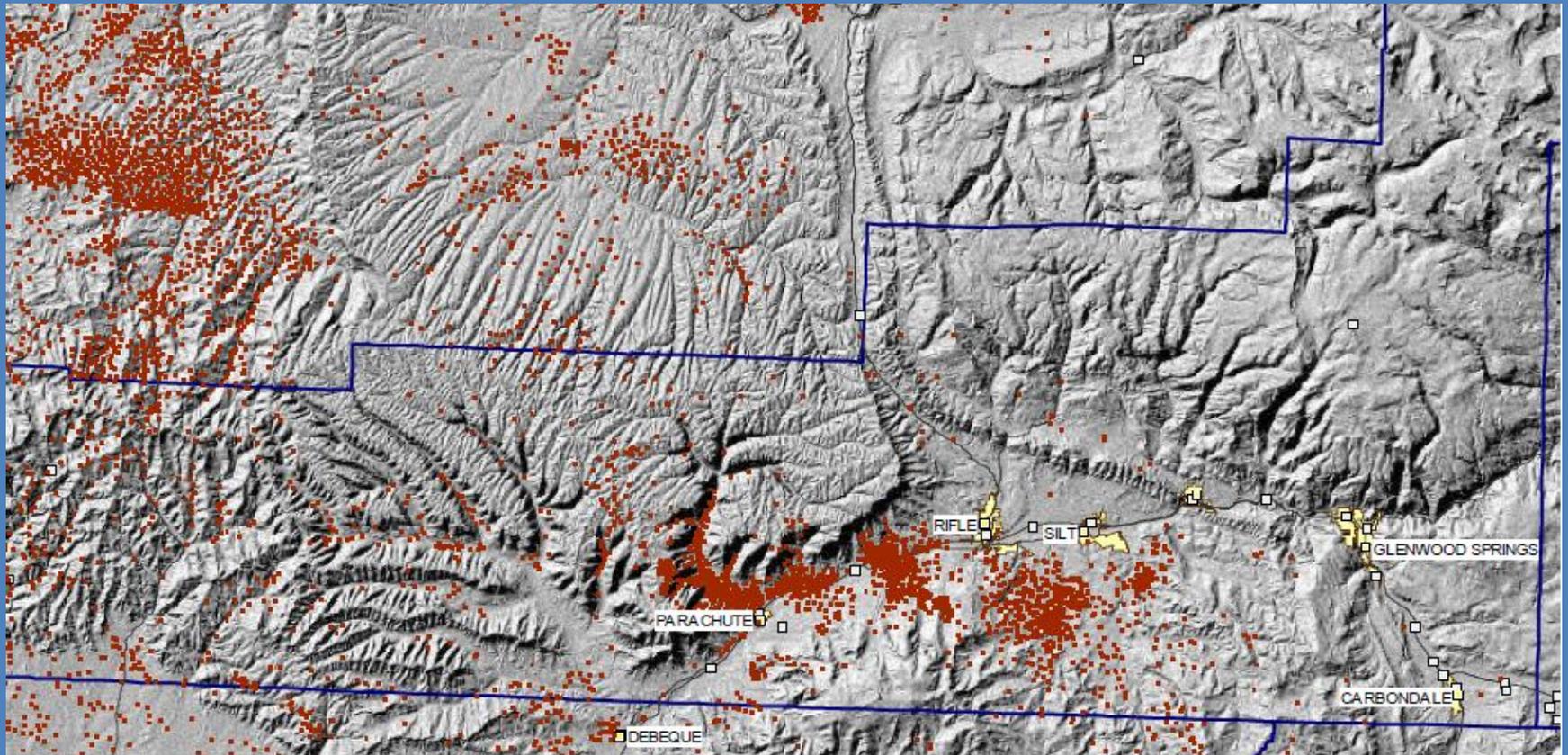


Garfield County Gas Emissions Study

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Project Team

- Colorado State University
 - Jeff Collett (Atmospheric Science), PI
 - Jay Ham (Soil and Crop Sciences), co-PI
- Air Resource Specialists, Inc.
- Technical Advisory Committee
 - Representatives from industry, CDPHE, USEPA, NCAR, BLM
- Operations Committee

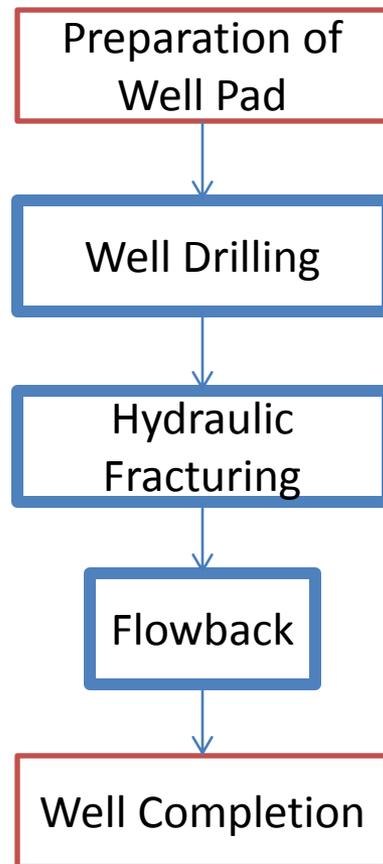


Project Timeline

- Sept 2011 – Initial meeting at CSU
- Oct 2011 – Meeting/field site tour in Garfield County
- Dec 2011 – Preproposal submitted
- Dec/Jan 2011/12 – Preproposal review and feedback
- Feb 2012 – Stakeholder meeting in Denver
- Mar/Apr, 2012 – TAC assembled
- May 8, 2012 – 1st TAC Meeting
- May 2012 – Final proposal submitted
- August 2012 – Citizen Group Meeting in Rifle
- **Aug/Sept 2012 – Finalize Funding (\$1.76 million)**
- **Fall 2012 – Launch study**
- **Fall 2015 – Complete study**

General Study Overview

Air emissions from natural gas extraction operations are not well characterized



Main objectives:

- quantify emissions of chemical compounds (especially VOCs) during well development operations
- characterize how these compounds are dispersed in the atmosphere in the downwind plume near the site

Experimental Design Choices

24 emission characterization experiments

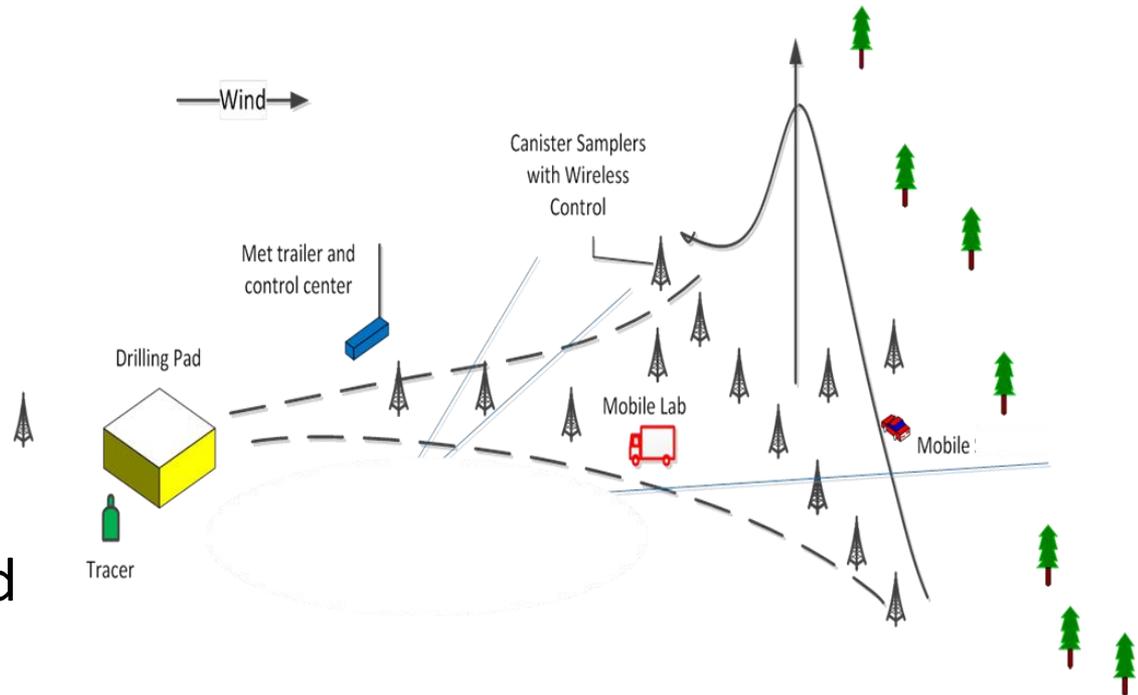
Operation * Operator * Season * Replication

Technical Objectives

- Quantify air emissions at pad or remote operations site during activity
 - Mass of each compound released vs. time (e.g., g/s)
 - Detailed operator information about on-site activity
 - Primary focus on air toxics
 - Secondary focus on CH₄ and ozone precursors
- Measure and model the spatial extent of the dispersing plume
 - Concentration vs. distance from source
 - Up to a few km

General Approach

- Multiple, independent approaches
 - Tracer method
 - Dispersion modeling
- Combination of time-integrated and continuous measurements to observe temporal and spatial variability
- Mobile and fixed sampling platforms



Measurement Platforms and Species



Mobile 4WD Plume Tracker

- C_2H_2
- CH_4
- TVOCs
- GPS



CSU Mobile Lab

- VOCs
- CH_4 /NMHC
- NO_x
- CO
- Met. Data



Other Downwind Measurements

- VOCs
- C_2H_2
- Carbonyls
- Met. Data

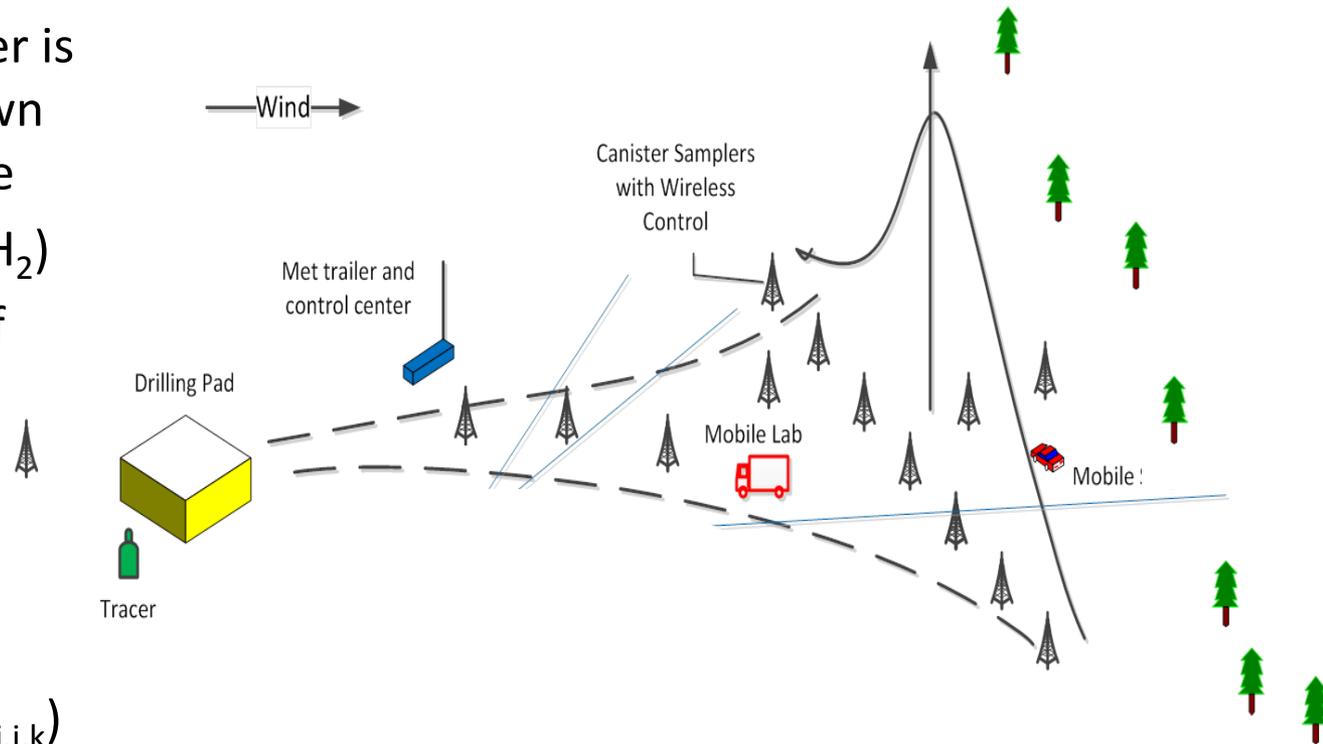


Upwind measurements

- VOCs
- C_2H_2
- Carbonyls

Tracer Ratio Method

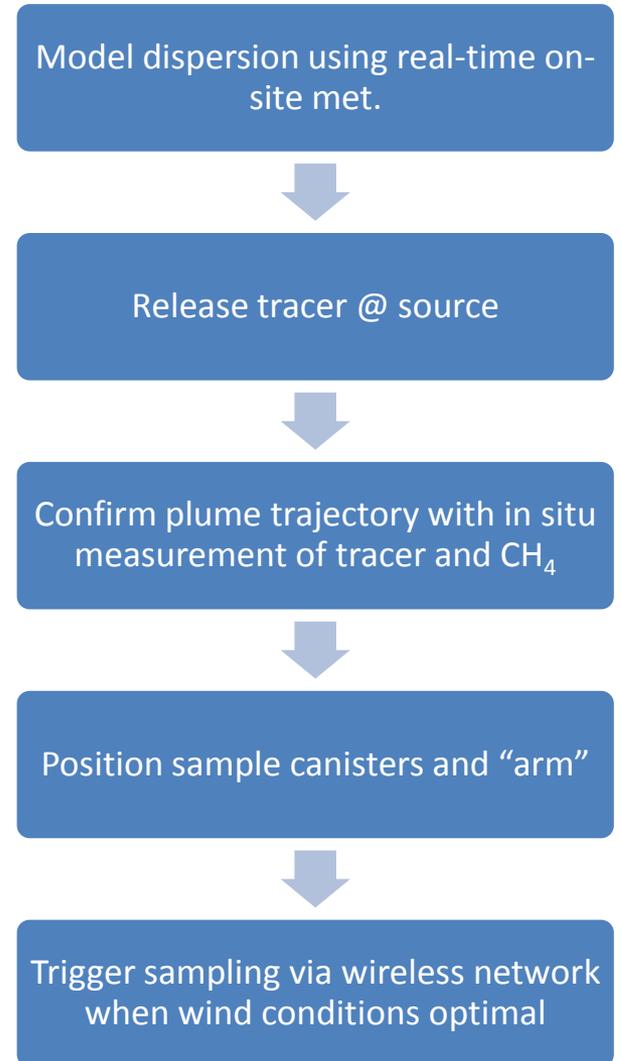
- Conservative tracer is released at a known rate (Q_T) at source
 - Acetylene (C_2H_2)
- Concentrations of tracer (C_T) and compounds of interest ($C_{i,j,k}$) measured in downwind plume
- Emission rates ($Q_{i,j,k}$) calculated from Q_T and the ratio of concentration between C_2H_2 and the compound of interest (e.g., C_i/C_T).



$$Q_i = Q_T \frac{C_i}{C_T}, \quad Q_j = Q_T \frac{C_j}{C_T}, \quad Q_k = Q_T \frac{C_k}{C_T}, \quad \dots$$

Tracer Ratio Method (continued)

- Theoretical Assumptions
 - Release point for tracer is the same as VOC emissions location
 - Turbulent processes transporting tracer and VOCs are the same
 - No chemical transformation between release point and sample point
- Measurement Requirements
 - Must accurately measure mass flow of the tracer and the VOC/tracer concentration ratios
- Key Advantages
 - Don't need to capture entire plume
 - Provides independent estimate of emissions for use in dispersion modeling



Inverse Modeling of Emissions

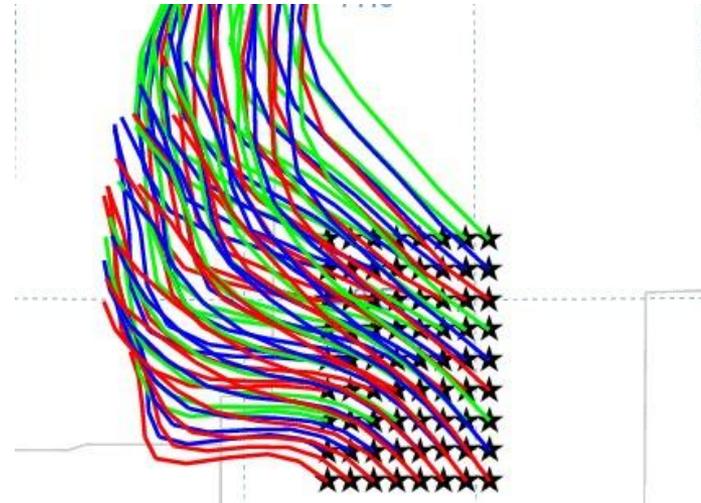
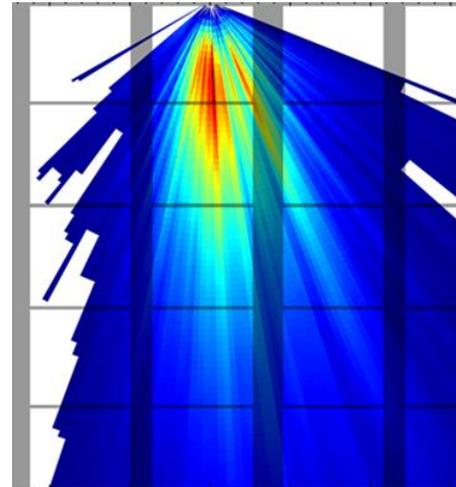
Infer emissions at source based on concentrations measured at multiple points downwind

- Backward Lagrangian Stochastic (bLS)
 - Generates “parcel” trajectories backward in time and space: emission is inferred from touchdown.
 - Need wind speed and direction, stability, gas concentration, and coordinates of source and instrumentation
- Solution of the advection- diffusion Equation.
 - Assumes wind profile shapes, homogenous source, roughness...
 - e.g., Huang, C.H. 1979. A theory of dispersion in turbulent shear flow. *Atmospheric Environment*, **13**, 453–463.

$$\chi(x, y, z) = \chi_{\text{bgd}} + \int_{\text{all } x_s \text{ and } y_s} S(x_s, y_s, z_s) D(x, y, z | x_s, y_s, z_s) dx_s, \quad (1)$$

Predicting Downwind Transport

- Once emissions have been quantified, the advection dispersion model can be used in forward mode to predict concentrations at greater distances from the site
 - Evaluate model performance at setback requirements
- Field data could be combined with regional transport models to predict transport and chemistry at greater distances
 - AERMOD, CALPUFF, HYSPLIT
 - WRF-CHEM, CAMx



VOC Measurements

- VOCs are measured online and offline
 - Online: PTRMS (Proton Transfer Reaction Mass Spectrometer)
 - 100 millisecond response time
 - Offline
 - Canisters and GC-MS/FID
 - Cartridges and HPLC



Canister/cartridge VOC Measurements



- Ozone precursor analysis will be performed on all collected canisters
 - Provides measure of key air toxic volatile organic compounds (VOC) as well as key ozone precursors
 - Matches current Garfield County analysis approach
- Full EPA-method air toxics VOC analysis will be conducted on a subset of canisters
 - Includes many additional halogenated compounds not typically seen in oil and gas emissions
- Cartridge samplers will be used for measurements of formaldehyde and larger carbonyls



VOCs (O₃ precursors)

PAMS Target List of VOCs (EPA TO-12 Method - Speciated)

Ethylene	c-2-Pentene	<i>2,2,4-Trimethylpentane*</i>
Acetylene	2,2-Dimethylbutane	n-Heptane
Ethane	Cyclopentane	Methylcyclohexane
Propylene	2,3-Dimethylbutane	2,3,4-Trimethylpentane
Propane	2-Methylpentane	<i>Toluene*</i>
Isobutane	3-Methylpentane	2-Methylheptane
1-Butene	2-Methyl-1-Pentene	3-Methylheptane
n-Butane	<i>n_Hexane*</i>	n-Octane
t-2-Butene	Methylcyclopentane	<i>Ethylbenzene*</i>
c-2-Butene	2,4-Dimethylpentane	<i>m&p-Xylenes*</i>
Isopentane	<i>Benzene*</i>	<i>Styrene*</i>
1-Pentene	<i>Cyclohexane*</i>	<i>o-Xylene*</i>
n-Pentane	2-Methylhexane	n-Nonane
Isoprene	2,3-Dimethylpentane	Isopropylbenzene
t-2-Pentene	3-Methylhexane	n-Propylbenzene
m-Ethyltoluene	p-Ethyltoluene	1,3,5-Trimethylbenzene
o-Ethyltoluene	<i>1,2,4-Trimethylbenzene*</i>	n-Decane
1,2,3-Trimethylbenzene	m-Diethylbenzene	p-Diethylbenzene
n-Undecane		

Some EPA TO-15 Air Toxics Compounds Measured on subset of canisters

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	Tetrahydrofuran	1,2-Dibromoethane
Bromoethene	1,1,1-Trichloroethane	Chlorobenzene
Trichlorofluoromethane	1,2-Dichloroethane	Ethylbenzene
Acetone	Benzene	m&p-Xylenes
Propanal	Carbon tetrachloride	Styrene
Isopropyl alcohol	Cyclohexane	o-Xylene
1,1-Dichloroethene	1,4-Difluorobenzene	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

Draft experiment matrix design

- Allocation of 24 experiments for different processes, location, seasons (or meteorological conditions)
 - Will be discussed in detail at next TAC meeting

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

EPA Project Participation Option

- EPA ORD interested in adding resources to enhance project
 - Equipment
 - Methods and SOPs
 - Personnel
- High value additions
 - Forward looking infra red (FLIR) camera
 - Tracer release capability
 - C₂H₂ + CH₄ cavity ringdown analyzer
 - Mobile sampling capability
 - Sampling above the surface with tethered balloon
 - Many SOPs available or in progress

Quality Assurance

- Field and Laboratory blanks and replicates
- Instrument calibrations and blanks
- Flow checks
- Use of EPA methods where applicable (e.g., TO-15 for GC-MS and canisters)
- SOPs for:
 - Preparing and extracting samples (e.g., Carbonyl cartridges, VOC canisters)
 - Sample handling and chain of custody
 - Sample analysis methods (e.g., GC-MS/FID)
 - Tracer release
 - Continuous CH₄, C₂H₂, and TVOC measurements
 - PTR-MS VOC speciation
 - Data analysis and data management

Study products

- Quantitative emissions (with uncertainties)
 - By development stage (drilling, fracturing, flowback)
 - Across multiple operations
 - For a broad suite of air toxics and ozone precursors and methane
 - Suitable for impact assessments
 - Air quality
 - Health
- Validation of dispersion model accuracy
 - Variety of meteorological conditions
 - Accuracy of concentration predictions at setback distances
- Peer-reviewed publications
- Validated data set for use in future assessments/studies

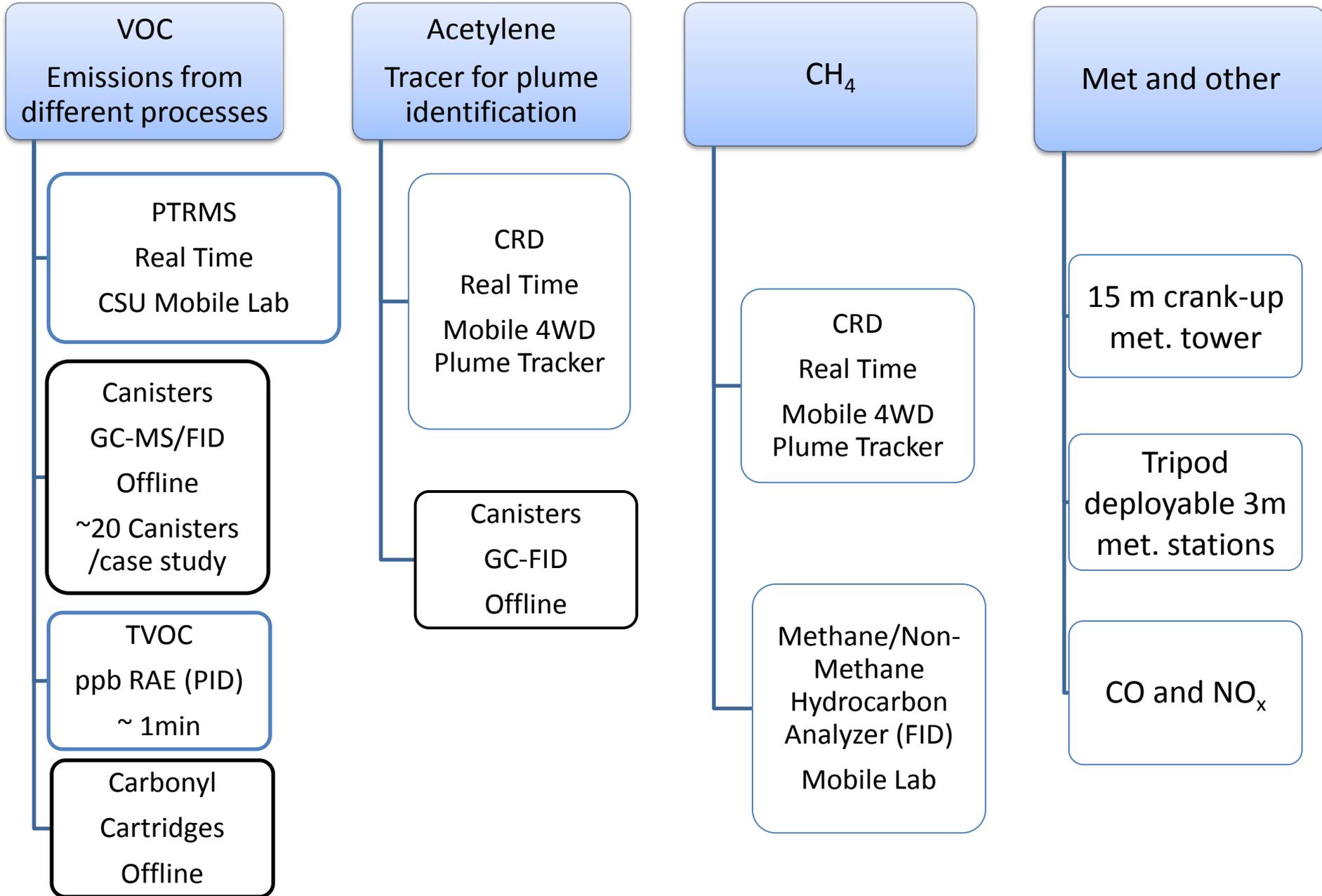
Study communications - highlights

- Internal
 - Data will reside at CSU. Available to the investigative team and discussed with the TAC.
 - TAC will consult on project results, any proposed project design changes, and any possible need for early disclosure of findings.
 - Progress reports and final project report will be provided to TAC. Following TAC comment, a revised final report will be provided to study sponsors and the public.
- Media/public
 - An initial press release will communicate study goals, general approach, and timeline. A public open house will be organized.
 - A post-study press release will outline published study findings.
 - Intermediate press communications limited to general comment about study objectives, design, and status. No results will be communicated to press w/o TAC approval.

Next steps

- Finalize study funding
 - Total budget of \$1.76MM
 - \$800K pledged in industry contributions
- Launch study (Fall 2012)
 - Form operations committee
 - Media/public information
 - Acquire equipment and conduct pilot field monitoring
 - Identify sites and conduct field measurements
 - Periodic public updates and TAC reviews
 - Analyze and publish findings in peer-reviewed journals
- Complete study (Fall 2015)
 - Publish final study report
 - Public presentation of findings

Measurements



Online VOC measurements HS PTR-QMS 500

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

Carbonyl Compounds Measured

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	