



FINAL REPORT

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

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4. Introduction

Investigations of inversion episodes in the Uintah Basin have shown that formaldehyde and other carbonyls are key precursors to wintertime ozone formation (Edwards et al., 2014). Three principal categories of carbonyl sources exist. These include: i) combustion-related primary emissions, ii) non-combustion primary emissions, and iii) secondary formation in the atmosphere from photochemical reactions involving organic compounds. Combustion-related emissions of formaldehyde have been characterized to some extent (e.g., Stutz et al. (2011)), and EPA emission factors for formaldehyde are available for some oil and gas-related combustion processes (see Literature Review). 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.

In contrast, non-combustion primary emissions of carbonyls from oil and gas processes are completely uncharacterized. To our knowledge, no publicly available 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 (Stoeckenius et al., 2014). Since very little is known about non-combustion sources of carbonyls in oil and gas fields, and it is not yet even clear whether or not they are important relative to combustion-related and photochemical sources, measurements to determine the importance of non-combustion carbonyl emissions are warranted. This document reports on measurements of carbonyl emissions from combustion-related and non-combustion oil and gas sources in the Uintah Basin. We discuss these measurements in the context of past work, and determine the effect of including our measurement results in a photochemical model of ozone.

5. Literature Review

5.1. Speciation Profiles

For photochemical modeling studies, several different volatile organic compound (VOC) speciation profiles have been developed and applied for oil and gas emission sources in Uintah Basin. Currently available speciation profiles are shown in Table 1.

Table 1. Available CB05 VOC emission speciation profiles applied for oil and gas activities in the Uintah Basin. Data are shown as split factors.

SCC	Source type	pro_code	pro_desc	ALDX	BENZENE	FORM	IOLE	OLE	PAR	TERP	TOL	UNR	XYL	CH4	ETHA
Default_spc (EPA, 2015)	Oil well tanks - flashing & standing /working/ breathing	2487	Composite of 7 Emission Profiles from Crude Oil Storage Tanks - 1993	0.0034	0.0104	2E-05	0.0003	0.0072	0.7900	0.0082	0.0231	0.1135	0.0127	-	0.0417
	Gas well truck loading	0051	Flares - Natural Gas	-	-	0.2	-	0.15	0.15	-	-	0.15	-	0.2	0.3
	Natural Gas; Heaters	0051	Flares - Natural Gas	-	-	0.2	-	0.15	0.15	-	-	0.15	-	0.2	0.3
	Natural Gas; Compressor Engines	0051	Flares - Natural Gas	-	-	0.2	-	0.15	0.15	-	-	0.15	-	0.2	0.3
	Natural Gas;	0051	Flares - Natural Gas	-	-	0.2	-	0.15	0.15	-	-	0.15	-	0.2	0.3
	Miscellaneous Engines	0051	Flares - Natural Gas	-	-	0.2	-	0.15	0.15	-	-	0.15	-	0.2	0.3
	Natural Gas; Artificial Lift	0051	Flares - Natural Gas	-	-	0.2	-	0.15	0.15	-	-	0.15	-	0.2	0.3
	Natural Gas;	0051	Flares - Natural Gas	-	-	0.2	-	0.15	0.15	-	-	0.15	-	0.2	0.3
Natural Gas Liquids; Tank Losses; Gas Plant Truck Loading	0051	Flares - Natural Gas	-	-	0.2	-	0.15	0.15	-	-	0.15	-	0.2	0.3	
2310121110	Hydraulic Fracturing Pumps	1207	Well Heads (Water Flood) Composite	0.0029	0.0028	1E-05	0.0002	0.0039	0.7547	0.0069	0.0296	0.1084	0.0373	-	0.0651
231001****	Oil well tanks - flashing & standing /working/ breathing	2487	Composite of 7 Emission Profiles from Crude Oil Storage Tanks - 1993	0.0034	0.0104	2E-05	0.0003	0.0072	0.7900	0.0082	0.0231	0.1135	0.0127	-	0.0417
ARMS_spc (AECOM, 2013)	Oil well tanks - flashing & standing /working/ breathing	9001	Natural gas dehydrators, pneumatic devices, oil and condensate tanks	-	-	-	-	0.9224	-	-	0.0219	0.0335	0.0190	0.0010	0.0023
	Gas well truck loading	9003	Natural gas dehydrators, pneumatic devices, oil and condensate tanks	-	-	-	-	0.1387	-	-	0.0033	0.0477	0.0006	0.6819	0.1278
	Natural Gas; Heaters	9003	Natural gas dehydrators, pneumatic devices, oil and condensate tanks	-	-	-	-	0.1387	-	-	0.0033	0.0477	0.0006	0.6819	0.1278
	Natural Gas; Compressor Engines	9003	Natural gas dehydrators, pneumatic devices, oil and condensate tanks	-	-	-	-	0.1387	-	-	0.0033	0.0477	0.0006	0.6819	0.1278
	Natural Gas;	9003	Natural gas dehydrators, pneumatic devices, oil and condensate tanks	-	-	-	-	0.1387	-	-	0.0033	0.0477	0.0006	0.6819	0.1278
	Miscellaneous Engines	9003	Natural gas dehydrators, pneumatic devices, oil and condensate tanks	-	-	-	-	0.1387	-	-	0.0033	0.0477	0.0006	0.6819	0.1278
	Natural Gas; Artificial Lift	9003	Natural gas dehydrators, pneumatic devices, oil and condensate tanks	-	-	-	-	0.1387	-	-	0.0033	0.0477	0.0006	0.6819	0.1278
	Natural Gas;	0051	Flares - Natural Gas	-	-	0.2	-	0.15	0.15	-	-	0.15	-	0.2	0.3
231003****	Natural Gas Liquids; Tank Losses; Gas Plant Truck Loading	0051	Flares - Natural Gas	-	-	0.2	-	0.15	0.15	-	-	0.15	-	0.2	0.3
2310121110	Hydraulic Fracturing Pumps	1207	Well Heads (Water Flood) Composite	0.0029	0.0028	1E-05	0.0002	0.0039	0.7547	0.0069	0.0296	0.1084	0.0373	-	0.0651
231001****	Oil well tanks - flashing & standing /working/ breathing	2487	Composite of 7 Emission Profiles from Crude Oil Storage Tanks - 1993	0.0034	0.0104	2E-05	0.0003	0.0072	0.7900	0.0082	0.0231	0.1135	0.0127	-	0.0417
WRAPIII_spc (WRAP, 2015)	Gas composition - CBM; Pneumatic Devices, Fugitives, Dehydrators, etc	UNT01	Gas composition - CMB wells	-	-	-	-	0.0030	-	-	-	2E-05	-	0.9812	0.0112
	Natural Gas; well fugitives; truck loading; Pneumatic Pumps etc	UNT02	Gas composition - conventional wells	-	0.0020	-	-	0.2174	-	-	0.0035	0.0017	0.0017	0.5470	0.1192
	Oil well heaters/tanks	UNT03	Oil well tanks - flashing & standing /working/ breathing	-	0.0034	-	-	0.8555	-	-	0.0689	0.0258	0.0430	0.0001	0.0006
	Natural Gas Liquids; Tank Losses; Gas Plant Truck Loading	UNT04	Flashing gas composition for condensate	-	0.0003	-	-	0.8608	-	-	0.0003	0.0159	0.0001	0.0318	0.0285

Data used in EPA's SPECIATE VOC speciation profiles applied for oil and gas emission sources in the Uintah Basin (i.e., Default_spc in Table 1) are derived from:

- Pro_code 0051: Flares – Natural Gas: This profile is based on composite survey data and engineering evaluation of literature data (EPA, 1980; Taback, 1978).
- Pro_code 1207: Well Heads (Water Flood) Composite: Data are from the Oklahoma Glen Sand formation, which is at a depth of 1500 feet. Nine samples were taken in stainless steel canisters and analyzed using a GC with cryogenic sample pre-concentration and flame ionization detection (EPA, 1990; Viswanath and Van Sandt, 1989).
- Pro_code 2487: Composite of 7 Emission Profiles from Crude Oil Storage Tanks – 1993: This profile was developed by normalizing emissions to equal 100% for the sum of the 55 PAMS (Photochemical Assessment Monitoring Stations) pollutants + MTBE (Methyl tertiary-butyl ether) measured (EPA, 2015a).

None of these sources include measurements of carbonyl compound emissions, so the source of the listed carbonyl speciation in the Default_spc profile is unclear. In Default_spc (Table 1), the application of flaring profiles (e.g., 0051 with ~ 20% of total VOC emissions partitioned to formaldehyde) to non-flaring oil and gas emission sources in the Uintah Basin is almost certainly incorrect.

In the Utah Bureau of Land Management's Air Resource Management Strategy (ARMS) study (Table 1), chemical speciation profiles were developed for oil and gas processes in Uintah Basin that have a notable contribution to VOC emissions—including natural gas dehydrators, pneumatic devices, and oil and condensate tanks—based on chemical composition analyses provided by Utah Department of Environment Quality (pro_code 9001, 9002, 9003 in Table 1; AECOM (2013)).

In the WRAP III study (Table 1), basin-specific VOC speciation profiles were developed based on gas composition analysis of produced gas, condensate and flashing gas obtained from operator surveys (Adelman, 2013). For the Uintah Basin, those basin-specific profiles (pro_code UNT01, 02, 03, and 04) were applied for some source categories, including blowdowns, completions and fugitive emissions. For other O&G sources in the basin, profiles from EPA's SPECIATE database were used. It is not clear whether carbonyl emissions allocated in these speciation profiles were based on actual measurements.

Pro_codes developed in the BLM-ARMS or WRAP III studies that assume zero emissions of carbonyls could lead to an underestimation of actual emissions. A top-down emission inventory for oil and gas emissions in Uintah Basin, developed from whole-basin methane emission measurements and ratios of methane to other emitted compounds measured in ambient air, showed a notable amount of formaldehyde/aldehyde emissions (Ahmadov et al., 2015), perhaps showing that neglect of carbonyl emissions in the ARMS-BLM and WRAP III Uintah Basin – specific profiles is not reasonable. On the other hand, use of ambient air carbonyl concentrations to derive emission rates likely results in the inclusion of both primarily emitted carbonyls and carbonyls that were produced secondarily in the atmosphere as primary emissions, which would result in an overestimation of real primary emissions.

5.2. Other Available Information

Several emission measurement campaigns for oil and gas processes have measured hydrocarbons, but no carbonyl emission measurements have been included. Viswanath and Van Sandt (1989) presented a comprehensive emission measurement dataset for hydrocarbons from many oil and gas field facilities in Tulsa County, Oklahoma. Hendler et al. (2009) reported measurements of hydrocarbon emissions from oil and condensate storage tanks at wellheads and gathering site tank batteries in East Texas. McKenzie et al. (2012) showed an analysis of hydrocarbon measurements conducted in Garfield County, Colorado around well-pads to estimate health risks for exposures to air emissions. Currently, emission measurement campaigns for oil and gas fields are being conducted by the Collett Research Group in Garfield County and the North Front Range, Colorado (<http://collett.atmos.colostate.edu/research-projects.html>). Again, these studies focus on hydrocarbons, but none have included measurements of carbonyls.

Ambient carbonyl concentration data have been collected at some monitoring stations located in cities in Colorado, Texas and California for health risk assessment, but are not suitable for characterizing oil and gas field emissions (Board, 2015; Eisele, 2009; Haney and Reddick, 2013). Jolly (2004) assessed the importance of carbonyl compounds in ozone formation in Houston-Galveston and found that at two of five monitoring stations in this study, formaldehyde and acetaldehyde were the two most important species contributing to total carbonyl reactivity in forming ozone. Again, these ambient monitoring data show the importance of carbonyls to air quality in oil and gas-producing areas, but are not useful for calculating the actual emission fluxes of carbonyl compounds from oil and gas production facilities. Airborne formaldehyde measurements made during the Texas Air Quality Study in 2000 indicated that formaldehyde and ozone production were more associated with petrochemical facilities, rather than power plant and mobile source emissions (Wert et al., 2003). Formaldehyde emissions were measured from burning flares and smoke stacks of large refinery and chemical manufacturing facilities in Houston and Texas City during the “Formaldehyde and Olefin from Large Industrial Sources” (FLAIR) campaign conducted in 2009 (Stutz et al., 2011). These emissions data do show that carbonyls are emitted from flares, but are probably not directly applicable to the relatively small oil and gas production facilities in Uintah Basin. Air quality research campaigns focused in the Uintah Basin collected carbonyl data during winter 2012, 2013 and 2014 at several monitoring stations to study unique radical source of ozone formation in the basin, but these data also do not constitute emissions measurements (Lyman et al., 2013; Stoeckenius et al., 2014).

AP-42, Compilation of Air Pollutant Emission Factors (EPA, 2015b), provides instruction on using the TANKS model to estimate air emissions from organic liquid storage tanks. This emission model could be applied for estimating VOC speciation emission profiles of oil/condensate storage tanks in the Uintah Basin. However, the ability of TANKS to accurately estimate carbonyl emissions is uncertain.

6. Methods

6.1. Field Measurements

We collected carbonyls with BPE-DNPH sorbent cartridges following Uchiyama et al. (2009). The first portion of the cartridge was packed with BPE-coated silica, which captures ozone and reduces sampling artifacts. The second portion of the cartridge was 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 kept DNPH cartridges refrigerated or on ice, except when installed for sampling.

We used a Class I Div 1 vacuum pump to pull sample exhaust gas from the emission source being tested and through the BPE-DNPH cartridges. Mass flow controllers regulated the flow rate through the cartridges. The sample line that connected the emission source to the cartridges was heated to 50°C with a Class I Div 1 heat trace and insulated to avoid condensation in the line. The system was connected to and housed within a small trailer and powered by a generator. The heated sample lines were 80 feet long and the generator had a 100-foot cord, allowing the generator to be well over 100 feet from any well site combustion source.

For measurements of emissions from sources with an exhaust pipe, we attached a two-inch or three-inch diameter extension pipe to the exhaust. Carbon steel and stainless steel extension pipes were used. The extension pipes were manufactured by Cameron Measurement Systems in Vernal, Utah. We inserted a thermal mass flow meter (Fox model FT3-061ESSSTE4DDMB) into this pipe to measure the total exhausted gas flow. To measure the concentration of carbonyls in the exhaust gas, we pulled a 1 L min⁻¹ subset of the extension pipe flow through the heated line and the BPE-DNPH cartridge. Flow, temperature, and other data were collected using a Campbell Scientific CR1000 data logger.

After a cartridge had been analyzed in the laboratory, we calculated the emission rate as:

$$\text{Emissions } (\mu\text{g s}^{-1}) = \text{Carbonyl Concentration in Exhaust Gas } (\mu\text{g m}^{-3}) \\ \times \text{Exhaust Gas Flow Rate } (\text{m}^3 \text{ s}^{-1}).$$

For measurements of emissions from sources without an exhaust line (e.g., leaks), or sources with an exhaust line too small to use the extension pipes (e.g., pneumatic pumps), we measured emissions via bag sampling. We used a Teflon bag to enclose the component to be measured. We flooded the bag with a constant, known flow of nitrogen. We sealed the bag around the component to be tested with adhesive tape. We pulled gas from the bag at one liter per minute through the heated line and BPE-DNPH sorbent cartridges. We measured oxygen and total combustible gas concentrations in the bag as proxies for measurement of flow into the bag due to intrusion of outside air and flow due to the leak itself. We then calculated emissions as:

$$\text{Emissions } (\mu\text{g/s}) = \text{Carbonyl Concentration in Bag } (\mu\text{g m}^{-3}) \times [\text{Nitrogen Flow Rate } (\text{m}^3 \text{ s}^{-1}) + \text{Flow Rate Due to Intrusion of Outside Air } (\text{m}^3 \text{ s}^{-1}) + \text{Flow Rate Due to the Leak Itself } (\text{m}^3 \text{ s}^{-1})]$$

Figures 1 and 2 show diagrams of the flow tube and bag sampling methods. We used a handheld natural gas detector to identify leaks or pneumatic device emissions for subsequent bag sampling.

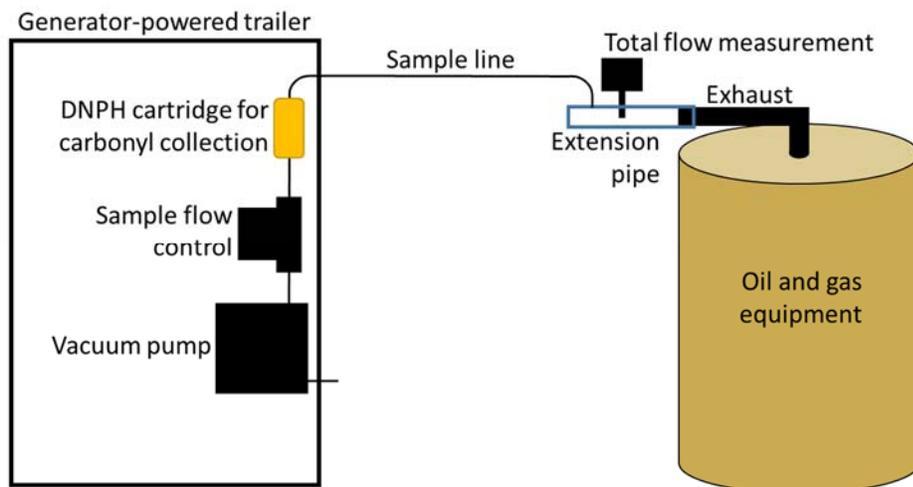


Figure 1. Diagram of flow tube measurement technique for liquid storage tanks, glycol dehydrators, or other equipment with an exhaust or vent line.

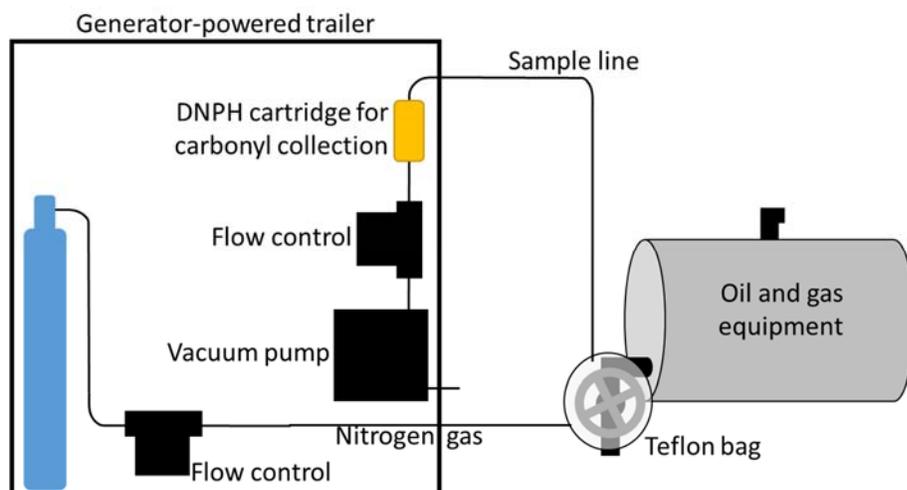


Figure 2. Diagram of bag measurement technique for pneumatic device emissions or leaks.

Each sample was collected over about 30 minutes. We collected field blanks on each day of sampling. Field blank BPE-DNPB cartridges were handled and analyzed exactly the same as normal field samples, but they were removed immediately after being connected to sampling apparatuses in the field. Before each sampling period, we checked the sampling apparatus for leaks by plugging the sample inlet with a gloved hand and ensuring that the flow rate dropped to zero. We checked flow rates indicated on flow controllers and sampling pumps against a NIST traceable standard during the study.

6.2. Laboratory Analysis

We kept BPE-DNPB cartridges refrigerated before analysis, and analyzed them within 14 days of sampling. To prepare samples for analysis, we flushed cartridges with a 5 mL solution of 75% acetonitrile and 25% dimethyl sulfoxide to release DNPB-carbonyls into solution. The solution was collected into 5 mL volumetric flasks, and we brought the flasks to a volume of 5 mL using 0.5-1 mL of the

acetonitrile/dimethyl sulfoxide solution. Finally we pipetted 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 analyzed samples using a Hewlett Packard series 1050 HPLC with a Restek Ultra AQ C18 column and a diode array detector. We used a mixture of acetonitrile and water as the eluent. We prepared standards by diluting commercially-available carbonyl-DNPH standards, and calibrated the instrument each day with a five-point calibration curve. We ran an additional standard at the beginning and end of each analysis batch to check for retention time drift or other errors.

We analyzed a laboratory blank during each laboratory analysis period. Laboratory blank cartridges were processed and analyzed just like normal samples, but were not taken to the field.

6.3. Air Quality Model Configuration

6.3.1. VOC speciation profiles for oil and gas emissions in Uintah Basin

We modified the 2005 update of the Carbon Bond V (CB05) speciation profiles for emissions from vent gas for oil tank batteries and raw gas composition at well heads based on our emission measurement data combined with hydrocarbon emission data from our literature search. In this document, we refer to this modified speciation profile as “BRC profiles.” Carbonyls compounds that we measured were grouped into three CB05 species for WRF-CAMx simulations: i) formaldehyde (FORM), ii) acetaldehyde (ALD2) and iii) and higher aldehydes (ALDX).

For the oil tank batteries emission profile, we combined carbonyl data averaged over 11 samples collected at liquid storage tanks with hydrocarbon data averaged over ten sites found in Hendler et al. (2009) for oil tank battery emissions. All data were converted to $\mu\text{g s}^{-1}$ as available in Hendler et al. (2009) before calculating the weight % for each species.

For the emission profile for raw gas at well heads, we combined carbonyl data averaged over four measurements of emissions from raw gas-powered pump jack engines with hydrocarbon data averaged over nine samples found in Viswanath and Van Sandt (1989) for well head emissions. All data were converted to $\mu\text{g m}^{-3}$ as available in Viswanath and Van Sandt (1989) before calculating weight % for each species.

We also measured carbonyl emissions at glycol dehydrators but have not found hydrocarbon emission data for similar sources in our literature search; therefore, in our modeling sensitivity tests with the BRC profiles, we only modified speciation profiles for oil tank batteries and raw gas at the well head.

We conducted sensitivity tests with different VOC speciation profile sets for oil and gas emissions in the Uintah Basin with WRF-CAMx simulations. Those profile sets included:

- Default profiles available in the EPA SPECIATE 4.3 database (EPA, 2015b)
- ARMS profiles introduced by AECOM (2013)
- WRAP Phase III profiles (WRAP, 2015)
- BRC profiles based on carbonyl measurement data and the literature search as described above.

We performed all of the test runs with listed VOC speciation profiles with the same bottom-up emission inventory (discussed in detail below) and compared them with a top-down inventory (Ahmadov et al., 2015). In the simulations utilizing the top-down inventory, only VOC oil and gas emissions in the Uintah Basin differed from the other simulations; other emission sources were identical. For simulations using BRC profiles, we kept everything same as the WRAPIII profiles except that UNT02 and UNT03 profiles were substituted by the profiles that we derived for raw gas at well heads and oil tank batteries, respectively.

Table 2. Available CB05 VOC emission speciation profiles applied for oil and gas activities in Uintah Basin, in addition to a speciation profile developed from emissions measurements collected during this study. Data are shown as split factors.

SCC	Source type	pro_code	pro_desc	ALDX	BENZENE	FORM	IOLE	OLE	PAR	TERP	TOL	UNR	XYL	CH4	ETHA	MEOH	PRPA	ALD2	
Default	Oil well tanks - Flushing & standing/work/breathing Gas well truck loading Natural Gas; Heaters Natural Gas; Compressor Engines Natural Gas; Miscellaneous Engines Natural Gas; Artificial Lift Natural Gas; Miscellaneous Engines Natural Gas Liquids; Tank Losses; Gas Plant Truck Loading Hydraulic Fracturing Pumps Oil well tanks - Flushing & standing/work/breathing	2487	Composite of 7 Emission Profiles from Crude Oil Storage Tanks - 1993	0.0034	0.0104	2E-05	0.0003	0.0072	0.7900	0.0082	0.0231	0.1135	0.0127	-	0.0417	-	-	-	
		0051	Flares - Natural Gas	-	-	0.2	-	-	0.15	-	-	-	0.15	-	0.2	0.3	-	-	-
		0051	Natural Gas; Heaters	-	-	0.2	-	-	0.15	-	-	-	0.15	-	0.2	0.3	-	-	-
		0051	Natural Gas; Compressor Engines	-	-	0.2	-	-	0.15	-	-	-	0.15	-	0.2	0.3	-	-	-
		0051	Natural Gas; Miscellaneous Engines	-	-	0.2	-	-	0.15	-	-	-	0.15	-	0.2	0.3	-	-	-
		0051	Natural Gas; Artificial Lift	-	-	0.2	-	-	0.15	-	-	-	0.15	-	0.2	0.3	-	-	-
		0051	Natural Gas; Miscellaneous Engines	-	-	0.2	-	-	0.15	-	-	-	0.15	-	0.2	0.3	-	-	-
		0051	Natural Gas Liquids; Tank Losses; Gas Plant Truck Loading	-	-	0.2	-	-	0.15	-	-	-	0.15	-	0.2	0.3	-	-	-
		1207	Well Heads (Water Flood) Composite	0.0029	0.0028	1E-05	0.0002	0.0039	0.7547	0.0069	0.0206	0.1084	0.0373	-	0.0651	-	-	-	-
		2487	Composite of 7 Emission Profiles from Crude Oil Storage Tanks - 1993	0.0034	0.0104	2E-05	0.0003	0.0072	0.7900	0.0082	0.0231	0.1135	0.0127	-	0.0417	-	-	-	-
ARMS	Oil well tanks - Flushing & standing/work/breathing Gas well truck loading Natural Gas; Heaters Natural Gas; Compressor Engines Natural Gas; Miscellaneous Engines Natural Gas; Artificial Lift Natural Gas; Miscellaneous Engines Natural Gas Liquids; Tank Losses; Gas Plant Truck Loading	9001	Natural gas dehydrators, pneumatic devices, oil and condensate tanks	-	-	-	-	-	0.9224	-	0.0219	0.0335	0.0190	0.0010	0.0023	-	-	-	
		9003	Natural gas dehydrators, pneumatic devices, oil and condensate tanks	-	-	-	-	-	0.1387	-	0.0033	0.0477	0.0006	0.6819	0.1278	-	-	-	
		9003	Natural gas dehydrators, pneumatic devices, oil and condensate tanks	-	-	-	-	-	0.1387	-	0.0033	0.0477	0.0006	0.6819	0.1278	-	-	-	
		9003	Natural gas dehydrators, pneumatic devices, oil and condensate tanks	-	-	-	-	-	0.1387	-	0.0033	0.0477	0.0006	0.6819	0.1278	-	-	-	
		9003	Natural gas dehydrators, pneumatic devices, oil and condensate tanks	-	-	-	-	-	0.1387	-	0.0033	0.0477	0.0006	0.6819	0.1278	-	-	-	
		9003	Natural gas dehydrators, pneumatic devices, oil and condensate tanks	-	-	-	-	-	0.1387	-	0.0033	0.0477	0.0006	0.6819	0.1278	-	-	-	
		9003	Natural gas dehydrators, pneumatic devices, oil and condensate tanks	-	-	-	-	-	0.1387	-	0.0033	0.0477	0.0006	0.6819	0.1278	-	-	-	
		0051	Flares - Natural Gas	-	-	0.2	-	-	0.15	-	-	-	0.15	-	0.2	0.3	-	-	-
		0051	Flares - Natural Gas	-	-	0.2	-	-	0.15	-	-	-	0.15	-	0.2	0.3	-	-	-
		1207	Well Heads (Water Flood) Composite	0.0029	0.0028	1E-05	0.0002	0.0039	0.7547	0.0069	0.0206	0.1084	0.0373	-	0.0651	-	-	-	-
2487	Composite of 7 Emission Profiles from Crude Oil Storage Tanks - 1993	0.0034	0.0104	2E-05	0.0003	0.0072	0.7900	0.0082	0.0231	0.1135	0.0127	-	0.0417	-	-	-	-		
WRAP-III	Gas composition- CBM; Pneumatic Devices, Fugitives, Dehydrators, etc Natural Gas; well fugitives, truck loading, Pneumatic Pumps etc Oil well heaters/tanks Natural Gas Liquids; Tank Losses; Gas Plant Truck Loading	UNT01	Gas composition- CMB wells	-	-	-	-	-	0.0030	-	-	2E-05	-	0.9812	0.0112	-	-	-	
		UNT02	Gas composition- conventional wells	-	0.0020	-	-	-	0.2174	-	0.0035	0.0017	0.0017	0.0017	0.5470	0.1192	2.01E-04	0.1073	
		UNT03	Oil well tanks- flashing & standing/work/breathing	-	0.0034	-	-	-	0.8555	-	0.0689	0.0258	0.0430	0.0001	0.0006	-	-	-	
		UNT04	Flashing gas composition for condensate	-	0.0003	-	-	-	0.8608	-	0.0003	0.0159	0.0001	0.0318	0.0285	-	-	-	
BRC	Gas composition- CBM; Pneumatic Devices, Fugitives, Dehydrators, etc Natural Gas; well fugitives, truck loading, Pneumatic Pumps etc Oil well heaters/tanks Natural Gas Liquids; Tank Losses; Gas Plant Truck Loading	UNT01	Gas composition- CMB wells	-	-	-	-	-	0.0030	-	-	2E-05	-	0.9812	0.0112	-	-	-	
		UNT02_BRC	Gas composition- conventional wells	2.27E-05	0.0005	5.8E-05	0.001107	-	0.2417	-	0.0009	0.0003	0.0025	0.5470	0.0508	-	0.1326967	7.9E-06	
		UNT03_BRC	Oil well tanks- flashing & standing/work/breathing	2.2E-06	0.0016	1.28E-07	0.002627	-	0.4655	-	0.0025	0.0006	0.0025	0.2216	0.0996	-	0.1985761	1.7E-06	
		UNT04	Flashing gas composition for condensate	-	0.0003	-	-	-	0.8608	-	0.0003	0.0159	0.0001	0.0318	0.0285	-	-	-	
Top-down	Source type All Oil & Gas source emission within Uintah and Duchesne	pro_code	pro_desc	ALDX	BENZENE	FORM	IOLE	OLE	PAR	TERP	TOL	UNR	XYL	CH4	ETHA	MEOH	PRPA	ALD2	
-NA-	-NA-	0.0001	0.0004	0.0005	-	0.0001	0.1774	-	0.0009	0.0306	0.0001	0.7394	0.0428	0.0068	-	0.0006			

6.3.2. Model configurations

We used WRF, CAMx, and SMOKE to model meteorology, chemistry, and emissions during 15-20 January 2013.

6.3.2.1. WRF model

We ran WRF simulations with a 12-4-1.3 km nested domain (Figure 3). We only used model results of the finest domain (1.3 km gridded resolution) for CAMx runs. Our WRF model configuration mostly followed the well-tested configurations of Neemann et al. (2015), which included: the Thompson cloud microphysics scheme (Thompson et al. (2008), unmodified), the Kain-Fritsch cumulus-ensemble scheme (Kain (2004); 12-km domain only), the treatment of long-wave and short-wave radiation based on Iacono et al. (2008), the Mellor-Yamada-Janjic scheme (Janjic, 1994) for the atmospheric boundary layer and the Noah scheme (Chen and Dudhia, 2001) for the land surface model. NAM-12km analysis data were used as initial and boundary conditions for WRF simulations. We applied analysis nudging with NAM data for air above the planetary boundary layer and nudging with MADIS data for the surface layer. The default NAM-12km initial snow field (snow depth and snow water equivalent) within the Uintah Basin and outside the basin was replaced by observational data (Neemann et al., 2015) and SNODAS 30s data (NOHRSC, 2004), respectively, to better represent initial snow cover for the entire finest domain. WRF vertical resolution was configured with 40 eta levels starting from the surface to zero hPa (Figure 3). The first layer above the ground had a thickness of 18m.

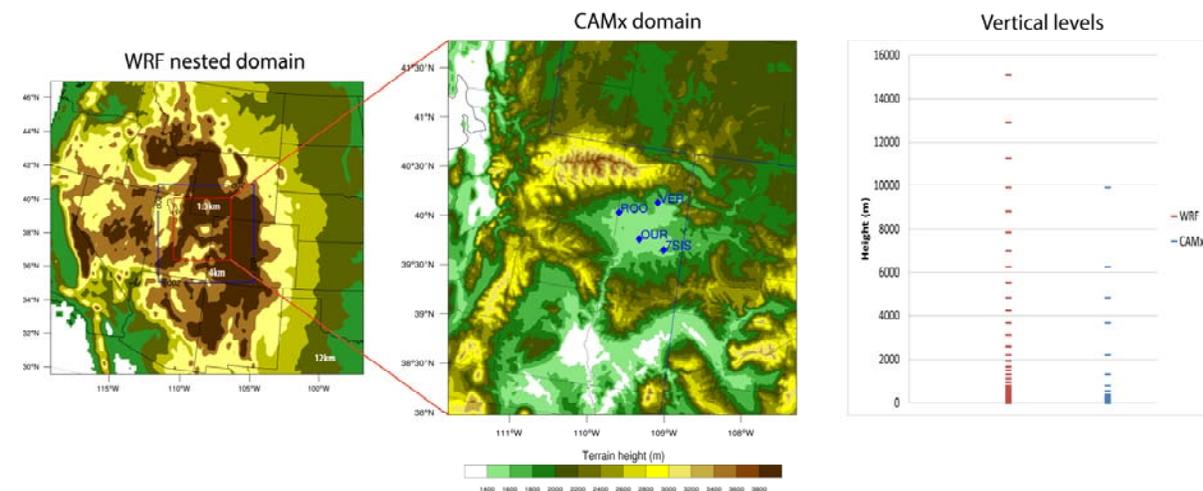


Figure 3. WRF-CAMx domain and vertical resolution configurations.

6.3.2.2. CAMx model

For chemistry simulations, we ran CAMx model version 6.1 using version 6 of Carbon Bond (CB6; Yarwood et al. (2010)) for gas-phase chemistry, Tropospheric Ultraviolet & Visible Radiation Model (TUV; NCAR (2011)) for photolysis rate calculations, the Zhang model (Zhang et al., 2003) for dry deposition, and no surface model. The 40 vertical layers of WRF runs were interpolated into 21 vertical layers of CAMx runs for computational efficiency. We kept the first 10 CAMx layers the same as the WRF layers, and expanded the 11 following CAMx layers over 30 WRF layers (Figure 3).

6.3.2.3. Emission inventories

Bottom-up emissions of most source sectors were obtained from the Utah Bureau of Land Management (BLM) inventory developed for the Air Resource Management Strategy (ARMS) modeling project (AECOM, 2013). Bonanza power plant emissions and stack parameters were obtained from the National Emission Inventory for year 2011 (2011 NEI version 1 available at <http://www.epa.gov/ttnchie1/net/2011inventory.html>). We updated the ARMS inventory, which is for base year 2010, with the 2011 NEI where appropriate. Other updates made to the ARMS inventory include extrapolating emissions from oil and gas sectors from base year 2010 to model year 2013 using scale factors derived from well counts and oil and gas production growth rate data over the three years.

We developed spatial surrogates for our 1.3 km horizontal resolution domain using ArcGIS software, employing the most updated data obtained from the Census Bureau, the Federal Emergency Management Agency, the National Land-Cover Dataset, the Utah Division of Oil, Gas and Mining, and other sources.

We processed the emission inventory through SMOKE model version 3.5. We used temporal surrogates developed by AECOM (2013) for oil and gas activities in the Uintah Basin for our simulations.

We adopted top-down emissions from Ahmadov et al. (2015) for oil and gas VOC emissions in the Uintah Basin only. This emission inventory approach was based on estimates of methane emissions derived from in situ aircraft measurements and a regression analysis for multiple VOC species relative to methane concentration measurements at the Horsepool monitoring site in the Uintah Basin.

7. Results and Discussion

7.1. Quality Control

Field blanks during the study averaged $0.1 \mu\text{g}$ per sample, which equates to an emission rate of $0.005 \pm 0.002 \mu\text{g s}^{-1}$ (mean \pm 95% confidence interval), assuming a total exhaust flow rate that is the average of exhaust flow from all measured samples. Laboratory blanks were always zero, so a confidence interval could not be calculated. Laboratory calibration spikes averaged $105 \pm 5\%$ recovery.

7.2. Measurement Results

We consistently detected emissions of carbonyls from all measured oil and gas equipment, except from equipment that vented raw natural gas. Figures 4 and 5 show that emissions from pneumatic pumps consistently yielded carbonyl emissions that were below detection. We also measured emissions from well-site building vents, where emissions within the buildings were expected to be mostly raw gas, and we failed to detect any carbonyl emissions from these sources, either. This is in spite of measurable total organic compound emissions from these sources, as indicated by our handheld natural gas detector.

Each source type measured had different carbonyl speciation in exhaust gas (Figure 4). Formaldehyde made up the majority of carbonyls emitted from pumpjack engines, while acetaldehyde was the most abundant carbonyl emitted from glycol dehydrators. Hexaldehyde, 2,5-dimethylbenzaldehyde, and

propionaldehyde were also commonly emitted from pumpjack engines. Liquid storage tanks and glycol dehydrators, on the other hand, tended to emit acrolein/acetone (acrolein and acetone were not adequately separated by our HPLC and were thus reported together), propionaldehyde, and butyraldehyde. Since carbonyl compounds have different chemical properties and different abilities to produce ozone-forming radicals, the speciation of carbonyl emissions can be expected to impact air quality.

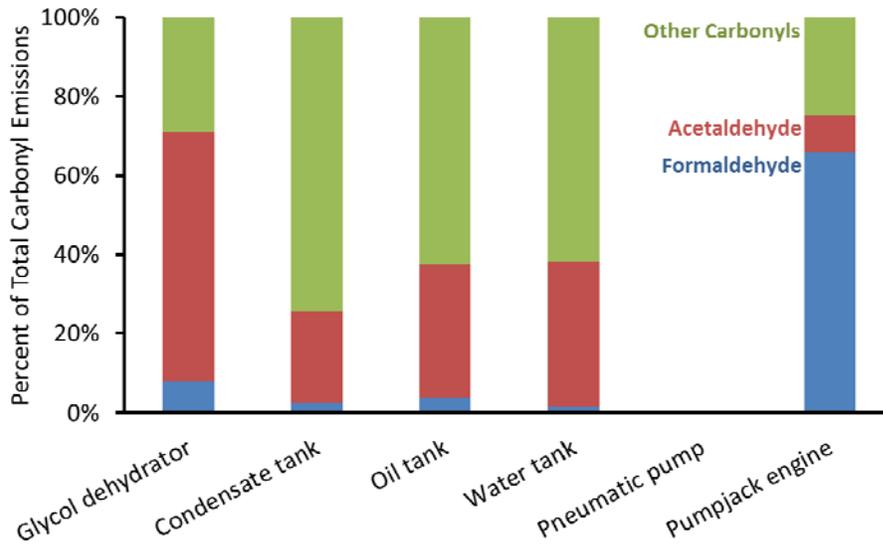


Figure 4. Speciation of carbonyl emissions from well-site oil and gas equipment.

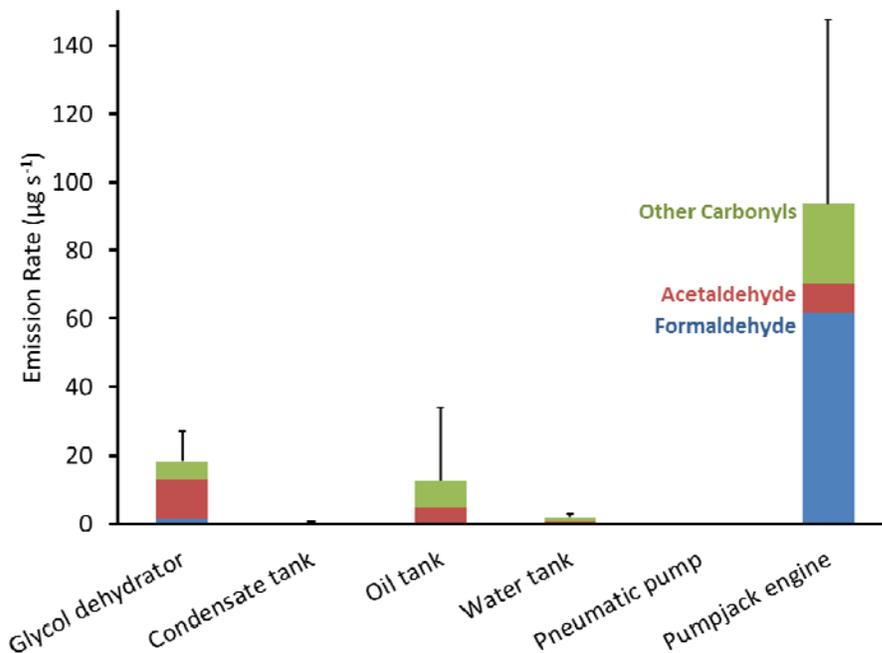


Figure 5. Carbonyl emissions from well-site oil and gas equipment. Each colored portion of each bar shows average emissions for that compound or set of compounds. The top of each bar is the average total carbonyl emissions. Whiskers represent 95% confidence intervals.

Figure 5 shows that emissions from pumpjack engines were several times greater than emissions from all other measured sources. This is due mostly to greater total exhaust flow from pumpjack engines compared to other measured sources. Figure 6 shows that concentrations of the sum of formaldehyde and acetaldehyde in exhaust gas from glycol dehydrators and pumpjack engines were similar. In other words, the amount of carbonyls per exhaust volume was similar. Exhaust flow rates from pumpjack engines were much higher than exhaust flow rates from other sources, however, leading to greater overall emissions.

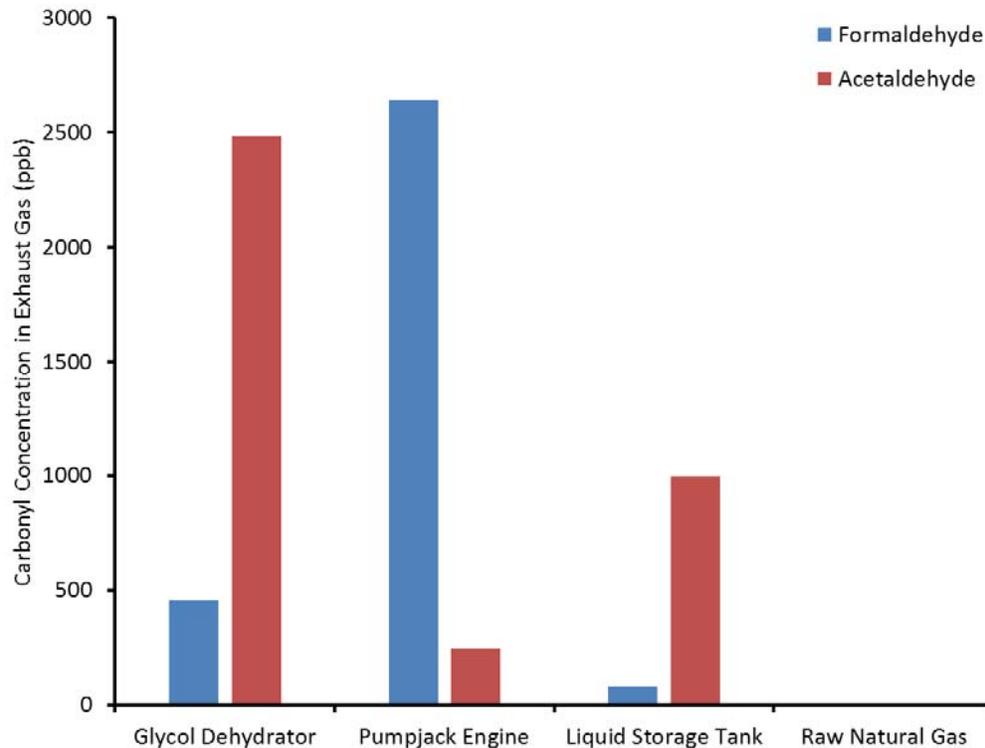


Figure 6. Concentrations of formaldehyde and acetaldehyde in exhaust gas from well-site oil and gas equipment.

Raw natural gas emissions of carbonyls were below detection, indicating that carbonyl concentrations in raw natural gas are low. Emissions from liquid storage tanks and glycol dehydrators, on the other hand, were consistently detected. Thus, carbonyls must be added to or generated by natural gas production processes, either within or prior to storage tanks and dehydrators. This study made no attempt to elucidate the source of carbonyls in these processes. Carbonyl emissions were measured from liquid storage tanks on wells where glycol, methanol, and other chemicals were added at the well head, and degradation of these chemicals may have resulted in carbonyl formation. Carbonyl emissions were also measured from storage tanks where chemicals were not added at the well head or at any point prior to the storage tank, however, indicating that other processes can produce carbonyls.

It is not clear from this study which of the measured equipment types is responsible for the most carbonyl emissions throughout the entire Uintah Basin. Pumpjack engines emitted more carbonyls on a per-unit basis, but the number of units in the Basin is not known with certainty. If there are many more liquid storage tanks in the Basin than pumpjack engines, liquid storage tanks may contribute more carbonyls to the atmosphere even though their per-unit emissions are much lower. Better information about the number and location of each equipment type in the Basin is needed to accurately assess the overall importance of each type of equipment measured.

This project was carried out with logistical support from several oil and gas companies. We collected measurements in cooperation with and according to the safety and logistical requirements of these companies. Because of this, measurements at some sites were collected differently than others. For some condensate tanks, a 60-foot polymer line was attached to the end of the tank exhaust, and we measured carbonyl emissions from the downstream end of this line. We suspect the use of this line may have resulted in the loss of some carbonyls. Figure 7 shows that emissions from condensate tanks utilizing a downstream polymer line were lower than condensate tanks overall, though it is not certain whether this was due to differences in actual emissions or interferences created by use of the polymer line.

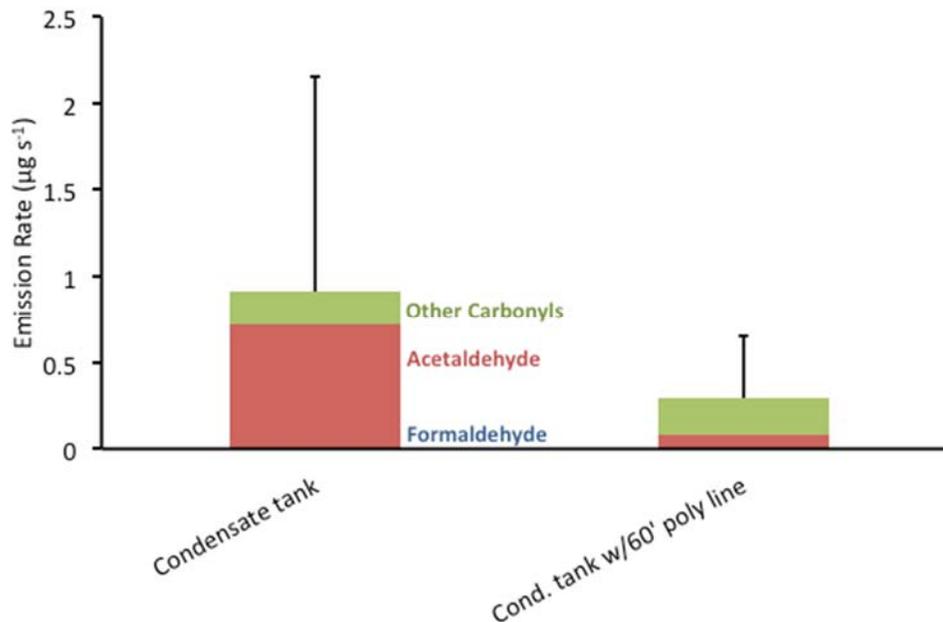


Figure 7. Carbonyl emissions from normally-operated condensate tanks, and from condensate tanks that incorporated a 60-foot polymer line between the normal tank exhaust location and the location of exhaust measurement. Each colored portion of each bar shows average emissions for that compound or set of compounds. The top of each bar is the average total carbonyl emissions. Whiskers represent 95% confidence intervals.

Exhaust from liquid storage tanks operated by different companies was plumbed differently, forcing us to adapt our emissions measurement system to fit different configurations. In some cases, we measured emissions from liquid storage tanks after a pressure-relief valve that kept the tank at a pressure greater than ambient. In other cases, we bypassed pressure-relief valves and measured emissions without them. Figure 8 shows the results of a test wherein we measured emissions from two tanks, once at each tank when the pressure relief valve was in place and once when it had been bypassed. Bypassing the pressure relief valve did result in higher carbonyl emissions, but the difference was not statistically significant.

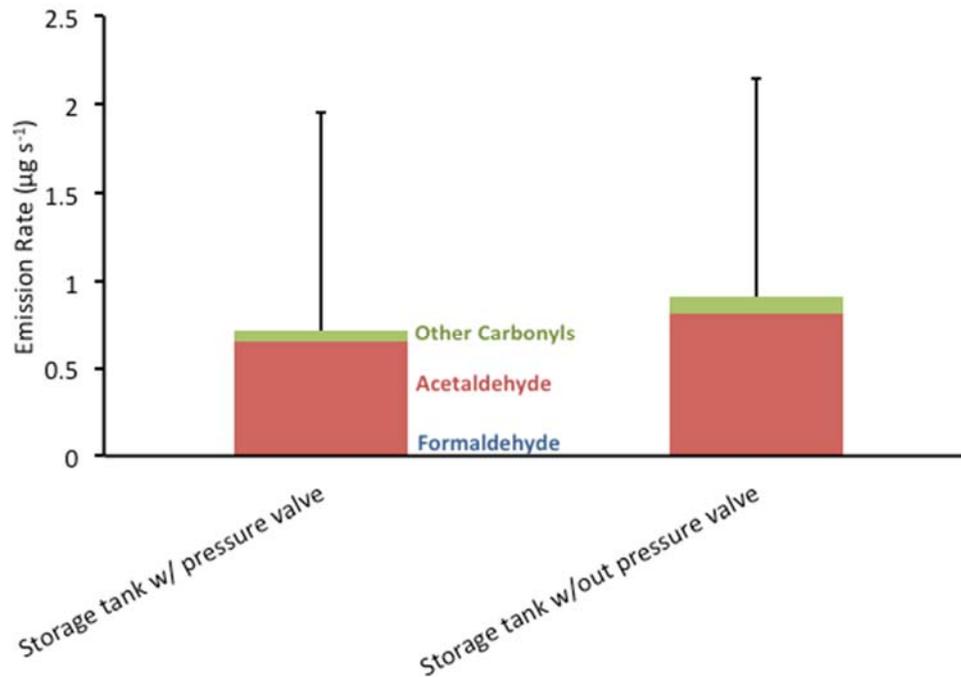


Figure 8. Carbonyl emissions from two liquid storage tanks that incorporated a pressure-relief valve, and from the same two storage tanks, but with the pressure-relief valve bypassed during measurements. Each colored portion of each bar shows average emissions for that compound or set of compounds. The top of each bar is the average total carbonyl emissions. Whiskers represent 95% confidence intervals.

7.3. Limitations of Measurements

Very few measurements of carbonyl emissions from oil and gas sources have been made before this study, and this study provides much-needed information to understand the sources of carbonyls during Uintah Basin winters. Measurements collected in this study have a number of limitations, however:

- While measurements were collected from well sites belonging to several different companies, the total number of measurements was few. This study included 11 glycol dehydrator measurements, 12 condensate tank measurements, 5 oil tank measurements, 6 water tank measurements, 8 raw gas measurements, and 4 pumpjack engine measurements. More measurements from more pieces of equipment are needed to confirm the results obtained in this study. Figure 5 shows that 95% confidence intervals for emissions measurements were large relative to average emission rates. This is partly because the equipment measured exhibited substantial variability, but it is also because the number of measurements was small. More measurements will result in greater confidence in average emission rates.
- Measurements were collected only from well-site equipment. No measurements of emissions from other equipment, such as compressor stations, midstream glycol dehydrators, gas processing facilities, oil and gas waste disposal facilities, etc., have been collected. We also did not measure emissions from well-site burners and heaters. Carbonyl emissions from these sources are completely uncharacterized, and the emission rates we measured may not be representative of emissions from these sources.

- Measurements were collected of carbonyl compounds only. To apply these measurements to VOC speciation profiles needed for air quality modeling, we must assume non-carbonyl organic compound emissions from these facilities are similar to those measured in other studies. Also, measurements of alcohols were not collected, and are needed because alcohols may degrade into carbonyls in the atmosphere.

7.4. Application of Measurement Results in an Air Quality Model

Our analysis focused on the Ouray and Seven Sisters sites, which are close to oil and gas activities, so we could see the more obvious effects of VOC speciation profiles on ozone concentrations.

At both sites, the model run that used the default speciation profiles (Table 2) yielded the highest ozone concentrations (Figure 9). These profiles apply a flaring profile, which speciates 20% of total VOC into formaldehyde, to non-flaring source categories, and we surmise that the high formaldehyde emissions generated by these profiles leads to higher ozone. The remaining runs strongly underestimated ozone concentrations, especially by the end of the studied episode when observed ozone started to build up (Figure 9). Although ozone predicted by the model run that utilized the default speciation profile agreed better with the observed data, we hypothesize that it was “right for the wrong reason,” especially given the application of a flaring speciation profile to non-flaring emission sources.

The runs utilizing the WRAP-III and BRC profiles yielded almost same results (Figure 4) although the UNT02 and UNT03 significantly differed from UNT02-BRC and UNT03-BRC, respectively, on most of the modeled species (Table 2). The two profiles agreed well, however, in that the carbonyl emissions of both were very low compared with hydrocarbon emissions. The model run that utilized the ARMS profiles predicted higher O₃ concentration compared to the WRAP-III and BRC runs. This is likely due to the fact that some of the non-flaring emission sources were still inappropriately assigned with a flaring profile in the ARMS profiles (Table 2).

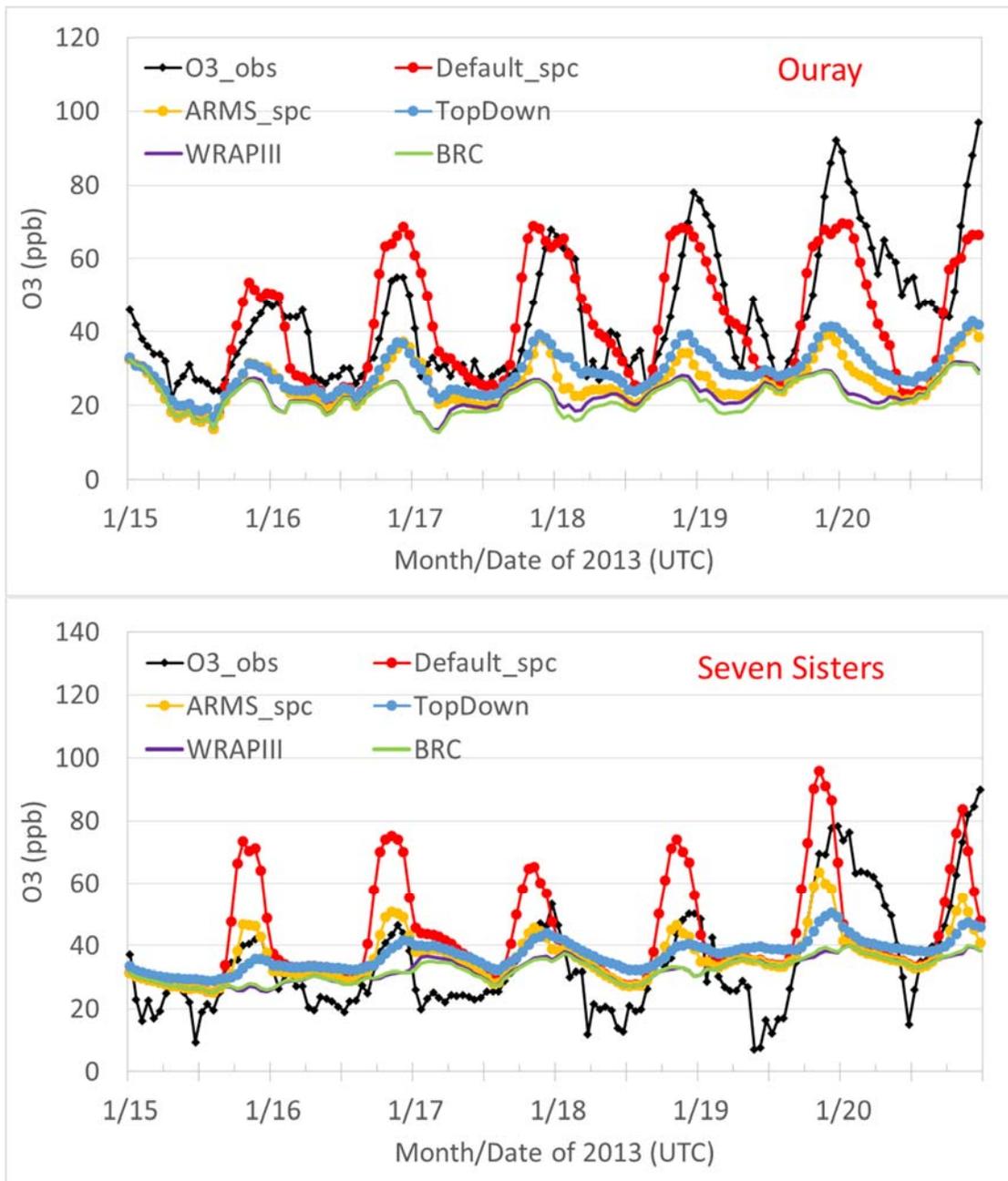


Figure 9. Temporal evolution of simulated and observed ozone concentration at Ouray (top) and Seven Sisters (bottom). Ozone concentrations were produced by CAMx simulations that were identical except that they utilized different emissions inventories. Default_spc, ARMS_spc, WRAPIII, and BRC utilized the same bottom-up inventory, but allocated VOC emissions with different speciation profiles. TopDown utilized the VOC emissions inventory developed by Ahmadov et al. (2015). Information about each profile is given in Table 2 and the text. O3_obs indicates ozone observations at the two sites.

The model run that utilized emissions from Ahmadov et al. (2015) yielded higher ozone than the WRAP-III and BRC runs, possibly because of higher formaldehyde emissions. Total formaldehyde emissions from oil and gas activities over the entire Uintah Basin are about 268 ton/yr according to the inventory that utilized the WRAPIII speciation profiles and are 576 ton/yr in the Ahmadov et al. (2015) inventory.

Since formaldehyde emissions in the latter inventory were derived based on the regression of ambient air formaldehyde with methane concentrations collected at a monitoring site, we believe carbonyl emissions in this inventory include both primarily emitted carbonyls and carbonyls that were actually produced secondarily in the atmosphere. In other words, the Ahmadov et al. (2015) inventory likely incorrectly categorizes secondary carbonyl production as primary carbonyl emissions, resulting in an overestimate of actual emissions.

Because of the obvious inaccuracies in the default speciation profiles (discussed above), and the fact that our own measurement results match low-carbonyl profiles best, we feel that use of the default profiles is inappropriate. Model runs utilizing the default profiles probably better match observed high ozone because the extra formaldehyde generated by the default profiles compensates for other deficiencies in the model that are preventing ozone buildup. Any of a number of model deficiencies could be confounding our results with low-carbonyl profiles and leading to low modeled ozone. These could include an overestimation of NO_x, which could lead to too much nighttime NO_x titration, meteorological errors that lead to too much dilution of generated ozone and precursors, not enough total VOC emissions or alcohol emissions, or other factors.

8. Conclusions

Carbonyls are emitted from combustion-related and non-combustion equipment used by the oil and gas industry in the Uintah Basin. The processes by which carbonyls are added to or generated within non-combustion equipment are not clear. Emissions of carbonyls from all of measured equipment types are low, and emissions inventories that incorporate our emissions measurement results are not able to simulate observed high wintertime ozone. The following additional work is suggested:

- More measurements of carbonyl emissions. Additional measurements are needed from the same types of equipment measured in this study to confirm this study's results. Measurements from additional sources are also needed, including but not limited to compressor stations, midstream glycol dehydrators, gas processing facilities, oil and gas waste disposal facilities, heaters, burners, and flares. Measurements of speciated hydrocarbon emissions and alcohol emissions should be made simultaneously with carbonyl emissions measurements.
- Additional verification of air quality models used to simulate wintertime ozone production. Current models may be unable to simulate high ozone during winter inversions because of other model inadequacies, rather than because of incorrect carbonyl emissions. Specific tasks could include:
 - Verification that meteorological simulations accurately simulate the vertical and horizontal structure of inversions, including air transport within the inversion and transport of clean air into the inversion. Verification of other meteorological phenomena simulated by models could also be pursued, such as cloud cover.
 - Comparison of modeled ambient air concentrations of a number of key chemicals with measurements from many sites within the Basin, rather than just the Horsepool site. Comparisons of measured and modeled concentrations of carbonyls, hydrocarbons, and reactive nitrogen compounds would provide a wealth of information to help determine whether models are accurately simulating emissions and chemistry.

9. Final Dataset

A final dataset of collected measurement data, in Microsoft Excel format, is available with this report. Please contact Seth Lyman at seth.lyman@usu.edu to obtain a copy of the final dataset.

10. Acknowledgements

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