

Background

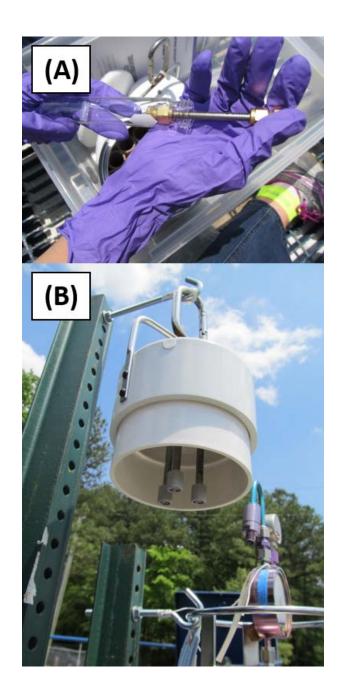
The United States Environmental Protection Agency (EPA) Region 6 – Dallas and Region 8 – Denver are home to burgeoning oil and natural gas (ONG) production activities. Emissions of volatile organic compounds (VOCs) and hazardous air pollutants (HAPs) from these activities are poorly estimated, contribute to increased ozone levels in the ambient air, and are a cause of concern for nearby communities. Fenceline monitoring, which serves as the interface between source measurements and ambient air quality measurements, can be an effective approach towards obtaining VOC and HAP emission data on a facility basis.

Introduction

Draft EPA Methods 325A and 325B, which focus on low-cost measurement and analysis of time-averaged fenceline concentrations of benzene around petrochemical refineries, were used as part of a method evaluation study around two active ONG pads in the Denver-Julesburg Basin (DJB) in northern Colorado and in the Barnett Shale (Barnett) in northern Texas. This study represents a first step in understanding the value of the passive sampler (PS) approach to help inform VOC and HAP concentrations around upstream energy production operations.

All sample analysis was performed by the same EPA laboratory using similar PS sorbent tubes, which was critical in assessing sample performance in the two different cities . Figure 1(A) shows an individual PS sorbent tube. Additionally, PSs were sent to other commercial laboratories for analysis as another quality indicator. Collocated samples were routinely collected during each 14-day deployment. Figure 1(B) shows three collocated PS sorbent tubes placed under a protective sampler hood.

Figure 1: Basic passive sampling equipment including (A) sorbent tube and (B) sampling shelter hood



Site Descriptions

Three sampling sites were used in this study and consisted of one urban-scale site and two rural-scale ONG production pads. The urban site was located in Downtown Denver on the roof of an air monitoring station, as shown in Figure 2(A) near a busy intersection with a strong mobile source signal. The DJB production pad in Figure 2(B) was located in a rural area with significant ONG production activities north of Denver. The other ONG production pad was located northeast of Dallas in the Barnett Shale and is shown in Figure 2(C).

Figure 2: Sampling locations at (A) Downtown Denver, (B) DJB pad, and (C) Barnett pad



These sampling sites were selected to compare urban concentrations to rural concentrations using the PS approach. The Downtown Denver and DJB sites are located at an elevation of approximately 5,300ft above mean sea level, so potential effects of altitude can be assessed. Other variables such as ambient temperature and relative humidity were compared between the sampling sites in both Denver and Dallas in this pilot study.

<u>References</u>:

EPA.2013. 40 CFR Part 60, subpart OOOO Oil and Natural Gas Sector: Reconsideration of Certain Provisions of New Source Performance Standards. US Environmental Protection Agency http://www.gpo.gov/fdsys/pkg/FR-2013-09-23/pdf/2013-22010.pdf (accessed January 2015) U.S. EPA, Method 325A-Volatile Organic Compounds from Fugitive and Area Sources: Sampler Deployment and VOC sample collection, pp 704-736 in 40 CFR Part 63, Subpart UUU [EPA-HQ-OAR-2010-0682; FRL-9720-4], RIN 2060-AQ75, Petroleum Refinery Sector Risk and Technology Review and New Source Performance Standards. U.S. EPA, Method 325B-Volatile Organic Compounds from Fugitive and Area Sources: Sampler Preparation and Analysis, pp 737-813 in 40 CFR Part 63, Subpart UUU [EPA-HQ-OAR-2010-0682; FRL-9720-4], RIN 2060-AQ75, Petroleum Refinery Sector Risk and Technology Review and New Source Performance Standards. Thoma, E.D.; Jiao, W.; Brantley, H.L.; Wu, T.; Squier, W.C.; Mitchell, B.; Oliver, K.D.; Whitaker, D.A.; Mukerjee, S.; Gross-Davis, C.A.; Schmidt, H.; Landy, R.; Diem, A.; Shine, B.; Escobar, E.; Amin, M.S.; Modrak, M. South Philadelphia Passive Sampler and Sensor Study: Interim Report; Proceedings of the 108th Annual Conference of the Air & Waste Management Association, June 23-26, 2015, in Raleigh, North Carolina.

Measurement of VOCs Using Passive Sorbent Tubes Near Oil & Natural Gas Production Pads in Colorado and Texas

Adam P. Eisele¹, Michael C. Miller², Donald W. Smith², Eben D. Thoma³, Shaibal Mukerjee⁴, Karen Oliver⁴, Don Whitaker⁴ & Halley Brantley⁵ ¹U.S. EPA Region 8, Wynkoop St., Denver, CO 80202 ²U.S. EPA Region 6, 1445 Ross Ave., Dallas, TX 75202 ³U.S. EPA Office of Research and Development, National Risk Management Laboratory, 109 TW Alexander Drive, RTP, NC 27711 ⁴U.S. EPA Office of Research and Development, National Exposure Research Laboratory, 109 TW Alexander Drive, RTP, NC 27711 ⁵ORISE Fellow, U.S. EPA Office of Research and Development, National Risk Management Laboratory, 109 TW Alexander Drive, RTP, NC 27711

Colorado

From November 2013 until February 2014, five 14-day deployments were collected at the Downtown Denver site using three PS locations (Loc 1, Loc 2, & Loc 3) on the roof of a permanent air monitoring station. Figure 3(A) shows an aerial view of the monitoring station roof with three colored dots that represent geo-referenced PS locations.

From March 2014 until September 2014, thirteen 14-day deployments were collected at six PS locations (Loc 4 – Loc 9) surrounding an active production pad in the DJB. This pad consisted of eight wells, seven separators, ten storage tanks, one vapor recovery unit, and four enclosed combustors. A north-south access road ran along the eastern extent of the pad, which included frequent heavy-duty truck traffic. A produced water treatment facility was operated on the southern end of the pad, but was later removed in July 2014. Figure 3(B) shows that six colored dots representing each PS location fit within a 100m radius. This pad is located near a number of other production pad facilities as well as a gas processing plant.

Figure 3: Aerial view of (A) Downtown Denver site and (B) DJB production pad

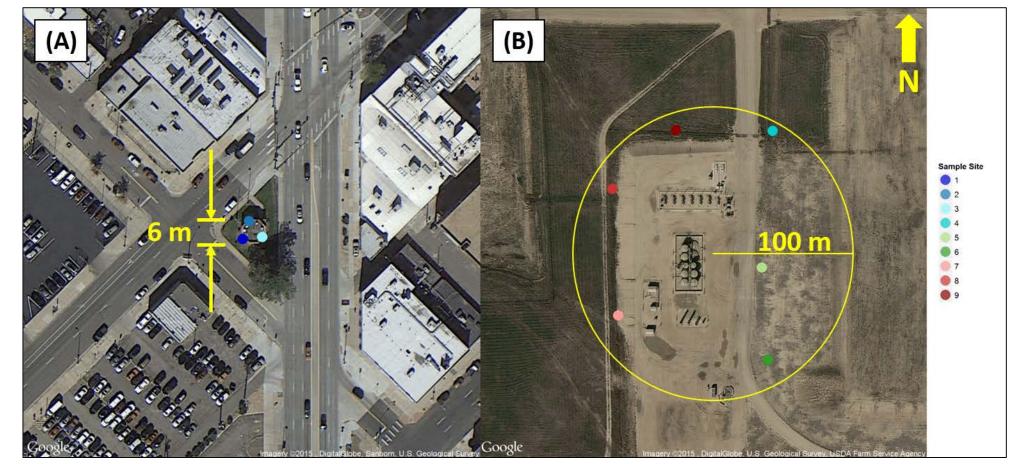
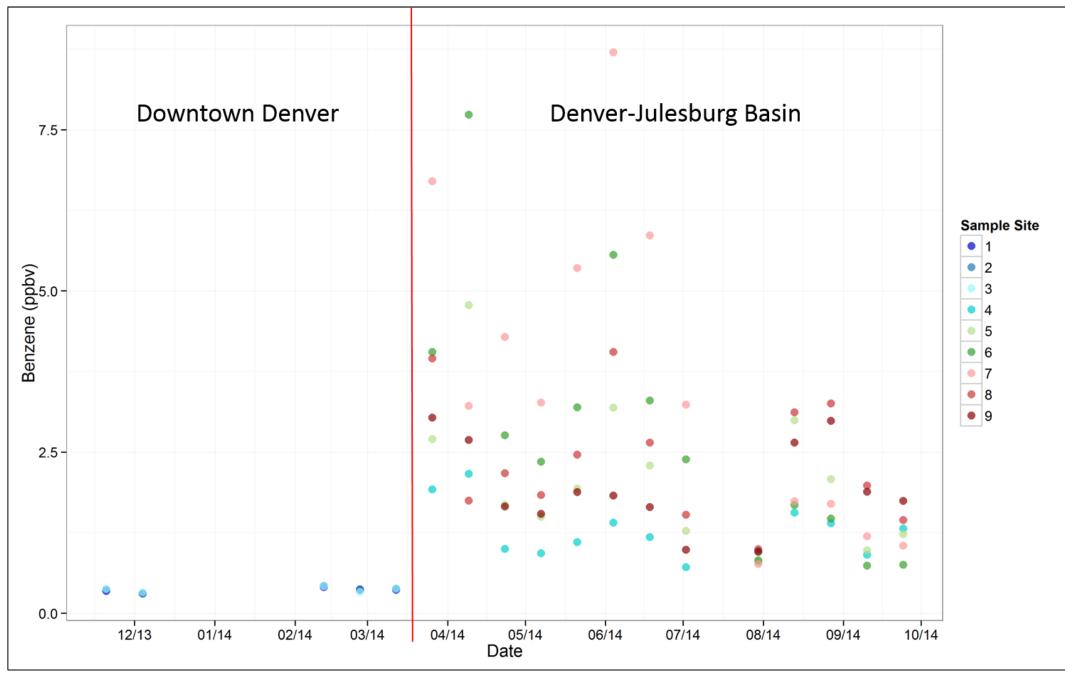


Figure 4 shows the benzene concentrations measured during every deployment and at each PS location in Downtown Denver and the DJB pad, which corresponds to the colored dots in Figure 3. Benzene concentrations measured in Downtown Denver were fairly uniform over the five 14-day deployments at the three PS locations with combined average and median values of 0.37 ppbV and 0.36 ppbV (n=15), respectively. At the DJB pad, PS Loc 7 showed the highest benzene concentrations with average and median values of 3.62 ppbV and 3.24 ppbV (n=13), respectively. PS Loc 4 showed the lowest benzene concentrations of the six PS locations with average and median values of 1.28 ppbV and 1.18 ppbV (n=13), respectively.

Figure 4: Benzene concentrations measured at the Downtown Denver and the DJB production pad sites



Seasonal impacts did not appear to impact benzene concentrations at the DJB pad, although additional monitoring would be required to examine this issue in greater detail. Using local meteorology on the roof of the air monitoring station, winds were generally out of the north at the Downtown Denver site. No predominate wind patterns were present at the DJB pad over the course of the 14-day deployments. According to the site operator, the DJB production pad was shut down for approximately one month starting in early June. ONG extracted from the Denver-Julesburg Basin is considered "wet gas" due to the high VOC to methane ratio. This may account for the higher benzene concentrations measured at the DJB pad when compared to the Barnett pad, as well as considerably higher production of condensate/oil liquids.

Starting in October 2013 and running through September 2014, nineteen 14-day deployments were collected at the Barnett Shale production pad site using ten PS locations (Loc 1 – Loc 10) that surrounded the facility. Two of these PS locations, Loc 9 and Loc 10, served as gradient measurement locations that were > 200m away from the pad. Figure 5 shows ten colored dots representing each of the ten PS locations. The Barnett pad consists of one well, one separator, three storage tanks, and one lift compressor. This site is in a rural area north of Dallas and near multiple ONG production operations, but distant from mobile source routes. Overall, the ten Barnett PS locations fall within a 250m radius which is considerably larger than the Downtown Denver and DJB production pad locations.



Seasonal impacts may indicate an indirect relationship with ambient temperature and benzene concentrations, although additional measurements and more complete data are needed to confirm this estimation. Using local meteorology, winds were predominantly out of the southeast. PS Loc 08 is upwind of immediate sources on the production pad when taking into account the predominant wind direction, which is supported by the lowest benzene concentrations measured on the pad. The Barnett Shale is considered a "dry gas" field, which is composed almost entirely of methane. The average production of natural gas at the Barnett production pad is considerably higher than the DJB pad, but liquid production is significantly less. Background concentrations of benzene were not determined in this pilot scale study.

Texas

Figure 5: Aerial view of Barnett Shale production pad

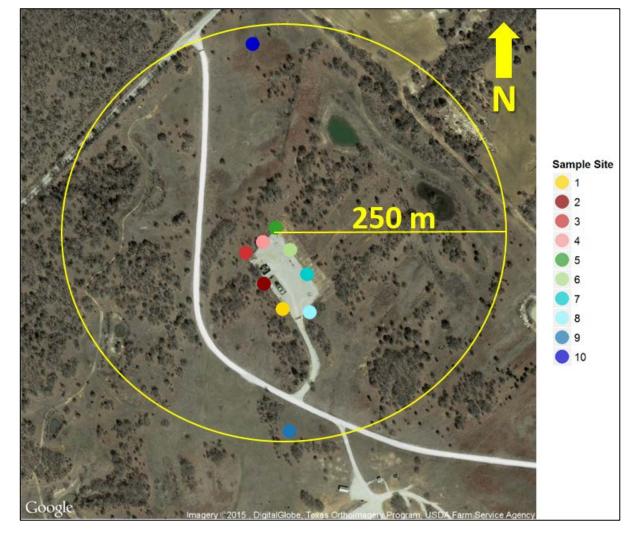
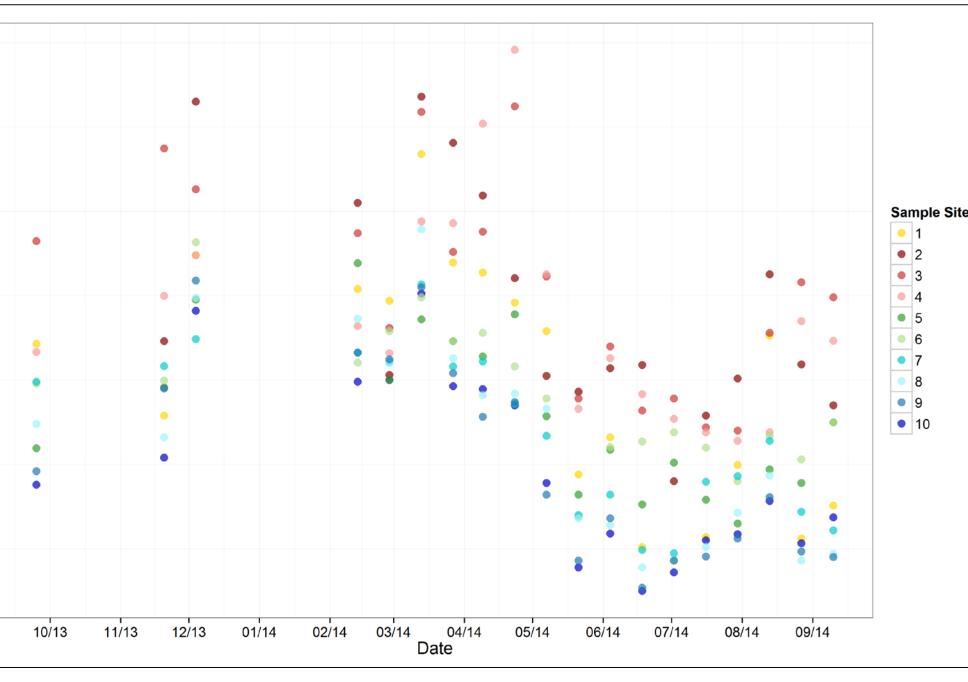


Figure 6 shows the benzene concentrations measured during every deployment and at each PS location at the Barnett production pad, which corresponds to the colored dots in Figure 5. PS Loc 3 had the highest benzene concentrations out of the eight PS locations on the production pad with an average and median of 0.26 ppbV (n=19). PS Loc 08 had the lowest benzene concentrations on the pad with an average and median of 0.16 ppbV and 0.17 ppbV (n=19), respectively. PS Loc 9 and Loc 10 showed the lowest benzene concentrations, with a similar average of 0.15 ppbV and medians of 0.13 ppbV and 0.14 ppbV (n=19), respectively.

Figure 6: Benzene concentrations measured at the Barnett production pad site



of f	umbe factors vities
	•
eac Figu Bari dete agre	olicate h 14-c ires 7 nett lo ermin eemer n a hig
0.45 0.40 0.35 0.30 0.30 0.30 0.25 0.00 0.10 0.15 0.00 0.00 0.00	Reg n=9
moi mea PS a ope	s pilot hitorir asurer approa ration ly due

The authors would like to thank EPA colleagues Patti Tyler, Michael Morton, Cindy Reynolds, Carole Braverman, Ron Landy, Howard Schmidt, Carol Ann Gross-Davis, Motria Caudill, Joe Delwiche, and Ray Merrill. We appreciate the site access coordinated through the Colorado Department of Public Health and Environment, an industry collaborator, and the U.S. Forest Service. Thanks to Eastern Research Group and Alion Science and Technology for analytical and logistical assistance. Primary funding for this effort was provided by the U.S. EPA ORD's Regional Method (RM), Regional Applied Research Effort (RARE), and Air, Climate, and Energy (ACE) programs.

Factors Influencing Results

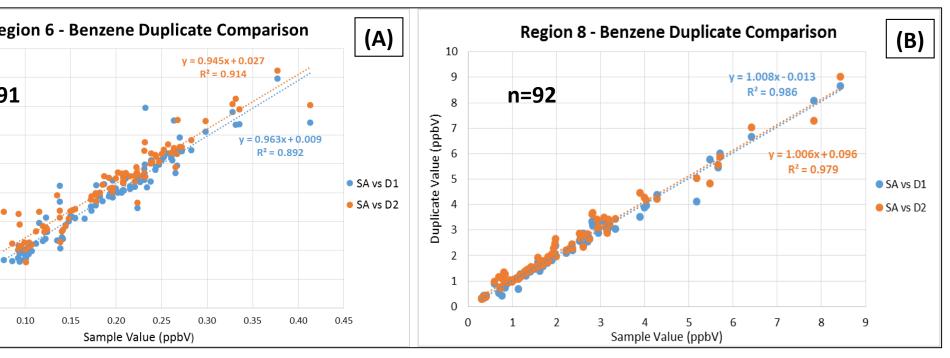
A number of factors impact PS concentrations during 14-day deployments. The following list s, although not entirely comprehensive, must be considered during data analysis at ONG production pads during PS activities:

- meteorological conditions experienced during 14-day deployment;
- background concentrations of the target VOCs;
- PS distance to potential sources; mobile source traffic patterns and vehicle types;
- temporary ancillary operations on site;
- product composition and production rates;
- well shut-in and other maintenance activities; and,
- neighboring emission sources off site.

Quality Assurance

e PSs, which consist of Duplicate 1 (D1) and Duplicate 2 (D2), were deployed during day sample period and collocated with primary samples (SA) at most PS locations. 7(A) and 7(B) show strong agreement between benzene duplicate samples from the ocation and the combined results from the CAMP/DJB locations, with coefficients of nation greater than 0.892 and 0.979, respectively. The strong duplicate-to-sample ent suggests that the collocated sample results throughout the study were replicated gh level of confidence. Field blank and field spike sorbent tubes were also deployed.

Figure 7. Benzene Duplicate Comparison at (A) Barnett and (B) CAMP/DJB



Conclusions

study demonstrated that EPA Draft Methods 325A and 325B can be followed for VOC ng at the fenceline of ONG production pads to obtain 14-day air quality ments. This study represents a first step in understanding the value of the low-cost bach to help to help inform VOC concentrations around upstream energy production ons. Differences in concentrations of benzene observed between study locations are e to PS proximity to relative to source, condensate and natural gas production rates, product composition, and specific site operations. Meteorological parameters retrieved from nearby stations to the Barnett, Denver, and DJB locations may have a significant influence on PS concentrations measured at each location.

Acknowledgements

Disclaimer

The views expressed in this poster are those of the authors and do not necessarily represent the views or policies of the U.S. Environmental Protection Agency. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.