Characterizing Air Emissions from Natural Gas Drilling and Well Completion Operations in Garfield County, Colorado

a proposal from

Colorado State University
Prof. Jeffrey L. Collett, Jr., PI (collett@atmos.colostate.edu; 970-491-8697)
Prof. Jay Ham, co-PI

Project period: 8/1/2012 – 7/31/2015

Project Budget: $1,763,218

July 27, 2012

1. Introduction

Recent and ongoing technological improvements, including directional drilling and hydraulic fracturing, have yielded large increases in economically recoverable natural gas resources in the U.S. One area experiencing rapid growth in natural gas development is Garfield County, Colorado.   In order to evaluate potential impacts of air emissions from natural gas development in the region, it is first necessary to determine the quantity and composition of emissions from the various phases of well development. That is the purpose of the work proposed here, which brings together a team of leading U.S. air quality researchers to experimentally determine air emissions from typical well drilling and completion activities in the region.

Natural gas development includes both well development and production phases. The focus of this project is characterization of emissions from well development. Well development includes pad preparation, well drilling, and well completion activities. Previous analyses suggest that the greatest air emissions are likely associated with well completion activities, which include hydraulic fracturing ("fracking") and flowback phases. During the fracking process, water, sand, and various chemicals are injected into a drilled well to aid the release of natural gas. The fracking process is followed by a period of flowback, where injected water and chemicals flow back to the surface along with well condensate (a mix of liquid hydrocarbons) and natural gas.

A variety of pollutants can be released to the atmosphere as part of well development activities. Included are the so-called BTEX compounds (benzene, toluene, ethylbenzene, and xylenes), along with a wide variety of other volatile hydrocarbons. Together with methane, these compounds comprise a complex mix of volatile organic compounds (VOC).   Other emissions of interest include nitrogen oxides (NO_x), which can also be produced through local traffic and power generation activities.

The primary focus of the proposed work is the characterization of VOC emissions from various stages of well development. VOC emissions will be characterized both with respect to their composition and their mass emission fluxes.   Planned VOC speciation efforts include a combination of on-line and off-line measurement techniques to provide valuable observations of temporal and spatial variability of speciated VOC concentrations downwind of emission sources. VOC mass emission fluxes will also be characterized using on-line and off-line approaches.

In order to better constrain emission fluxes in the complex terrain and meteorology found in Garfield County, two complementary measurement approaches will be utilized. The primary approach involves

the release of a gaseous tracer (e.g., C_2H_2, acetylene) from the source accompanied by downwind measurements of the ambient concentration ratios of methane and individual VOCs to the tracer. This method eliminates the need to capture the full emissions plume, providing improved accuracy of emissions characterization. The second approach to characterizing emissions utilizes a combination of meteorological measurements coupled with upwind and downwind VOC concentration measurements. An inverse model is then used to estimate what emission rates would have been necessary to produce the observed downwind concentrations under the measured meteorological conditions. This method provides an independent check on emissions fluxes determined by the tracer approach. Once fluxes have been accurately quantified, a larger scale dispersion model (forward mode simulation) can be used to predict the trajectory and concentration maps of VOCs the downwind plume. Because emissions determined by the tracer method do not involve the use of a dispersion model, we are able to make use of those emissions fluxes and ambient VOC concentrations to test the ability of dispersion models to accurately predict downwind transport and dispersion of emitted pollutants.

Along with the planned VOC emissions characterization, we also plan to make complementary measurements of other key gas phase compounds. Emissions of methane (CH_4), an important greenhouse gas, will be characterized. The interactions of VOCs, NO_x, and sunlight in the atmosphere are the primary determinants of atmospheric ozone levels. NO_x will therefore be quantified in the experiments to provide a basis for possible future efforts to model impacts of natural gas development activities on regional ozone concentrations. Carbon monoxide (CO) will also be measured to help assess periods where combustion sources are potentially important contributors to measured VOC concentrations. The NO_x and CO measurements represent relatively low cost, but high value additions to the planned study.

While the proposed work does not directly consider potential health impacts of emissions associated with natural gas well development, the speciated emission fluxes quantified in the study and the dispersion of those emissions (both modeled and observed) will provide a solid basis for other investigators to make a robust health impact assessment. Likewise, study findings will be valuable inputs to future studies of potential impacts of well development on regional scale ozone formation.

2. <u>Measurement approach</u>

The goals of the proposed measurements are two-fold: 1) quantify the emissions of different chemical compounds (especially VOCs) during well development operations, and 2) characterize how these compounds are dispersed in the atmosphere in the downwind plume near the site. A conservative tracer will be released from the site to quantify emissions by use of a tracer ratio method (see below). These emissions will then be used in numerical simulations of atmospheric dispersion to predict concentration fields of species of interest downwind of the source. Measurements of species concentrations upwind and downwind of the source will also be used, in an inverse modeling approach, to independently determine emission fluxes of those compounds.

2.1 Quantifying Emissions with the Tracer Ratio Method

Emissions (mass released per unit time) will be measured using a modified version of the *tracer ratio method* described by Lamb et al. (1995). The tracer ratio technique has been used to quantify emissions from a variety of sources at landfills, urban sites, and agricultural operations. The tracer ratio method is well suited for isolated sites with unsteady emission rates and complex surrounding terrain. The approach is straightforward in principle; a gaseous tracer is released at a known rate, Q_T, at the source location (i.e., drilling pad, or centralized fracking station), then air samples are collected at

multiple sites in the plume (typically 50 to 500 m downwind). Where feasible, VOC sample canisters will also be collected at prescribed setback distances to provide additional validation of dispersion model performance over policy-relevant spatial scales. Subsequent analysis of the air samples provides the concentration of the tracer, C_T, and the concentrations of other compounds, (C_i, C_i, C_k, …) that were released in the same plume (e.g., individual VOCs, CH_4, etc.). Because the release rate of the tracer is known, the emission rate of the other compounds (Q_i, Q_j, Q_k, …) can be determined from the ratio of the two compounds,

$$\quad\quad \text{—} \quad\quad\quad \text{—} \quad\quad\quad \text{—} \quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad (1)$$

In practice, obtaining these data takes a considerable field effort because the direction and shape of the plume changes rapidly with meteorological conditions (especially wind speed and direction). Thus, supporting measurements are needed to determine the geometry of the downwind plume so real-time monitoring equipment and air sampling canisters can be properly positioned. A diagram of the basic sampling approach given in Lamb et al. (1995) is reprinted here.
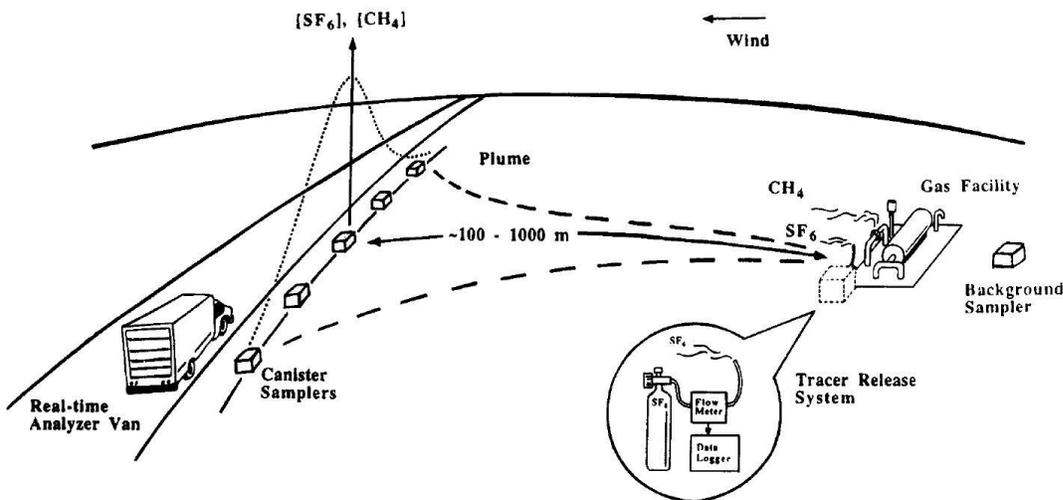

FIGURE 1. Schematic of the tracer ratio emission measurement method showing the tracer release at the source of interest, the use of the mobile analyzers to locate and sample the methane/tracer plumes, and the deployment of canister samplers for upwind and downwind measurements.

Figure 1. Schematic of the tracer ratio emission measurement method from Lamb et al. (1995). The proposed work would add additional field measurement systems to this configuration to enhance capabilities and quality assurance.

2.2 Adapting the Tracer Ratio Method for Garfield County Gas Sites

Once a site has been chosen for measurement, a 15-m crank-up meteorological (met) tower and a suite of 3 m surface met stations will be deployed downwind of the facility to obtain real-time atmospheric conditions. The tower will include two 3D sonic anemometers for measuring friction velocity and the Monin-Obhukov length (a measure of boundary layer stability). Sensitivity analysis shows that these are the two most important parameters affecting any type of near field modeling, especially the inverse modeling of emissions. Met observations also will provide inputs to a local scale dispersion model that will predict the current plume trajectory and extent. Once the operation of interest is underway, the C_2H_2 tracer will be released close to the source of the emissions. A 4WD vehicle carrying real-time C_2H_2,

methane, and total VOC analyzers will traverse the potential sample area (as predicted with a plume forecast model) to determine the actual location of the downwind plume.

A series of sampling canisters (up to 20, depending on the experiment) will then be deployed on 2m tripods along sampling transects in the plume at distances ranging from 50 to 800 m downwind depending on the terrain, with a few canisters deployed in very close proximity to the emission source (e.g., condensate tank vent) and a few very near the location of a mobile laboratory where continuous measurements are conducted. The canisters will be equipped with solenoid valves controlled by a wireless sensor network. Thus, the canisters will not start sampling immediately but be "armed" so they can start sampling on command.

At a location near the center of the plume, remotely-actuated sampling canisters will be deployed at 2, 5, and 12 m on the crank-up tower to obtain vertical concentration profiles. A subset of the tripods will also be equipped with cartridge samplers for carbonyls sampling. A mobile laboratory with a suite of real-time analyzers (PTR-MS system for VOC speciation, methane/non-methane hydrocarbon analyzer, NO_x analyzer, CO analyzer) will also be parked in the plume to obtain real-time information on multiple compounds. Upwind canister samplers will also be deployed to determine local background conditions. Additionally, a few days before the start of a specific operation and experiment, a few canister samples will be manually collected to assess the background concentrations of VOCs in the area near the operation before the start of the activities.

Using data from the meteorological tower, the mobile laboratory truck, and the C_2H_2 tracer analyzer on the plume-tracking vehicle, the field team will determine when conditions are optimal and activate canister and cartridge sampling using the wireless sensor network. This whole process (plume characterization, canister and mobile lab deployment, and sampling) will be repeated multiple times during an experiment to capture the temporal variation in emissions. After each canister sampling period is completed (e.g., 15 to 60 min) the canisters will be retrieved and returned to the laboratory for chemical analysis and the calculation of emissions (Q_i, Q_j, Q_k, … , Eq. 1).

To provide additional quality assurance on the plume location, trajectory, and characteristics; a fast response open-path CH_4 analyzer (Li-Cor 7700) will be deployed on the 15m crank up tower. This will help verify if the tower is in the plume as well as quantify temporal variation CH_4 concentrations (data are collected at 20Hz). The 3D sonic anemometers and open path CH_4 analyzer will help quantify the degree of stationarity in the surface boundary layer and help determine when the canisters should be opened for sampling. The combination of spatial coverage provided by the canisters and continuous measurements from the mobile lab, plume mapping vehicle, and open-path CH_4 analyzer will provide powerful tools for accurately and continuously characterizing emissions throughout specific well development activity periods.

2.3 Dispersion Modeling

Data from the field experiments will also be used as inputs to dispersion models of atmospheric transport. These models can estimate emissions when used in inverse "backward" mode or predict the extent of downwind transport in normal "forward" mode. Inverse dispersion models can be used to infer emissions at the source based on concentration data collected at multiple points downwind (i.e., the canister sampling points). Thus, the concentration data from the field experiments will be used in both three-dimensional Gaussian and Backward Lagrangian stochastic (BLs) inverse models to estimate emissions (Q_i, Q_j, Q_k, …). These emission measurements will be independent of the tracer ratio estimates, because the tracer concentration data will not be used. Thus, emissions determined from the

inverse modeling approach will be compared to the tracer ratio technique as a form of quality assurance.

Once the emissions rates of the different compounds have been quantified, it will be possible to estimate the extent of the downwind transport using dispersion models operating in the normal "forward" mode. Local scale transport (e.g., 1 to 4 km) will be estimated using the same three-dimensional Gaussian models used for inverse modeling along with emissions fluxes determined from the tracer method. Data from the forward mode simulations will provide maps of chemical concentration as a function of distance from the source. This could be very useful in examining the suitability of setback requirements. By including some samples at distances corresponding to current setback requirements, we will have both numerical simulations and direct observations of VOC concentrations at that distance.

The forward simulations also will quantify how transport is affected by weather conditions and variations in local terrain. Results could help determine what type of meteorological conditions should be avoided when working in close proximity to populated areas. The sensitivity of the model to different inputs and the resultant level of uncertainty will be evaluated using MonteCarlo methods (Loubet et al., 2010). It should be noted that Jay Ham, co-PI on this proposal, is actively cooperating with Drs. Lamb and Loubet on other research projects. The expertise of these scientists will be consulted when making measurement and modeling decisions regarding the proposed work.

Because the proposed work is focused on emissions measurement, the modeling effort will be limited to the local scale (i.e., within a few km of the site). However, the results obtained from this work are also suitable for use in regional models to predict transport over larger areas (e.g., county or multi-county scale) using more traditional air quality dispersion models (e.g., AERMOD, CALPUFF) or regional scale chemical transport models (e.g., CMAQ, WRF-CHEM).

2.4 Measurement platforms

As described above, several measurement platforms are planned for inclusion in the planned experiments. These include a 15 m meteorological and sampling tower, a 4WD vehicle equipped for plume mapping, a mobile lab that can be parked in the plume for more sophisticated on-line characterization of emitted pollutants, and a suite of field-deployable canisters and cartridge samplers for VOC, carbonyls, and tracer sampling across the region of expected plume impact. Table 1 lists these measurement platforms and the instrumentation to be deployed as part of each package.

Table 1. Field deployment measurement systems

Meteorology and sampling tower	4WD plume mapping vehicle	CSU Mobile Lab	Other
Tower trailer with crank-up 15 m met tower including two 3D sonic anemometers and basic meteorological sensors	Fast instrument for simultaneous, real-time measurements of C_2H_2 tracer and CH_4 (Picarro, CRD)	On-line PTR-MS system for real-time VOC speciation	20 tripod-deployable, remotely actuated VOC sampling canisters
Real-time CH_4 analyzer deployed on met tower (LI-COR 7700)	Vertically adjustable inlet for CH_4 and C_2H_2 sampling up to 10 m	NO_x and CO analyzers	Cartridge samplers to be deployed on a subset of tripods for carbonyls measurement

Mounting positions (3 heights) on 15 m tower for remotely actuated VOC sample canisters	Real-time total VOC analyzer (ppbRAE)	CH_4/non-methane hydrocarbon analyzer (FID)	
Tripod deployable 3 m met stations (3) with basic wind speed, wind direction, and meteorological sensors	GPS and data acquisition	Gas calibration and data acquisition	

2.5 Chemical Measurements

Canister samples will be collected upwind, near the emission source and downwind in-plume for measurement of speciated VOCs. Most will be deployed on 2-m tripods, but several canisters will also be deployed on the 15-m crank-up tower to document vertical VOC concentration profiles. The standard canister chemical analysis approach will include analysis of ozone precursors. This method, adopted by Garfield County in 2008 for ambient VOC speciation, is well suited to characterizing a wide range of VOCs important for ozone production as well as those air toxic compounds (including BTEX) suggested in previous measurements to be most abundant in the vicinity of natural gas extraction operations. The method used for this analysis is similar to EPA method TO-12, with the addition of a gas chromatograph (GC) for the speciation of VOCs. A similar approach has been described in USEPA (1998). A list of compounds to be quantified by this approach is given in Table 2. EPA Method TO-15, designed for air toxics analysis, will also be used for the analysis of approximately 20% of collected canisters, focusing on those with the highest VOC concentrations from each experiment. The suite of VOCs to be analyzed by method TO-15 is described in Table 3. While most expected air toxic VOCs are anticipated to be among those speciated with the ozone precursor analysis, inclusion of the TO-15 analysis will ensure we are not overlooking other important VOC air toxics not previously identified as major emissions from regional gas operations. Canister VOC analyses will be completed using a Hewlett-Packard GC/MS-FID system in the CSU Atmospheric Chemistry analytical laboratory. Atmospheric carbonyl concentrations will be determined by sampling onto DNPH-coated cartridges followed by elution and analysis (EPA Method TO-11a) using an Agilent HPLC system equipped with absorbance and mass spectrometric detectors. In addition to the standard TO-11a carbonyls suite, we will also look for the presence of glutaraldehyde which is sometimes used in fracking and other well applications as a biocide. A list of carbonyls slated for HPLC analysis is given in Table 4. The use of mass spectrometry (MS) in HPLC and GC analyses will improve the confidence of identified compounds and provide improved capability for identification of unknown emissions.

Table 2. List of target ozone precursor VOCs (modified from EPA, 1998)

Compound Name	Compound Name	Compound Name	Compound Name
Ethylene	*trans*-2-Pentene	2,3-Dimethylpentane	*n*-Nonane
Acetylene	*cis*-2-Pentene	3-Methylhexane	Isopropylbenzene (cumene)
Ethane	2,2-Dimethylbutane	2,2,4-Trimethylpentane (isooctane)	*n*-Propylbenzene
Propylene	Cyclopentane	*n*-Heptane	*m*-Ethyltoluene (1-ethyl-3-methylbenzene)
Propane	2,3-Dimethylbutane	Methylcyclohexane	*p*-Ethyltoluene (1-ethyl-4-methylbenzene)

Isobutane	2-Methylpentane	2,3,4-Trimethylpentane	1,3,5-Trimethylbenzene
1-Butene	3-Methylpentane	Toluene	*o*-Ethyltoluene (1-ethyl-2-methylbenzene)
n-Butane	1-Hexene	2-Methylheptane	1,2,4-Trimethylbenzene
trans-2-Butene	*n*-Hexane	3-Methylheptane	*n*-Decane
cis-2-Butene	Methylcyclopentane	*n*-Octane	1,2,3-Trimethylbenzene
Isopentane	2,4-Dimethylpentane	Ethylbenzene	*m*-Diethylbenzene
1-Pentene	Benzene	*m/p*-Xylene	*p*-Diethylbenzene
n-Pentane	Cyclohexane	Styrene	*n*-Undecane
Isoprene (2-methyl-1,3-butadiene)	2-Methylhexane	*o*-Xylene	*n*-Dodecane

Table 3. List of target air toxic VOCs (modified from EPA method TO-15)

Compound Name	Compound Name	Compound Name
Propene	1,1-Dichloroethane	4-Methyl-2-pentanone
Dichlorodifluoromethane	Vinyl acetate	cis-1,3-Dichloropropene
Chloromethane	2-Butanone	trans-1,3-Dichloropropene
Dichlorotetrafluoroethane	n-Hexane	Toluene
Acetaldehyde	cis-1,2-Dichloroethene	1,1,2-Trichloroethane
Vinyl chloride	Ethyl acetate	2-Hexanone
1,3-Butadiene	Bromochloromethane	Dibromochloromethane
Bromomethane	Chloroform	Tetrachloroethene
Chloroethane	Tetrahydofuran	1,2-Dibromoethane
Bromoethene	1,1,1-Trichloroethane	Chlrorobenzene
Trichlorofluoromethane	1,2-Dichloroethane	Ethylbenzene
Acetone	Benzene	m&p-Xylenes
Propanal	Carbon tetrachloride	Styrene
Isopropyl alcohol	Cyclohexane	o-Xylene
1,1-Dichloroethene	1,4-Difluorbenzene	Bromoform
1,1,2-Trichloro-1,2-2-trifluoroethane	2,2,4-Trimethylpentane	1,1,2,2,-Tetrachloroethane
Methylene chloride	n-Heptane	4-Bromomofluorobenzene
3-Chloro-1-propene	Trichloroethene	4-Ethyltoluene
Carbon disulfide	1,2-Dichloropropane	1,3,5-Trimethylbenzene
trans-1,2-dichloroethene	1,4-Dioxane	1,2,4-Trimethylbenzene
tert-Butyl methyl ether	Bromodichloromethane	Benzyl chloride
Propene	1,1-Dichloroethane	4-Methyl-2-pentanone
Dichlorodifluoromethane	Vinyl acetate	cis-1,3-Dichloropropene
Chloromethane	2-Butanone	trans-1,3-Dichloropropene

Table 4. List of target carbonyls to be measured (modified from EPA Method TO-11a)

Compound Name	Compound Name	Compound Name
Formaldehyde	Acetaldehyde	Acetone
Propionaldehyde	Butyr/Isobutyraldehyde	Benzaldehyde
Isovaleraldehyde	Valeraldehyde	*o*-Tolualdehyde
m-Tolualdehyde	*p*-Tolualdehyde	Hexaldehyde
2,5-Dimethylbenzaldehyde	Glutaraldehyde	

Because both operational emissions and meteorology can vary strongly in time, real-time measurement techniques are critical to documenting variability between the "snapshots" provided by the canister and

cartridge measurements. A variety of instruments are included in the field deployment package to document this variability.

A Proton Transfer Reaction – Mass Spectrometer (PTR-MS) system will be deployed in the CSU mobile lab to characterize temporal variability in a wide variety of VOC concentrations. A quadrupole PTR-MS system (Ionicon, Model HS-PTR-QMS 500) will be used in the study, due to its simplicity of operation, fast time response (100 ms) and suitability for trace level analysis (MDL ~ 5 pptv). The PTR-MS system will measure, in real time, ambient concentrations of a wide variety of VOC compounds, including many of particular interest in the study such as BTEX, a variety of carbonyls and ketones, and polycyclic aromatic hydrocarbons (PAH). A partial list of compounds to be measured by PTR-MS is summarized in Table 5. While the PTR-MS does not measure all VOCs of interest, ratios of VOC concentrations obtained from the canister measurements can be used with PTR-MS observations to construct surrogate timelines of concentration variability for the full suite of VOCs characterized in canister samples.

Table 5. List (partial) of VOCs measured continuously by PTR-MS (modified from http://www.certech.be/files/FileLibraryFile.php?ID=4882)

Type of Compound	Examples
Alkanes	Octane, Decane
Cycloalkanes	Cyclopropane, Cyclopentane, Cyclohexene, 1,3-Butadiene
Alkenes	Propylene (Ethylene measurable with O_2^+ source)
Alkynes	Propyne (Acetylene measurable with O_2^+ source)
Aromatic Compounds	Benzene, Toluene, Xylenes, Styrene, Ethylbenzene
Polycyclic Aromatic Hydrocarbons (PAHs)	Naphthalene, Fluorene, Anthracene
Isoprenoids	Monoterpenes, Isoprene
Ethers	Methyl Tertiary Butyl Ether
Aldehydes	Acetaldehyde, Hexanal, Methacrolein, Benzaldehyde
Ketones	Acetone, Methyl Ethyl Ketone, Methyl Vinyl Ketone, Chloroacetone, Bromoacetone, Hexanone
Carboxylic Acids	Acetic Acid, Propionic Acid, Butyric Acid, Isobutyric Acid, Valeric Acid, Isovaleric Acid, Caproic Acid

The CSU mobile lab will also be equipped with a high sensitivity Flame Ionization Detector (PEAK Laboratories, Model PEAK Performer 1 FID) to make measurements of CH_4 and Non-methane hydrocarbons (NMHC). The sample analysis time for this instrument is 400 seconds with MDL of 500 ppt for methane and 800 ppt for NMHCs. This will allow for near-real time observations of methane and NMHC concentrations on board the lab. Data collected from this instrument will complement the VOC measurements made using the PTR-MS and also help validate observations from the 4WD plume tracking vehicle.

The 4WD plume tracking vehicle will be equipped with a methane and acetylene analyzer (Picarro, Model G2203). The Picarro G2203 uses Cavity Ring Down Spectroscopy (CRDS) to make fast and

accurate measurements of CH$_4$ and C$_2$H$_2$, which will enable the operators of the 4WD vehicle to track the emission plume. The observations will also provide an excellent basis for quantifying methane emission rates by the tracer ratio method. The plume tracking information will be used for the activation of sample collection by the canisters at the appropriate time and locations. This instrument is simple to setup and operate and it is vibration and shock resistant and thus designed to operate while the 4WD vehicle is mobile. The measurement interval for both compounds is 2 seconds with MDLs of 9 ppb and 1.8 ppb for methane and acetylene respectively. Measurements of the concentrations of total VOCs (TVOCs) will also be collected in the 4WD vehicle, using a photo-ionization detector device (RAEsystems, Model ppbRAE 3000). This is a very compact instrument that is capable of making 5 second measurements of TVOCs within a range of 1 ppbv to 10000 ppmv. It can run for 16 hours on batteries and includes a wireless transmitter for real-time data communication. The suite of VOCs included in this measurement is dependent on the type of lamp used as the ionization source and the compound used for the calibration of the system. The standard lamp used would include compounds such as benzene, toluene, ethyl benzene, xylenes, methyl ethyl ketone and acetone in the suite of TVOC measurement.

2.6 Planned experiments

Emissions characterization during the project will focus on 3 activity types: well drilling, hydraulic fracturing, and flowback. A total of 24 emissions characterization experiments are planned for the study in order to assess variability in activity emissions between sites, operators, and in different seasons. The exact representation of each activity type and the locations of monitored operations will be determined in consultation with the project Technical Advisory Committee (TAC) described below. Special attention will be paid to evolving well development approaches, including the use of centralized fracking and flowback operations. Table 6 shows a hypothetical breakdown of such experiments discussed as a starting point for experimental design at the first TAC meeting. Resources and experiments may be reallocated to certain operation types after an initial TAC review of early measurements and conditions.

Table 6. Hypothetical breakdown of 24 emission characterization experiments

Season	Operation Type	Number of Experiments
Warm season	Well drilling	3
	Hydraulic Fracturing	5
	Flowback	5
Cold season	Well drilling	2
	Hydraulic Fracturing	3
	Flowback	3

A number of factors must be considered in selecting locations and times for planned experiments. These include the complexity of operations, access to the site and regions downwind, the nature of local terrain and anticipated meteorology, the availability of site operations information, and other factors. In general, sites will be selected where emissions are dominated by a single activity, where there is good access to on-site operational information, where local terrain is not overly complex, and where there is good access to terrain downwind of operations.

The TAC and the investigative team continue to discuss technical issues related to experiment planning and will do so throughout the project. Once the project is funded, a project operations committee (POC) will also be constituted to facilitate the planning and execution of specific experiments. The POC will contain members from local industry and local and state government with "on the ground"

knowledge of industry practices, local meteorology and air quality issues, and well development schedules. Close coordination with the POC and with industry cooperators is essential to the success of the project and will be of the highest priority.

Detailed information regarding on-site activities during measurement periods will be provided by industry cooperators to ensure accurate attribution of quantified emission fluxes to particular activity types. Close cooperation with industry cooperators will enable the study to better characterize well development emissions and how they are tied to specific technological approaches and activities than has been possible in many previous studies, especially those that have relied on fenceline monitoring approaches.

3. Project team

The project will be conducted by a team of air quality, emissions, and dispersion modeling experts from Colorado State University (CSU) and Air Resource Specialists, Inc. (ARS). Dr. Jeffrey L. Collett, Jr., Professor and Head of the CSU Department of Atmospheric Science, will serve as overall project Prinicipal Investigator (PI). Dr. Collett, an expert in atmospheric chemistry and air quality, will oversee all project operations and his group will be the lead for planned chemical measurements. Dr. Jay Ham, Professor in the CSU Department of Soil and Crop Sciences, will serve as project co-PI. Dr. Ham is an expert on measurement of emissions fluxes and will oversee tracer releases, meteorological measurements, project plume mapping and dispersion modeling activities. CSU's team will also include other faculty, graduate students, and postdoctoral scientists who will carry out field and laboratory operations. Included among these individuals are new CSU Professor Allen Robinson (relocating summer 2012 from Carnegie Mellon University), who has worked extensively on air emissions from shale gas operations in the Marcellus Shale region; Dr. Arsineh Hecobian, who has been instrumental in project design and planning and who will manage planned field deployments; Dr. Taehyoung Lee, who will participate in field experiments and operate the PTR-MS system for real-time VOC measurements; and Dr. Marek Uliasz, an expert in local to regional scale transport and dispersion modeling. ARS will provide project expertise in the deployment of continuous gas analyzers, assist in the deployment of automated VOC sampling canisters, and be responsible for data archival. Mr. Mark Tigges will serve as project manager for ARS operations.

The CSU/ARS project team will be aided in project planning and execution by a Technical Advisory Committee (TAC). The TAC will consist of approximately 6-8 members representing industry, government, academic, and non-governmental organizations. Each member of the TAC will be required to have technical expertise in air quality/air emissions. The TAC will serve as a resource for the project team, providing expert advice about industry operations, emission characterization needs and strategies, and regional air quality. The project team will consult with the TAC regularly, keeping them apprised of project progress and consulting with them in cases where significant deviations from original project plans appear warranted. Initial TAC membership includes Ms. Cindy Allen, Team Lead, Environmental, EnCana Oil & Gas (USA) Inc.; Mr. Korby Bracken, Air Quality Manager, Anadarko Petroleum; Mr. Adam Eisele, Environmental Engineer, U.S. EPA; Dr. Shauna Kocman, Hydrologist/Environmental Engineer, Colorado River Valley, Bureau of Land Management; Mr. Gordon Pierce, Program Manager, Technical Services Program, Air Pollution Control Division, Colorado Department of Public Health and Environment; and Dr. Christine Wiedinmyer, Research Scientist II, National Center for Atmospheric Research.   The first meeting of the TAC was held in Fort Collins on May 08, 2012. The focus of this meeting was discussion of final project design and the completion of a project communications plan. Members of the TAC have also had an opportunity to review and provide input to this proposal.

As mentioned above, once the project is funded we also plan to constitute and convene a Project Operations Committee (POC). The POC is anticipated to include approximately 4-6 members from industry cooperators, Garfield County government, and CDPHE. The POC is expected to provide the investigative team with practical knowledge and insight into local operational plans, industry practices, and air quality issues. The POC will play an important role in coordinating experiment planning with local operators and in working with the investigative team to keep the local community apprised of study operations.

Industry cooperators also represent an important part of the overall study team. Close cooperation with regional producers is a hallmark of this study and is critical to ensuring the generation of representative emissions data that can be accurately attributed to the various phases of well development.

4. Quality Assurance

4.1 Modeling plan

This project involves the use of different models to support various aspects of the research, including: 1) a real-time near-field model to predict plume location and extent when the field team is placing sampling canisters, mapping the tracer with the mobile unit, etc…, 2) inverse modeling to determine emissions from the site based on plume canister concentrations and met data, and 3) forward mode dispersion models to map the downwind extent of the plume. Once the research team has been fully assembled (PIs, supporting research scientists, post docs, and graduate students), the group will develop a detailed written plan outlining the specifics of each modeling effort. This document will be reviewed by the TAC. As the project progresses, it is anticipated that the modeling plan will be modified as the team learns what type of models perform best. Each field experiment, especially the first few tests, will provide vital information to optimizing the modeling effort (i.e., type of model, required spatial and temporal resolution, and required field measurements to reduce uncertainty). All the models used in this study will include sensitivity analyses. Thus, all model predictions will be accompanied by an uncertainty estimate.

4.2 Study plan

Prior to the deployment of instruments to the field, the investigative team will develop documents outlining the planning, implementation, and data assessment phases of the project. Procedures to be followed for the assembly of the information in each document will be based on guidelines provided in EPA documents QA/G-4 (Guidance for the Data Quality Objectives Process) and QA/G-5 (Guidance for Quality Assurance Project Plans). The project goal has been defined in this proposal. The organization, schedule, and the use of data to support project objectives will be discussed in depth in a work plan (WP) document, which will also include a Data Quality Objective (DQO) document. Furthermore, each instrument planned for use in the study will be furnished with a Standard Operating Procedures (SOP) or Research Protocol (RP) document, as appropriate, where the capabilities and limitations of the instrument, operating procedures, and the specific needs for data quality checks for each instrument (e.g., blank measurements, calibrations, maintenance, etc…) will be discussed. A document outlining how the data acquired will be analyzed (both in the field and in the laboratory), reviewed and validated for quality assurance and assessed for uniformity of reporting format will be assembled that will include all data types collected with various instruments used during the experiments. This document will also furnish guidelines for the reporting of the uncertainties of each measurement. A Quality Assurance Project Plan (QAPP) will be produced based on guidelines from EPA QA/G-5 document and shared with

members of the TAC. TAC members will be kept apprised of emerging study results, the overall progress of the project, and adherence to established DQOs.

5. Project timeline

The project is slated to begin in August 2012 and continue through July 2015. Acquisition and testing of new equipment will take place in summer/fall 2012. An initial, pilot field deployment is planned for Fall 2012. The main experiment phase will begin in spring 2013 and continue through fall 2014. Detailed data analysis, determination of VOC emissions and dispersion model performance, and preparation of peer-reviewed publications and a project final report are planned for the first half of 2015.

6. Project deliverables

The overall goal of this project is to produce a high quality, peer-reviewed assessment of air emissions and dispersion from well drilling, hydraulic fracturing, and flowback activities in Garfield County, CO. Given the great interest in eventual use of such data for assessing impacts of emissions on air quality and public health, the project has been designed with complementary approaches to ensure the delivery of high quality emissions data for a wide range of compounds, including those of concern as air toxics and as precursors to photochemical smog production. The following set of deliverables is planned for the project:

- Interim status reports and a final report describing project activities and project findings.
- A data set containing measured time and space-resolved species concentrations for each emission characterization experiment and associated emission fluxes for those species as determined by study methods.
- Manuscripts prepared for peer-reviewed scientific journal publication describing the study design and findings.

7. Opportunities for project enhancement

Discussions have been initiated with EPA's Office of Regional Development (Dr. Eben Thoma) with respect to possible ORD participation in a subset of planned emissions monitoring experiments. EPA ORD has developed a mobile sampling platform that characterizes plume dimensions and concentration fields and has expressed an interest in deploying this system to Garfield County to complement the measurements planned by the CSU/ARS project team. The EPA mobile platform includes a fast acetylene/methane analyzer, canister sampling capabilities for VOC measurement, and a forward looking infrared camera (FLIR) for infrared imaging of emission sources. The addition of the FLIR and a second mobile, fast acetylene/methane analyzer would greatly aid plume identification and mapping efforts. EPA's participation, if invited, would come at no additional cost to the project. Several details of a potential collaboration remain to be discussed with ORD, study sponsors, and industry cooperators, including issues related to site access for EPA personnel and data sharing agreements. The study team and the TAC both see key possible benefits to collaboration with ORD. The TAC has advised CSU to explore possible arrangements for collaboration with ORD once the study is underway. Collaboration options will be considered by the TAC at a future meeting.

8. References

Lamb, B.K., McManus, J.B., Shorter, J.H., Kolb, C.E., Mosher,B., Harriss, R.C., Allwine, E., Blaha, D., Howard, T.,Guenther, A., Lott, R.A., Siverson, R., Westberg, H.,Zimmerman, P., 1995. Development of

atmospheric tracer methods to measure methane emissions from natural gas facilities and urban areas. Environmental Science and Technology 29, 1468–1479.

Loubet, B.; Ge´nermont, S.; Ferrara, R. M.; Bedos, C.; Decuq, C.;Personne, E.; Fanucci, O.; Durand, B.; Rana, G.; Cellier, P. 2010. An inverse model to estimate ammonia emissions from fields. Eur. J. Soil Sci., 61:793-805.

U.S. Environmental Protection Agency. National Exposure Research laboratory. Human Exposure and Atmospheric Science Division, Technical Assistance Document (TAD) for Sampling and Analysis of Ozone Precursors. (EPA Publication 600-R-98/161; 1998; http://www.epa.gov/ttn/amtic/files/ambient/pams/newtad.pdf).