

## Upstream Oil and Gas Emissions Measurement Project

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### ABSTRACT

In recent years, Colorado has seen ozone levels that exceed national ambient air quality standards with levels increasing at several sites. It is thought that volatile organic compound (VOC) emissions from the prevalent upstream oil and gas operations may contribute in part to these exceedances. In 2008, EPA Region 8 requested OAQPS assistance in quantifying VOC emissions from upstream oil and gas facilities as currently there is limited data, particularly regarding fugitive emissions, from these operations. Oil and gas fields provide very challenging emission testing issues due to the large number and variety of emissions points including separators, dehydrators, generators, gas-powered pneumatics, injection wells, heaters, compressors/engines, storage tanks, and produced water ponds along with activities such as well drilling, well completion, well work over, and loading/unloading of oil/produced water into trucks. Though interested in VOC data for all these emission points, Region 8 wanted to first focus on quantifying VOC emissions from the produced water ponds. Our project team (EPA OAQPS, EPA ORD and their contractors, Region 8, Colorado, and Wyoming) chose to use EPA Other Test Method 10 (OTM 10), an optical remote sensing-based technique, with two open-path Fourier transform infrared (OP-FTIR) instruments in a four corners configuration to provide mass emission flux estimates for a representative alkane mixture. To supplement the alkane mixture flux assessment, FTIR spectra for select VOC compounds that were individually quantifiable were analyzed for concentration and reported as flux estimates using a ratio approach. VOC concentrations were determined at a point along two of the FTIR beam paths using summa canisters with EPA Method TO-14A and TO-15 analysis to provide additional information on the overall VOC emissions from the ponds. The data from this study is currently under internal review by EPA.

## INTRODUCTION

EPA Region 8 and, in particular, the State of Colorado is home to numerous upstream oil and gas operations. In recent years, Colorado has seen ozone levels that exceed national ambient air quality standards with levels increasing at several sites. It is thought that emissions of volatile organic carbon (VOC) ozone precursor compounds from upstream oil and gas operations may contribute in part to these exceedances. With the anticipated increase in oil and gas operations in this area of the country coupled with new lowered ozone standards, exceedances may potentially increase. The VOC including hazardous air pollutants (HAPS) is a concern to the public and press which has prompted inquiries to the affected state agencies and EPA Region 8. In addition, emissions from upstream oil and gas operations include a significant proportion of methane, an additional concern as regulating agencies consider greenhouse gas emissions quantification, reporting, and control.

There is significant uncertainty regarding fugitive emissions from upstream oil and gas production operations which start with drilling, well completion and work-over activities, to well-site operations through to midstream production and waste handling. Models exist to estimate emissions from some of these emission sources such as amine units, glycol dehydrators and oil/condensate storage tanks, but these modeled emissions represent only a fraction of the emissions from oil and gas production activities. Development and application of tools to quantify both VOC and methane emissions would help (1) better assess emission contributions from upstream oil and gas operations, (2) in development of a more robust inventory of oil and gas operation emissions from which mitigation options can be quantified and compared. This can ultimately lead to more effective control of ozone precursors and greenhouse gases and protection of air quality.

Oil and gas fields, however, provide very unique and challenging testing issues due to their large variety and quantity of emissions sources. For example, one 30 mile by 15 mile section of Garfield County in Colorado contains over 3,000 well sites and Weld County in Colorado contains over 10,000 well sites. Producing oil or gas well sites each require various combinations of supporting process equipment such as separators, dehydrators, generators, natural gas powered pneumatic devices, injection wells, heaters, compressors/engines, storage tanks, and produced water ponds. In addition to all these potential emissions sources, there are also a variety of activities such as well drilling, well completion, well work over, and loading/unloading of oil/produced water into trucks which have the potential to generate organic emissions.

The project team with representatives from EPA OAQPS, EPA ORD and their contractor (ARCADIS U.S., Inc.), EPA Region 8, and the states of Colorado and Wyoming are working on a multi-phased research effort to measure emissions from upstream oil and gas operations. This paper describes the first phase of the project addressing an immediate need of Region 8 and its states to improve understanding of VOC emissions from produced water evaporation ponds. These emissions data will help

stakeholders increase understanding regarding the accuracy of their emission inventories and further residual risk knowledge and potential environmental impact of this source category. This testing may also provide a basis for future protocols for testing this source category.

## METHODS

Two produced water evaporation pond facilities in Colorado were each tested for four days each over a two week period from August 6 to 15, 2008. The first site consisted of a large evaporation pit and two holding ponds of approximately three acres each (see Figure 1). As explained by the site operator, water produced by the upstream oil and gas operations is delivered by truck and is pumped into receiving tanks where it is heated to yield the first stage of separation. It is then transferred to an oil/water separator (for the second stage of separation). Recovered oil is stored for later sale. The water then passes through the skim pond and into the North Pond (the one enclosed by the red box in Figure 1) which utilizes aerobic bacteria to reduce hydrocarbons. Water is pumped back and forth between the North and South Ponds and agitators are located across the bottom of each pond to aid the mixing. Water from the South Pond is eventually pumped out of the South Pond (frac water) and trucked or piped back to the field to be used again.



Figure 1. First test site.

The second site tested was much less complex and is shown in Figure 2. Here, the produced water is transported to the facility via a pipeline and into tanks on the northern side of the pond for a one-stage separation using chemical demulsifying agents prior to being pumped into the pond. The brown areas north of the pond and tanks are racks of used pipes, another likely source of hydrocarbons.

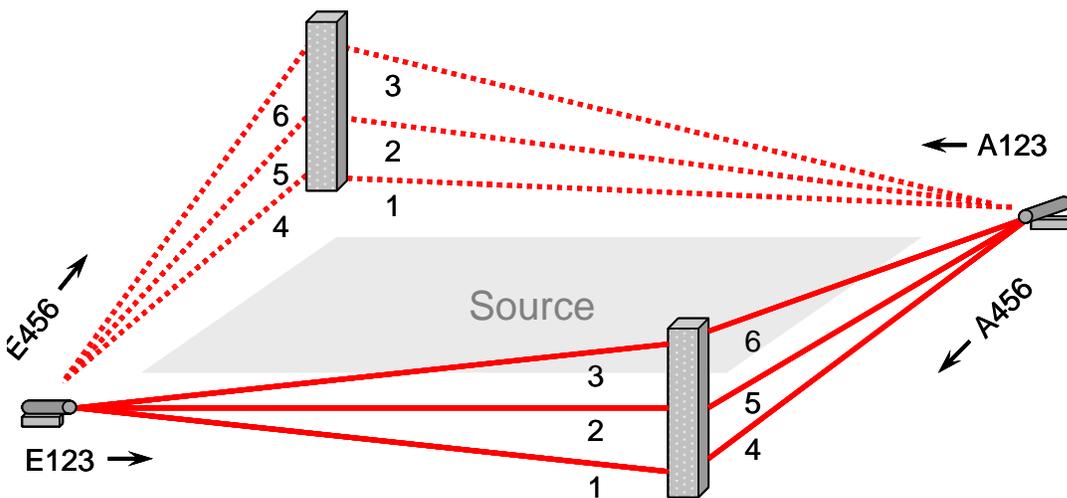


**Figure 2. Second test site.**

For this project, the estimate of pollutant mass emission flux from the facility sources was produced using EPA method OTM 10.<sup>1,2,3</sup> OTM 10 utilizes ground-based optical remote sensing technologies and multiple non-intersecting beam paths in a vertical plane downwind from the emission source to obtain a mass-equivalent plume map. This concentration plume map, in conjunction with wind speed and direction, is used to obtain the mass rate flux of pollutant(s) passing through the vertical plane. The measured flux is used to estimate the emission rate of the upwind source being characterized. For this measurement program, two open-path Fourier transform infrared (OP-FTIR) instruments deployed at each in a “four-corners configuration” yielding four vertical measurement planes (see Figure 3).

The measurement approach included two steps: (1) acquisition and analysis of path-integrated concentration (PIC) data of air pollutants along multiple beam paths using OP-FTIR, and (2) the vertical radial plume mapping (VRPM) analytical approach of

OTM 10 which calculates the mass emission flux estimate for the upwind source. The acquisition of PIC data was accomplished using three beams for each of the four flux planes. The two OP-FTIR instruments (A and E) were set up around the pond sources as shown by the red lines in Figures 1 and 2. In the four corners configuration, the four flux planes provide continuous measurement coverage under changing wind directions. The flux planes are labeled with a letter (A or E) representing the OP-FTIR system along with the beam paths (1,2,3 or 4,5,6) to form unique identifiers. Alternating scans were made between the two VRPM planes of each OP-FTIR. At both facilities, the position of the VRPM flux measurement planes were chosen to maximize the capture of fugitive emissions from the ponds taking into account the suspected source locations and site constraints.



**Figure 3. Four-corners Measurement Configuration.**

For this project, OP-FTIR data reduction focused on of the PIC values of a representative alkane mixture (AM, including straight-chain and bent-chain alkanes C-4 to C-8, butane, pentane, hexane, heptane, octane) by spectroscopic analysis of the infrared absorption features in the C-H stretch spectral region around  $2950\text{ cm}^{-1}$ . Spectral analysis of each individual compound is not possible due to the similarity in the shapes of there absorption band. In addition, individually quantifiable hydrocarbons species (e.g., methane) were analyzed if present at concentrations above the MDL for the OP-FTIR

In addition to the OTM 10 measurements, evacuated summa canister samples were collected at both sites to provide supporting information on VOC concentration levels proximate to the OTM 10 flux planes and to provide an estimate of trace VOC emissions fluxes by using an OP-FTIR/summa canister ratio technique. Summa canister sampling and analysis was utilized since the samples collected and analyzed using Methods TO-14A and TO-15<sup>4</sup> yield lower method detection limits (MDL) for most target compounds than the path-integrated measurements done with OP-FTIR, thus providing useful information on concentrations of trace VOCs . Canisters were placed at an approximate 1 m height near the location of the lowest beam paths of the respective

VRPM planes (paths 1 or 4 shown in Figure 3). Three samples were collected at a time: two canisters were co-located at a location near the midpoint of the downwind VRPM plane, and one canister was deployed near the midpoint of the upwind VRPM plane. On some days, two sets of samples were collected, one in the morning and one in the afternoon. A total of 28 canister samples were collected between the two sites.

## RESULTS

For this project, we used an OTM 10 VRPM calculation producing an approximately four-minute rolling average for flux value for each of the four vertical planes. Calculations of the alkane mixture flux through the measurement plane were conducted only when specific data quality indicators (wind speed, wind direction, path averaged concentration ratios and instrument operation) were met. To calculate the net flux for the emission source within the four vertical plane configurations, the measured fluxes for the two downwind vertical planes were added together and the fluxes of the two upwind vertical planes were subtracted as background. This was accomplished using 20-minute averages for each flux plane; the reason for this longer averaging time was the upwind and downwind plane pairs are not time synchronized for the 4-minute average time periods, so it is necessary to average several successive primary flux values to ensure that the net flux calculation is composed of temporally comparable results. This allowed robust determination of net flux of the ponds confined by the 4-plane configuration at times when very low background (upwind planes) fluxes are measured. At other times, emission fluxes from a source external to the configuration, such as the skim pond at the first site, could be accurately measured.

Where methane and other VOC were detected by OP-FTIR, the OP-FTIR spectra were also used to determine the concentrations of methane and those VOCs at the two sites. The methane and VOC concentrations were ratioed to the alkane mixture concentrations from the same time period to produce an estimate of the methane and VOC fluxes.

The summa canister samples analyzed by EPA Methods TO-14A and TO-15 were used to estimate flux concentrations of trace VOC that were not detected by OP-FTIR as well as several VOC that were detected by the FTIR. In a manner similar to FTIR methane flux determinations, the trace VOC concentrations determined using the summa canisters and Methods TO-14A and 15 were ratioed to the alkane mixture concentrations from co-located FTIR beam at the same time period to produce flux estimates. Though the summa canister/TO-14A and 15 measurements provides better detection limits for the trace VOC than the OP-FTIR measurements, they have a higher level of uncertainty with regard to emission flux because they represent only a single point sample while the FTIR multi-beam PIC data average over the spatial heterogeneities of the emission plumes.

Preliminary results from these measurement techniques will be presented at the conference.

## REFERENCES

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