Build sampling system	■	■	■									
Finalize lab protocols	■	■	■									
Literature review		■	■	■	■							
Emissions measurements				■	■	■	■	■	■	■		
Report preparation										■	■	■
Deliverables												
Interim report						■						
Final report												■
Final dataset												■

Table 1. Schedule of work to be performed and deliverables.

7. Budget and Budget Justification

The total cost for this project is \$75,000. A breakdown of costs is given in Table 2. Labor and fringe benefits costs include costs for the PI to manage the project, an air quality specialist to prepare field sampling equipment and supervise field sampling, an air quality modeler to perform plume dispersion inverse modeling, and several undergraduate students to perform field and laboratory work. Materials and parts costs include BPE-DNPH cartridges and accessories, battery-powered air sampling pumps, Teflon bags, and field and laboratory consumables. Travel costs include travel to field sites.

Labor and fringe benefits	\$45,251
Materials and parts	\$20,430
Travel	\$2,500
Indirect costs (10%)	\$6,818
TOTAL	\$75,000