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Advancing Understanding of Emissions from  
Oil and Natural Gas Production Operations  
to Support EPA's Air Quality Modeling  
of Ozone Non-Attainment Areas

FINAL SUMMARY REPORT

Regional Applied Research Effort Program

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Table of Contents:

Page

EXECUTIVE SUMMARY.....	1
1. BACKGROUND.....	3
2. PROJECT OVERVIEW.....	6
3. FIELD CAMPAIGN.....	7
3.1. Background.....	7
3.2. Site Description.....	8
3.3. Campaign Schedule.....	9
3.4. Experimental Methods.....	9
3.4.1. IMACC Passive Fourier Transform Infrared Radiometer (PFTIR).....	9
3.4.2. TELOPS Mid-Wave Infrared Hyper-Spectral Imager (HSI).....	10
3.4.3. Optical Gas Imaging Camera.....	10
3.4.4. Instrument Calibration Procedures.....	10
3.4.5. Combustion Efficiency Calculations.....	12
3.5. Data Products and Reports.....	14
3.6. Results.....	14
3.6.1. Site #5 Emissions Data.....	15
3.6.2. Combustion Efficiency Estimates at Various Sites.....	17
3.6.3. Evaluation of PFTIR and His Sensing Approaches for ECD Assessment.....	19
4. EPA SPECIATE DATABASE.....	20
4.1. Background.....	20
4.2. SPECIATE Database Description.....	20
4.3. SPECIATE Data Processing and Entry Approach.....	23
4.3.1. Data Collection.....	23
4.3.2. Documentation.....	24
4.3.3. Data Format.....	24
4.3.4. Speciation Data Quality.....	24
4.4. Study or Measurement Datasets.....	26
4.4.1. RARE ECD Study.....	26
4.4.1.1. Background.....	26
4.4.1.2. Results.....	26
4.4.2. WRAP Phase III VOC Speciation Profiles.....	27
4.4.2.1. Background.....	27
4.4.2.2. Methodology.....	27
4.4.2.3. Results.....	28
4.4.3. Uintah and Ouray Indian Reservation Tribal Minor Source Registration.....	30
4.4.3.1. Background.....	30
4.4.3.2. Methodology.....	31
4.4.3.3. Results.....	34
4.4.4. Denver-Julesburg Basin Direct Measurement Study.....	35
4.4.4.1. Background.....	35
4.4.4.2. Methodology.....	36
4.4.4.3. Results.....	37
4.4.5. East Texas Oil Field Speciation Data.....	37
4.4.5.1. Background.....	37
4.4.5.2. Methodology.....	38
4.4.5.3. Results.....	38
4.4.6. San Joaquin, California Oil and Gas Speciation Data.....	39
4.4.6.1. Background.....	39
4.4.6.2. Methodology.....	40
4.4.6.3. Results.....	41

4.5. Results of SPECIATE Work.....	42
5. SUMMARY.....	44
6. WORK PRODUCTS and FUTURE WORK.....	46
APPENDIX A: PHOTOGRAPHS OF MEASUREMENT SITES.....	48
APPENDIX B: SPECIATION PROFILES.....	55
APPENDIX C: LIST OF PRODUCERS IN UINTAH and OURAY RESERVATIONS.....	62

<u>Figures:</u>	<u>Page</u>
Figure 1: IMACC PFTIR Radiometer.....	10
Figure 2: TELOPS Mid-Wave Hyper-Spectral Imager.....	11
Figure 3: Overhead View of Site#5 with Measurement Configurations.....	15
Figure 4: TELOPS Chemical Map Example Images .....	17
Figure 5: Daily Calculated Combustion Efficiency from PFTIR.....	18
Figure 6: Overlay of WRAP Basins.....	27

<u>Tables:</u>	<u>Page</u>
Table 1: Initial List of Target Compounds for Study .....	8
Table 2: Latitude, Longitude, and Date of Data Acquisition of Each Measurement Site.....	9
Table 3. Summary of PFTIR Concentration Determinations (ppm-m) at Site #5.....	16
Table 4: Number of Individual Profiles to Develop Composite Profile.....	28
Table 5: Number of Different Samples for each Operator Profile.....	33
Table 6: Number of Profiles for Each Oil and Natural Gas Production Emission Source.....	34
Table 7: Number of Profiles for Each Oil and Natural Gas Production Emission Source .....	37
Table 8: Number of Profiles for Each Oil and Natural Gas Production Emission Source .....	39
Table 9: Number of Profiles Collected from each California Study.....	40
Table 10: Number of Profiles for Each Oil and Natural Gas Production Emission Source .....	40
Table 11: Number of Individual Profiles Developed from Each Study Reviewed for This Project.....	43

Abbreviations:

A&WMA	Air and Waste Management Association
ACE	Air, Climate, and Energy Research Program
API	American Petroleum Institute
ASTM	American Society for Testing and Materials
bbbl	barrels of oil
BPA	Beaumont-Port Arthur
BTEX	Benzene, Toluene, Ethyl-benzene and Xylenes
CARB	California Air Resources Board
CO <sub>2</sub>	Carbon Dioxide
CO	Carbon Monoxide
CAS	Chemical Abstract System
CAA	Clean Air Act
CHIEF	Clearing House for Inventories and Emission Factors
CBM	Coal-Bed Methane
CFR	Code of Federal Regulations
CE	Combustion efficiency
DFW	Dallas-Fort Worth
DJ	Denver-Julesburg
ECDs	Enclosed Combustor Devices
EPA	Environmental Protection Agency
E&P	Extraction and Production
FIP	Federal Implementation Plan
FY	Fiscal Year
FID	Flame Ionization Detection
FTIR	Fourier Transform Infrared
GC	Gas Chromatography
GOR	Gas Oil Ratio
GRI	Gas Research Institute
GPS	Global Positioning System
GHGs	Greenhouse Gases
HAPs	Hazardous Air Pollutants
HVS	High Volume Sampler
HGB	Houston-Galveston-Brazoria
H <sub>2</sub> S	Hydrogen Sulfide
HSI	Hyper-Spectral Imaging
IMACC	Industrial Monitor and Control Corporation
IPAMS	Independent Petroleum Association of Mountain States
IR	Infrared
IRMS	Isotope Ratio Mass Spectrometer
MS	Mass Spectrometry
CH <sub>4</sub>	Methane
NAAQS	National Ambient Air Quality Standards
NEI	National Emissions Inventory
NESHAP	National Emission Standards for Hazardous Air Pollutants

NSPS	New Source Performance Standards
NSR	New Source Review
NO <sub>x</sub>	Nitrogen Oxides
NAICS	North American Industry Classification System
OAQPS	Office of Air Quality Planning and Standards
OIG	Office of Inspector General
ORD	Office of Research and Development
OSP	Office of Science and Policy
OGI	Optical Gas Imaging
PM	Particulate Matter
PM <sub>10</sub>	Particulate Matter less than 10 microns
PM <sub>2.5</sub>	Particulate Matter less than 2.5 microns
ppb	parts per billion
ppm	parts per million
ppmv	parts per million by volume
PFTIR	Passive Fourier Transform Infrared
PAMS	Photochemical Assessment Monitoring System
PECASE	Presidential Early Career Award for Scientists and Engineers
QA	Quality Assurance
ROG	Reactive Organic Gases
RARE	Regional Applied Research Effort
SBIR	Small Business Innovation Research
SO <sub>2</sub>	Sulfur Dioxide
TCEQ	Texas Commission on Environmental Quality
TERC	Texas Environmental Research Consortium
TOG	Total Organic Gas
TMS	Tribal Minor Source
U.S.	United States
VMT	Vehicle-Miles Traveled
VOCs	Volatile Organic Compounds
WEA	Western Energy Alliance
WRAP	Western Regional Air Partnership

## Executive Summary

Environmentally responsible development of national energy assets requires well-developed emissions inventories and measurement techniques to verify emissions and to understand the effectiveness of emissions control strategies. To properly model the energy production sector impacts on air quality, it is also critical to have accurate activity data, emission factors, and chemical speciation profiles for volatile organic compounds (VOCs) and nitrogen oxides (NO<sub>x</sub>). The upstream oil and gas sector, specifically well pad operations, presents many challenges in this regard. The vast number and variety of potential emission sources, coupled with company-specific differences in engineering and maintenance practices, and the natural variability in product composition make it difficult to understand and properly represent emissions from well pads. Advancements in understanding this source sector require both speciated inventory development and measurement techniques that can assess the emissions in the field.

This report describes an United States (U.S.) Environmental Protection Agency (EPA) effort that aimed to improve the understanding of well pad emissions, the capability of different measurement methods, and identify areas where future work is needed. Funded through the EPA Office of Research and Development (ORD) Regional Applied Research Effort (RARE) program (awarded 2014 to 2016), EPA Region 8, ORD, and the Office of Air Quality Planning and Standards (OAQPS) conducted a two-phase project to explore a novel measurement approach for a potentially important oil and gas source, and gather source emission information to advance the EPA SPECIATE database. The SPECIATE database is a key tool used by air quality modelers to predict areas of ozone non-attainment. The emphasis of this RARE project was on product-related VOC emissions from on-going well pad operations.

Currently, there is little information on the potential emissions from non-optimally operating emissions control systems, called enclosed combustion devices (ECDs), on well pads, and how often the ECDs do not function properly. Fugitive emissions of VOCs can originate from leaks and from potentially ineffective control systems, such as ECDs. In the case of ECDs, it is possible that byproducts of incomplete combustion may produce more highly reactive ozone precursor species. As a result, the first phase of this RARE project consisted of a limited-scope field effort that investigated new remote sensing techniques for off-site assessment of ECDs on well pads.

For both compliance and scientific purposes, the ability to quickly and easily assess ECD operations from off-site vantage points is potentially important. The exploratory methods study described in this report represents the first attempt to assess well pad ECD emissions using an optical remote sensing approach. The limited-scope field demonstration was executed over a five-day period in September 2014 and produced observations on 10 well pads in the Denver-Julesburg (DJ) Basin Colorado. The demonstration showed that it may be possible to effectively assess the operational states of ECDs using remote sensing approaches for compliance purposes, but improved technologies and further method development are necessary. Of the 10 well pads investigated, at least one demonstrated clear evidence of improper ECD operations and these measurements are described in this report. The demonstration also indicated the challenges in measuring and collecting emissions from these sources that are suitable for use in the SPECIATE database and representing the emissions for air quality models to predict air quality impacts. In

particular, the data acquired from the field study were not of high enough quality or quantity for this purpose. Although this methods demonstration project was not successful in robust quantification of emissions of highly reactive VOCs from ECDs with current remote sensing systems, it identified a need for additional research to more efficiently measure emissions from ECD operations and update emission speciation profiles in SPECIATE for both properly operating and malfunctioning ECD systems and to improve our understanding of the prevalence of the latter.

The second phase of this RARE project focused on data synthesis work from existing oil and gas studies to improve speciated emissions information for this sector. This component of the project contributed significantly to improvements to EPA's SPECIATE database. This database is used to develop emissions inventories and is a key tool for air quality modelers to predict non-attainment areas that may be impacted by oil and gas development. The data synthesis portion gathered information on VOC emissions from multiple internal and external projects. These data were utilized to develop process-related VOC speciation profiles that were incorporated into EPA's SPECIATE database for multiple basins and to improve SPECIATE's representation of oil and gas processes. This report and associated Excel spreadsheet provides background information on these efforts, summarizes results, and provides information on areas for potential future work. While this project produced over 90 new VOC speciation profiles for various oil and gas processes, it identified gaps in understanding how to link the profiles to inventories or whether there is a potential need to develop and utilize site- or process-specific VOC speciation profiles for interpreting ambient measurement data and creating model-ready emissions for photochemical modeling applications.

## 1 BACKGROUND

The establishment of accurate emissions inventories and the development of field observation techniques that can help verify emissions and the effectiveness control strategies are key factors that support environmental responsible development national energy assets. In particular, well-developed speciated source emission profiles and source activity data that includes knowledge of the malfunction frequency of control strategies assist modeling efforts that investigate energy production sector impacts on air quality. The upstream oil and gas sector, specifically well pad operations, presents many challenges in this regard. The vast number and variety of potential emission sources, coupled with company-specific differences in engineering and maintenance practices, and the natural variability in product composition make it a difficult to understand and properly represent emissions from well pads. Advancements in understanding this source sector require both speciated inventory development and measurement techniques that can assess emissions in the field.

The Intermountain West is an important source of domestic energy resources. Operations involved in the extraction, production, and distribution of oil and natural gas have significant environmental impacts. One of the primary environmental impacts associated with oil and natural gas production is related to air emission releases of a number of air pollutants. The primary air pollutants released include NO<sub>x</sub>, VOCs, particulate matter (PM), sulfur dioxide (SO<sub>2</sub>), Greenhouse Gases (GHGs), and Hazardous Air Pollutants (HAPs). In the case of NO<sub>x</sub> and VOCs, these pollutants are important precursors to the formation of ground-level ozone. Ozone is one of the criteria pollutants regulated by EPA under the Clean Air Act (CAA). Studies have indicated that the emissions associated with the oil and natural gas sector are highly uncertain because little information exists on the emissions from this source category. In particular, a recent EPA Office of Inspector General (OIG) Report found that EPA has limited directly-measured air emissions data for oil and natural gas sources, and approximately half of EPA's oil and natural gas emission factors are rated below average or unrated because of insufficient or low quality data.<sup>1</sup>

This report describes a U.S. EPA effort that aimed to improve information on emissions and measurement methods and identify areas where future work is needed. Funded through the EPA RARE program (awarded 2014 to 2016), EPA Region 8, ORD, and OAQPS conducted a two-phase project to explore a novel measurement approach for a potentially important oil and gas source and gather source emission information to advance the EPA SPECIATE database. The SPECIATE database is a key tool used by air quality modelers to predict areas of ozone non-attainment. The emphasis of this RARE project was on product-related VOC emissions from on-going well pad operations.

To reduce the emissions released during the production of oil and gas, most well pads in EPA Region 8 use control devices, such as ECDs. These control devices are generally assumed to

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<sup>1</sup> EPA Needs to Improve Air Emissions Data for the Oil and Natural Gas Production Section, Report No. 13-P-0161, February 20, 2013, Office of Inspector General, EPA.

have collection and control efficiencies in excess of 95 percent.<sup>2</sup> Properly maintained and controlled oil and gas extraction and production (E&P) processes are important for limiting the amount of pollutants released into the air, thereby protecting human health and the environment. However, recent observations, including visibly smoking ECDs and infrared (IR) camera footage, suggest that under some operating conditions, capture and control efficiency can be substantially lower than 95 percent. As a result, it is possible that these poorly maintained E&P processes can emit VOCs, including air toxics and precursors to ozone, at potentially significant levels. For ECDs that may not be operating at designed destruction efficiencies, there is also uncertainty in the composition of combustion byproducts. The composition of the combustion byproducts or the speciation of the VOC emissions from these sources, as well as other oil and gas operations, are not only important for understanding the magnitudes of the individual VOC chemical species being emitted into the air, but are also important for interpreting ambient measurement data and creating speciated emission inventories for regional haze, climate, and photochemical air quality models. Currently, there is little information on the potential emissions and frequency of occurrence of non-optimally operating ECDs and the representation of ECD emissions. Therefore, research on emissions from well pad ECDs and other oil and gas operations is needed to improve emissions inventories, to better understand highly reactive VOC species for air quality modeling, and to aid in the design of future field measurement studies for the oil and gas sector.

One difficulty with assessment of upstream oil and gas sources is the large number of well pads in a given basin and the cost and complexity of executing on-site field measurements, which typically require prearranged site access with the oil and gas operator. This mode of operation can allow for effective investigation of nominally operating systems, but may obstruct the study of “as-encountered” systems for the purpose of establishing control effectiveness and the frequency of process malfunctions. Many well pads are close to public roadways and in theory can be somewhat effectivity assessed with regard to gross malfunctions using remote observation approaches. For both compliance and scientific purposes, the ability to quickly and easily assess ECD operations from off-site vantage points is potentially important.

The first phase of this RARE project consisted of a limited-scope, exploratory methods study that represents the first attempt to assess well pad ECD emissions using an optical remote sensing approach. In addition to methods development objectives, a goal of the field study was to produce emissions measurements suitable for use in the SPECATE database and representing the emissions for air quality models to predict air quality impacts.

The second phase of this RARE project focused on data synthesis work from existing oil and gas studies to improve EPA’s SPECIATE database. The SPECIATE database is a key tool for air quality modelers to assess impacts of oil and gas development in non-attainment areas. Photochemical air quality models are used to simulate the transport of air pollution and are important tools in the regulatory process. Within these models, the predictions of major pollutants, such as ozone, NO<sub>x</sub>, VOCs, and PM, are represented using simplified chemical mechanisms and emissions inventories. The common chemical mechanisms within models either

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<sup>2</sup> Control Techniques Guidelines for the Oil and Natural Gas Industry (Draft), EPA-453/P-15-001, U.S. Environmental Protection Agency, Office of Air and Radiation, Office of Air Quality Planning and Standards, Sector Policies and Programs Division, Research Triangle Park, North Carolina, August 2015.

group compounds based on reactivity with hydroxyl radicals or break compounds into functional groups. Further, the emissions inventories are based on the EPA's National Emissions Inventory (NEI), which contains estimates of total anthropogenic emissions of NO<sub>x</sub>, VOCs, PM, and other pollutants in the United States. To utilize the NEI for the models, speciated emission profiles found in the SPECIATE database are routinely used to convert the total emissions from specific sources in the emissions inventory into the speciated emissions needed for models.

To improve the predictions of air quality models, the second phase of this RARE effort reviewed and expanded upon the Total Organic Gas (TOG) speciation profiles stored in EPA's SPECIATE Database for oil and gas sources to ensure that the most recent and representative profiles are available to the community.

## 2 PROJECT OVERVIEW

The objective of this project was to advance understanding of speciated VOC emissions from upstream oil and gas production operations. Specifically, the project aimed to advance information on methods for off-site remote assessment of ECDs and fugitive emissions, and improve EPA's SPECIATE database for this sector. These objectives were accomplished through a collaborative effort with EPA Region 8, ORD, and OAQPS to build upon VOC measurement and database development projects currently in progress at EPA. In particular, the project leveraged and built upon a previous effort in EPA Region 8, using funds and the time of one of EPA's winners of the Presidential Early Career Award for Scientists and Engineers (PECASE). The PECASE project entitled "*Detection and Quantification of Component Level Emissions at Oil and Natural Gas Production Well Pads Using Remote/Direct Measurements*" fed into the design of a field campaign, while the SPECIATE program<sup>3</sup> provided the basis for developing and adding oil and gas VOC speciation profiles to EPA's SPECIATE Database.

The project occurred in two phases. The first phase of the project consisted of a limited-scope field campaign in the DJ Basin that provided the first demonstration of two experimental off-site remote sensing measurements to assess control efficiency and emissions of highly reactive VOCs from ECDs at well pads. The two instrument used were: (1) a Passive Fourier Transform Infrared (PFTIR) radiometer (IMACC, LLC, Round Rock, TX, USA), and (2) a mid-wave infrared hyper-spectral imaging (HSI) camera (Telops, Quebec City, QC, CANADA). The field campaign was conducted over a course of five days in September 2014. The second phase of the project utilized the information gathered from multiple oil and gas measurement studies to improve the VOC speciation profiles used for emissions inventory development and within air quality models. EPA's SPECIATE program develops and maintains a repository (i.e., SPECIATE Database) of VOCs and PM speciation profiles of air pollution sources or weight fractions of chemical species of both VOCs and PM.

This report summarizes the activities and results from this two-phase RARE project.

### 3 FIELD CAMPAIGN

#### 3.1 Background

For the first phase of this project, EPA Region 8 and ORD conducted a pilot demonstration field campaign in the DJ Basin to investigate remote assessment of ECD performance using two off-site observation approaches. Previous EPA field studies have shown that methane and VOCs can be emitted from well pad sources that are improperly maintained or controlled.<sup>3,4,5,6</sup> ECDs are commonly used as control devices to control VOC emissions from well pad sources such as atmospheric storage tanks. To support energy development practices with minimal environmental impacts, it is important to develop easy-to-use and reproducible measurement techniques that can verify the effectiveness of ECD operation in the field. Remote sensing systems may provide a means to improve understanding of ECD operation without direct onsite sampling of the combustion plume.

The goals of the field campaign were to demonstrate and evaluate the performance of measurement technologies to characterize emissions from ECDs at upstream oil and gas production sites, and to the extent feasible, provide speciated emissions information from the ECDs, and assess the combustion efficiency of the ECDs. The initial list of target compounds for the campaign is presented in Table 1.

The pilot campaign was executed over a course of five days in September 2014 and aimed to collect emissions data for the compounds listed in Table 1 from ECDs at multiple well site locations in an active natural gas field in Weld County, Colorado. The campaign utilized two primary instruments that could characterize ECD performance on well pads from remote vantage points, including (1) a PFTIR radiometer (IMACC, LLC, Round Rock, TX, USA), and (2) a mid-wave infrared HSI camera (Telops, Quebec City, QC, Canada). The two technologies have been used in previous studies to characterize emissions from industrial flares.<sup>7</sup> An optical gas

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<sup>3</sup> Brantley, H.L.; Thoma, E.D.; Squier, W.C.; Guven, B.B.; Lyon, D. Assessment of Methane Emissions from Oil and Gas Production Pads Using Mobile Measurements; *Environ. Sci. Technol.*, **2014**, *48*, 14508-1451, doi: 10.1021/es503070q.

<sup>4</sup> Modrak, M.T.; Amin, M.; Ibanez, J.; Lehmann, C.; Harris, B.; Ranum, D.; Thoma, E.D. ; Squier, B.C. Understanding Direct Emission Measurement Approaches for Upstream Oil and Gas Production Operations, Control No. 2012-A-411-A&WMA, *Proceedings of the 105th Annual Conference of the Air & Waste Management Association*, June 19-22, 2012, San Antonio, Texas.

<sup>5</sup> Thoma, E.D.; Squier, B.; Olson, D.; Eisele, A.; DeWees, J.; Segall, R.; Amin, M.; Modrak, M. 2012, Assessment of Methane and VOC Emissions from Select Upstream Oil and Gas Production Operations Using Remote Measurements; Control No. 2012-A-21-A&WMA, *Proceeding of the 105th Annual Conference of the Air & Waste Management Association*, June 19-22, 2012, San Antonio, Texas.

<sup>6</sup> Brantley, H.L.; Thoma, E.D.; Squier, W.C.; Eisele, A.P. Remote and Onsite Direct Measurements of Emissions from Oil and Natural Gas Production, Abstract # 551, *Proceedings of the 108th Annual Conference of the Air & Waste Management Association*, June 23-26, 2015, Raleigh, North Carolina.

<sup>7</sup> Texas Commission on Environmental Quality, PGA No. 582-8-862-45-FY09-04, Tracking No. 2008-81 with Supplemental Support from the Air Quality Research Program TCEQ Grant No. 582-10-94300, *TCEQ 2010 Flare Study Final Report*. David Allen, Vincent Torres, University of Texas at Austin, The Center for Energy and Environmental Resources, August 1, 2011 (accessed January, 2015).

<http://www.tceq.texas.gov/assets/public/implementation/air/rules/Flare/2010flarestudy/2010-flare-study-final-report.pdf>. Last Accessed: June 2016

imaging (OGI) camera (GF-320, FLIR Systems, Inc., Boston, MA, USA) was also deployed to provide complementary qualitative data on the ECD emissions. Additionally, measurements of ECD temperature were collected remotely using the OGI camera and a hand-held infrared thermometer (Fluke Corporation, Everett, WA, USA).

**Table 1. Initial List of Target Compounds for Study**

Compound	Instrument
Butane	Passive FTIR
Ethene	Passive FTIR
Propene	Passive FTIR
Methane	Both <sup>1</sup>
Benzene	Mid-Wave Hyper-Spectral Imager
Toluene	Mid-Wave Hyper-Spectral Imager
Xylenes	Mid-Wave Hyper-Spectral Imager
Ethylbenzene	Mid-Wave Hyper-Spectral Imager
Total Hydrocarbons (aggregate of compounds with carbon number greater than 4)	Both
Carbon Monoxide	Both
Carbon Dioxide	Both
Water Vapor	Both
Ammonia	Passive FTIR
Nitrous Oxide	Both
Nitrogen Dioxide	Both

<sup>1</sup>Both = Passive FTIR and Mid-Wave Hyper-Spectral Imager

Remote sensing measurements were conducted from safe and appropriate offsite observing locations on the side of public roadways, and the sites were selected based on a combination of factors including ease of observation and the results of OGI imaging that indicated the potential presence of ECD operational issues. This research effort was not part of any enforcement or compliance activity.

The subsequent sections describe the measurement technologies, including details of instrument operation, deployment, and data analysis methods, as well as a discussion of data results from the campaign.

### **3.2 Site Description**

Measurements were conducted in Weld County, Colorado, which is located approximately 50 miles northeast of the Denver Metropolitan area. A total of ten well pads were surveyed during the campaign. Both instruments were not able to collect data at all ten sites because of time and resource limitations. Both instruments were only employed together at three of the ten sites. The general locations of the sites were in areas with a large density of active well sites. Measurements were collected from the side of public roadways adjacent to the emission source, with approximately four well sites surveyed per day. Table 2 outlines the location of each

measurement site and information related to the data collected by each of the instruments. The rows filled in yellow represent sites that had data from both instruments. Photographs of the site locations are included in Appendix A.

Table 2. Latitude, Longitude, and Date of Data Acquisition of Each Measurement Site.

Site	Latitude	Longitude	Date	Time [Local]	Number of ECDs at Site	Instrument
Site #1	40.3197 N	-104.5688 W	09/08/2014	13:00	1	PFTIR
Site #2	40.2040 N	-104.8147 W	09/08/2014	15:30	2	PFTIR
Site #3	40.1889 N	-104.7582 W	09/09/2014	08:00	3	PFTIR
Site #4	40.3343 N	-104.6232 W	09/10/2014	10:00	2	PFTIR/HSI
Site #5	40.1314 N	-104.6896 W	09/11/2014	09:30	2	PFTIR/HSI
Site #6	40.1168 N	-104.7078 W	09/11/2014	12:00	4	PFTIR
Site #7	40.1314 N	-104.6896 W	09/11/2014	12:30	10	HSI
Site #8	40.1167 N	-104.6922 W	09/11/2014	14:30	4	PFTIR/HSI
Site #9	40.1221 N	-104.6973 W	09/11/2014	16:00	1	HSI
Site #10	40.3385 N	-104.7934 W	09/12/2014	09:00	2	PFTIR

### 3.3 Campaign Schedule

The field campaign was conducted from September 8-12, 2014 in Weld County, Colorado. Data were collected with the PFTIR during each day of the campaign, and with the mid-wave infrared HSI on September 10-11, 2014. Table 2 outlines the date and time of the data acquisition for each instrument over the course of the campaign.

### 3.4 Experimental Methods

The instruments utilized during the field campaign, calibration procedures and combustion efficiency calculations are discussed in the following sub-sections.

#### 3.4.1 IMACC Passive Fourier Transform Infrared Radiometer (PFTIR)

The Industrial Monitor and Control Corporation (IMACC) was responsible for all on-site measurement activities using the PFTIR. The PFTIR radiometer analyzes thermal radiation emitted by hot gases in the ECD plume. During the measurement process, the instrument does not transmit an infrared light source through the measurement plane. Instead, infrared energy emitted from the hot gases from the source is the infrared signal, and the instrument acts as a receiver. This approach is possible because the emissions spectra of hot gases are very similar to their absorption spectra, and can therefore be used for identification and quantification of species through emission spectroscopy, just as with absorption spectroscopy. The PFTIR has been used successfully on large open industrial flares, but this was the first attempt to use the approach on smaller (lower temperature) ECDs with high duty cycles. The PFTIR was chosen for the current study instead of active open-path Fourier Transform Infrared (FTIR) monitoring (where the instrument transmits and receives an infrared source) because of potential difficulties of transmitting and receiving an infrared source through a small, elevated plume, and the need for site access and support infrastructure to position the required beam retroreflectors.

Data from the IMACC PFTIR radiometer were used primarily to determine the combustion efficiency of the flares at each site. Data from the PFTIR were also used to provide information on the constituents present in the flare plumes. However, the PFTIR measurement approach cannot provide actual gas concentrations. To obtain actual gas concentrations, accurate knowledge of both the path length through the plume and plume temperature are required. For this reason, gas concentrations determined for the project are considered estimated values obtained using estimated values of path length through the plume and plume temperature. The raw PFTIR data were post-processed using IMACC proprietary software.

The instrument was deployed from the back of a field trailer, and was mounted on a mechanical positional scanner. At each measurement site, the trailer was oriented to provide a clear line of sight between the PFTIR and the emissions source detected during the pre-measurement OGI camera survey. Measurements were collected at 0.5 per centimeter ( $\text{cm}^{-1}$ ) spectral resolution, and the instrument field of view was approximately 14 inches in diameter. Each data point was averaged for 30 seconds, with analyte concentrations in units of parts per million-meter (ppm-m). Because many of the plumes measured during the campaign showed weak infrared signal due to overall low combustion throughput, often times it was not possible to make a valid measurement. A data filter was developed to eliminate data points with insufficient infrared signal. Due to the lack of sustained infrared signal from many ECDs, the PFTIR was not as effective as compared to industrial flare applications. The PFTIR was deployed during each day of the field campaign at a total of eight well pad sites. Figure 1 presents the IMACC PFTIR radiometer.



Figure 1. IMACC PFTIR Radiometer.

### 3.4.2 TELOPS Mid-Wave Infrared Hyper-Spectral Imager (HSI)

TELOPS was responsible for all on-site measurement activities using the HSI. The mid-wave infrared HSI is a standoff instrument that uses FTIR technology. Incoming infrared radiation from the vicinity of the source being monitored is modulated using a Michelson interferometer located inside the instrument. A high-resolution spectrum is then recorded for each pixel of a focal plane array detector. By comparing the measured spectrum to a series of reference spectra of known gases, the constituent species can be identified and quantified. The instrument has a nominal spectral range of 3 to 5 microns, with spectral resolution of  $0.25 \text{ cm}^{-1}$  wavenumber. The instrument field of view consists of 128 by 128 pixels, with individual pixel size ranging from

approximately 5 to 166 cm<sup>2</sup>, depending on the distance from the instrument to the source. Data collected with the instrument are used to create quantitative chemical imaging sequences, showing the column density, in units of ppm-m, for detected compounds in the instrument field of view. Figure 2 shows the Telops mid-wave hyper-spectral imager, and an example chemical map showing carbon monoxide column density.



Figure 2. TELOPS Mid-Wave Hyper-Spectral Imager.

The instrument was mounted on a heavy-duty tripod, and was deployed from the back of a field vehicle, which housed the data acquisition/control computer. The instrument was deployed at each measurement site in a location that provided a clear line of sight to the emissions source, as determined during the pre-measurement infrared camera survey. Measurements were collected with the mid-wave hyper-spectral imager during two days of the field campaign (September 10-11) at a total of five well pad sites.

### 3.4.3 Optical Gas Imaging Camera

The OGI camera was deployed to provide complementary, qualitative data on ECD flares. The camera was deployed at each site concurrently with the PFTIR and HSI, and operated by EPA Region 8 personnel. The OGI was used to confirm that hydrocarbon<sup>8</sup> emissions were present in the flare plume, and utilized to document any potential changes in the plume characteristics during the measurement period. Although the camera was used at times to collect videos simultaneously while data were being collected with the other instrumentation, the camera was not operated continuously due to limitations in the capacity of the camera flash drive. Data collected with the OGI were considered non-critical for this project.

### 3.4.4 Instrument Calibration Procedures

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<sup>8</sup> “Hydrocarbons” are VOC species that consist entirely of hydrogen and carbon and include most of the primary VOC emissions species from oil and gas operations, including alkanes and aromatic species. Hydrocarbon does not include oxygenated VOC species that are typically formed via oxidation of hydrocarbons, however, some oil and gas production activities also emit oxygenated VOC directly, e.g., formaldehyde is formed as a contamination product from methanol, and both formaldehyde and methanol are emitted directly to the atmosphere. The instruments used in this study were not able to detect oxygenated VOC emissions.

After the instrumentation was deployed, calibration procedures were conducted prior to collection of measurements. At the beginning of each day, the PFTIR team performed a series of calibrations using a custom-designed calibration cart that contained a telescope and various calibration materials. The PFTIR team performed a black body calibration using a black body with an infrared source of known spectral radiance, an infrared source calibration to determine atmospheric transmission loss between the flare plume and the PFTIR, a cold source calibration to determine radiance generated by the atmosphere between the flare plume and the PFTIR, and a sky background calibration to determine the background radiance from the sky. The calibrations were typically done once per day (at the first site of each day), although the sky background calibration was conducted more frequently when sky conditions varied during the measurement period. Deployment of the PFTIR and completion of the pre-measurement calibrations were completed at each site in one to two hours.

The HSI camera also required preliminary system setup and calibration. The initial system setup and calibration were completed at the first site where the HSI was deployed in approximately 90 minutes. System setup and calibration at subsequent sites were generally completed in 5 to 10 minutes.

After deployment and system calibrations were completed, information collected during a pre-deployment OGI camera survey was used to locate the ECD emissions, and align the PFTIR and mid-wave HSI on the source. Measurements were collected at each site for one to four hours, depending on the frequency and duration of emissions observed from the ECD. The data collected were analyzed for pollutants listed in Table 1, along with combustion efficiencies using data from the PFTIR.

### **3.4.5 Combustion Efficiency Calculations**

Several EPA regulations, including New Source Performance Standards (NSPS)<sup>9</sup> and National Emission Standards for Hazardous Air Pollutants (NESHAP),<sup>10</sup> require facilities to use good air pollution control practices to minimize the emissions released into the environment. Because not all waste gas emissions can be prevented or recovered, various control technologies are used to reduce the impact of these waste streams. For instance, EPA regulations require facilities to install control devices, such as flares, on operations that emit waste gases into the atmosphere. A flare is a mechanical device used to combust and thereby destroy volatile organic compounds, toxic compounds, and other pollutants from oil and gas operations, refineries, and other industrial facilities. Many flares employ steam or air as assist gases to improve flame stability and to promote mixing of oxygen within the vent gas to ensure combustion occurs without smoke. Completeness of combustion in a flare is governed by flame temperature, residence time in the combustion zone, turbulent mixing of the gas stream components to complete the oxidation reaction, and available oxygen for free radical formation. Combustion is complete if all VOCs are converted to carbon dioxide and water. Incomplete combustion results in some of the VOCs being unaltered or converted to other organic compounds such as aldehydes or acids.

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<sup>9</sup> EPA NSPS: <https://www.epa.gov/compliance/demonstrating-compliance-new-source-performance-standards-and-state-implementation-plans>. Last Access Date: June 2016.

<sup>10</sup> EPA NESHAP: <https://www.epa.gov/compliance/national-emission-standards-hazardous-air-pollutants-compliance-monitoring>. Last Access Date: June 2016

There are many parameters that affect the combustion efficiency of a flare. One important parameter is the heating value of the gases that are to be combusted, often measured in British Thermal Units per standard cubic foot (BTU/scf). Generally, it is easier to maintain a stable flame and achieve high efficiency for gas streams with higher heating values. The NSPS and NESHAP requirements regulate the net heating value and require that gases contain at least 300 BTU/scf if they are being combusted in an air- or steam-assisted flare. If this heating value minimum cannot be met by the vent gases alone, then supplemental gas, such as natural gas, must be added.

The current regulations require control devices to achieve 98 percent destruction efficiency. However, because most of the flare data is reported in terms of combustion efficiency, it was necessary to estimate a combustion efficiency equivalent to 98 percent destruction efficiency as a means for determining good performance for flares. Note that destruction efficiency is a measure of how much of the hydrocarbon is either fully or partially oxidized; and combustion efficiency is a measure of how much of the hydrocarbon is fully oxidized to yield carbon dioxide and water vapor.

Based on a series of flare performance studies conducted in the early 1980s, the EPA concluded that properly designed and operated flares achieve good combustion efficiency (e.g., greater than 98 percent conversion of organic compounds to carbon dioxide).<sup>11</sup> However, flares operating outside “their stable flame envelope” produced flames that were not stable or would rapidly destabilize, causing a decrease in both combustion and destruction efficiency (i.e., 40 Code of Federal Regulations (CFR) 60.18 and 40 CFR 63.11(b)). Other EPA studies also found that the combustion efficiency will always be less than or equal to the destruction efficiency; and a flare operating with a combustion efficiency of 98 percent can achieve a destruction efficiency in excess of 99.5 percent.<sup>12</sup> The relationship between destruction and combustion efficiency is not constant and changes with different compounds. However, these studies estimate that a 1.5% difference is a reasonable assumption.<sup>13</sup>

One of the goals of the project was to evaluate the combustion efficiency of ECDs at oil and gas well pads using data collected with the PFTIR. When ECDs are operating properly, efficient combustion is achieved by converting hydrocarbons to carbon dioxide and water. However, inefficient combustion occurs when the oxygen supply to the ECD is insufficient, forming products of incomplete combustion such as carbon monoxide, intermediate hydrocarbons, and carbonyls. Carbonyls include formaldehyde and other aldehydes that are HAPs and are also highly reactive precursors of ozone. Combustion efficiency (CE) is defined as the ratio of the mass concentration of carbon dioxide to the sum of the concentrations of carbon dioxide, carbon monoxide, and total hydrocarbons in the plume and is expressed using the following equation (1):

$$\text{Combustion Efficiency (\%)} = \frac{[\text{Carbon Dioxide}]}{[\text{Carbon Monoxide}] + [\text{Carbon Dioxide}] + [\text{Total Hydrocarbons}]} \quad (1)$$

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<sup>11</sup> EPA Flare Report: <https://www3.epa.gov/airtoxics/flare/2012flaretechreport.pdf>. Last Access Date: June 2016.

<sup>12</sup> EPA Flare Report: <https://www3.epa.gov/airtoxics/flare/2012flaretechreport.pdf>. Last Access Date: June 2016.

<sup>13</sup> EPA Flare Report: <https://www3.epa.gov/airtoxics/flare/2012flaretechreport.pdf>. Last Access Date: June 2016.

The fundamental output of the remote sensing instruments used in this project was the gas concentration times the path length of the gas, or ppm-m. Since the path length of all gases in the plume is the same, the path length cancels in the ratio given in the equation above. Consequently, for the CE calculation, knowledge of the actual path length through the measured plume is not necessary. At this time, only the PFTIR had the capability of generating CE values but the HSI protocols for determination of CE values are under development by the manufacturer.

### **3.5 Data Products and Reports**

Reporting requirements for this project included relative concentrations of the target compounds listed in Table 1 measured with the PFTIR, estimated concentrations of the target compounds measured with the PFTIR, concentrations of the target compounds measured with the HSI, combustion efficiency calculations for each site using data from the PFTIR instrument, Global Positioning System (GPS) coordinates of each site and measurement locations, and videos from each site collected with the OGI. Personnel from IMACC and TELOPS were responsible for all data acquisition with the PFTIR and HSI respectively, with oversight by Arcadis. Personnel from EPA Region 8 were responsible for data acquisition with the OGI. Deliverables included:

- Interferograms collected with the PFTIR;
- Interferograms collected with the HSI;
- GPS coordinates of each site and each measurement location; and
- OGI videos.

After the data were analyzed and validated, IMACC and Telops submitted a short-form report of the results and a project data package to Arcadis. Arcadis compiled the information and submitted a report and project data package to EPA. Additionally, the descriptions of the measurement technology and results of the field campaign were reported and presented at the June 2015 Air and Waste Management Association (A&WMA) Conference in Raleigh, North Carolina<sup>14</sup>.

### **3.6 Results**

The instruments were deployed at a total of ten representative well pads during the field campaign (see Table 2). Both instruments collected data at three of the 10 sites, otherwise data were collected by only one of the instruments. As a general observation, it was apparent to the field teams during deployment that the emission signals observable by the remote sensing instruments were fairly weak at most of the well pads. The amount of gas flowing to and combusted by the ECD raises the temperature of the ECD stack and the emitted plume. If the temperature of the emitted plume becomes too low, the radiated signal to the PFTIR or HSI becomes insufficient for acquisition of usable data. Since the load on the ECD is time-dependent (increases during periodic separator dumps), the signal available to the remote sensing equipment changes with time. One result of the pilot study is the observation that remote assessment of lower temperature ECDs is a more difficult task than higher temperature facility

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<sup>14</sup> [https://cfpub.epa.gov/si/si\\_public\\_record\\_report.cfm?dirEntryId=309972&subject=Health%2520Research&showCriteria=0&searchAll=Environmental%2520Justice&sortBy=revisionDate](https://cfpub.epa.gov/si/si_public_record_report.cfm?dirEntryId=309972&subject=Health%2520Research&showCriteria=0&searchAll=Environmental%2520Justice&sortBy=revisionDate) [Access Date: June 2016].

flares. For the equipment configurations and source strengths encountered in this pilot study, the emission signals were marginal in many cases. For this reason, the effective detection limits of specific compounds are variable and the quantity of usable data was generally low.

At Sites 1 and 10, the ECDs were not sufficiently active during the observation period to execute the measurement (although emissions were detected during the pre-deployment gas imaging camera survey). As a result, no usable data were collected from the PFTIR. Analysis of data collected with the PFTIR indicated that most of the ECDs showed relatively high combustion efficiency values (close to, or exceeding 0.95), with little to no detected hydrocarbon emissions. However, data collected with both instruments at Site #5 indicated emissions of hydrocarbons greater than emissions found at the other sites. A summary of the data collected at Site #5 is included below.

### 3.6.1 Site #5 Emissions Data

Data were collected at Site #5 with the PFTIR and HSI for approximately 2.5 hours on September 11, 2014. The PFTIR and HSI were deployed approximately 45 and 78 meters, respectively, from an active ECD stack at the site. Figure 3 presents an overhead view of Site #5, showing the location of the PFTIR and HSI during the measurements.



Figure 3. Overhead view of Site #5 with measurement configurations.

The PFTIR detected emissions of several hydrocarbons from the stack. A summary of path-integrated concentrations determined from data collected with the PFTIR is presented in Table 3. The table shows that most of the lighter alkanes and alkenes were detected in emissions from the site, with relatively higher concentrations of methane, ethane, and pentane.

Measurements collected with the HSI also indicated the presence of hydrocarbons in emissions from Site #5. Specifically, analysis of the data detected methane, propane, and butane, as well as carbon monoxide and formaldehyde. Figure 4 presents quantitative chemical map sequences for several compounds detected at Site #5. The top of the ECD stack is located in the lower right hand portion of each image. The maps present a spatial distribution of path-integrated concentrations (in units of ppm-m) across the ECD plume. The figures in the left column represent the path-integrated concentrations during the burst and the figures in the right column represent the path-integrated concentrations during the fade out combustion stages. The burst and fade correspond to flash gases that were routed to an ECD as result of a separator dumping liquids to atmospheric storage tanks.

Table 3. Summary of PFTIR concentration determinations (ppm-m) at Site #5.

<b>Compound</b>	<b>Minimum</b>	<b>Maximum</b>	<b>Average</b>
Carbon Dioxide	2,960	61,500	18,300
Carbon Monoxide	0	510	184
Methane	92.0	485	258
Ethane	0	224	58.3
Propane	0	36.4	10.8
Pentane	0	197	50.7
Ethene	0	80.0	40.4
Propene	0	53.2	21.0
Cyclopentene	0	57.1	35.8
Total Hydrocarbons <sup>1</sup>	92.0	3140	1170

<sup>1</sup>Computed as carbon-weighted sum of all C1 through C5 hydrocarbons

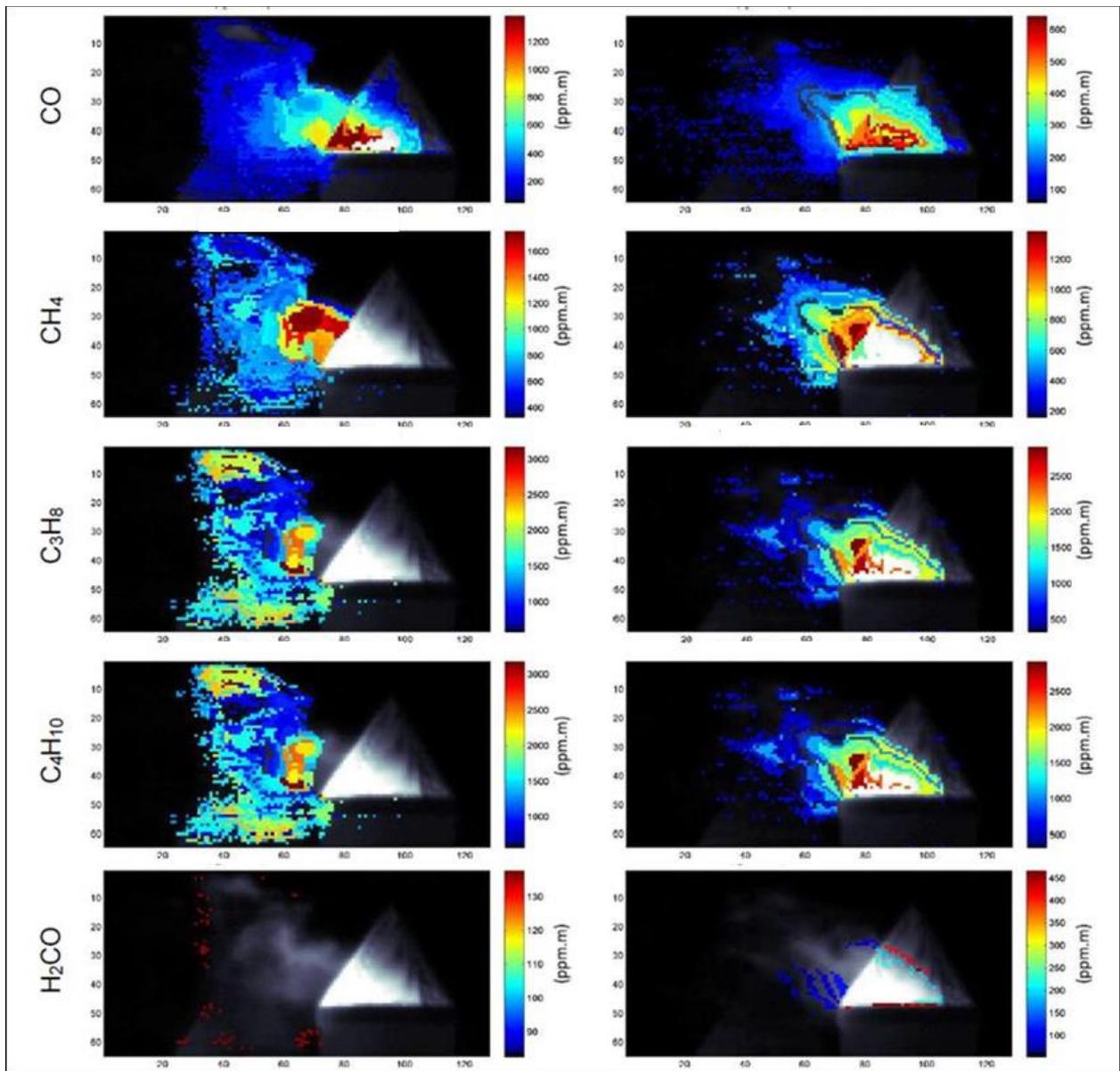


Figure 4. Quantitative chemical map sequences of carbon monoxide, methane, propane, butane, and formaldehyde emissions from enclosed combustion device at Site #5 during combustion stages, burst of heavy fuel load (left) and as the fuel load fades out (right).

### 3.6.2 Combustion Efficiency Estimates at Various Sites

The combustion efficiency of the ECDs at each site was determined from the field measurements using Equation 1. Daily plots of CE values for data that passed quality assurance (QA) acceptance criteria from four of the six sites measured using PFTIR are presented in Figure 5. The preliminary QA acceptance criteria were based on an analysis of sufficient signal level from the source as determined by the strength and spectral analysis fit quality of the observed plume compound (CO for example), compared to the noise level in the analysis region. The determination (amount of CO) must exceed the residual noise by several factors to be considered a robust detection. Insufficient signal can be caused by number of factor such as misalignment

of the observation region of the instrument (not looking at the plume), insufficient plume size and temperature, or the absence of the compound of interest in the plume. Standard definitions of PFTIR detection sensitivity and QA acceptance criteria for small intermittent sources such as ECDs is the subject of future work.

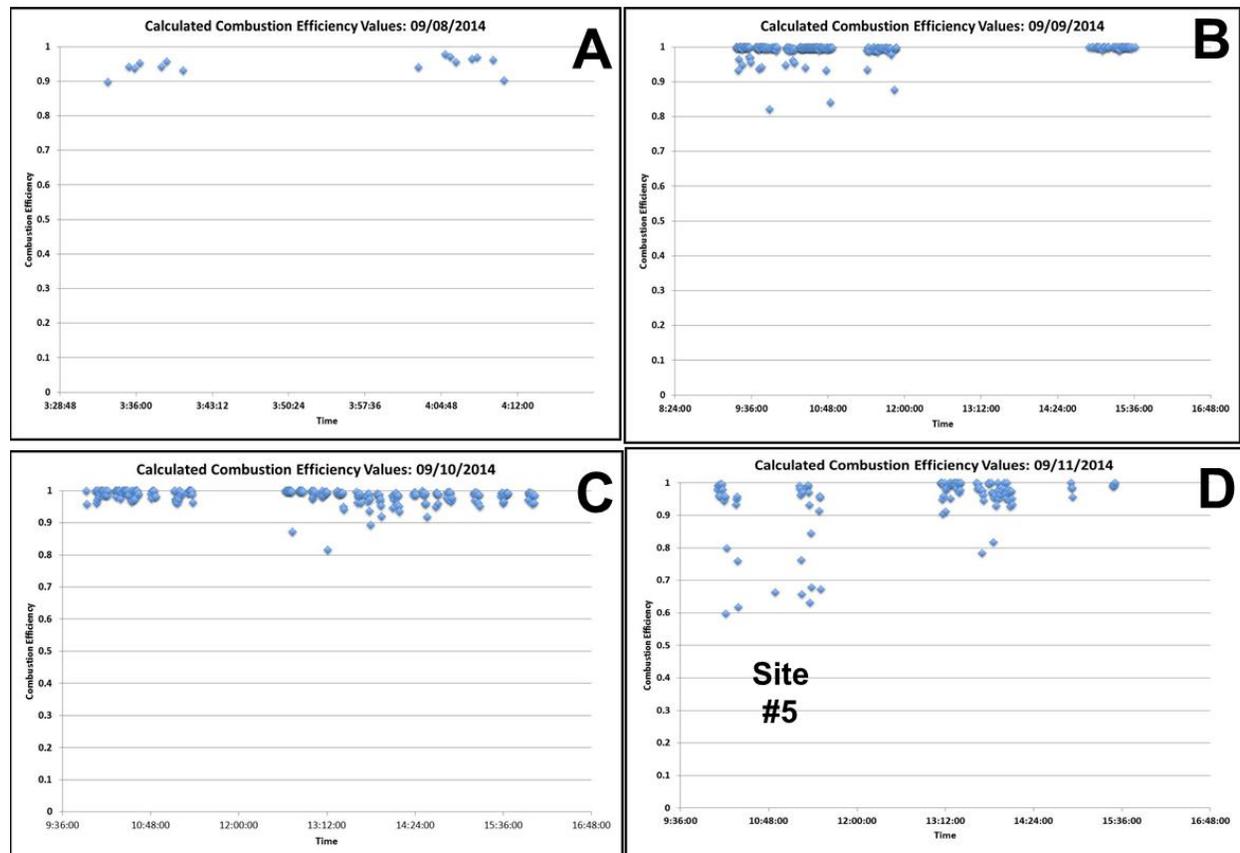


Figure 5. Daily calculated combustion efficiency values from PFTIR data. Plots shown for September 8 (A), September 9 (B), September 10 (C), and September 11 (D).

For the study sites, the majority of the calculated CE values are close to, or greater than 98%. There are periods of time where the CE appears to fall below 90% and this is most obvious at Site 5 (Figure 5D). These time periods of relatively lower CE values directly correspond with the observation of increased measurable hydrocarbon emissions from this site (see Table 3). From simultaneous OGI observations, these time periods could potentially be related to flash emission events. In general, when high CE values are registered by the PFTIR, the presence of speciated hydrocarbon emissions could not be confirmed (e.g., Table 3), as concentrations were most likely below instrument detection limits. Regarding accuracy of CE estimates for ECDs, significant uncertainty exists from a method development standpoint. Due to the small flare size and low temperatures encountered, the determination of CE is generally more difficult than for larger flare systems.<sup>15</sup> Additional method development work would be required to determine the

<sup>15</sup> Texas Commission on Environmental Quality, *TCEQ 2010 Flare Study Final Report*. See: <http://www.tceq.texas.gov/assets/public/implementation/air/rules/Flare/2010flarestudy/2010-flare-study-final-report.pdf> (accessed January, 2015).

absolute accuracy of the CE measurement for ECDs. The apparent time dependency of the CE is believed to be real, however the magnitude of these drops and the accuracy with which it is determined carries significant uncertainty. Future studies conducted on the use of PFTIR for remote ECD CE assessments would focus on the relationship between the ECD temperature, plume size, and variability, with respect to PFTIR effective field of view.

### **3.6.3 Evaluation of PFTIR and HSI Remote Sensing Approaches for ECD Assessment**

In general, the remote sensing approaches used in the field campaign were found to be potentially useful for offsite observation of ECD operation for research purposes, if direct onsite measures were not available. However, clear improvements in the instrumentations and methods would be required to improve signal strength understanding of measurement uncertainty since the signals from ECDs are not strong and are temporally variable. Limitations were found in ease of execution (setup and use of equipment), data analysis throughput, and observable ECD temperature ranges. Due to the lack of sustained infrared signal from many ECDs, the PFTIR was not as effective as compared to industrial flare applications. The accuracy of CE determination with the PFTIR approach requires additional investigation and may be complicated by the small size and variability of the ECD plume. As evidenced from Figure 4, the HSI approach provides a superior diagnostic of plume heterogeneity compared to the single element (non-imaging) PFTIR. However, the vast amount of data provided by the HSI approach make even simple determination of CE challenging, and requires significant method development work. Both techniques are best characterized as high-asset value research tools requiring significant set up time and data processing resources, making them relatively impractical for routine use. In the future, other types of emerging multi-channel remote sensing approaches may provide what is essentially a combination of aspects of the two instruments used in the campaign, but in a more implementable form. Development of one multi-channel remote sensing approach for flare CE measurements is the subject of a recently announced EPA ORD Phase II Small Business Innovative Research Award.<sup>16,17</sup>

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<sup>16</sup> U.S. EPA Phase II SBIR award; *Development of Real-Time Flare Combustion Efficiency Monitor*, 2014, Providence Photonics, LLC: Baton Rouge, LA, USA (Accessed February 2015)  
[http://cfpub.epa.gov/ncer\\_abstracts/index.cfm/fuseaction/outlinks.sbir/fullList/Yes/showYear/current](http://cfpub.epa.gov/ncer_abstracts/index.cfm/fuseaction/outlinks.sbir/fullList/Yes/showYear/current).

<sup>17</sup> Zeng, Y. 2012. White Paper on A Calibration/Verification Device for Gas Imaging Infrared Cameras. Providence, June 25, 2012. <http://www.providenceeng.com/services/technology/Optical-Gas-Imaging> (accessed February 2015).

## 4 EPA SPECIATE DATABASE

### 4.1 Background

For the second phase of this project, EPA Region 8, ORD, and OAQPS utilized information from multiple oil and gas measurement studies, to evaluate total organic gas (TOG) speciation profiles associated with oil and natural gas sector. The TOG speciation profiles are important for interpreting ambient measurement data and developing model-ready emissions for photochemical modeling applications. This modeling provides the foundation for air quality management decisions and is a critical input to air quality models used to demonstrate attainment of the National Ambient Air Quality Standards (NAAQS) or the prediction of air quality impacts.

Photochemical air quality models are used to simulate the transport of air pollution and are important tools in the regulatory process. Within these models, the predictions of major pollutants, such as ozone, NO<sub>x</sub>, VOCs, and PM, are represented using simplified chemical mechanisms and emissions inventories. The common chemical mechanisms within models either group compounds based on reactivity with hydroxyl radicals or break compounds into functional groups. Further, the emissions inventories are based on the EPA's National Emissions Inventory (NEI), which contains estimates of total anthropogenic emissions of NO<sub>x</sub>, VOCs, PM, and other pollutants in the United States. To utilize the NEI for the models, speciated emission profiles are routinely used to convert the total emissions from specific sources in the emissions inventory into the speciated emissions needed for models.

To improve the predictions of air quality models, a goal of this project included reviewing and expanding upon the TOG speciation profiles stored in EPA's SPECIATE Database<sup>18</sup> for oil and gas sources to ensure that the most recent and representative profiles are available to the community. SPECIATE is a key tool used to develop speciated emission inventories for regional haze, PM, GHGs, and photochemical air quality modeling. The Database can also be used for estimating hazardous and toxic air pollutant emissions from PM and organic gas primary emissions. It should be noted that most HAPs emissions are developed using test data or emissions factors that are more specific to a detailed process and pollutant.

Prior to this project, the SPECIATE database contained non-location-specific speciation profiles for the oil and gas sector. Many of these profiles were based on test data collected in 1989, 2000, or 2004, and added to the SPECIATE Database in 1989, 1999, 2007, 2010, or 2013. In general, the speciation profiles covered the following oil and gas areas or processes (year included either represents date of test data (DT) or date added to SPECIATE (DA)):

- External Combustion Boiler (DA=1989): Residual Oil; Distillate Oil; Natural Gas; Refinery Gas
- Natural Gas: Production (DA=2013); Transmission (DA=2013); Distribution (DT=2004); Extraction (DA=2013); Turbine (DA=1989), Flares (DA=1989); Internal Combustion Engine (DA=1989)

- Crude Oil Production (DA=1989): Fixed Roof Tank; Gathering Tanks; Storage Tanks Composite
- Oil Field (DT=1989/DA=2013): Pipeline Tanks; Extraction Wells; Gage Tank; Shipping Tank; Surge Tank; Compressor; Separator; Dehydration Tank; Vapor Recovery; Sump
- Oil and Gas Production (Fugitives) (DA=1989): Unclassified; Valves and Fittings - Liquid Service; Valves and Fittings - Gas Service
- Oil and Gas Extraction (DT=2004): Conventional; Non-Conventional; Services
- Well Heads (Water Flood) Composite (DA=1989)
- Petroleum Storage Facilities Composite (DA=1999)
- Liquefied Petroleum Gas Composition (DT=2000)
- Well Heads (Gas Drive) (DA=1989)
- Reciprocating Diesel Engine (DA=1989)

Initially, a large number of the non-basin specific profiles were used in the 2011 NEI.<sup>19,20</sup> However, improvements were made in more recent versions of the 2011 NEI to associate sources to more basin-specific speciation profiles. Given this information, it is important to develop more recent and process-specific speciation profiles for the oil and gas sector.

This project amended an existing EPA Work Assignment for the analysis and additions to the SPECIATE Database specifically related to TOG emissions from oil and gas operations. With contract support, this project surveyed the community for measurement data, reports, and publications associated with TOG emissions associated with these sources. This included information and data from:

1. RARE ECD Study;
2. WRAP Phase III Speciation Profiles;
3. Uintah and Ouray Indian Reservations Tribal Minor Source Registrations;
4. Denver-Julesburg Basin Direct Measurement Study;
5. East Texas Oil Field Speciation Data; and
6. San Joaquin, California Oil and Gas Speciation Data.

The data were consolidated into EXCEL spreadsheets, developed into speciation profiles, reviewed for completeness and representativeness, analyzed for differences among the available profiles, and prepared for entry into the SPECIATE Database. Other than the RARE ECD Study, these profiles will be included in the SPECIATE version 4.5 public release, planned for fall of 2016. The RARE ECD Study did not provide usable profiles because it was difficult to determine whether all of the targeted compounds were properly measured by the instruments. This was a result of either the emission signals observable by the remote sensing instruments being too weak at the well pads, or the limitation of the measurements.

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<sup>19</sup> 2011 NEI Emissions Inventory Technical Support Document: [http://www.epa.gov/ttn/chief/emch/2011v6/2011v6.1\\_2018\\_2025\\_base\\_EmisMod\\_TSD\\_nov2014\\_v6.pdf](http://www.epa.gov/ttn/chief/emch/2011v6/2011v6.1_2018_2025_base_EmisMod_TSD_nov2014_v6.pdf). Last Accessed: June 2016.

<sup>20</sup> 2011 v6.1 Emissions Modeling Platform Technical Support Document: [https://www.epa.gov/sites/production/files/2015-08/documents/2011v6.1\\_2018\\_2025\\_base\\_emismod\\_tsd\\_nov2014\\_v6.pdf](https://www.epa.gov/sites/production/files/2015-08/documents/2011v6.1_2018_2025_base_emismod_tsd_nov2014_v6.pdf). Last Accessed: June 2016.

The subsequent sections describe the SPECIATE Database, the datasets utilized for this project, the data processing and SPECIATE Database entry methodology, and an overview of the TOG speciation profiles developed from this project.

## **4.2 SPECIATE Database Description**

EPA develops and maintains a repository (i.e., SPECIATE Database) of TOG and PM speciation profiles of air pollution sources or weight fractions of chemical species of both TOGs (e.g., VOCs) and PM. The SPECIATE Database was computerized in 1988 and the first electronic version was distributed to the user community in 1993. The development and continuous update of the SPECIATE Database support EPA's ORD Air, Climate, and Energy Research Program (ACE).<sup>21</sup> In particular, this effort supports the assessment of impacts associated with air pollutants at various spatial scales, and provides data and tools to develop and evaluate approaches to prevent and reduce emissions of pollutants to the atmosphere.<sup>22</sup>

The SPECIATE Database is available to the public through EPA's Clearing House for Inventories and Emission Factors (CHIEF) website. In general, the most recent version of the database, SPECIATE 4.4, includes comprehensive speciation of TOG profiles from oil and gas fugitive emissions, gasoline vehicle exhaust, VOC emissions from the dairy industry (including silages, other feedstuffs, and animal waste), gasoline vapor from enclosed fuel tanks, PM profiles from the Kansas City Light-Duty Vehicle Emissions Study, outdoor wood boiler aerosol emissions, and commercial aircraft jet engine PM emission profiles. The SPECIATE 4.4 Database contains the following total number of profiles and unique species:

- 3,600 PM profiles;
- 1,879 organic gas profiles;
- 249 Other Gases profiles;
- 2,346 unique species; and
- Composite profiles for 58 (47 PM and 11 TOG) source categories.

The SPECIATE version 4.5 is expected to be available to the public in fall of 2016. The SPECIATE Database is used in conjunction with an inventory of VOC and PM, such as the NEI, in order to provide the model-ready species required for air quality modeling. The species needed are dependent on the chemical mechanism and air quality model. The NEI provides emissions of criteria air pollutants and their precursors. The NEI also contains HAPs, specific pollutants (such as benzene), and classes of pollutants (such as PM, VOC, and NOx) that may be determined through source-specific emission measurements, mass balance, source-specific models, emissions models, or emission factors.

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<sup>21</sup> ACE Action Plan: <https://www.epa.gov/sites/production/files/2014-06/documents/strap-ace2012.pdf>. Last Accessed: June 2016.

<sup>22</sup> ACE Overview: [https://yosemite.epa.gov/sab/sabproduct.nsf/CB83B5741E45F33085257A3300579242/\\$File/ACE+for+SAB\\_BOSC+071012final.pdf](https://yosemite.epa.gov/sab/sabproduct.nsf/CB83B5741E45F33085257A3300579242/$File/ACE+for+SAB_BOSC+071012final.pdf). Last Accessed: June 2016.

The data from SPECIATE may also be used to estimate HAPs in the inventory, or may be used as inputs to models such as in EPA's Oil and Gas Tool.<sup>23</sup> For example, a speciation profile containing benzene, toluene, ethyl benzene and xylenes (BTEX) can be used to estimate these HAPs from VOC for a particular process by computing VOC to BTEX factors from the TOG speciation profile and applying them to the VOC emissions for the county and process. The data from SPECIATE also provide an easy way to develop emissions inventories, to quickly analyze and determine source sectors that are major contributors to nationwide emissions of specific VOC compounds that are important for ozone formation and toxics exposure, and to provide the information needed to conduct air quality modeling.<sup>24</sup>

### **4.3 SPECIATE Data Processing and Entry Approach**

EPA has developed some guidance documents outlining a quality assurance plan and procedures for collecting and presenting source profile data to assess whether the data should be incorporated into the SPECIATE Database.<sup>25,26,27</sup> EPA is currently working to update the guidance in a Standard Operating Procedures Document.<sup>28</sup> The following sections explain the general data processing and entry approach for the development of speciation profiles for the SPECIATE Database.

#### **4.3.1 Data Collection**

In general, profiles are defined as the mass fractions of chemical species that make up a source-specific emission stream. The VOC profiles should include the mass fractions of each of the species present, including species that cannot be identified. When all organic gas species are present (e.g. methane), these profiles are referred to as TOG profiles.

Profile data must contain information on the chemical abundance of each species noted above. These data can be defined as the fraction of mass emissions of VOC/TOG or the mass emission rate of each species (e.g. pounds per ton (lb/ton); grams per vehicle-miles traveled (g/VMT), etc.). In addition to the estimate of central tendency for each species (e.g. mean, median), an estimate of the variability of each species should also be provided (e.g. standard deviation). Available information on the analytical uncertainty for individual test profiles should be identified and described separately.

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<sup>23</sup> <https://www.epa.gov/air-emissions-inventories/oil-and-gas-101-overview-oil-and-gas-upstream-activities-and-using-epas>. Last Accessed: June 2016.

<sup>24</sup> Simon, et. al., "The Development and Uses of EPA's SPECIATE Database", Atmospheric Pollution Research 1 (2010) 196-06 (<http://www3.epa.gov/ttnchie1/software/speciate/atmospheric.pdf>).

<sup>25</sup> SPECIATE Version 4.4 Quality Assurance Project Plan (QAPP), EPA Contract No. EP-D-08-100, WA 4-02, July 15, 2013.

<sup>26</sup> Protocol for Expansion of the SPECIATE Database, EPA Contract No. 68-D-00-265, WA No. 4-46, May 30, 2005.

<sup>27</sup> SPECIATE Version 4.4 Database Development Documentation, EPA Contract No. EP-D-08-100, WA No. 4-14, February 19, 2014. [https://www3.epa.gov/ttn/chief/software/speciate/speciate\\_version4\\_4\\_finalreport.pdf](https://www3.epa.gov/ttn/chief/software/speciate/speciate_version4_4_finalreport.pdf)

<sup>28</sup> SPECIATE Version 4.4 Database Development Documentation, EPA Contract No. EP-D-08-100, WA No. 4-14, February 19, 2014. [https://www3.epa.gov/ttn/chief/software/speciate/speciate\\_version4\\_4\\_finalreport.pdf](https://www3.epa.gov/ttn/chief/software/speciate/speciate_version4_4_finalreport.pdf). Last Accessed: June 2016.

The specific details of the data processing for each dataset are discussed below in section 4.4 of this report.

### **4.3.2 Documentation**

The primary reference for the profile is cited as the source of documentation. The “document” column in the “Reference Table” of the SPECIATE database is used to store this information. The “notes” column in the Reference Table of the SPECIATE database also contains additional descriptive information on the profile.

### **4.3.3 Data Format**

The data were formatted into a template developed by EPA and available on the SPECIATE Database Documentation website.<sup>29</sup> The template allows for the data to be easily added to the SPECIATE database. All the information requested in the template was provided by EPA or developed by the SPECIATE contractor, including references, test methods, analytical methods, Chemical Abstract System (CAS) numbers, data quality ratings, normalization basis, etc.

### **4.3.4 Speciation Data Quality**

Recommendations for or against inclusion of profiles into SPECIATE are based on a number of factors including whether there any available data for a particular process in the database. In some situations, the perceived overall quality of the profiles is used. There are no simple criteria that can be set to scrutinize speciation data for inclusion in the SPECIATE database. The supporting information (metadata) housed within SPECIATE is therefore critically important. Also, communication with the principal investigator involved in producing the data is essential.

The SPECIATE database provides structure sufficient to thoroughly document profiles and the underlying analyses. EPA guidance recommends that data housed in the SPECIATE Database originate from one of the following sources:

- Peer-reviewed data appearing in journal articles;
- Products of other EPA projects; or
- A select group of expert scientists in consultation to the EPA.

In addition, EPA guidance provides a profile rating criteria to assist is determining the overall quality of the profiles for inclusion into the SPECIATE Database. Each profile will have a quality rating that is assigned by the profile developer. The quality rating protocol is documented on SPECIATE Database Documentation website.<sup>30</sup> The profile ratings developed for newly added source profiles are based on the following criteria:

- V-rating (profile vintage): The vintage of the profile reflects measurement technology and methodology. For profiles before year 1980, score = 1; 1980-1990, score = 2; 1991-2000, score = 3; 2001-2005, score = 4; and after year 2006, score = 5.

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<sup>29</sup> [http://cfpub.epa.gov/si/speciate/ehpa\\_speciate\\_documentation.cfm](http://cfpub.epa.gov/si/speciate/ehpa_speciate_documentation.cfm). Last Accessed: June 2016.

<sup>30</sup> [http://cfpub.epa.gov/si/speciate/ehpa\\_speciate\\_documentation.cfm](http://cfpub.epa.gov/si/speciate/ehpa_speciate_documentation.cfm). Last Accessed: June 2016.

- D-rating (number of samples): This category is rated based on the number of samples: # of samples > 10, score = 4; 5-9 samples, score = 3; 3-4 and composite samples, score = 2; and 1-2 or unknown # of samples, score = 1.
- Quality Score: V-rating x D-rating.
- J-rating (expert judgment): Given a “1” (poor) to “5” (excellent) rating. This value is based on the information underlying each profile including, but not limited to:
  - Profile composition;
  - Relative ratios of species within the profile;
  - Sum of the speciated mass fractions; and
  - Supporting documentation.

It should be noted that speciation profiles can be based on an individual sample or an average of samples. Averaging speciation profiles is generally based on weighting and normalizing the individual profiles to generate a composite speciation profile. Composite profiles are needed because tests are often performed on different emission sources that represent the same type of operation, but perhaps at different times or different locations. When using the profiles in applications such as modeling, it is more practical to take an average of the different tests, rather than having to choose a single test.

The Quality Score is basically an objective rating and the J-rating is a subjective rating. Additional consideration in deciding whether to include the profile in SPECIATE includes:

- **Appropriate Method** – Reviewers experienced in analytical methods and application of speciation profiles will need to determine if characteristic compounds are present and properly measured. Sampling and analytical procedures need to be specific to the source and documented as thoroughly as possible.
- **Measurement Precision** – Low precision is expected for certain species; the data quality ratings should reflect this issue. In cases where the sampling or analytical methods are found to be wholly inappropriate for a given species, these data should not be included in SPECIATE.
- **Overall Test Program Confidence** – Results obtained from the test program should be consistent with expectations for that source, and if not, the differences should be sufficiently accounted for.
- **Source Category-specific Considerations** – For certain source categories, such as the pulp and paper industry, oxygenated compounds contribute significantly to organic gas emissions, thereby interfering with the proper characterization of the total TOG or VOC emissions. The solution is to collect fully speciated data using appropriate methods and to consolidate all organic gases into a total organic gas profile for normalization.

The overall rating and constituent ratings, as well as the expert judgment rating, are available to the user and auditor for consideration. Users may consider the ratings as well as the reference and summary information about the profiles housed in the profile tables to determine the suitability of a profile to the community’s needs.

## **4.4 Study or Measurement Datasets**

The following sections discuss the studies and datasets reviewed for this project to support or develop VOC speciation profiles for the SPECIATE Database. Either a quality assurance review of these datasets were conducted to determine whether the data were sufficiently supported for the entry into the SPECIATE Database, or the datasets were developed into profiles that could then be utilized in the SPECIATE Database.

### **4.4.1 RARE ECD Study**

#### **4.4.1.1 Background**

As discussed in the previous sections, the instruments deployed for the RARE ECD study collected data at a total of ten representative well pads in Weld County to characterize emissions from ECDs at upstream oil and gas production sites. Unfortunately, the emission signals observable by the remote sensing instruments were fairly weak at most of the well pads. This could have been a result of the limitation of the measurements or simply the absence of the compounds (i.e., ECDs were functioning properly). As a result, it was difficult to determine whether all of the targeted compounds were properly measured by the instruments. In addition, the field campaign focused on ambient measurements, as opposed to source-specific measurements. Given that inventories are for specific sources at an oil and gas well pad (i.e., condensate tanks, dehydrator vents, pneumatic devices), source-specific speciation data is needed for use in speciating the source-specific VOC emissions.

#### **4.4.1.2 Results**

Until additional data can be collected for these sources, the speciated emissions collected from this campaign will not be utilized to develop profiles for the SPECIATE Database. Future work could include:

- Developing a method to utilize the data collected from the RARE field campaign;
- Determining whether the data collected from the RARE field campaign represented all of the pollutants released from the sources;
- Investigating the speciated emissions profiles of properly maintained and controlled oil and gas E&P processes;
- Investigating the speciated emissions profiles of poorly maintained and controlled E&P processes.

This work would assist in determining whether the speciated emissions collected from the RARE field campaign are potentially representative of these types of sources. Further, this work could be compared to the current flare profile included in the SPECIATE Database that was based on data collected in 1989 to determine its representativeness.

## 4.4.2 WRAP Phase III VOC SPECIATION Profiles

### 4.4.2.1 Background

The Western Regional Air Partnership (WRAP) and the Western Energy Alliance (WEA), formerly the Independent Petroleum Association of Mountain States (IPAMS), sponsored the development of a Phase III regional oil and gas emission inventory for the Inter-Mountain West.<sup>31</sup> This effort focused on creating a comprehensive criteria pollutant emissions inventory for activities associated with oil and gas field operations in the basins throughout the study region for a baseline year (2006 for most basins) as well as future projection years. The inventory includes all point and area sources related to the oil and gas industry exploration and production operations at well sites and midstream (primarily compressors station and gas plants) sources, known through states' inventory efforts or disclosed by operators for the first time in the project data collection effort. Figure 6 shows oil and gas basins covered by the WRAP Phase III work with the state and county boundaries overlaid.

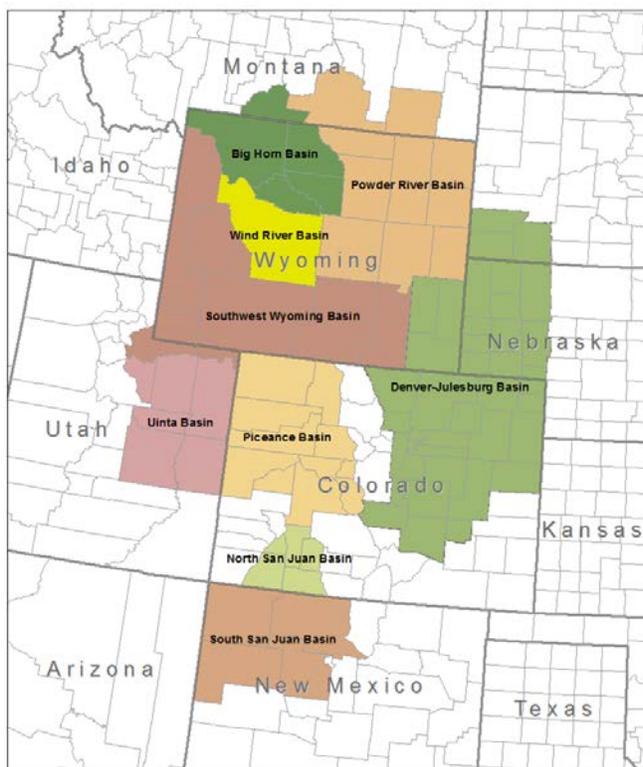


Figure 6. Overlay of the WRAP basins with state and county boundaries.

### 4.4.2.2 Methodology

To convert the raw emissions data into an emissions inventory that could support air quality activities, this effort collected gas composition analyses and developed oil and gas speciation profiles for different well types, processes, and basins in the Rocky Mountain States.<sup>32</sup> The gas

<sup>31</sup> WRAP Website: <http://www.wrapair2.org/emissions.aspx>. Last Accessed: June 2016.

<sup>32</sup> WRAP Phase III oil and gas speciation profiles Memorandum, Ramboll ENVIRON, Revised August 27, 2015

composition analyses were collected through operator surveys as part of the WRAP Phase III project. The data are based on oil and gas companies taking Gas Chromatography/Mass Spectrometry (GC/MS) analyses of their produced gas or in some cases running models such as E&P TANK using input measured compositions (again derived from GC/MS tests of hydrocarbon liquids). The gas composition data were gathered to develop 2006 base year oil and gas inventories, but may not necessarily reflect samples collected in 2006. While the samples could be from a different year, an assumption was made that the gas composition was not expected to vary much in time for a given basin. Survey respondents were instructed to provide “representative” gas compositions. However, no provisions were made to ensure that the collected compositions were statistically valid. Nevertheless, these data represent actual gas compositions collected by multiple companies in each of the WRAP basins and therefore represent an improvement over other potentially available data sources.

Each survey respondent’s gas compositions were averaged to obtain a representative operator-specific gas composition. Then, the composite weighted averaged profiles were developed by taking a weighted average of all operator specific compositions using the fraction of gas production ownership for each operator as the weighting factor. Table 4 shows the number of individual profiles across all survey respondents that were used to create the weighted average composite profile. Note that in some cases a straight average was calculated instead of a production weighted average (e.g., DJFLA) because information was not available to estimate a weighted average profile.

Table 4. Number of individual profiles averaged to develop composite profile.

P_NUMBER	Name	Number of Profiles
SSJCB	South San Juan Basin Produced Gas Composition from Coal-Bed Methane (CBM) Wells	4
SSJCO	South San Juan Basin Produced Gas Composition from Non-CBM Gas Wells	15
WRBCO	Wind River Basin Produced Gas Composition from Non-CBM Gas Wells	7
PRBCB	Powder River Basin Produced Gas Composition from CBM Wells	8
PRBCO	Powder River Basin Produced Gas Composition from Non-CBM Wells	11
DJFLA	Denver-Julesburg Basin Flashing Gas Composition for Condensate Tanks	16
DJVNT	Denver-Julesburg Basin Produced Gas Composition from Non-CBM Gas Wells	13
UNT01	Uinta Basin Produced Gas Composition from CBM Wells	3
UNT02	Uinta Basin Produced Gas Composition from Non-CBM Wells	28
UNT03	Uinta Basin Flash Gas Composition from Oil Tanks	1
UNT04	Uinta Basin Flash Gas Composition from Condensate Tanks	5
PNC01	Piceance Basin Produced Gas Composition from Non-CBM Gas Wells	20
PNC02	Piceance Basin Produced Gas Composition from Oil Wells	1
PNC03	Piceance Basin Flash Gas Composition for Condensate Tank	5
SWFLA	SW Wyoming Basin Flash Gas Composition for Condensate Tanks	6
SWVNT	SW Wyoming Basin Produced Gas Composition from Non-CBM Wells	23
PRM01	Permian Basin Produced Gas Composition for Non-CBM Wells	4

The composite weighted average profiles were normalized for organic gaseous species, excluding inorganic gases (e.g., carbon dioxide (CO<sub>2</sub>) and hydrogen sulfide (H<sub>2</sub>S)), to develop the profiles for the SPECIATE Database and Speciation Tool. SPECIATE species identification numbers were assigned to each profile based on name and engineering judgment. When there

were unknown groups (e.g., C10 compounds) in the profile, the species identification number for the lowest carbon number species in the group (i.e. C10 compounds) was applied to the profile. Finally, the WRAP Phase III basin-specific oil and gas speciation profiles were converted into the SPECIATE Database format.

#### **4.4.2.3 Results**

A total of 17 profiles related to oil and gas sector gaseous emissions were developed through this project (see Table 4). The specific profiles are provided in the accompanying EXCEL workbook, and referenced as “WRAP” in the worksheets. Appendix B also presents the final WRAP Phase III oil and gas speciation profiles. The SPECIATE profiles provided in Appendix B differ by basin and within basin by the type of emission stream.

The WRAP study suggested applications of the different types of profiles to associated source categories:

- Produced Gas Composition from non-CBM Wells: Applied to vented source emissions from non-CBM oil and gas wells in a basin for source categories such as completions, blowdowns, pneumatic controllers, pneumatic pumps, and fugitive leaks. This type of profile should not be applied to CBM well or tank emissions.
- Produced Gas Composition from non-CBM Gas Wells: Applied to vented source emissions from non-CBM gas wells in a basin for source categories such as completions, blowdowns, pneumatic controllers, pneumatic pumps, and fugitive leaks. This type of profile should not be applied to emissions from CBM wells, oil wells, or tanks.
- Produced Gas Composition from non-CBM Oil Wells: Applied to vented source emissions from non-CBM oil wells in a basin for source categories such as completions, blowdowns, pneumatic controllers, pneumatic pumps, casing head gas venting, and fugitive leaks. This type of profile should not be applied to emissions from CBM wells, gas wells, or tanks.
- Produced Gas Composition from CBM Wells: Applied to vented source emissions from CBM gas wells in a basin for source categories such as completions, blowdowns, pneumatic controllers, and fugitive leaks. This type of profile should not be applied to emissions from non-CBM wells or tanks.
- Flashing Gas Composition from Condensate Tanks: Applied to emissions in a basin from condensate tanks. This profile should not be applied to vented source emissions such as completions, blowdowns, pneumatic controllers, pneumatic pumps, and fugitive leaks.
- Flashing Gas Composition from Oil Tanks: Applied to emissions in a basin from oil tanks. This profile should not be applied to vented source emissions such as completions, blowdowns, pneumatic controllers, pneumatic pumps, and fugitive leaks.

### 4.4.3 Uintah and Ouray Indian Reservations Tribal Minor Source Registrations

#### 4.4.3.1 Background

In 2011, EPA promulgated the Indian Country Minor New Source Review Rule or Tribal Minor Source (TMS) New Source Review (NSR) Rule [40 CFR 49.151].<sup>33, 34</sup> The Rule is a preconstruction permitting program that serves two important purposes. First, it ensures that air quality in reservation areas of Indian country is not significantly degraded from the addition of new and modified sources of air pollution, such as factories, industrial boilers and power plants. In areas with unhealthy air, the Rule assures that new emissions do not slow progress toward cleaner air, or that new emissions do not significantly worsen air quality. Second, the Rule assures people that any new or modified industrial source in their neighborhoods will be as clean as possible, and that advances in pollution control occur concurrently with industrial expansion.

Tribal minor sources are defined in attainment areas as those sources with the potential to emit less than major source preconstruction permitting thresholds, but more than:

- 10 tons per year of carbon monoxide (CO), NO<sub>x</sub>, SO<sub>2</sub>, or PM, or
- 5 tons per year of VOCs, or
- 5 tons per year of particulate matter less than 10 microns (PM<sub>10</sub>), or
- 3 tons per year of particulate matter less than 2.5 microns (PM<sub>2.5</sub>), or
- 0.1 tons per year of lead, or
- 1 ton per year of fluorides, or
- 2 tons per year of H<sub>2</sub>S.

The TMS NSR rule, when promulgated, required registration of existing and new minor sources in reservation areas of Indian country until September 2, 2014, at which time new sources were required to obtain a minor source permit prior to construction [40 CFR 49.160].<sup>35</sup> EPA made a number of revisions to this rulemaking to extend the permitting deadline for new and modified minor sources in the oil and natural gas sector operating or proposing to operate in reservation areas of Indian country and other areas of Indian country for which tribal jurisdiction has been demonstrated.<sup>36</sup> The most recent February 24, 2016 deadline has been extended to October 3, 2016 for obtaining a permit. The revisions were necessary to avoid the potentially unnecessary burden of sources in the oil and natural gas sector needing to obtain source-specific permits while EPA develops a streamlined permitting solution for the source category, as contemplated in the Rule for certain source categories expected to be common and widespread throughout Indian country. The revisions also provided a level of certainty to the regulated industry, tribes and other parties pending final action on the streamlined permitting solution. Each registration requires the following information, as applicable:

- Identifying information;

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<sup>33</sup> <https://www3.epa.gov/air/tribal/tribalnsr.html>. Last Accessed: June 2016.

<sup>34</sup> [http://www.ecfr.gov/cgi-bin/text-idx?SID=b3c384e3b0e2672b9d150f1ff1bf4483&mc=true&node=se40.1.49\\_1151&rgn=div8](http://www.ecfr.gov/cgi-bin/text-idx?SID=b3c384e3b0e2672b9d150f1ff1bf4483&mc=true&node=se40.1.49_1151&rgn=div8). Last Accessed: June 2016.

<sup>35</sup> [http://www.ecfr.gov/cgi-bin/text-idx?SID=b3c384e3b0e2672b9d150f1ff1bf4483&mc=true&node=se40.1.49\\_1160&rgn=div8](http://www.ecfr.gov/cgi-bin/text-idx?SID=b3c384e3b0e2672b9d150f1ff1bf4483&mc=true&node=se40.1.49_1160&rgn=div8). Last Accessed: June 2016.

<sup>36</sup> 76 FR 38788, July 1, 2011, as amended at 79 FR 31045, May 30, 2014; 79 FR 34239, June 16, 2014.

- A description of source's processes and products;
- A list of all emissions units;
- Allowable and estimated actual annual emissions of each regulated NSR pollutant in tons per year (tpy) for each emissions unit listed (estimates must be based on actual test data or acceptable procedures, including source-specific emissions tests, mass balance calculations, published emission factors, or other engineering calculations);
- Information on fuels, fuel use, raw materials, production rates and operating schedules;
- Identification and description of any existing air pollution control equipment and compliance monitoring devices or activities; and
- Any existing limitations on source operation affecting emissions or any work practice standards for all NSR-regulated pollutants at the source.

The registrations are publically available for review. The EPA proposed a Federal Implementation Plan (FIP) under the Rule for oil and natural gas sector in September 2015 that, if finalized, will take the place of individual source permitting, unless a source opts for a site-specific permit. The proposed FIP, if finalized as proposed, would require new oil and natural gas production sources to comply with a suite of cost-effective regulations, as individually applicable, that reduce harmful air pollution from the oil and natural gas industry, in lieu of obtaining a site-specific permit prior to construction or modification.

#### **4.4.3.2 Methodology**

EPA Region 8 surveyed the TMS NSR registration data for oil and natural gas operations located on the Uintah and Ouray Indian Reservations. The registrations surveyed consisted of existing oil and natural gas sources with registration submissions between August 2011 and March 2015. Any registration data submitted for new sources or sources created or modified after this period were not included in this survey. It should also be noted that while the survey reviewed 2011 to 2015 submissions, the data may not always reflect emissions from these years. TMS NSR registration data do not need to be specific to a particular year, only representative of the expected emissions from the specific sources.

Approximately 5,200 registrations were surveyed for VOC emissions associated with oil and gas operations located on the Uintah and Ouray Indian Reservations. These registrations represented 23 different operators or companies, and consisted of crude petroleum and natural gas extraction facilities (North American Industry Classification System (NAICS) 211111), natural gas liquid extraction facilities (NAICS 211112), and support activities for oil and gas operations facilities (NAICS 213112). About 63 percent of registrations consisted of crude petroleum and natural gas extraction, about 37 percent consisted of natural gas liquid extraction, and less than 1 percent consisted of support activities for oil and gas operations.

The registrations provided extended composition analyses of the untreated natural gas stream, the tank emission stream, and the glycol dehydrator regenerator emission stream associated with each facility. The composition of each untreated natural gas stream was determined by lab analysis. The composition of each tank emission stream was determined using an emission model programs, such as the American Petroleum Institute's (API's) E&P Tanks or an analysis of the Gas Oil Ratio (GOR). These emission models require operating inputs that include

separator pressure and temperature and extended hydrocarbon analyses of pressurized liquid samples. The composition of the glycol dehydrator regenerator emission stream was determined using the Gas Research Institute (GRI-GlyCalc) emission model.<sup>37</sup> This emission model requires operating inputs that include the absorber tower pressure and temperature, the glycol circulation rate, and extended gas analysis of the input “raw” gas stream. The outputs of all these models provide speciated emission streams. No provisions were made to assess the quality or timing of the necessary pressurized liquid and raw gas stream lab analyses necessary to run these models. Further, no analyses were performed to assess the statistical “representativeness,” or ensure that the collected compositions were statistically valid. The estimated speciated emission streams were also based on emission calculations that did not account for controls being implemented. The majority of minor registered sources are uncontrolled at this time.

The registration forms do not provide details on the methods used in collecting and analyzing the samples for the oil and gas components. Nevertheless, these data represent actual gas compositions collected by multiple companies in the Uinta Basin, and are routinely collected across the oil and gas fields. Therefore, these data represent an improvement over other potentially available data sources and the current information available to the community.

An average composition for the untreated “raw” natural gas emission stream, the oil tank emission stream, the condensate tank emission stream, and the glycol dehydrator regenerator (also referred to as still vent) emission stream was determined for each operator using the data provided in the registrations. The average operator-specific profile calculated for each emission stream was then normalized for each operator. Where emission stream outputs were in terms of percentage by mole (mol%), the data were converted to percentage by weight (wt%) and normalized for TOG profiles (e.g., removing H<sub>2</sub>S, CO<sub>2</sub> or Nitrogen). This resulted in 37 average operator-specific composition profiles, which consisted of 15 untreated “raw” natural gas emission stream profiles, three oil tank emission stream profiles, 11 condensate tank emission stream profiles, and eight glycol dehydrator regenerator emission stream profiles. Table 5 presents the number of different samples used to calculate the operator-specific composition profiles for each emission stream.

The average operator-specific composition profiles developed for each operator and emission stream were then renamed into the classification established in the SPECIATE Database. For instance, “isomers of octane” from SPECIATE cover “n-Octane (C8)” output in the tank emission model. The re-classification was applied to methane, n-hexane, isomers of hexane, isomers of heptane, ethane, propane, isobutene, n-butane, isopentane, and n-pentane.

With assistance from Abt Associates, four “composite” speciated VOC profiles were developed using the 37 operator-specific composition profiles. A composite VOC profile was developed for each process emission source, including a composite profile for the untreated “raw” natural gas emission stream, the oil tank emission stream, the condensate tank emission stream, and the glycol dehydrator regenerator emission stream. Before creating the composite VOC profiles, the data were converted from volume percent (vol%) or mol% to wt%. The composite profiles were developed by combining the operator-specific profiles for a particular emission source and calculating the weighted average using oil/condensate production for tank emissions and natural

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<sup>37</sup> Gas Technology Institute, Des Plaines, USA; IL<http://sales.gastechnology.org/000102.html>.

gas production for untreated “raw” natural gas and glycol dehydrators. The production data are based on information collected during 2014 for the top 20 producers in the Uintah and Ouray reservations. Appendix C outlines the data used for weighting the profiles.

Table 5. Number of Different Samples for Each Averaged Operator-Specific Profile.

<b>Profile</b>	<b>Emission Stream</b>	<b>Number of Unique Profiles</b>
95336	Untreated Natural Gas	1
95337	Untreated Natural Gas	9
95338	Untreated Natural Gas	1
95339	Untreated Natural Gas	1
95340	Untreated Natural Gas	2
95341	Untreated Natural Gas	2
95342	Untreated Natural Gas	2
95343	Untreated Natural Gas	2
95344	Untreated Natural Gas	4
95345	Untreated Natural Gas	3
95346	Untreated Natural Gas	2
95347	Untreated Natural Gas	3
95348	Untreated Natural Gas	1
95349	Untreated Natural Gas	1
95350	Untreated Natural Gas	25
95351	Oil Tank Vent Gas	1
95352	Oil Tank Vent Gas	23
95362	Oil Tank Vent Gas	42
95353	Condensate Tank Vent Gas	2
95354	Condensate Tank Vent Gas	6
95355	Condensate Tank Vent Gas	7
95356	Condensate Tank Vent Gas	6
95357	Condensate Tank Vent Gas	2
95358	Condensate Tank Vent Gas	29
95359	Condensate Tank Vent Gas	59
95360	Condensate Tank Vent Gas	4
95361	Condensate Tank Vent Gas	4
95363	Condensate Tank Vent Gas	2
95364	Condensate Tank Vent Gas	6
95409	Glycol Dehydrator	7
95410	Glycol Dehydrator	2
95411	Glycol Dehydrator	3
95412	Glycol Dehydrator	3
95413	Glycol Dehydrator	2
95414	Glycol Dehydrator	1

95415	Glycol Dehydrator	2
95416	Glycol Dehydrator	27

#### 4.4.3.3 Results

A total of 37 operator-specific speciation profiles and four composite profiles representing weighted-average profiles for each of the emission streams/sources were developed from the Uintah Basin and Ouray Tribal Minor Source Registrations. Table 6 outlines the number of profiles for each oil and natural gas production emission source based on the data from the TMS NSR registrations. The specific profiles are provided in the accompanying EXCEL workbook, and referenced as “TMSR” in the worksheets. Appendix B also presents the final speciation profiles.

Table 6. Number of profiles for each oil and natural gas production emission source.

Emission Source Speciation	Number of Profiles
Untreated “Raw” Natural Gas	15
Oil Tank	3
Condensate Tank	11
Glycol Dehydrator Regenerator	8
Composite of Each Emission Stream	4
Total	41

The analysis of the registration data allowed for the development of VOC speciation profiles for oil and natural gas sources located on the Uintah and Ouray Indian Reservations. These speciation profiles have the following suggested applications:

- Untreated “Raw” Natural Gas Emission Stream: This profile should be applied to emission sources such as fugitive leaks, pneumatic controllers, and pneumatic pumps.
- Oil Tank Emission Stream: This profile should be applied to emissions sources from oil tanks (those with API Gravity of the sales oil <40 degrees) and include flash, working/breathing/standing emissions.
- Condensate Tank Emission Stream: This profile should be applied to emissions sources from condensate tanks (those with API Gravity of the sales oil >40 degrees) and include flash, working/breathing/standing emissions.
- Glycol Dehydrators Regenerator (Still Vent) Emission Stream: This profile should be applied to emissions sources from glycol dehydrator regenerator/still vents.

Given the similarity in approaches used for these and the WRAP III profiles, a comparison was done in species concentrations across similar emission sources for the individual and composite TMS NSR profiles and the Uintah Basin WRAP III profiles. The comparison is provided in the accompanying EXCEL workbook, and referenced as “Uintah\_Profile\_Comparison” in the worksheets. The comparison, provided in Appendix B, shows varying agreement by source type and species, with the raw gas profiles being the most consistent.

## 4.4.4 Denver-Julesburg Basin Direct Measurement Study

### 4.4.4.1 Background

In July 2011, EPA, with contract support from Arcadis, conducted a direct measurement study of production pad emissions in Weld County, Colorado.<sup>38, 39</sup> This effort was coordinated with Sage Environmental Consulting (Sage) and several industry operators. The study focused on the determination of instantaneous VOC and methane (CH<sub>4</sub>) emissions from production pads, with emphasis on oil and condensate tank emissions, using non-invasive measurement techniques, such as infrared video and real-time leak measurements coupled with subsequent laboratory analysis of acquired canisters. The general goals for the study were to improve the understanding of component-level emissions and speciation profiles from production pads using non-invasive measurement approaches. Another goal of the study was to improve the understanding of the performance of high volume sampling equipment for emissions that are VOC rich (defined here as combustible vapor less than ~95% CH<sub>4</sub>).<sup>40, 41</sup>

A total of 23 sites within Weld County, Colorado were selected for sampling. For each well pad, leak inspections were performed to identify emission points, and the identified emission points were sampled to determine the emissions rate and to estimate the mass emission rates of individual organic compounds. From the largest emission point on each well pad, at least one sample was acquired at the exit of the High Volume Sampler (HVS) using a leak-free, sub-atmospheric 6-liter stainless steel canister with a valve and passivated interior. The canister-derived concentration values were used with the measured HVS flow rates to calculate emission rates for individual and groups of compounds, including the US EPA Photochemical Assessment Monitoring (PAMS) Target (VOC, as well as percent level CH<sub>4</sub>, ethane, ethene, propene, and propane. The concentrations of total and speciated non-methane volatile organic compounds were determined using Gas Chromatography with Flame Ionization Detection (GC/FID) as described in EPA/600-R-98/161<sup>42</sup> coupled with American Society for Testing and Materials (ASTM) 1946/D1945 analysis<sup>43</sup> of methane, ethane, and propane. The calculation of the emission rate of total combustibles and total VOC emissions was accomplished by summing the

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<sup>38</sup> Understanding Direct Emission Measurement Approaches for Upstream Oil and Gas Production Operations, M. Modrak, M. Shahrooz, J. Ibanez, C. Lehmann, B. Harris, D. Ranum, E. Thoma, B. Squier, Air & Waste Management Association, 105<sup>th</sup> Annual Conference and Exhibition, June 19-22, 2012, Texas.

<sup>39</sup> Assessment of VOC and HAP Emissions from Oil and Natural Gas Well Pads Using Mobile Remote and Onsite Direct Measurements, Halley L. Brantley, E. D. Thoma, A.P. Eisele (2015); Journal of the Air & Waste Management Association, DOI: 10.1080/10962247.2015.10568.

<sup>40</sup> EPA Report, *Oil and Gas Production Pad Air Emission Study, Weld County, Colorado*, prepared by Arcadis under EP-C-09-027, (in preparation).

<sup>41</sup> U.S. EPA. *Greenhouse Gas Emissions Reporting From the Petroleum and Natural Gas Industry, Background Technical Supporting Document, supporting 40 CFR Part 98.230, 77 FR 11039 Subpart W – Petroleum and Natural Gas Systems*, at web site: [http://www.epa.gov/climatechange/emissions/downloads10/Subpart-W\\_TSD.pdf](http://www.epa.gov/climatechange/emissions/downloads10/Subpart-W_TSD.pdf). Last Accessed: June 2016.

<sup>42</sup> Technical Assistance Document for Sampling and Analysis of Ozone Precursors, EPA National Exposure Research Laboratory, Research Triangle Park, NC, September 1998. <https://www3.epa.gov/ttnamti1/files/ambient/pams/newtad.pdf> (Accessed: June 2016).

<sup>43</sup> American Society for Testing and Materials (ASTM). 2010. ASTM D1945-03. Standard Test Method for Analysis of Natural Gas by Gas Chromatography. West Conshohocken, PA: ASTM International. [www.astm.org](http://www.astm.org). doi:10.1520/D1945-03R10.

concentrations of individual measured species to achieve a total measured pollutant vol%, which was then multiplied by the total gas flow rate (converted to standard conditions). The calculation of speciated mass emissions was accomplished by first converting the VOC concentration results from parts per million by volume (ppmv) to units of micrograms per cubic meter ( $\mu\text{g}/\text{m}^3$ ) and converting the gas flow rate to standard gas flow.

From the 23 sites, a total of 106 emission points were measured by the instruments. Samples were acquired from condensate tank thief hatch leaks or other emission points prior to the control device. The average production pad consisted of five wells, 258 valves, 2,583 connectors, three condensate tanks, one produced water tank, four thief hatches, five pressure relief devices, three separators, and all sites contained one flare or combustor. One production pad contained a dehydration unit, and four each contained one vapor recovery unit. All sites were fitted with one ECD as per current State of Colorado requirements. Of the 23 sites surveyed, 19 processed field gas by a single stage three phase separator and four utilized a two stage separation process to further recover natural gas by reducing the net pressure by approximately 25 percent of the liquid sent to the condensate tanks via a buffer tank.

#### **4.4.4.2 Methodology**

The direct measurement study conducted in the Denver-Julesburg Basin collected data from produced water tanks, separators, well heads, dehydrators, and condensate tanks from oil and natural gas production operations.<sup>37,38,44</sup> However, only the data from the condensate tanks were used in this work because of the amount and quality of the available samples. There was not enough confidence in the data from the other sources because only a limited number of samples were collected. For instance, data referenced as separator emissions may be a pneumatic controller leak that happened to be near the separator. Additionally, the produced water tank only had one sample. Therefore, this work focused on the data collected from the condensate tanks.

The raw speciation data collected from the canister samples were used to develop VOC speciation profiles. The data were available in concentrations (ppb). Because the sum of adding methane, ethane, and all other measured species was so large relative to the unknown species, it was reasonable to use the sum of measured or known species as the normalization basis. Based on ideal gas law, for each canister sample (i.e., fixed volume), volume fraction (ppb) is equivalent to mole fraction for each species. By multiplying molecular weight to concentration (ppb), each species was converted into mass. The sum of these speciated masses was the normalization basis for each profile. Each speciated mass was divided by the sum of speciated masses to calculate the weight fraction, then converted to wt% by multiplying 100.

The composite profile was developed by taking the mean of the individual condensate tank profiles. By comparing the composite profile compositions using “mean” and “median” of each

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<sup>44</sup> U.S. EPA. “Technical Assistance Document for Sampling and Analysis of Ozone Precursors. (1998), At web site <https://www3.epa.gov/ttnamti1/files/ambient/pams/newtad.pdf> (accessed June 22, 2016). American Society for Testing and Materials (ASTM). ASTM D1945-03, “Standard Test Method for Analysis of Natural Gas by Gas Chromatography” West Conshohocken, PA: ASTM International. [www.astm.org](http://www.astm.org). (2010) doi:10.1520/D1945-03R10.

species, it was found that both methods resulted in very similar composite profile compositions. As a result, this work elected to use the “mean” to composite the condensate tank profiles.

#### 4.4.4.3 Results

A total of 27 speciation profiles and one composite profile for the condensate tank emissions were developed from the measurements collected in the DJ Basin. Table 7 presents the number of oil and natural gas production profiles for each emission source. The specific profiles are provided in the accompanying EXCEL workbook, and referenced as “DJBasinDMS” in the worksheets. Appendix B also presents the final speciation profiles.

Table 7. Number of profiles for each oil and natural gas production emission source.

Category	Number of Profiles
Condensate Tank	27
Composite	1
Total	28

The analysis of the measurement data allowed for the development of VOC speciation profiles for oil and natural gas sources located in the DJ Basin. These speciation profiles have the following suggested applications:

- Condensate Tank Emission Stream: This profile should be applied to emissions sources from condensate tanks. Samples were acquired from condensate tank thief hatch leaks or other emission point prior to the control device. All sites were fitted with one ECD as per current State of Colorado requirements.

#### 4.4.5 East Texas Oil Field Speciation Data

##### 4.4.5.1 Background

Measurements conducted by the National Oceanic and Atmospheric Administration (NOAA) and other research organizations during the 2000 Texas Air Quality Study (TexAQS 2000) suggested that the levels of VOC found in ambient air could not all be accounted for based on reported emissions estimates. As a result, the Texas Commission on Environmental Quality (TCEQ) began an intensive effort to identify, quantify, and reduce VOC emissions that had been underestimated in the past. In this effort, TCEQ identified oil and condensate storage tanks, through the use of remote sensing measurements, as a source category for potentially underestimated emissions (TCEQ, 2005). Oil and condensate storage tank emissions at wellhead and gathering sites are composed of working losses, breathing losses, and flashing losses. Working losses are vapors that are displaced from a tank during the filling cycle and breathing losses are vapors that are produced in response to diurnal temperature changes. Flashing losses are vapors that are released when a liquid with entrained gases experiences a pressure drop, as during the transfer of liquid hydrocarbons from a wellhead or separator to a storage tank that is vented to the atmosphere. This effort also resulted in a study that investigated and developed speciated VOC profiles and emissions factors for condensate storage tanks in Texas. The study is summarized below.

To support the TCEQ efforts, the Texas Environmental Research Consortium (TERC) study was conducted in 2005 to evaluate ozone control strategies for Dallas-Fort Worth (DFW), Houston-Galveston-Brazoria (HGB), and Beaumont-Port Arthur (BPA) by measuring speciated VOCs and developing average emission factors (in units of pounds of VOC per barrel of oil or condensate produced (pound per barrels of oil (lb/bbl)) from direct measurements of vent gas flow rates and chemical composition.<sup>45</sup> The measurements were made by directly monitoring the flow rates of gases escaping from storage tank vents and sampling the vent gases for chemical composition. Producers of oil and condensate from seven companies allowed the emission measurements at one or more wellhead or gathering sites. The storage tank battery sites generally consisted of one or more wellheads, one or more high pressure separators, and two or more storage tanks containing either water or liquid hydrocarbon (oil or condensate). The approximate age of the inspected tank batteries ranged from two to more than 50 years. The conditions of the storage tank batteries were found to vary quite a bit, with some older tanks being of bolted construction and the newer tanks being of welded construction. The welded tank batteries generally had piping for vent gas consolidation to a common vent. The storage tank capacities ranged from 300 to 500 barrels except for at one gathering station, which had tank capacities ranging from 5,000 to 10,000 barrels. Thirty-three tank batteries met the criteria for sampling vent gas emissions. Of the 33 tank batteries that were sampled, 27 transferred its liquid product by tanker truck, five by pipeline, and one by barge. The 2005 TERC study reported measurements of speciated VOC emissions made at 11 oil and 22 condensate tank battery sites in the BPA, DFW, and HGB areas during May-July, 2006.

#### **4.4.5.2 Methodology**

Prior to the commencement of this RARE project, EPA had collected the speciated VOC data from the 2005 Texas study. A total of 33 profiles were obtained from the TCEQ Texas study, including 11 oil tank battery vent gas profiles and 22 condensate tank battery vent gas profiles.<sup>46</sup> However, composite profiles of the oil tank and condensate tank profiles were not developed for the SPECIATE Database. As a result, the RARE project prepared two composite speciation profiles for entry into SPECIATE.

The Texas study had already calculated a mean speciation profile for the oil tank battery vent gas and condensate tank battery vent gas. However, the mean speciation profiles provided by the Texas study included the wt% of some measured gases that are not needed for the SPECIATE Database, including nitrogen and carbon dioxide. As a result, this work removed the nitrogen and carbon dioxide contributions from each mean profile and re-normalized the profiles by the sum of the remaining gases.

#### **4.4.5.3 Results**

A total of two composite profiles for tank batteries were developed from the measurements collected in the Texas study. Table 8 presents the number of oil and natural gas production

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<sup>45</sup> 2005 TERC Study Report: <http://files.harc.edu/Projects/AirQuality/Projects/H051C/H051CFinalReport.pdf>. Last Accessed: June 2016.

<sup>46</sup> 2005 TERC Study Report: <http://files.harc.edu/Projects/AirQuality/Projects/H051C/H051CFinalReport.pdf>: See Table 3-4 and Table 3-5 on pages 3-6 to 3-10. Last Accessed: June 2016.

profiles for each emission source. The specific profiles are provided in the accompanying EXCEL workbook, and referenced as “Texas” in the worksheets. Appendix B also presents the final speciation profiles.

The analysis of the measurement data allowed for the development of VOC speciation profiles for oil and natural gas sources located in East Texas. These speciation profiles have the following suggested applications:

- Oil Tank Battery Vent Gas
- Condensate Tank Battery Vent Gas

Table 8. Number of new composite profiles for each oil and natural gas production emission source.

Category	Number of Profiles
Oil Tank Battery Vent Gas	1
Condensate Tank Battery Vent Gas	1
Total	2

#### 4.4.6 San Joaquin, California Oil and Gas Speciation Data

##### 4.4.6.1 Background

California is an important region for oil and natural gas production in the United States. These sources are prominent in the California Air Resources Board (CARB) emission inventory of reactive organic gases (ROG) in the San Joaquin Valley.<sup>47</sup> Petroleum operations include extraction, storage, transport, and processing; all of which can have varying degrees of fugitive emissions of methane and other gas-phase organic carbon, including VOCs.

In accordance with the Request for Proposal issued by CARB, a study was completed in 1991 to characterize fugitive emissions from oil fields in California.<sup>48</sup> The Ventura, Elk Hills, and Wilmington fields in California were targeted for this study. At the time of the study, the major oil producers in this area included Shell, Chevron, Bechtel, Texaco, Union Oil, and THUMS Long Beach Company. The study investigated three source categories from California oil production facilities, including oil production fugitive emissions, utility engine exhaust, and farm and heavy-duty engine exhaust. Only the oil production fugitive emissions were reviewed for this project. The components of the oil production fugitive emissions sampled in this study included wellheads, pipelines, processing, and storage tanks. Samples from two secondary sumps were also collected from a flux chamber in SUMMA electro-polished, evacuated stainless steel canisters. Storage tank headspace samples were collected in evacuated steel canisters. Samples from other components were obtained by isolating the selected component(s) with a Teflon®

<sup>47</sup> Emissions of organic carbon and methane from petroleum and dairy operations in California’s San Joaquin Valley, *Atmos. Chem. Phys.*, 14, 4955–4978, 2014, [www.atmos-chem-phys.net/14/4955/2014/](http://www.atmos-chem-phys.net/14/4955/2014/), doi:10.5194/acp-14-4955-2014.

<sup>48</sup> Final Report on Development of Species Profiles for Selected Organic Emission Sources, Volume I: Oil Field Fugitive Emissions, Prepared by Albert C. Censullo, California Polytechnic State University, Contract No. A832-059, Prepared for California Air Resource Board, April 30, 1991. [https://inis.iaea.org/search/search.aspx?orig\\_q=RN:23071542](https://inis.iaea.org/search/search.aspx?orig_q=RN:23071542). Last Accessed: June 2016.

shroud, and collecting the shroud effluent in evacuated steel canisters. Additional samples from several sources were taken by direct connection of the evacuated canisters to pipe fittings in the distribution lines using Teflon tubing. Analysis for desired hydrocarbon constituents were performed using a variety of validated chromatographic methods. This study collected a total of 38 samples from the oil production facilities.

In 2003, the U.S. Geological Survey (USGS) completed an assessment of the oil and gas resource potential of the San Joaquin Basin Province of California.<sup>49</sup> Part of this assessment included the identification and characterization of natural gas types in the San Joaquin Basin.<sup>50</sup> To accomplish this goal, 66 gas samples were analyzed for C1 to C7 hydrocarbons, CO<sub>2</sub>, CO, Nitrogen, Oxygen, Argon, Helium, Hydrogen, and H<sub>2</sub>S using a Wason gas analyzer, and a customized Hewlett-Packard gas chromatograph. Stable carbon isotopes of methane, ethane, propane, butane and carbon dioxide were measured using a Hewlett-Packard gas chromatograph interfaced with a Micromass Optima continuous-flow isotope ratio mass spectrometer (IRMS). The results were also combined with analyses of 15 gas samples from previous studies. For the purpose of this resource assessment, each gas type was assigned to the most likely petroleum system. Three general gas types were identified on the basis of bulk and stable carbon isotopic composition, including thermogenic dry, thermogenic wet and biogenic. About 75 percent of the gas samples in this study were taken from oil fields, with the rest taken from gas fields, generally reflecting the dominance of oil and associated gas production over non-associated gas production in the San Joaquin Basin Province.

#### **4.4.6.2 Methodology**

Prior to the commencement of this RARE project, EPA had collected the speciated VOC data from the 1991 and 2003 California studies discussed above. A total of 39 profiles were obtained from the 1991 study<sup>51</sup> and 77 profiles were obtained from the 2003 study.<sup>52</sup> Table 9 outlines the numbers of profiles for each emission source from each study. However, composite profiles for each source type were not developed for the SPECIATE Database. As a result, the RARE project prepared the composite speciation profiles for entry into SPECIATE.

The data from the 1991 study were already presented in wt%. As a result, no manipulations were applied to the data. The composite profiles using the 1991 study were based on the mean of the original profiles. The mean was applied rather than the median for two reasons, including:

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<sup>49</sup> Petroleum Systems and Geologic Assessment of Oil and Gas in the San Joaquin Basin Province, California, USGS, Energy Resource Program, edited by Allegra Hosford Scheirer, 2007. <http://pubs.usgs.gov/pp/pp1713/>. Last Accessed: June 2016.

<sup>50</sup> Chapter 10, Petroleum Systems of the San Joaquin Basin Province – Geochemical Characteristics of Gas Types, Petroleum Systems and Geologic Assessment of Oil and Gas in the San Joaquin Basin Province, California, USGS, Lillis et al., 2007. [http://pubs.usgs.gov/pp/pp1713/10/pp1713\\_ch10.pdf](http://pubs.usgs.gov/pp/pp1713/10/pp1713_ch10.pdf). Last Accessed: June 2016.

<sup>51</sup> Final Report on Development of Species Profiles for Selected Organic Emission Sources, Volume I: Oil Field Fugitive Emissions, Prepared by Albert C. Censullo, California Polytechnic State University, Contract No. A832-059, Prepared for California Air Resource Board, April 30, 1991. See Table 7 to Table 13 on pages 37 to 43.

<sup>52</sup> Chapter 10, Petroleum Systems of the San Joaquin Basin Province – Geochemical Characteristics of Gas Types, Petroleum Systems and Geologic Assessment of Oil and Gas in the San Joaquin Basin Province, California, USGS, Lillis et al., 2007. See Table 10.2A and Table 10.2B on pages 24 to 29.

1. Some of the composites only had three to five individual profiles available. Therefore, no meaningful median profiles could be calculated; and
2. For those composites that were based on more than 20 individual profiles, it was found that the composites based on mean and median were very similar.

The data from the 2003 study were presented in mol%. As a result, the data were converted to wt% using the molecular weight of each species, and then normalized by the sum of the species. Multiple species were also renamed into the classification established in the SPECIATE Database. For instance, “C1” from the data was renamed to methane. The re-classification was applied to ethane, propane; isobutene; n-butane; isopentane (2-methyl butane); n-pentane; neopentane (2,2-dimethyl propane); n-hexane; n-heptane.

Table 9. Number of profiles collected from each California Study.

Category	Number of Profiles
1991 Study	
Oil Wells	9
Oil Tanks	17
Oil Separators	3
Oil Vapor Recovery	5
Oil Field - Dehydration Tank	1
Oil Field - Gage Tank	1
Oil Field - Sump, inlet end	1
Oil Field - Sump, outlet end	1
Oil Field - Sump	1
Total	39
2003 Study	
Gas Wells	20
Oil Wells	40
Oil and Gas Separators	9
Oil Well Tanks	3
Oil Well Casings	2
Gas and Oil Condensate Wells	3
Total	77

#### 4.4.6.3 Results

A total of ten composite profiles were developed from the measurements collected from the 1991 and 2003 California studies. Table 10 presents the number of oil and natural gas production profiles for each emission source. The specific profiles are provided in the accompanying EXCEL workbook, and referenced as “California” in the worksheets. Appendix B also presents the final speciation profiles.

The analysis of the measurement data allowed for the development of VOC speciation profiles for oil and natural gas sources located in San Joaquin, California. These speciation profiles have the following suggested applications: gas wells, oil wells, oil and gas separators, oil well tanks, oil well casings, gas and oil condensate wells, and oil vapor recovery operations.

Table 10. Number of composite profiles for each oil and natural gas production emission source.

Category	Number of Profiles
Oil Wells	2
Oil Tanks	1
Oil Separators	1
Oil Vapor Recovery	1
Gas Wells	1
Oil and Gas Separators	1
Oil Well Tanks	1
Oil Well Casings	1
Gas and Oil Condensate Wells	1
Total	10

#### 4.5 Results of SPECIATE Work

For the second phase of this project, EPA Region 8, ORD, and OAQPS, with contract support from Abt Associates, utilized the information gathered from the RARE ECD field campaign, as well as other oil and gas measurement studies, to expand upon the VOC speciation profiles associated with the oil and natural gas sector stored in EPA’s SPECIATE Database. This project reviewed data from the six different studies summarized above, and generated a total of 98 profiles associated with various oil and gas operations. These profiles will be included in the next release of the SPECIATE Database (version 4.5). Table 11 presents the number of individual profiles developed from each study reviewed for this project.

In a preliminary review of the data, the VOC speciated profiles vary by oil and gas basin, region of the United States, the type of pollutants emitted from the sources, and ratio of the pollutants emitted from the sources. It should be noted that all of these profiles represent uncontrolled sources. Table 11 presents the number of different species (including groups like “C10 compounds”) that comprised the profiles measured or developed from each of the studies. The number of species measured or used to speciate the VOC profiles ranged from 24 species to 59 species. A total of 87 different pollutants/groups were obtained among all the profiles developed for this project. Table 11 also presents the range of methane and highly reactive VOC contributions for each dataset. The specific profiles are provided in the accompanying EXCEL workbook. Appendix B also presents the percent contribution by weight of the various pollutants by profile developed for this project. The results presented in Appendix B are also grouped by various oil and gas components.

Based on these results, care should be taken in selecting the speciation profiles to apply to various source categories and basin to basin. When possible, the SPECIATE profiles specifically associated with operations or sources should be used to speciate the VOC emissions. The types of controls should also be carefully considered when selecting a speciation profile to develop speciated emissions for the oil and gas sector. For instance, a speciated profile associated with the control device should only be used to characterize the controlled portion of the VOC emitted from the emission stream. Profile developers should also use care and be specific when labeling and describing the profiles for SPECIATE to assist users in linking the profiles to inventory emissions. However, additional work is needed by EPA to develop a common set of terminology and metadata that could be used by profile developers for profile labels, assignments, and descriptions.

Table 11. Number of individual profiles developed from each study reviewed for this project.

Study	Types of Sources	# of Profiles	# of Species	Range of Methane Contribution [%]	Range of Reactive VOC Contribution [%] <sup>1</sup>
RARE ECD Study	Enclosed Combustor Devices	0	0	-	-
WRAP Study	Composite Profiles – Produced Gas for CBM Wells, Non-CBM Gas Wells and Oil Wells; Flashing Gas for Condensate Tanks and Oil Tanks	17	28	0.008-99.9	0.12-36.02
DJ Basin Direct Measurement Study	Individual Profiles of Oil and Natural Gas Production Condensate Tanks; and One Composite Profile	28	58	3.08-28.8	26.1-33.23
Utah Indian Reservations Tribal Minor Source Registrations	Individual Profiles of Oil and Gas Production – Untreated Natural Gas; Oil Tank Vent Gas; Condensate Tank Vent Gas; Glycol Dehydrator; and Four Composite Profiles	41	24	0.02-89.6	1.6-74.13
Texas Study	Composite Profiles of Oil Tank Battery Vent Gas and Condensate Tank Battery Vent Gas	2	33	15.9-37.3	17.42-22.2
California Studies	Composite Profiles of Gas Wells, Oil Wells, Oil and Gas Separators, Oil Well Tanks, Oil Well Casings, Gas and Oil Condensate Wells, and Oil Vapor Recovery Operations	10	59	30.7-96.3	2.3-24.1
Total		98	87 <sup>2</sup>		

<sup>1</sup> Represents the sum of benzene, ethane, xylenes (xylene/m&p-xylene/m-xylene/o-xylene/p-xylene), toluene, n-butane, 2,2,4-trimethylpentane, and ethylbenzene.

<sup>2</sup> This number represents the total number of different species among all of the profiles. Because the species overlap among the profiles or not all of the same species are covered in all profiles, this number will not represent of sum of the values in this column.

## 5 SUMMARY

This Fiscal Year (FY) 2014 to FY 2016 RARE project was a collaborative research effort between EPA Region 8, ORD and OAQPS to improve our understanding of remote measurement methods to assess VOC control devices and VOC emissions emitted from various oil and gas operations. The project also utilized information from multiple measurement projects to improve EPA's SPECIATE database. This report summarized the Region 8 RARE effort that aimed to improve information on upstream oil and production emissions and identify areas where future work is needed for this source sector.

The project occurred in two phases. The first phase of the project consisted of a pilot field campaign in the DJ Basin using off-site remote measurements to assess VOC control efficiency and emissions of highly reactive VOCs from ECDs at well pads. The goals of the campaign were to evaluate the performance of measurement technologies to characterize emissions from ECDs at upstream oil and gas production sites, to provide speciated emissions information from the ECDs, and to assess the combustion efficiency of the ECDs. The campaign was executed over a course of five days in September 2014 to collect emissions data from ECDs at multiple well site locations in a natural gas field of Weld County, Colorado. The campaign utilized two primary instruments, including a PFTIR radiometer (IMACC, LLC, Round Rock, TX, USA), and a mid-wave infrared HSI camera (Telops, Quebec City, QC, Canada).

The results of the pilot field campaign indicated that it is important to develop easy-to-use remote approaches for assessment of ECD operational states, as high combustion efficiencies cannot be assumed under all conditions. In general, the remote sensing approaches evaluated in this project were found to be potentially useful as research tools for off-site observation of ECD operation if more direct on-site measures are not available. However, clear improvements in the instrumentations and methods would be required to improve the signal strength of the measurement uncertainty, given that the signals from ECDs are not strong and are temporally variable. Limitations were found in ease of execution, data analysis throughput, and observable ECD temperature ranges. Due to the lack of sustained infrared signal from many ECDs, the PFTIR was not as effective as compared to industrial flare applications. The results of the field campaign also developed some limited knowledge on potentially emitted byproducts from improperly operated combustors and their associated VOC reactivity, and collected measurements to determine component-level emissions from oil and gas control-related devices. Of ten well pads investigated, at least one demonstrated evidence of improper ECD operations. However, the field study was not able to quantify the emissions of highly reactive VOC from these devices with a high-level of certainty.

The second phase of the project utilized information from oil and gas measurement studies to improve the VOC speciation profiles for multiple oil and gas basins used for emissions inventory development and air quality models. The goals of this phase of the project included reviewing and expanding upon the VOC speciation profiles stored in EPA's SPECIATE Database for oil and gas sources to ensure that the most recent and representative profiles are available to the community. The current version of the SPECIATE Database (v4.4) contains non-location-specific speciation profiles for the oil and gas sector. Many of these profiles were based on test data collected between 1989 and 2004. Further, the speciation profile generally used for oil and gas is based on data from 1989 and assumes that ethane and propane are 30 percent of the VOCs,

and formaldehyde and methane are 20 percent. This weighted profile of highly reactive VOCs may not be appropriate to use to generate speciated VOC emissions for most oil and gas operations because current data and research studies suggest that the speciation of VOC emissions can vary significantly among oil and gas operations and basins. Without more representative VOC speciation profiles to generate improved VOC emissions from these types of sources, the air quality model will have difficulties predicting air quality impacts from this source sector. As a result, this project reviewed data from a total of six different studies to develop more recent and process-specific speciation profiles for the oil and gas sector. The data were consolidated into EXCEL spreadsheets, developed into speciation profiles, reviewed for completeness and representativeness, analyzed for differences among the available profiles, and prepared for entry into the SPECIATE Database.

The results of the SPECIATE work generated a total of 98 profiles associated with various oil and gas operations within multiple oil and gas basins. These profiles will be included in the next release of the SPECIATE Database (version 4.5). In a preliminary review of the data, the VOC speciated profiles vary by oil and gas basin, region of the United States, the type of pollutants emitted from the sources, and ratio of the pollutants emitted from the sources. Based on these results, care should be taken in selecting the speciation profiles to apply to various source categories. When possible, the SPECIATE profiles specifically associated with operations or source should be used to speciate the VOC emissions. The types of controls should also be carefully considered when selecting a speciation profile to develop speciated emissions for the oil and gas sector. For instance, a speciated profile associated with the control device should only be used to characterize the controlled portion of the VOC emitted from the emission stream. Further, profile developers should use care and be specific when labeling and describing the profiles for SPECIATE to assist users in linking the profiles to inventory emissions. However, additional work is needed by EPA to develop a common set of terminology and metadata that could be used by profile developers for profile labels, assignments, and descriptions.

Better measurements and models not only help protect the environment, but also help facilitate efficient resource development by alleviating concerns where appropriate. Air emissions from oil and gas production sites vary based on a number of factors including the composition of the oil and gas product, age of well, production equipment designs, control devices, and equipment maintenance states. There is an ongoing need to improve emissions estimates, as well as to facilitate identification and remediation of compliance issues related to air quality.

## 6 WORK PRODUCTS AND FUTURE WORK

EPA Region 8, ORD, and OAQPS plan to continue this collaborative effort to further investigate the VOC emissions associated with oil and gas operations and cost-effective measurement tools that can facilitate leak detection and repair to protect human health and the environment.

Improving our understanding of the emissions from the oil and gas sector is important for environmentally responsible development of this energy sector. To accurately model the oil and gas sector impacts on air quality, it is also critical to have accurate activity data, emission factors and chemical speciation profiles for VOCs and NO<sub>x</sub>.

The results of this project will support EPA's priorities related to air quality and all three research themes outlined in ORD's ACE Strategic Research Action Plan 2012 – 2016, including assessing impacts associated with air pollutants, providing data and tools to prevent and reduce emissions of pollutants into the atmosphere, and developing improved air quality models. The results will also be widely applicable to state/tribal agencies and EPA regions with oil and natural gas production. The results of the project will be transferred to groups through journal articles and presentations produced by EPA and collaborators.

The information gathered from this project will be a step towards achieving effective monitoring, model predictions, and controls of oil and gas emissions, particularly for upstream oil and production emissions on well pads. However, the work from this project identified the need to continue this investigation in order to make additional improvements and to fill in data and measurement tools gaps, including:

- Importance to develop easy-to-use remote approaches for assessment of ECD operational states, as high CE cannot be assumed. In general, the remote sensing approaches used were found to be potentially useful as research tools for offsite observation of ECD operation if more direct onsite measures are not available. However, the limitations of the off-site remote sensing tools investigated for this project were included the ease of execution, data analysis throughput, and observable ECD temperature ranges.
- Importance to develop and utilize site- or process-specific VOC speciation profiles for interpreting ambient measurement data and creating model-ready emissions for photochemical modeling applications. In the past, speciation profiles generally used for oil and gas were based on older data and were not representative of the multiple processes that exist in the oil and gas operations. While this project develop a number of speciation profiles to represent a variety of oil and gas processes across multiple basins, limitations included labeling and describing the profiles for SPECIATE to assist users in linking the profiles to inventory emissions, and the need to develop a common set of terminology and meta data that could be used by profile developers for profile labels, assignments, and descriptions.
- Importance to properly account for the impact of controls on VOC speciation.
- Conduct photochemical grid modeling with the updated VOC speciation profiles to evaluate the model performance and understand the model's sensitivity to the new profiles.

The results of this project will also inform and aid EPA in the design of future field studies and emissions inventories in areas where oil and natural gas contribute significantly to regional air

quality issues. This project also directly addresses the OIG report's statements regarding the uncertainty and limitations of EPA's air emissions factors and data for oil and natural gas sources. Specifically, the project improved our knowledge of the emissions uncertainties associated with ozone precursors for oil and natural gas production sources.

## APPENDIX A: PHOTOGRAPHS OF MEASUREMENT SITES

### SITE #1



### SITE #2



### SITE #3



# SITE #4



**SITE #5**



**SITE #6**



**SITE #7**



# SITE #8



**SITE #9**

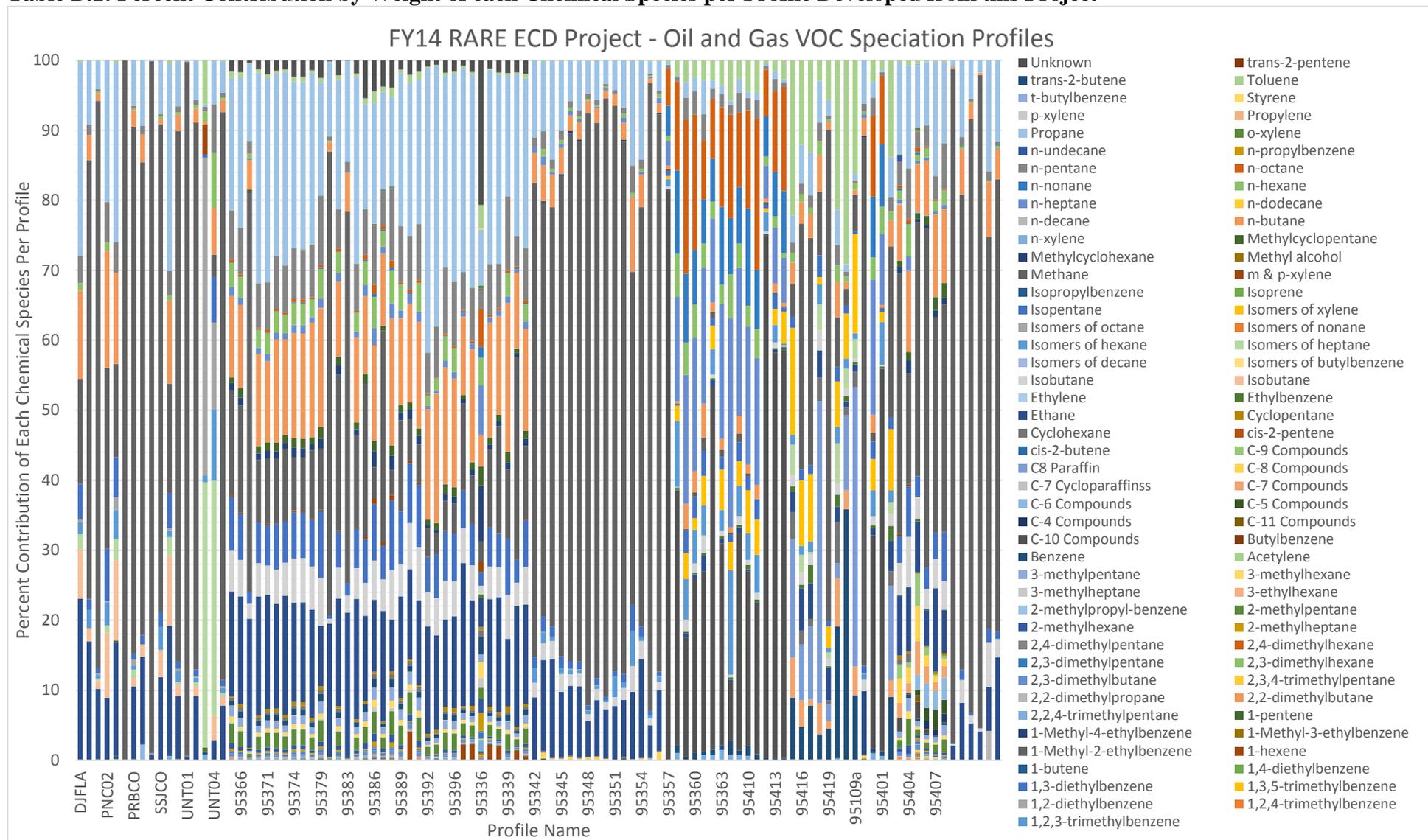


**SITE #10**

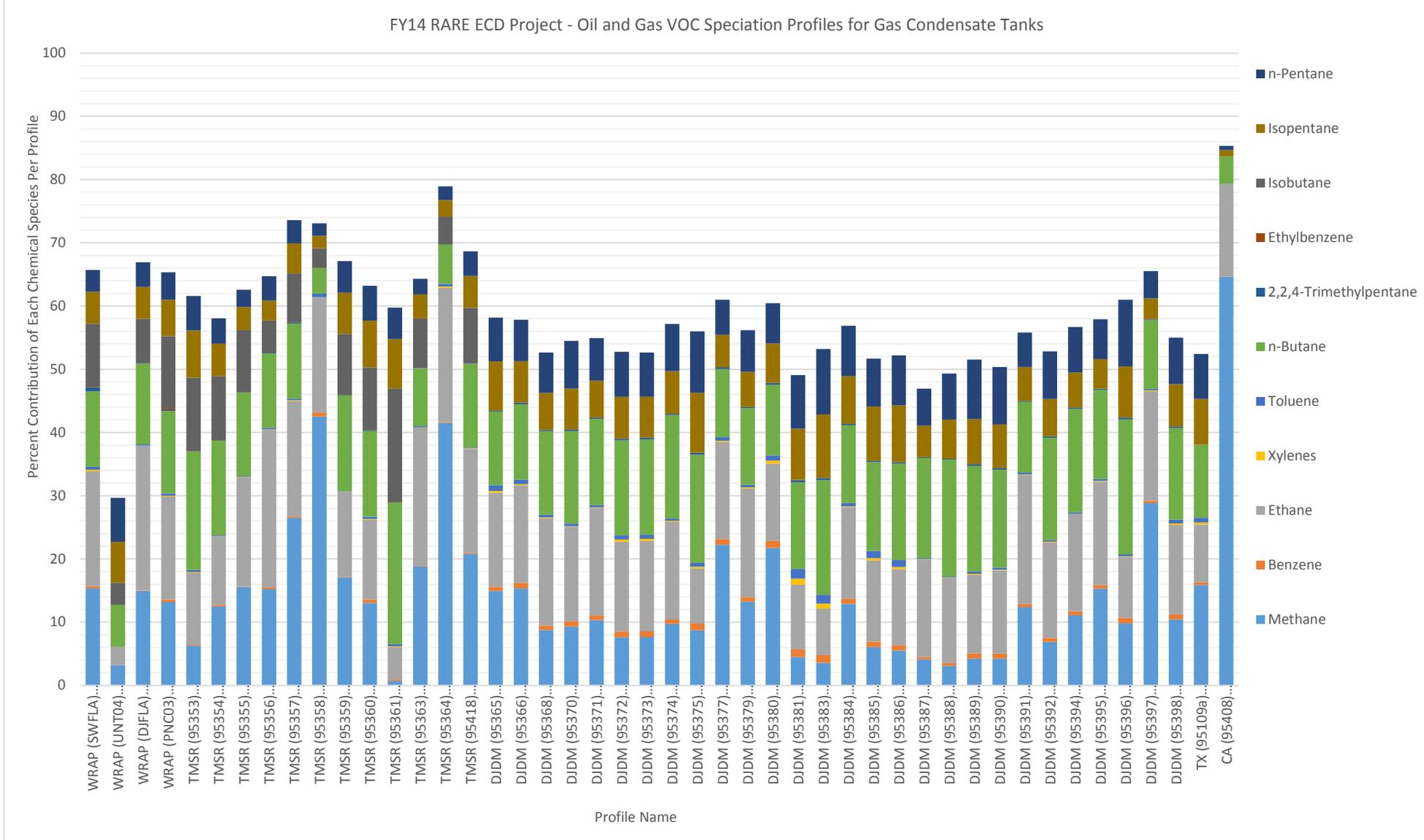


**APPENDIX B:**

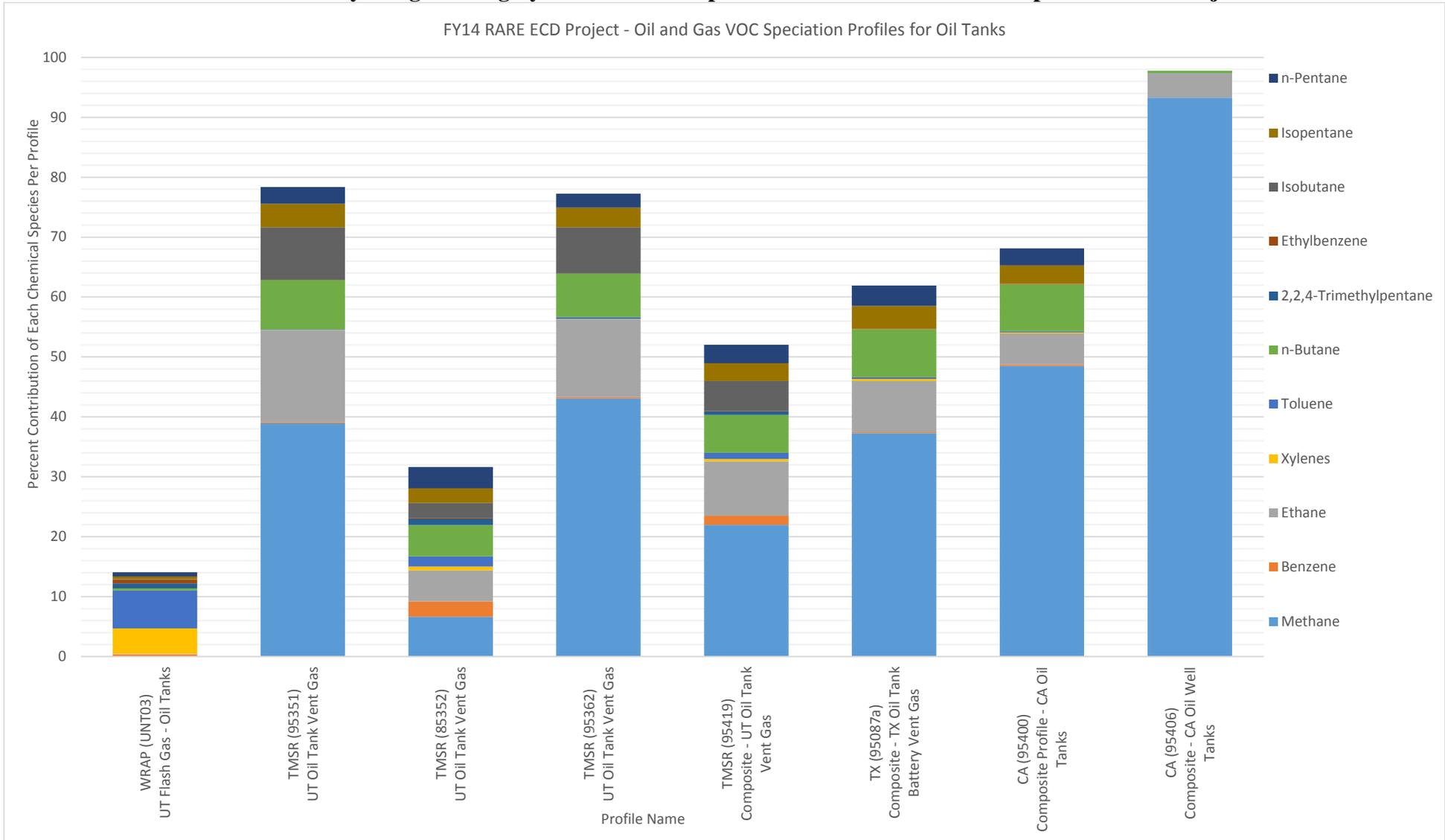
**Table B.1: Percent Contribution by Weight of each Chemical Species per Profile Developed from this Project**



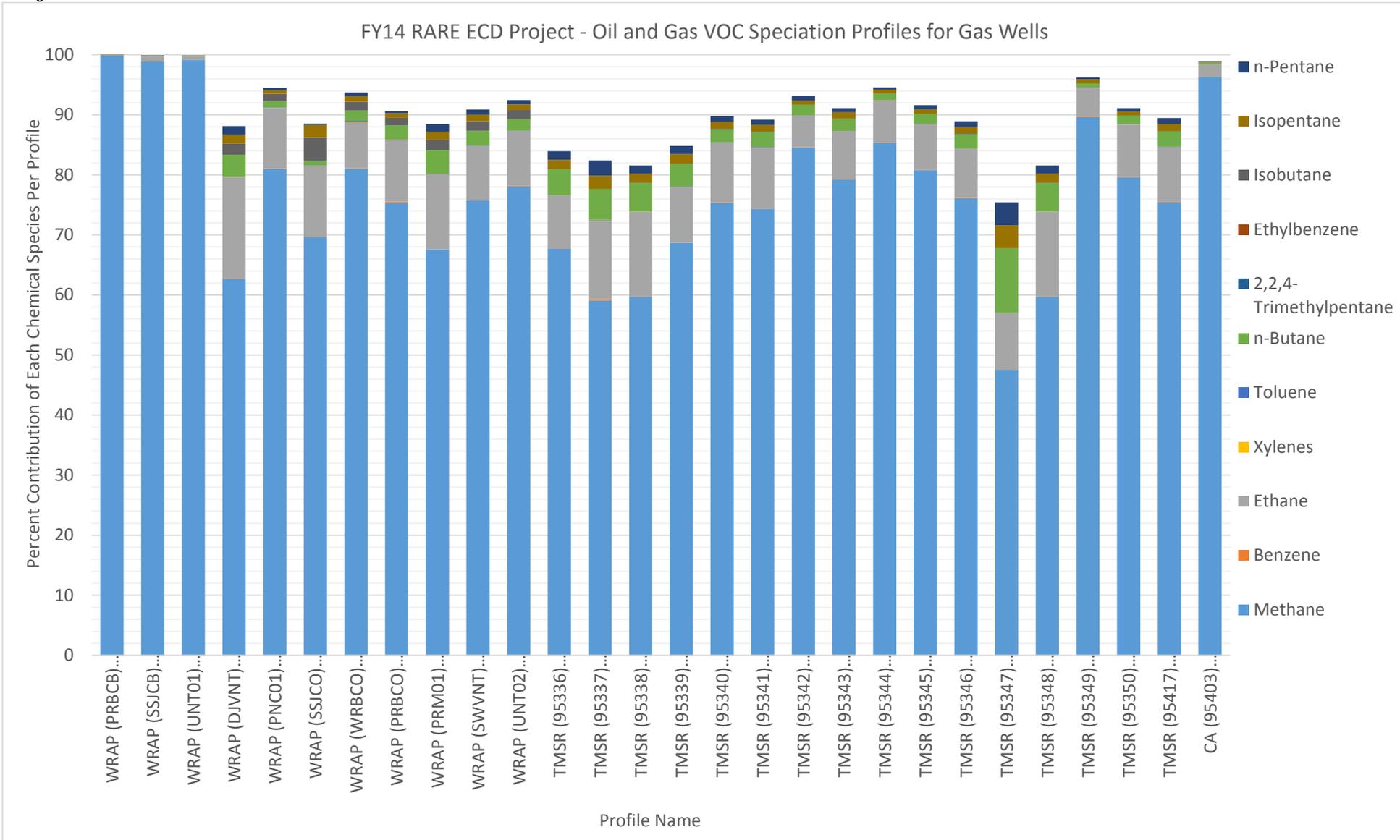
**Table B.2: Percent Contribution by Weight of Highly Reactive VOCs per Profile for Gas Condensate Tanks Developed from this Project**



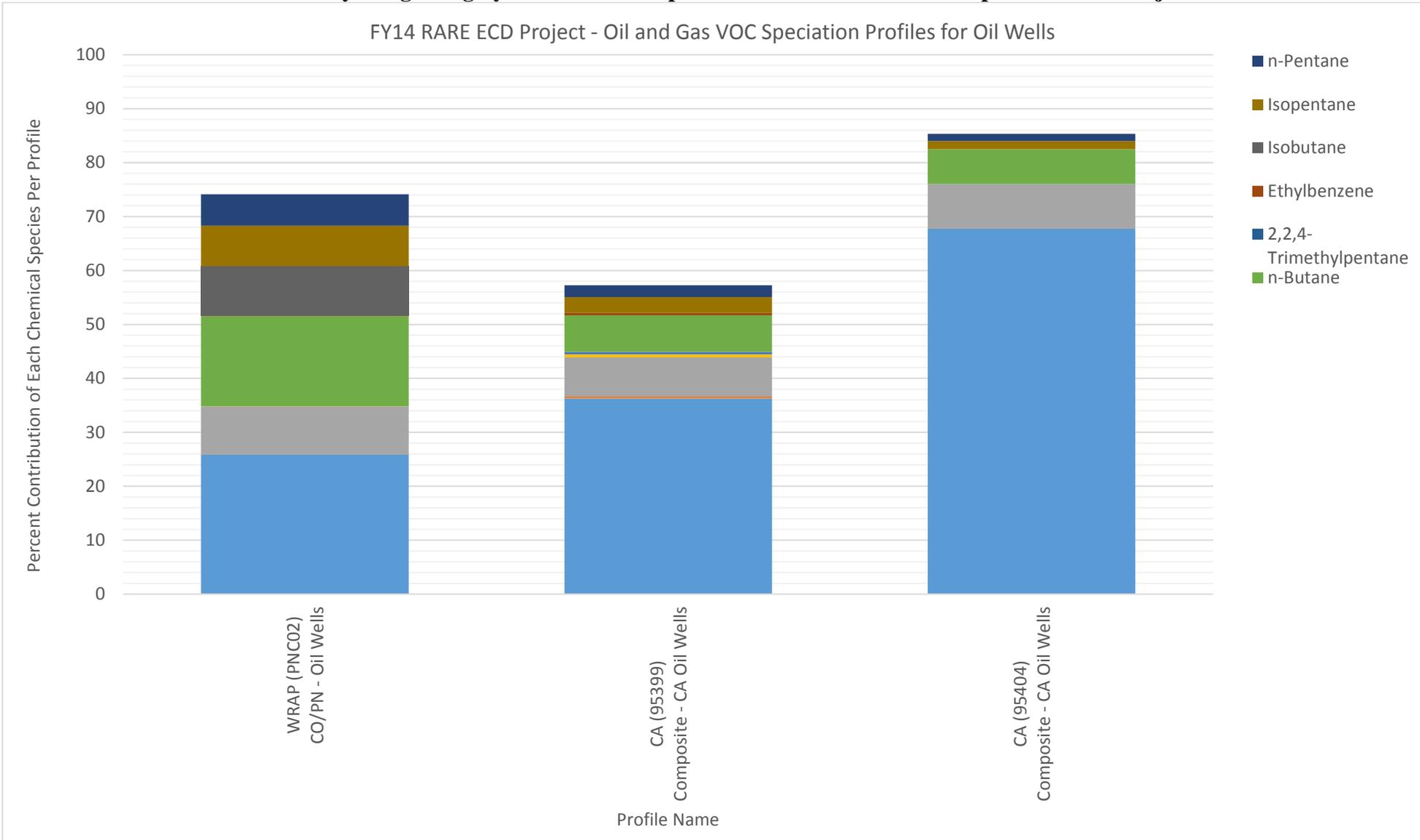
**Table B.3: Percent Contribution by Weight of Highly Reactive VOCs per Profile for Oil Tanks Developed from this Project**



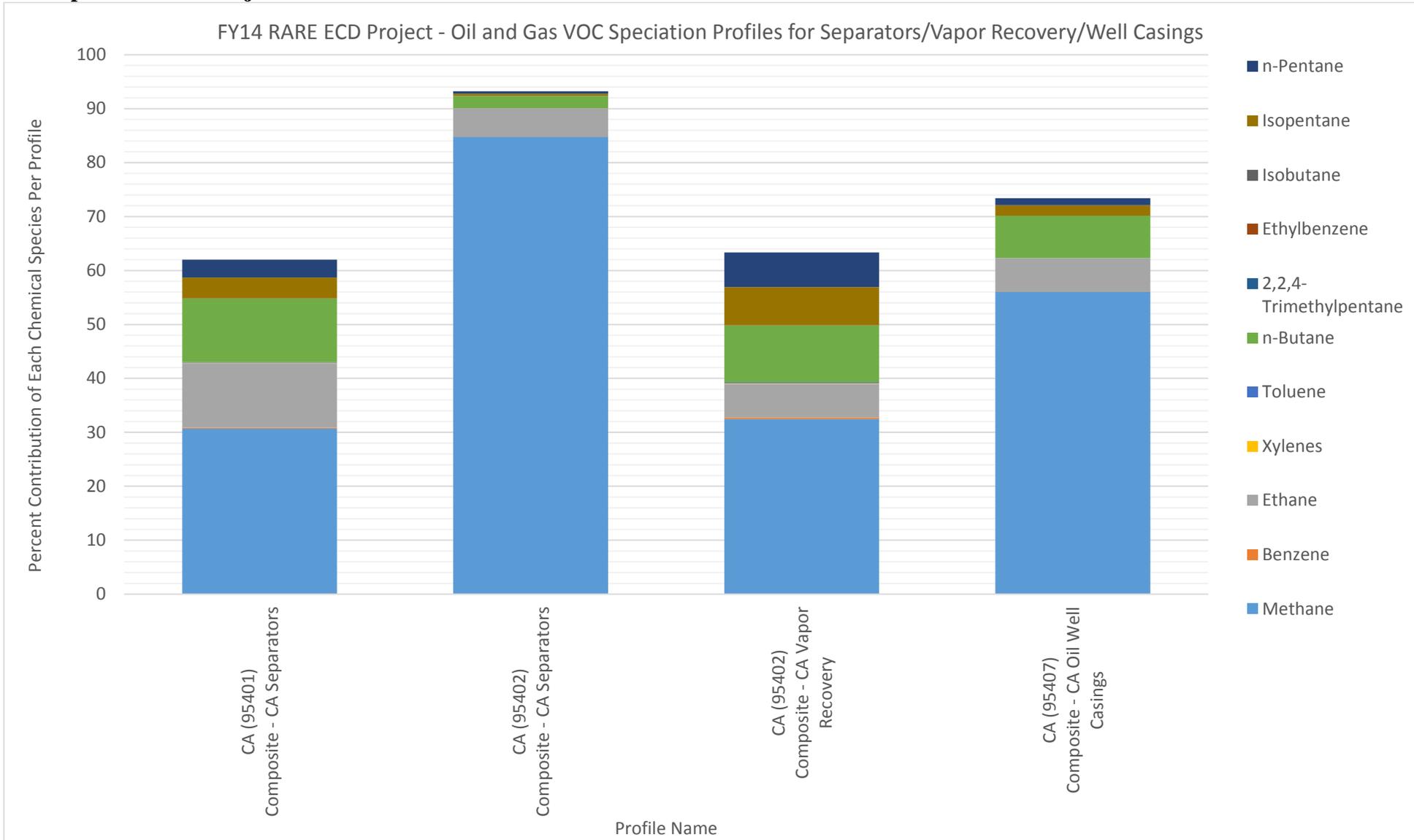
**Table B.4: Percent Contribution by Weight of Highly Reactive VOCs per Profile for Gas Condensate Tanks Developed from this Project**



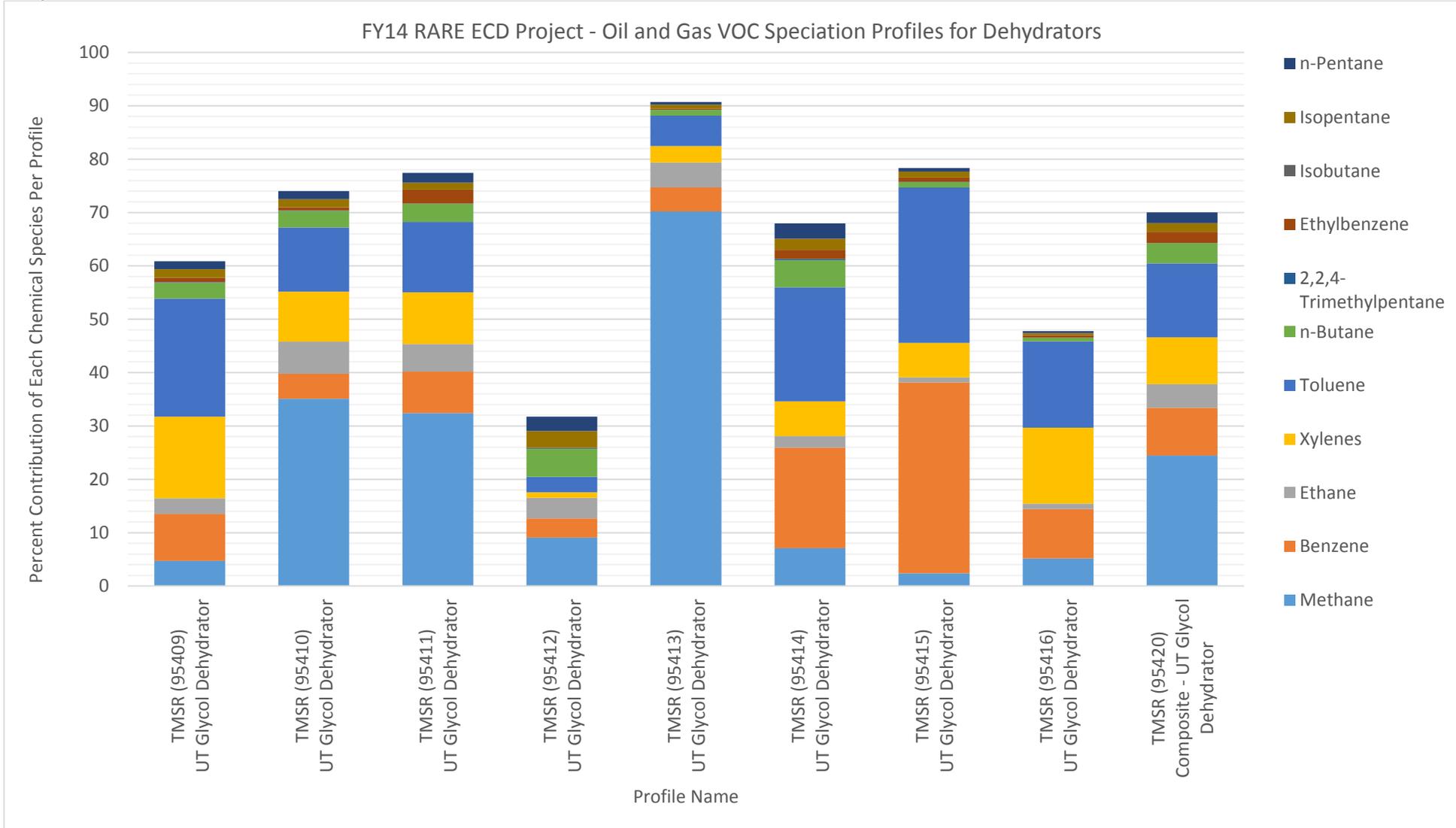
**Table B.5: Percent Contribution by Weight Highly Reactive VOCs per Profile for Oil Wells Developed from this Project**



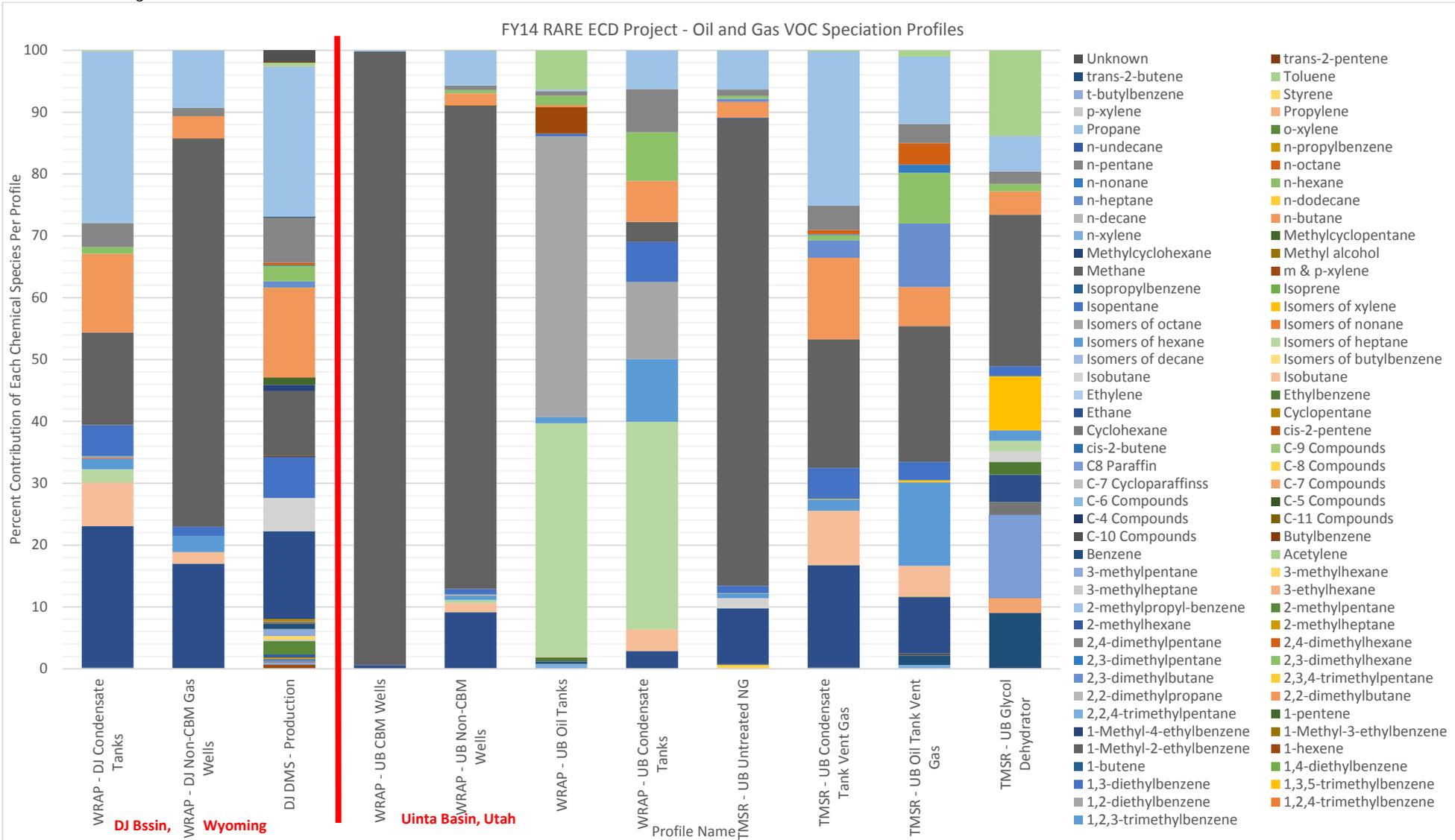
**Table B.6: Percent Contribution by Weight of Highly Reactive VOCs per Profile for Separators/Vapor Recovery/Well Casings Developed from this Project**



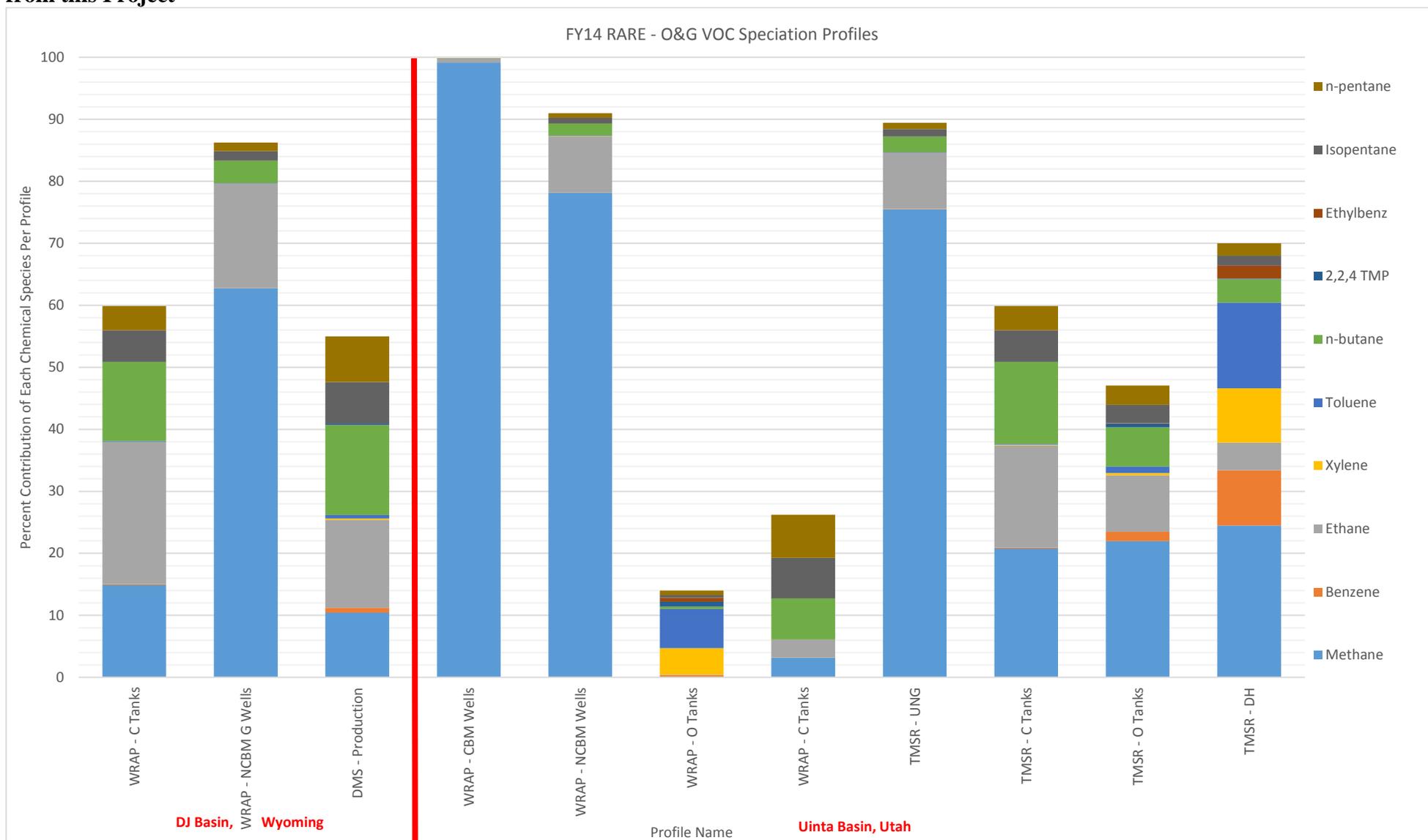
**Table B.7: Percent Contribution by Weight of Highly Reactive VOCs per Profile for Gas Condensate Tanks Developed from this Project**



**Table B.8: Percent Contribution by Weight of each Chemical Species per Profile for EPA Region 8-Specific Profiles Developed from this Project**



**Table B.9: Percent Contribution by Weight of Highly Reactive VOCs per Profile for EPA Region 8-Specific Profiles Developed from this Project**





**APPENDIX C: Top 20 Producers in the Uintah and Ouray Reservations – 2014**

Profile #	Name	2014 Data
<b>Production</b>		<b>Mcf</b>
95336	Natural Gas - Untreated - Oil Well - Axia Energy II, LLC	1406147
95337	Natural Gas - Untreated - Oil Well - Bill Barrett Corporation	11389526
95338	Natural Gas - Untreated - Oil Well - Crescent Point Energy U.S. Corp	2854439
95339	Natural Gas - Untreated - Oil Well - Enduring Resources, LLC	1213888
95340	Natural Gas - Untreated - Oil Well - EOG Resources, Inc.	35547477
95341	Natural Gas - Untreated - Oil Well - Koch Exploration Company	422013
95342	Natural Gas - Untreated - Oil Well - Newfield Production Company	11888643
95343	Natural Gas - Untreated - Oil Well - QEP Energy Company	24401675
95344	Natural Gas - Untreated - Oil Well - QEP Field Services Company	0
95345	Natural Gas - Untreated - Oil Well - Red Rock Gathering Company, LLC	0
95346	Natural Gas - Untreated - Oil Well - Rosewood Resources, Inc.	596571
95347	Natural Gas - Untreated - Oil Well - Ultra Resources, Inc.	1450111
95348	Natural Gas - Untreated - Oil Well - Ute Energy, LLC	0
95349	Natural Gas - Untreated - Oil Well - Whiting Petroleum Company	3664200
95350	Natural Gas - Untreated - Oil Well - XTO Energy, Inc	10740094
95409	Oil Field - Glycol Dehydrator - EOG Resources, Inc.	655458
95410	Oil Field - Glycol Dehydrator - Koch Exploration Company	3436
95411	Oil Field - Glycol Dehydrator - Newfield Production Company	7043408
95412	Oil Field - Glycol Dehydrator - QEP Energy Company	1074473
95413	Oil Field - Glycol Dehydrator - QEP Field Services Company	0
95414	Oil Field - Glycol Dehydrator - Ultra Resources, Inc.	1397871
95415	Oil Field - Glycol Dehydrator - Whiting Petroleum Company	9011
95416	Oil Field - Glycol Dehydrator - XTO Energy, Inc	97486
<b>Oil Produced</b>		<b>Barrels</b>
95353	Oil Field - Condensate Tank Battery Vent Gas - El Paso Midstream Group, Inc	0
95354	Oil Field - Condensate Tank Battery Vent Gas - Enduring Resources, LLC	10641
95355	Oil Field - Condensate Tank Battery Vent Gas - EOG Resources, Inc.	655458
95356	Oil Field - Condensate Tank Battery Vent Gas - Gasco Energy, Inc	74545
95357	Oil Field - Condensate Tank Battery Vent Gas - Kerr-McGee Oil and Gas Onshore LP	1042197
95358	Oil Field - Condensate Tank Battery Vent Gas - Koch Exploration Company	3436
95359	Oil Field - Condensate Tank Battery Vent Gas - QEP Energy Company	1074473
95360	Oil Field - Condensate Tank Battery Vent Gas - QEP Field Services Company	0
95361	Oil Field - Condensate Tank Battery Vent Gas - Rosewood Resources, Inc.	8091
95363	Oil Field - Condensate Tank Battery Vent Gas - Whiting Petroleum Company	9011
95364	Oil Field - Condensate Tank Battery Vent Gas - XTO Energy, Inc	97486
95351	Oil Field - Oil Tank Battery Vent Gas - Axia Energy II, LLC	1106170
95352	Oil Field - Oil Tank Battery Vent Gas - Bill Barrett Corporation	3151243
95362	Oil Field - Oil Tank Battery Vent Gas - Ultra Resources, Inc.	1397871