

Characterizing the emissions of volatile organic compounds (VOCs) from oil and natural gas operations in several U.S. shale plays

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I. Introduction

- Shale gas production
- Measurement details

II. Comparison of VOC composition

- Haynesville flights (F20130610 and F20130625)
- Karnack, TX EPA monitoring site to flight data from SENEX 2013 and TexAQS 2006
- Central, eastern, and western basins

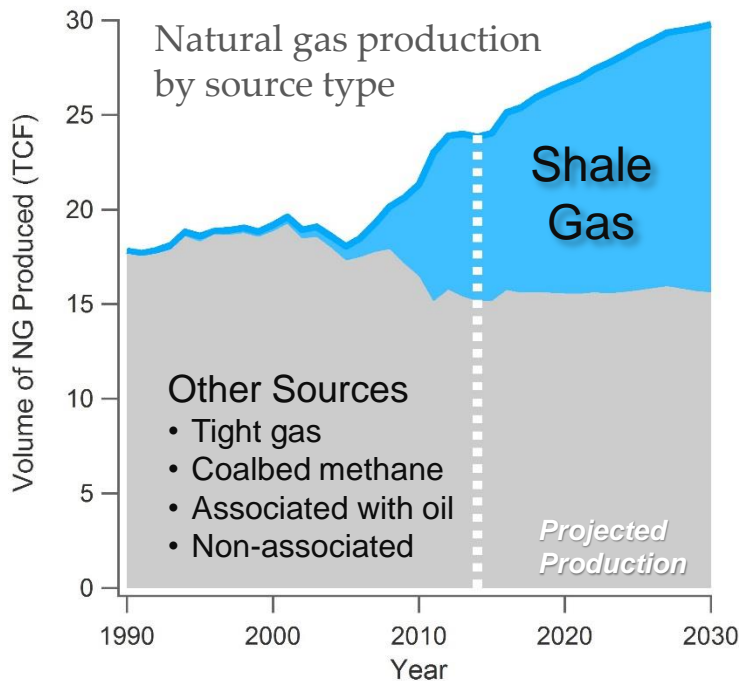
III. Long-term VOC trends at Karnack site in Haynesville shale play

I. Introduction: Oil and natural gas operations

Production and composition of raw natural gas

Natural gas production in U.S.

- Shale gas production in U.S. is at an historic high
- Accounts for 39% of NG production as of 2012



Data Source: U.S. EIA, AEO2012

Composition of raw natural gas

- Raw natural gas may contain significant amounts of non-methane hydrocarbons
- “Wet” natural gas contains higher proportions of non-methane hydrocarbons relative to CH_4

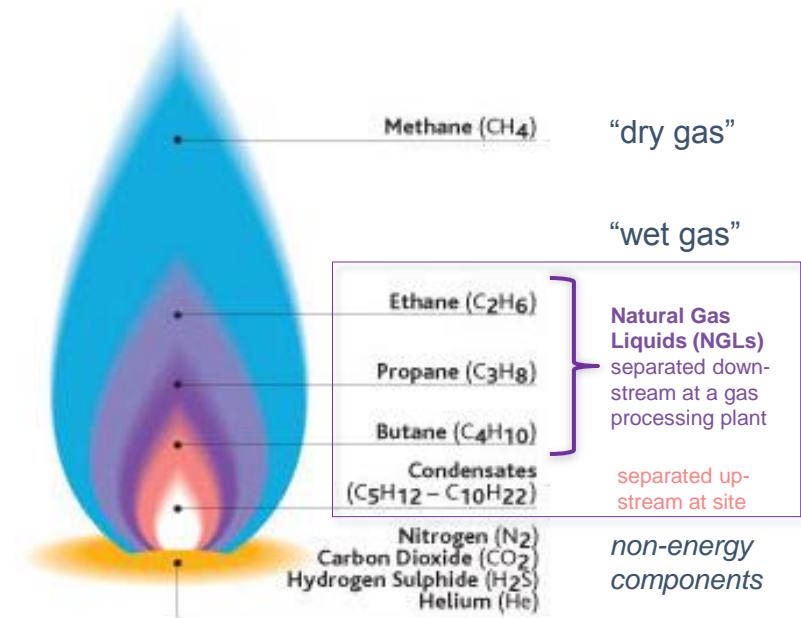


Image Source: Canadian Centre for Energy Information © 2009

I. Introduction: Measurement locations

Western, central, and eastern shale basins

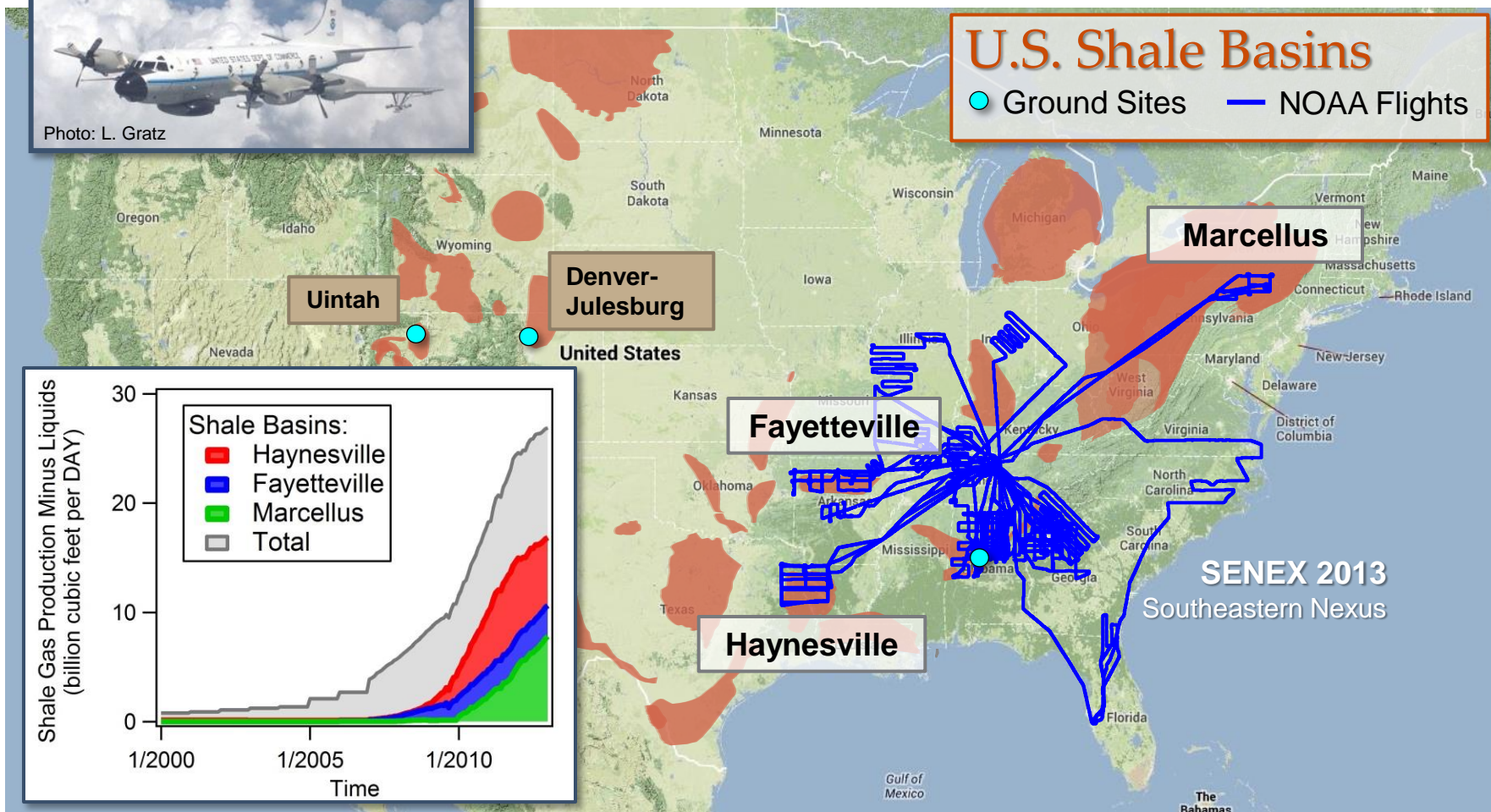
NOAA WP-3D



Photo: L. Gratz

U.S. Shale Basins

● Ground Sites — NOAA Flights



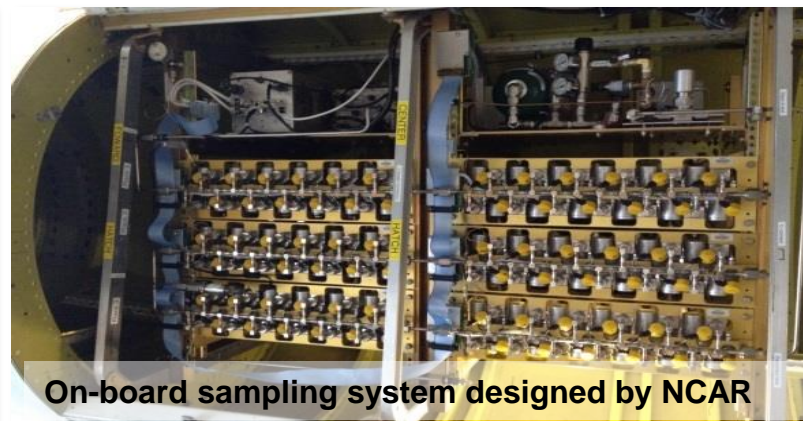
I. Introduction: Measurement techniques

VOCs from whole air samples and in-situ PTR-MS

- Continuous in-situ measurements of:
 - **Aromatic VOCs via proton transfer reaction-mass spectrometry (M. Graus)**
 - **Methane via infrared laser absorption (J. Peischl and T.B. Ryerson)**
- Discrete measurements of C2-C6 hydrocarbons via whole air sampler (WAS)
 - Post-flight analysis via gas chromatography-mass spectrometry (GC-MS)



Whole air sampling system located inside "AMPS pod"

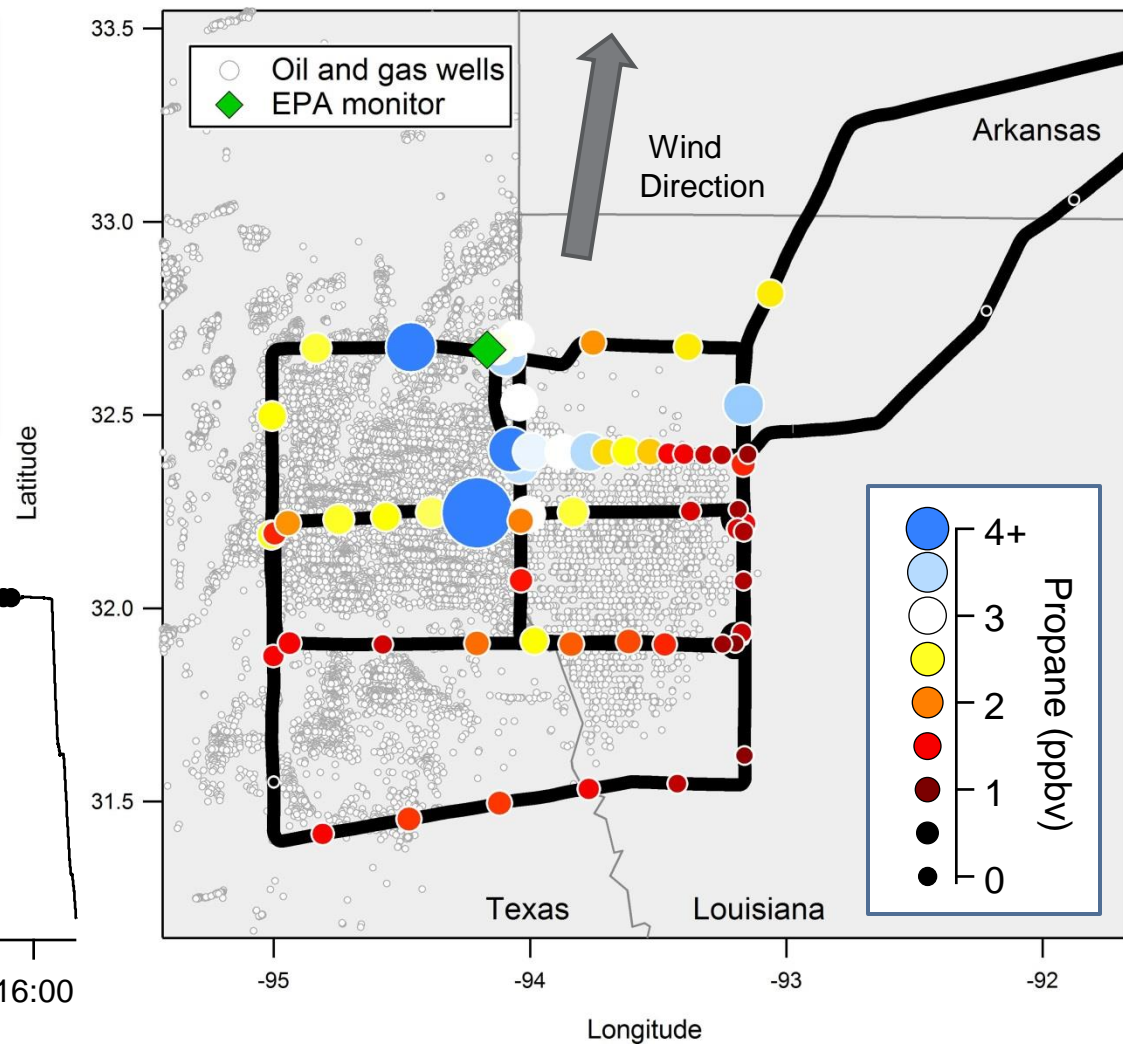
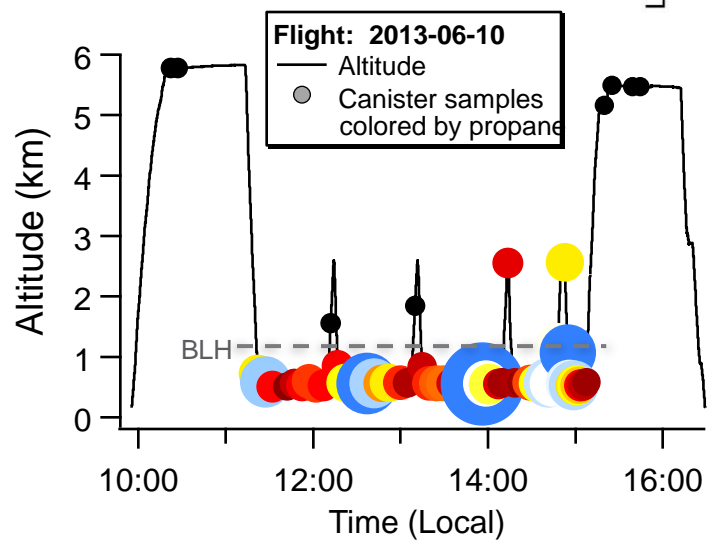
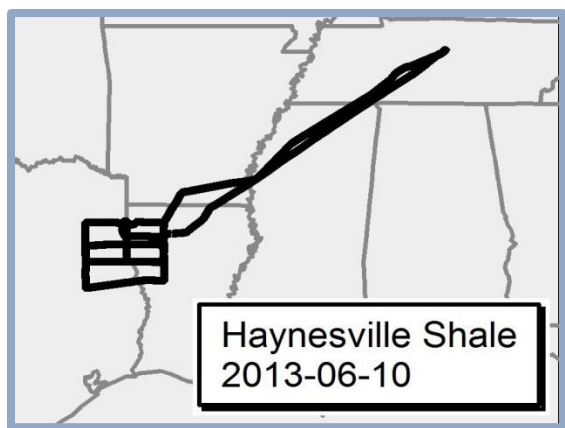


On-board sampling system designed by NCAR

- Samples collected in ~1 L stainless steel cylinders filled to ~3 atm
- 72 whole air samples collected per flight
- Filled automatically or with manual override for targeted analysis

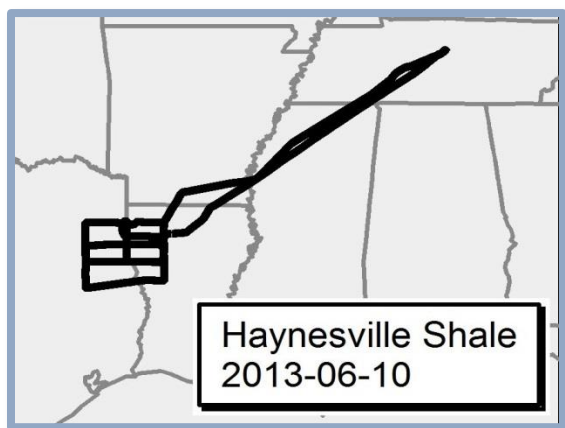
See Brian Lerner's poster
this evening for more details

II. VOC emissions in Haynesville Shale Basin Haynesville shale flight on 2013-06-10

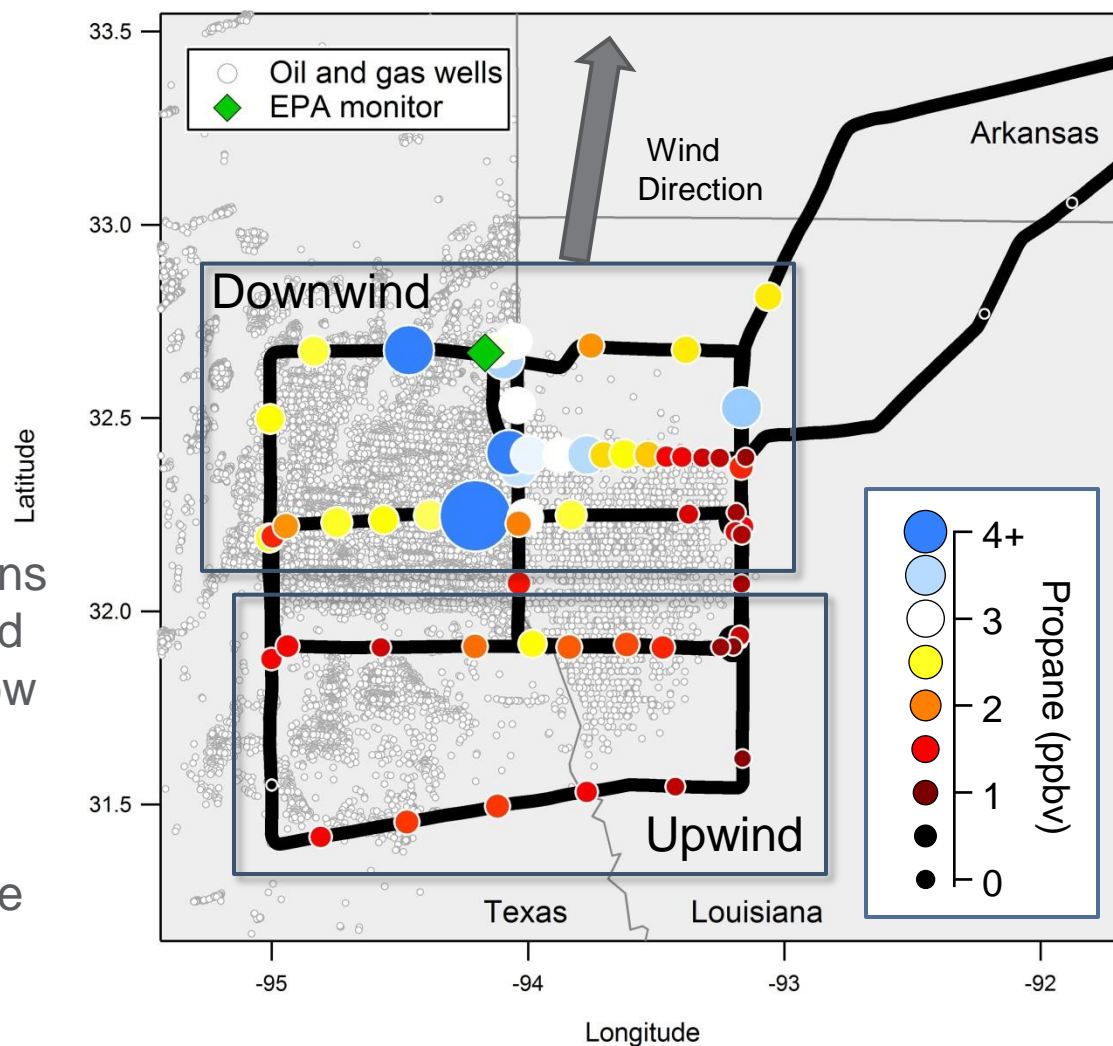


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Haynesville shale flight on 2013-06-10

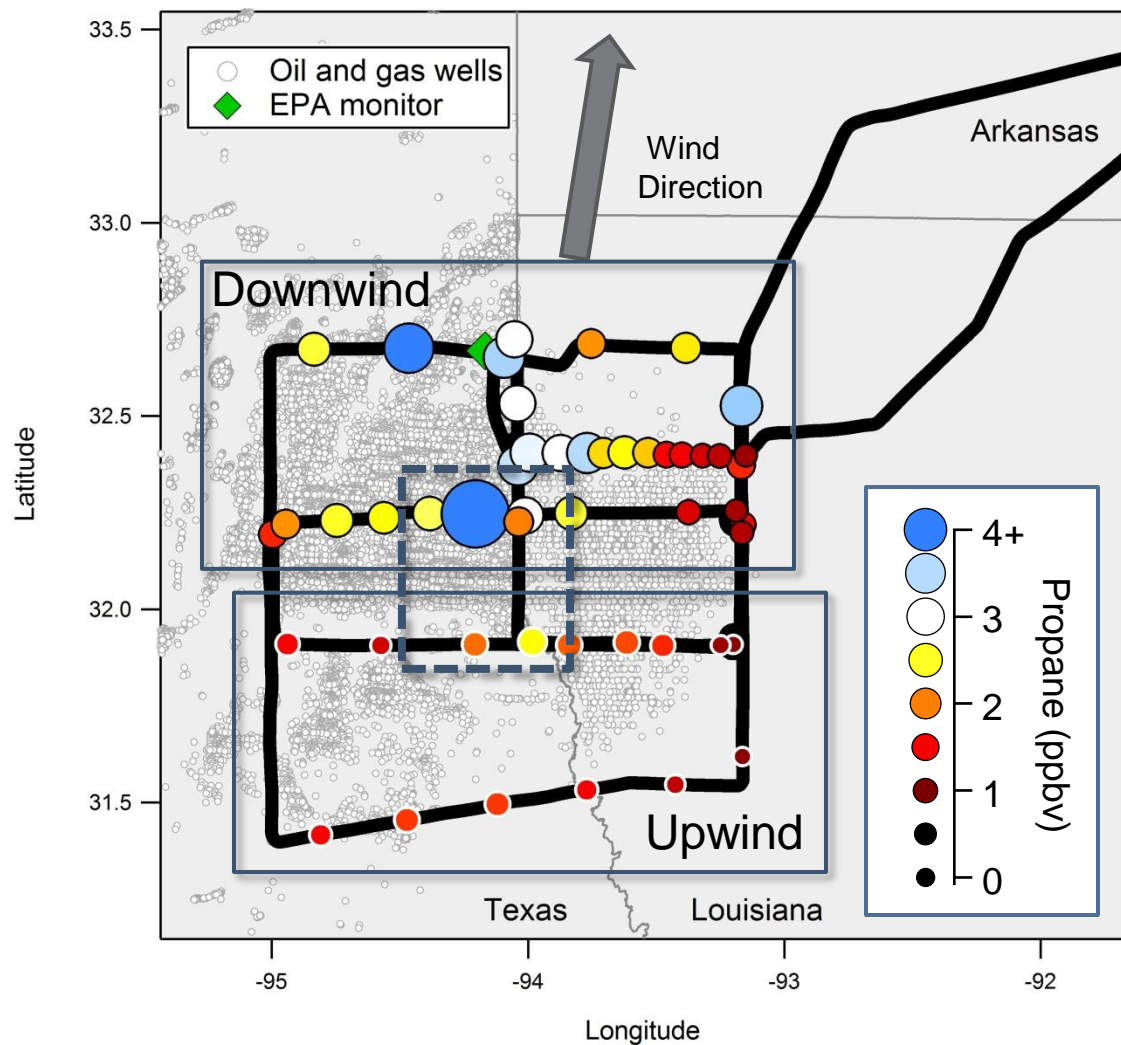
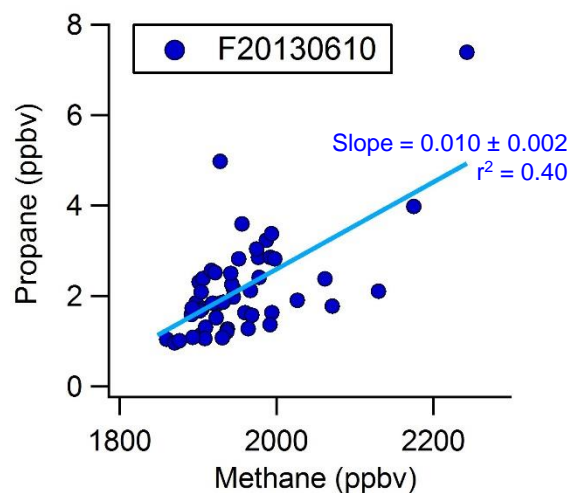
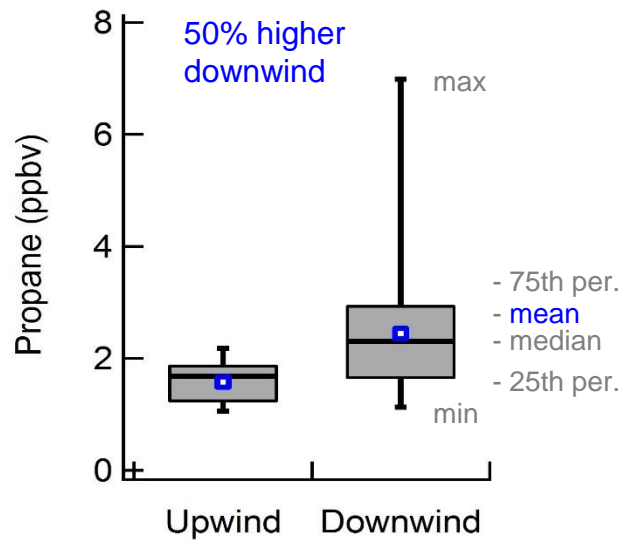


1. Assess propane emissions by comparing upwind and downwind samples for low altitude canisters only
2. Compare propane correlations with methane



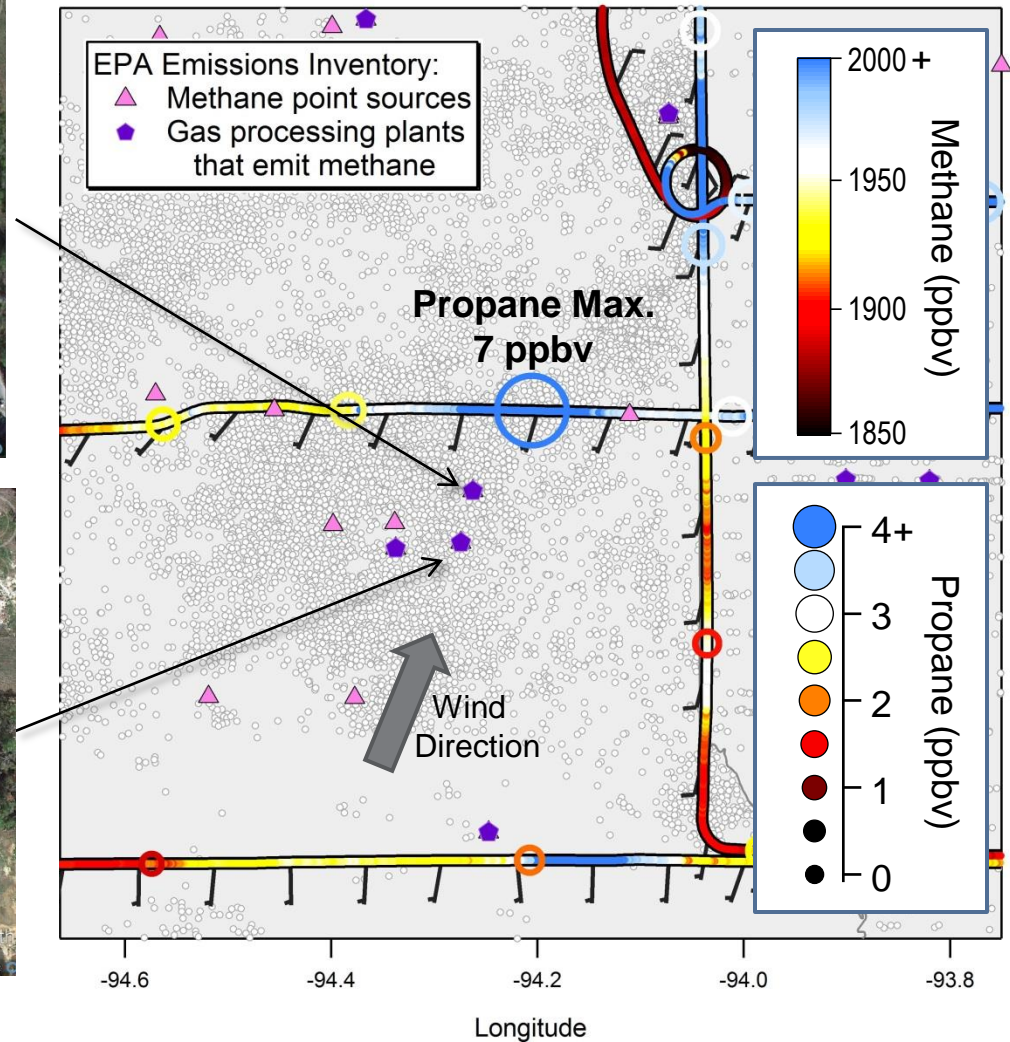
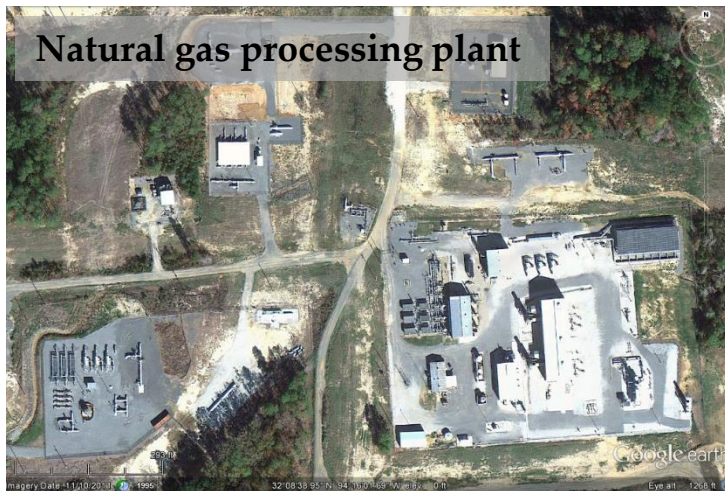
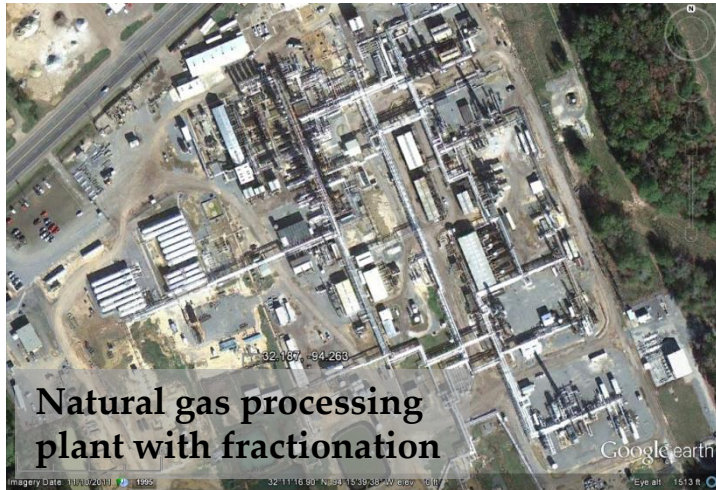
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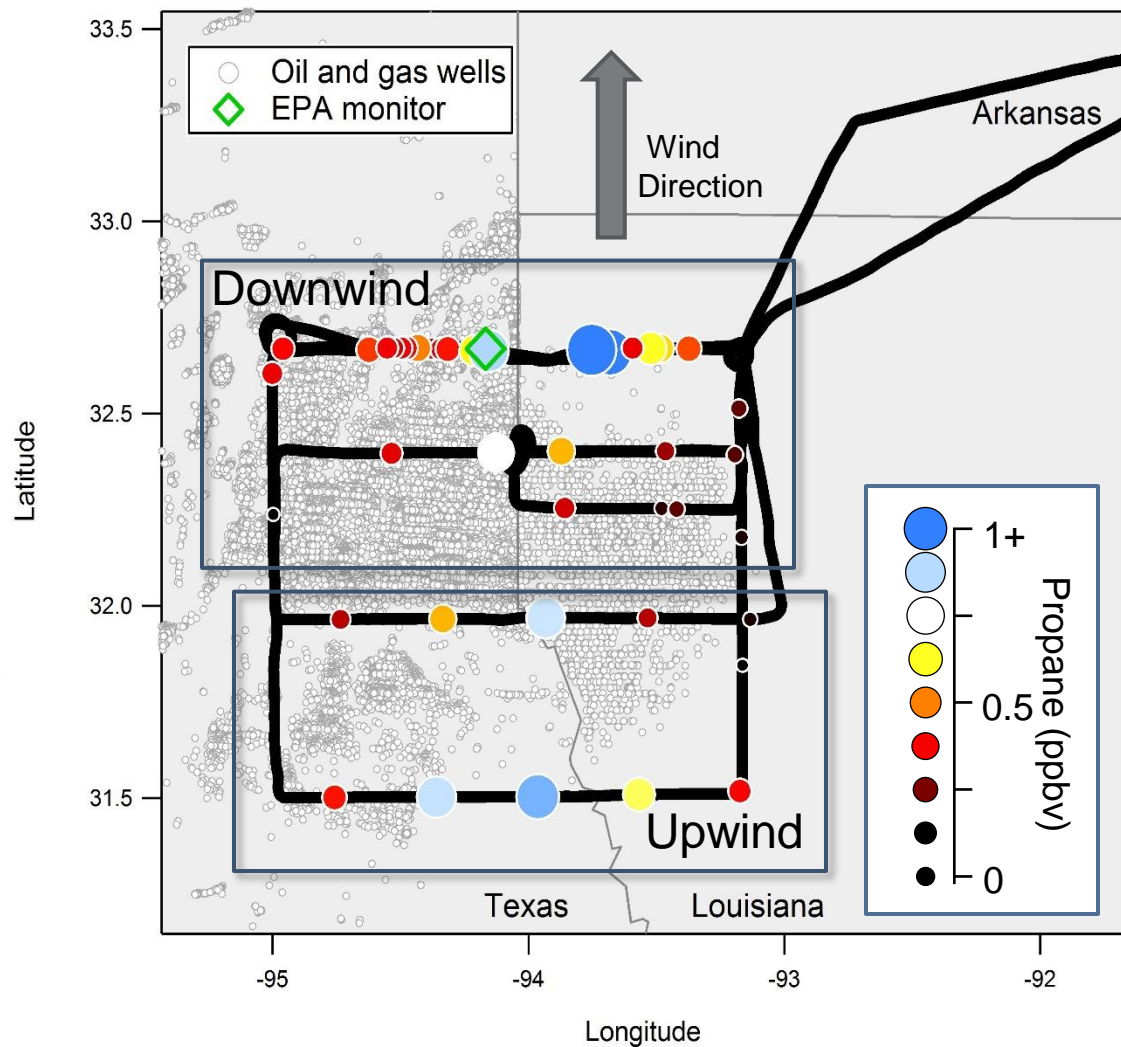
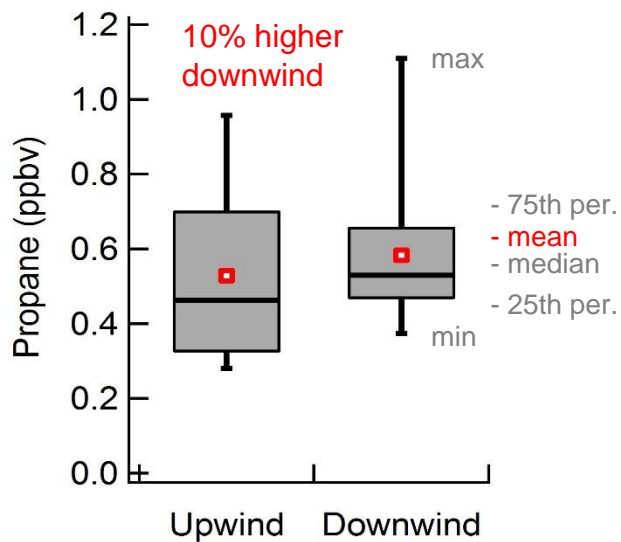
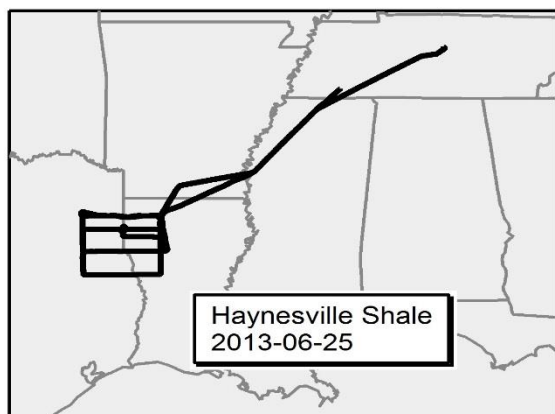
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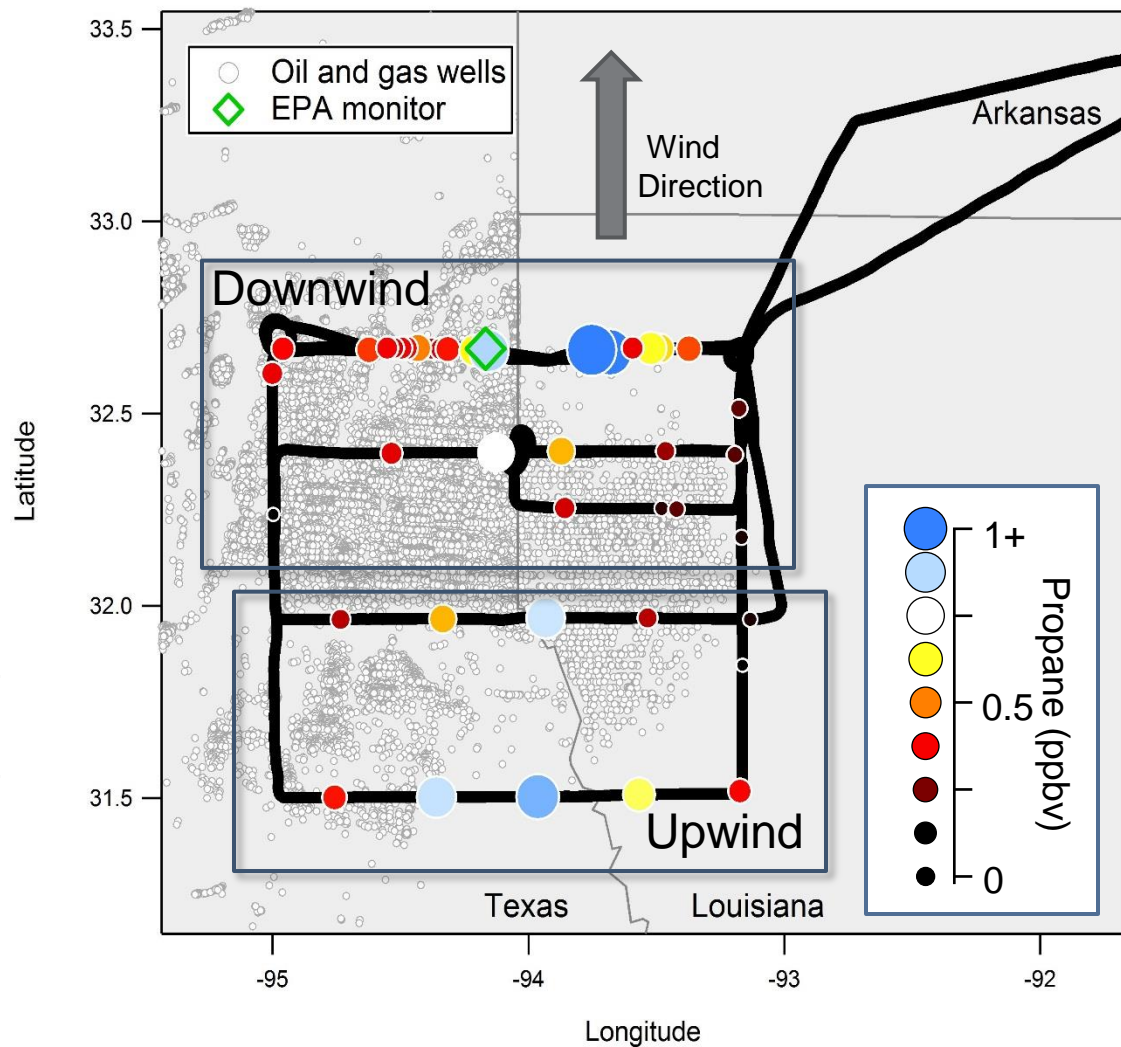
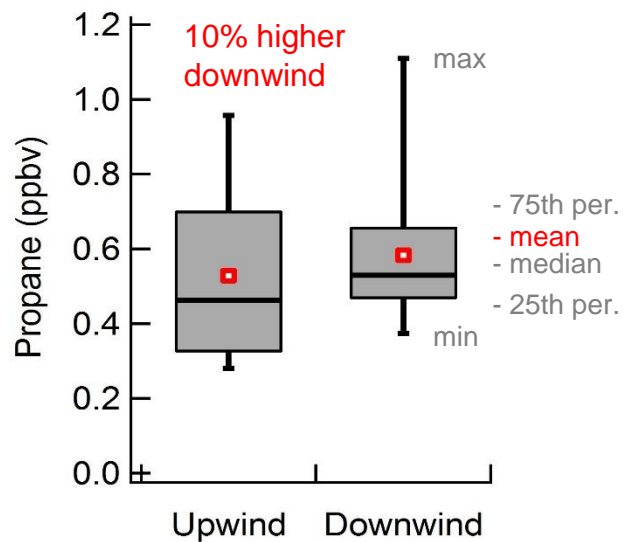
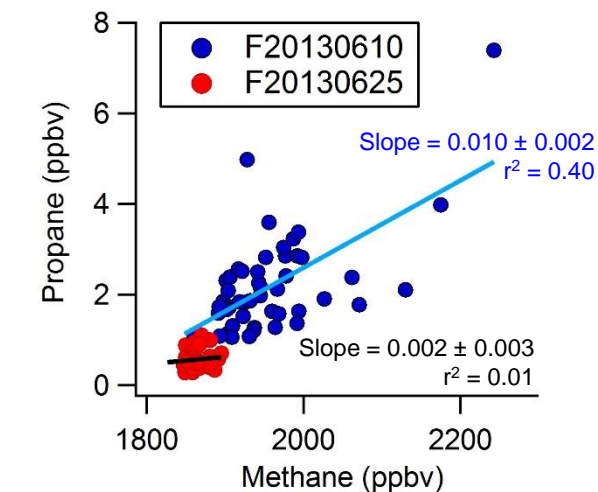
II. VOC emissions in Haynesville Shale Basin

Haynesville shale flight on 2013-06-25



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Haynesville shale flight on 2013-06-25



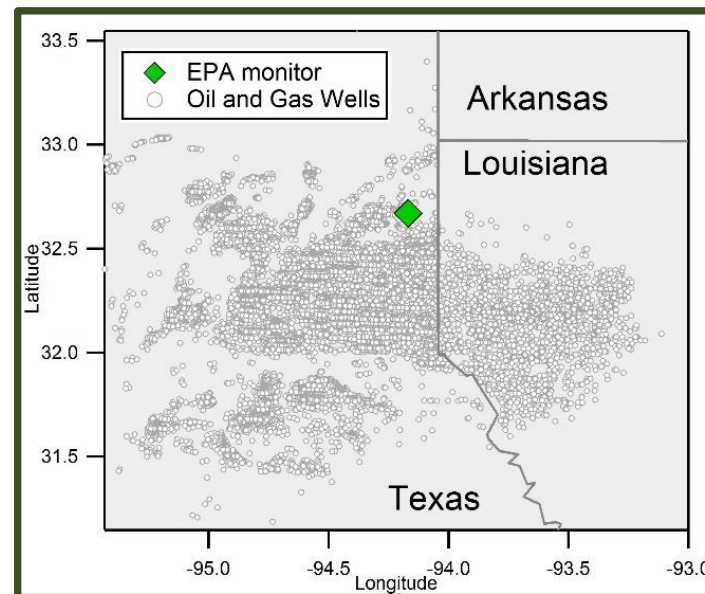
II. VOC emissions in Haynesville Shale Basin

Comparison of VOC composition

How does the Haynesville flight data compare to ground-based measurements?

◆ EPA monitoring site in Karnack, TX

- National Air Toxics Trends Station (NATTS)
- 1 whole air sample per week; 24-hr average
- Alkanes, alkenes, aromatics, isoprene and OVOCs



II. VOC emissions in Haynesville Shale Basin

Comparison of VOC composition

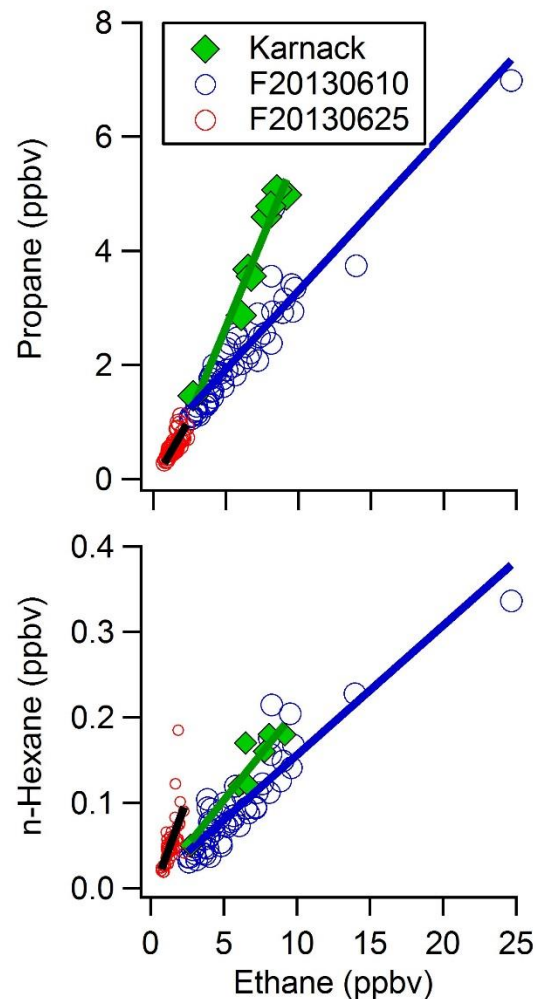
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- Data shown for June-July 2013

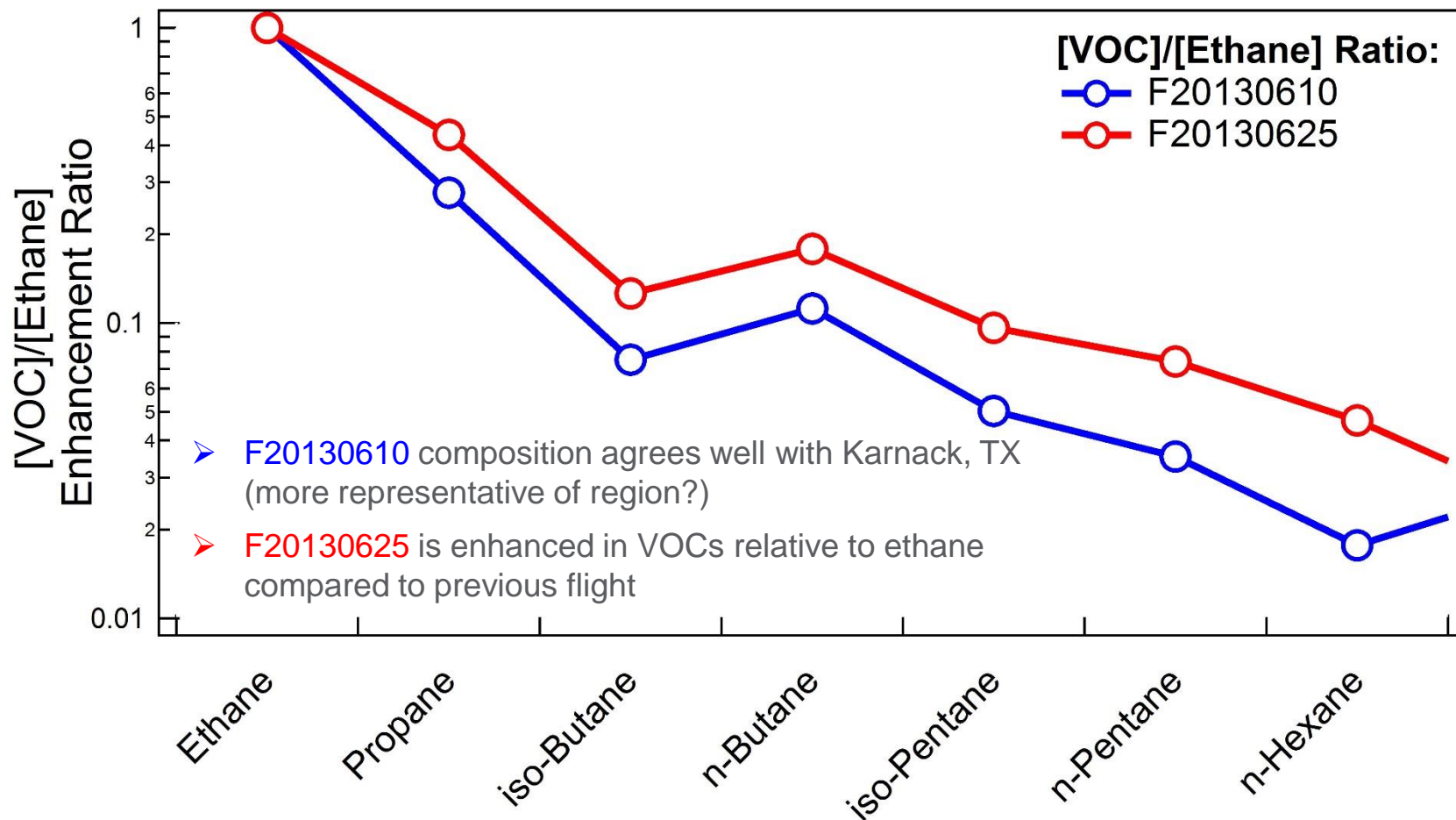
➤ Enhancement Ratios (ERs):

- ER is determined from slope of **VOC to ethane** correlation plot
- Ratios minimize the effects of air mass mixing and dilution and may be used to identify emission sources



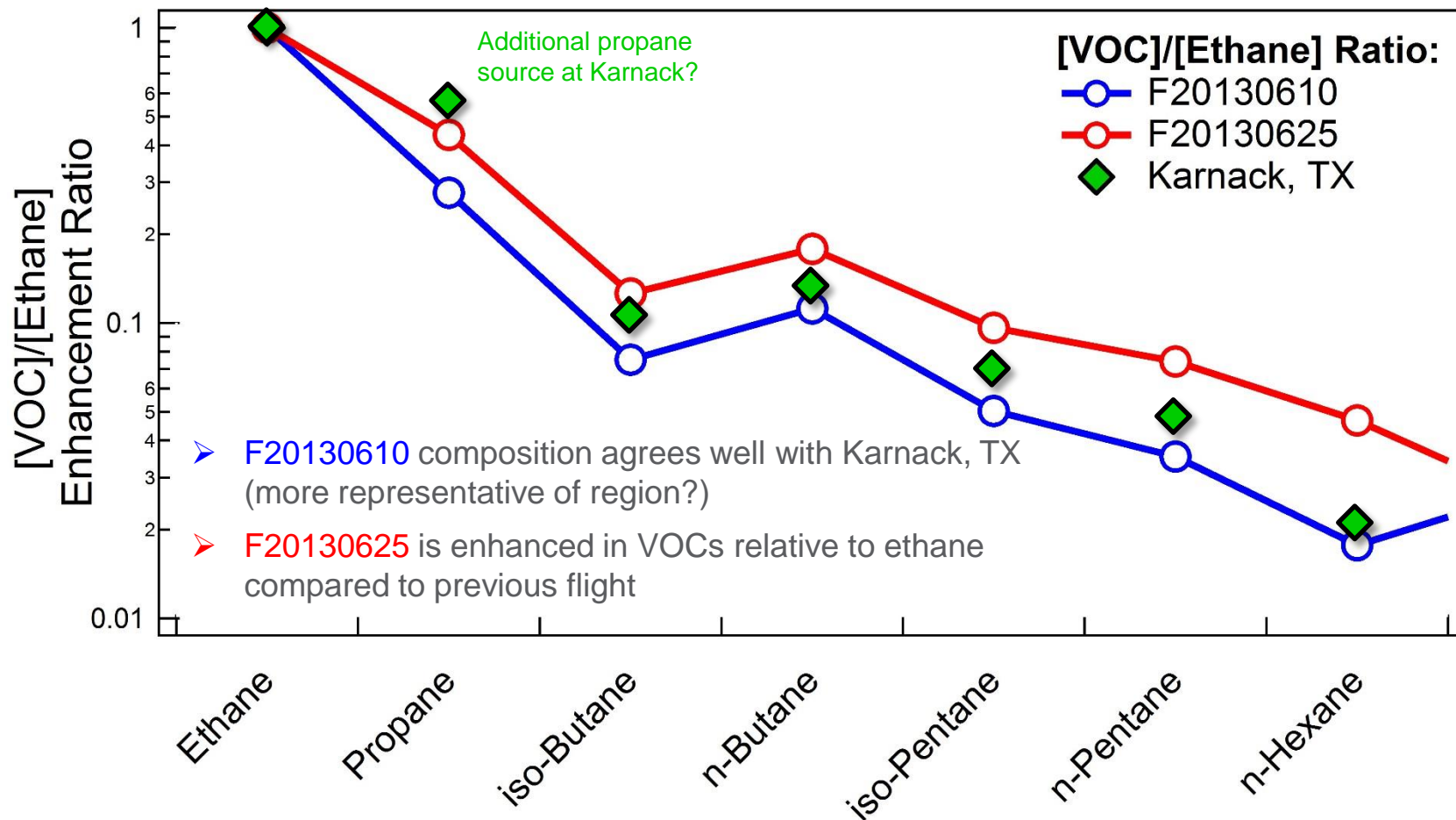
II. VOC emissions in Haynesville Shale Basin

Comparison of VOC composition to Karnack, TX site



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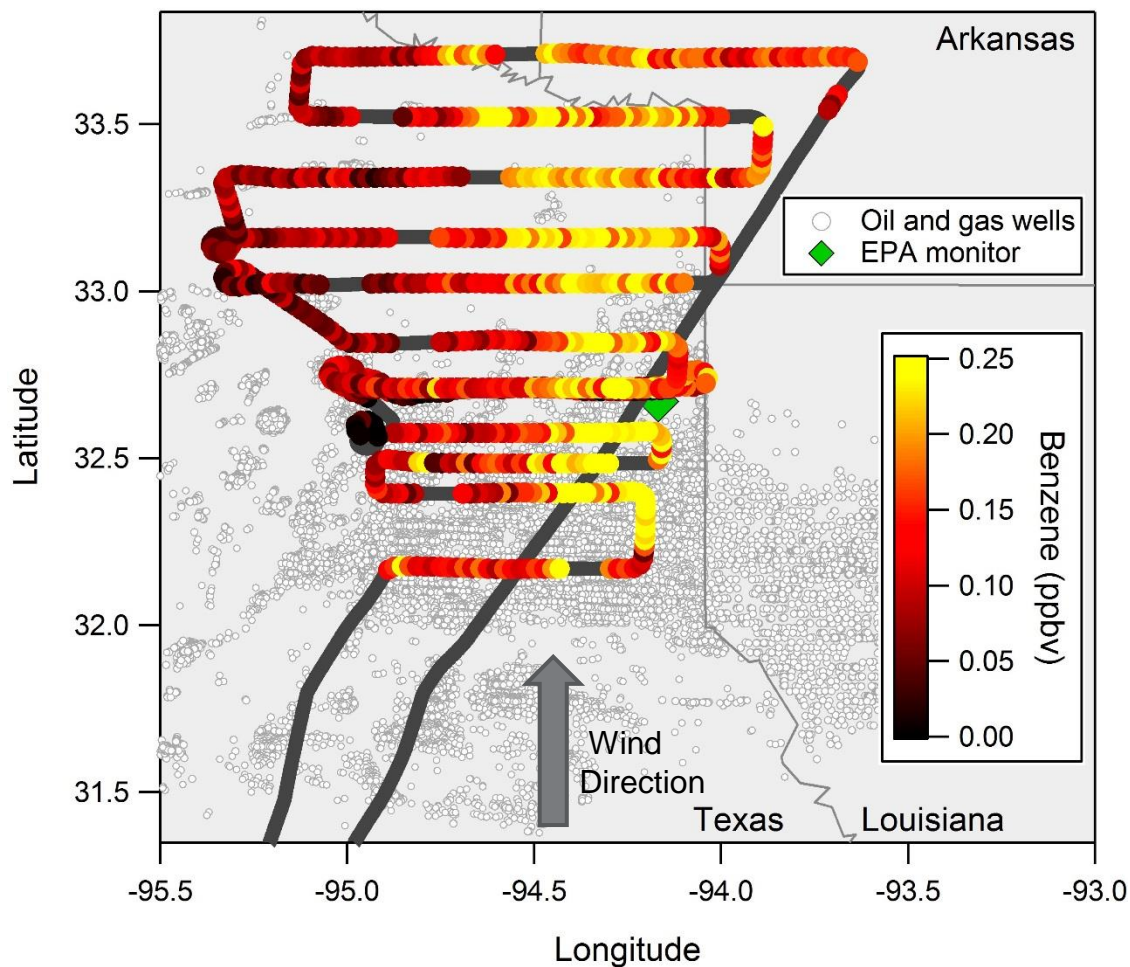
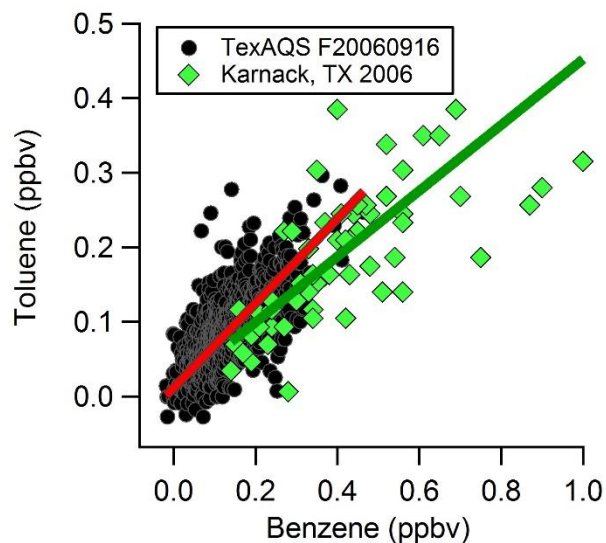
II. VOC emissions in Haynesville Shale Basin

Comparison of VOC composition to TexAQS 2006

➤ 2006 flight over Haynesville (TexAQS F20060916)

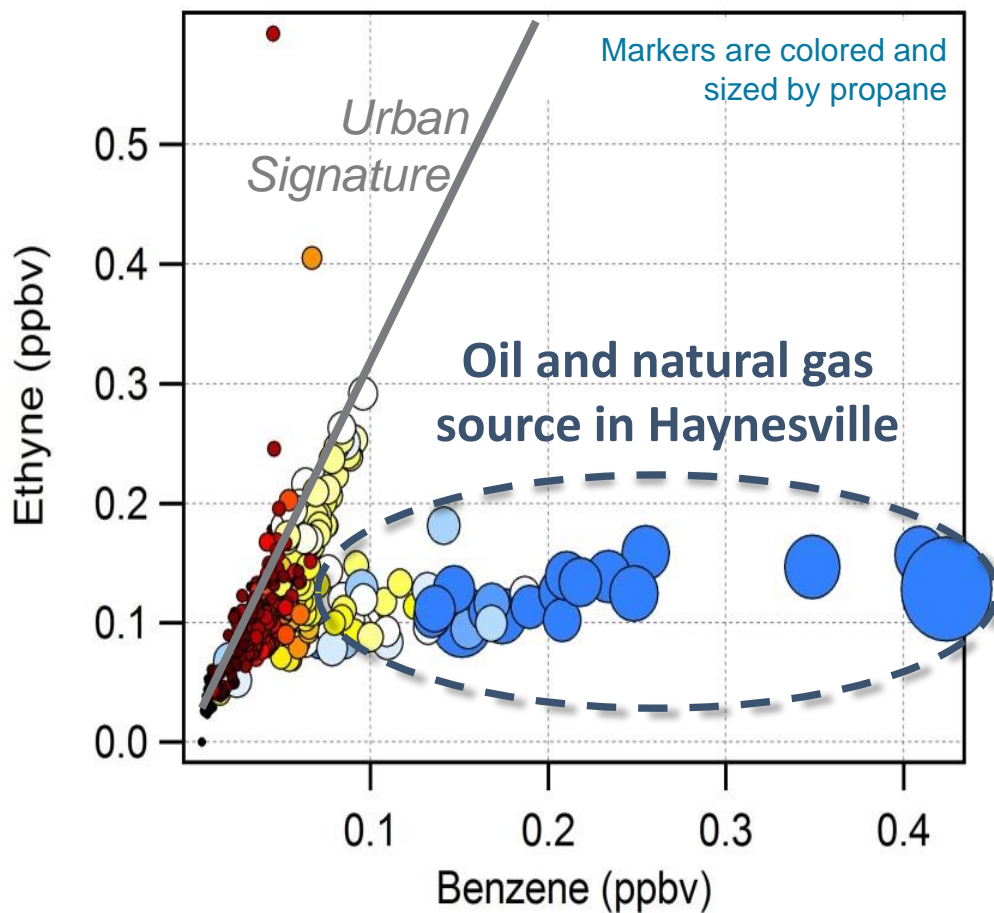
- WAS data not available
- Toluene/Benzene from PTR-MS (C. Warneke and J. de Gouw)

➤ Elevated benzene downwind of eastern Haynesville basin in 2006

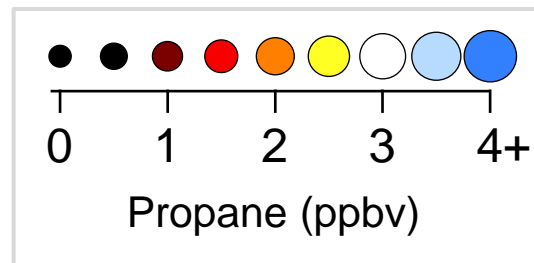


II. VOC emissions in Haynesville Shale Basin

Benzene source associate with oil and natural gas ops.



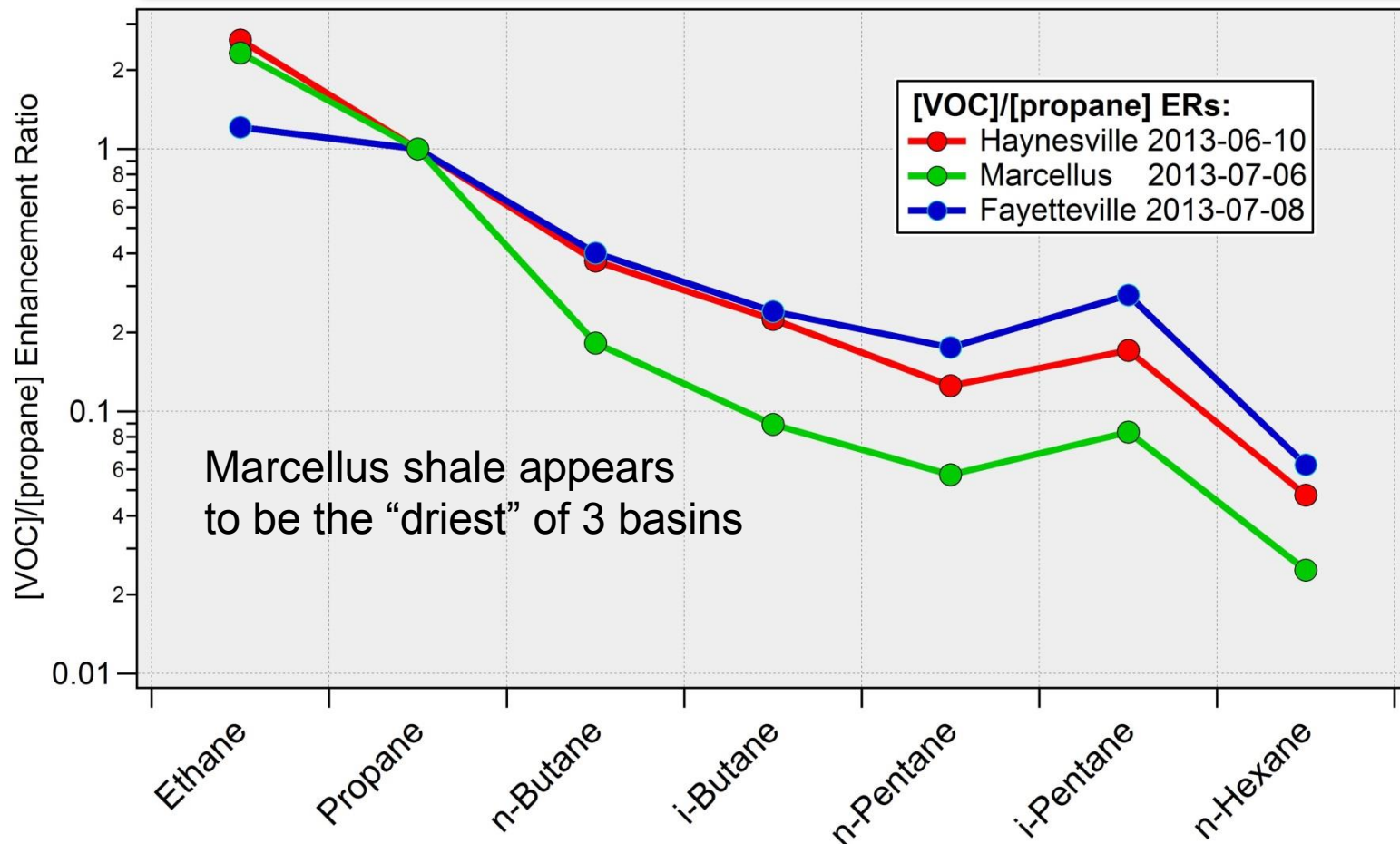
- Elevated benzene in HS is not associated with combustion sources (e.g., tailpipe emissions)
- Elevated benzene correlates with propane enhancements indicating a similar source (e.g., oil & natural gas operations)



II. Regional VOC emissions

Comparison of central and eastern shale basins

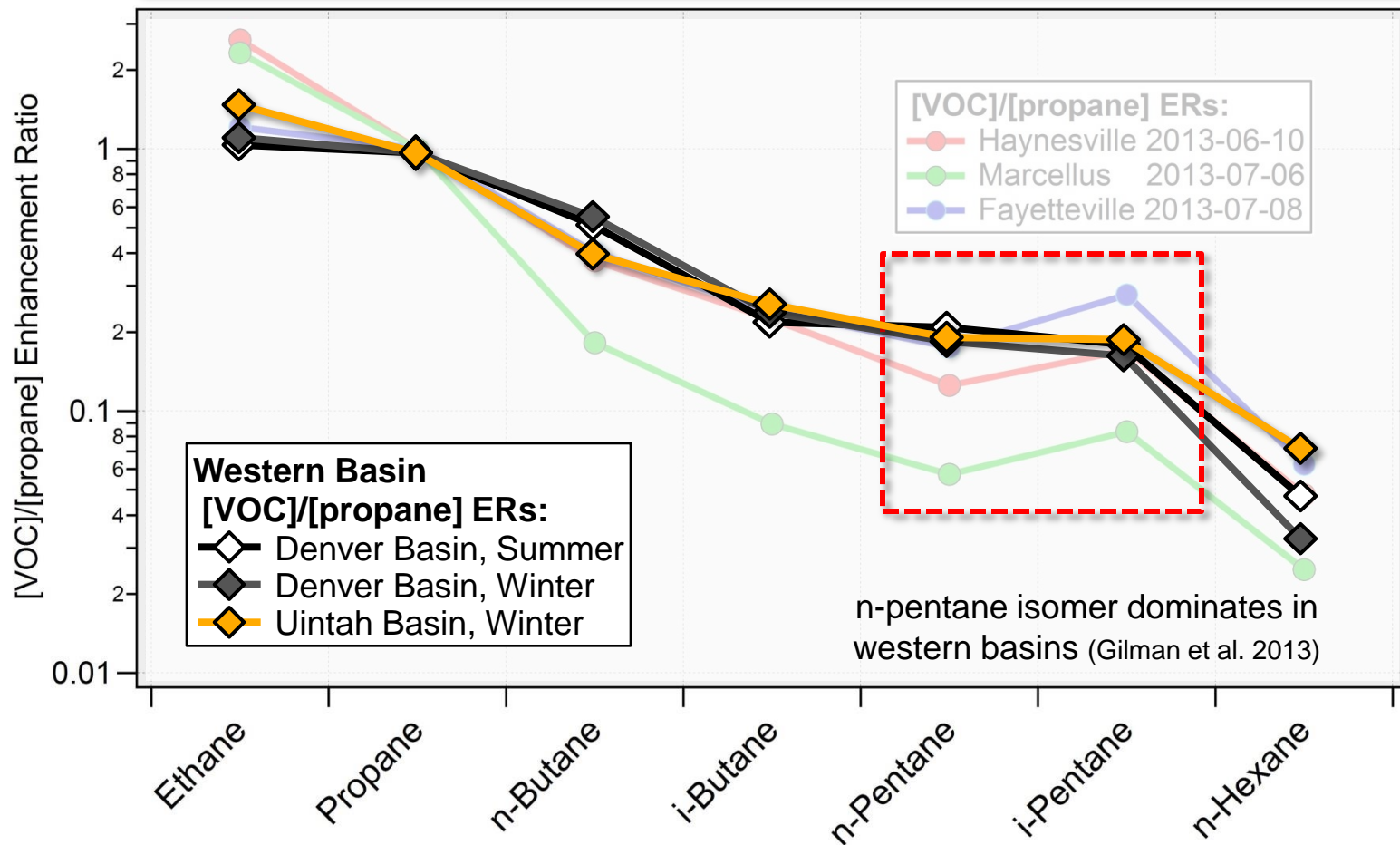
Each shale basin has a unique VOC profile



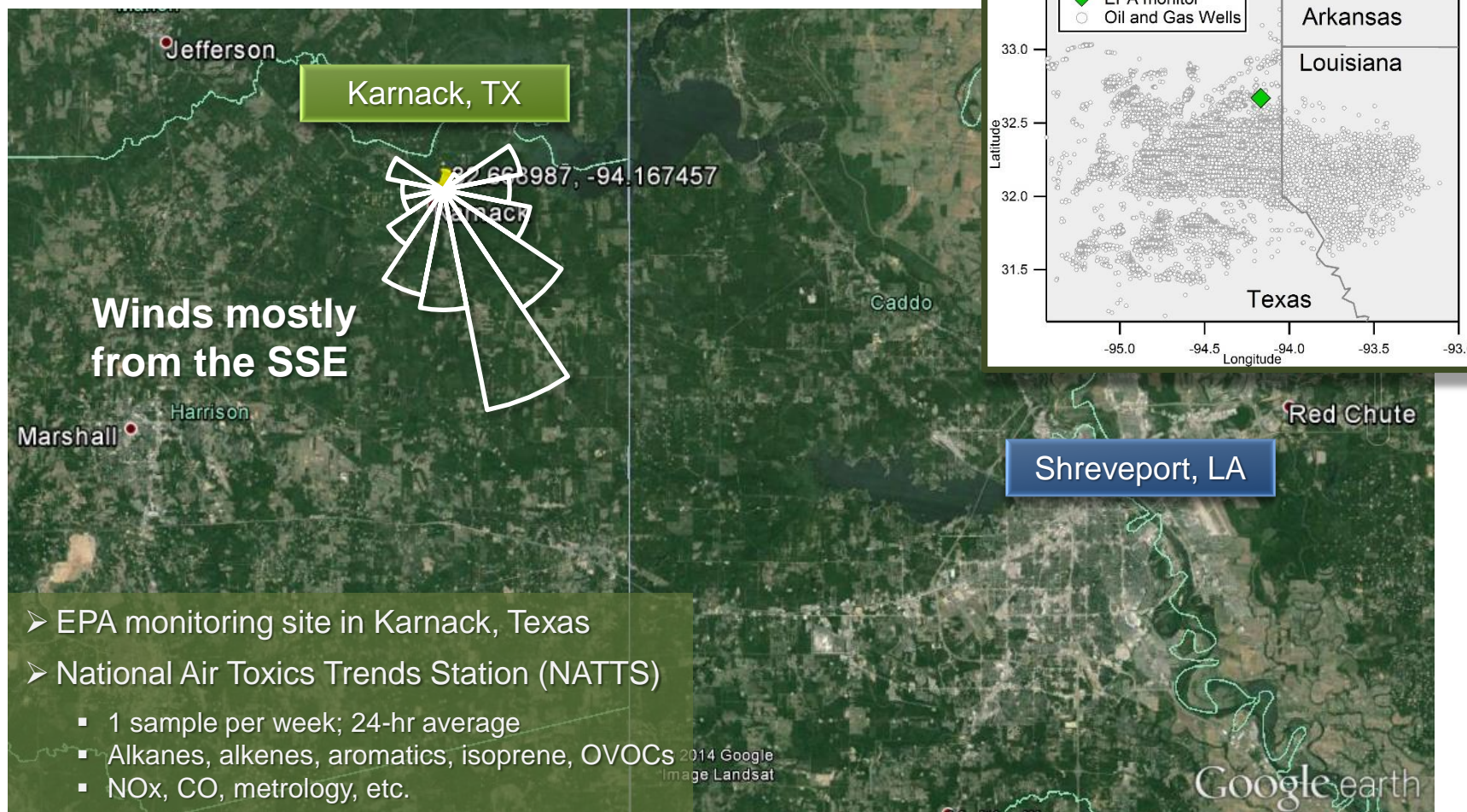
II. Regional VOC emissions

Comparison of all shale basins

Each shale basin has a unique VOC profile

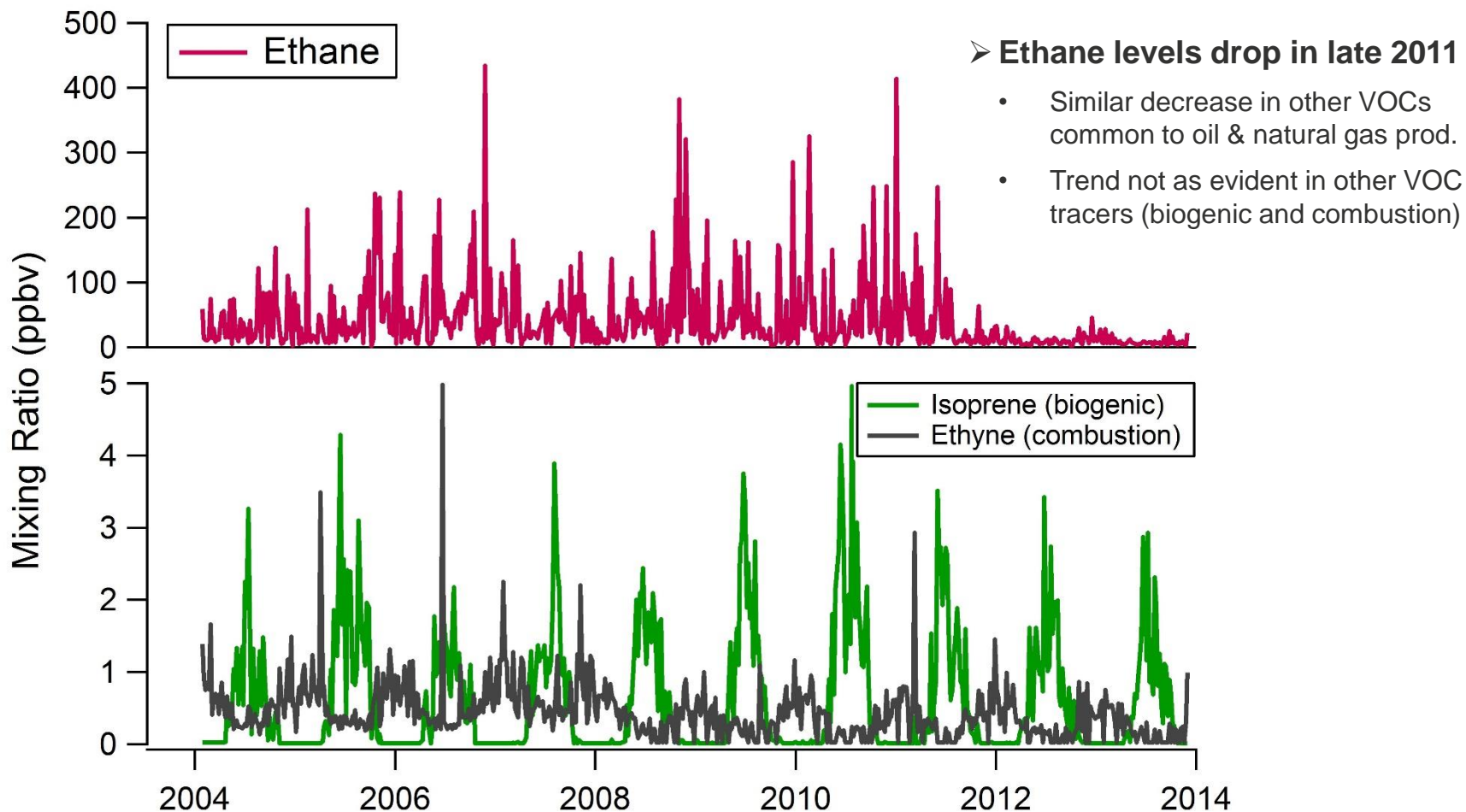


III. EPA monitoring site at Karnack, TX in Haynesville Shale VOC measurements from 2004-present



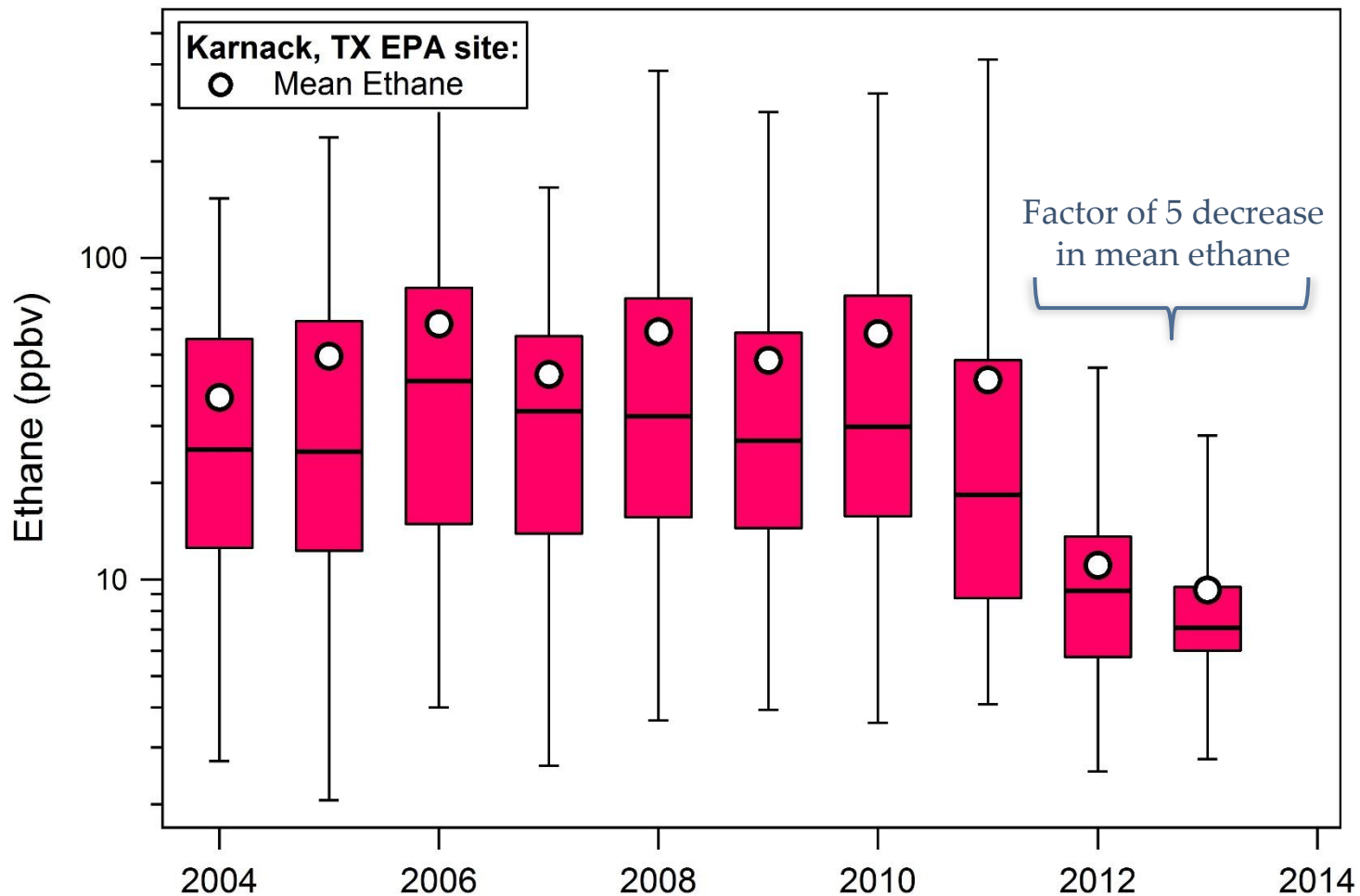
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VOC measurements from 2004-present



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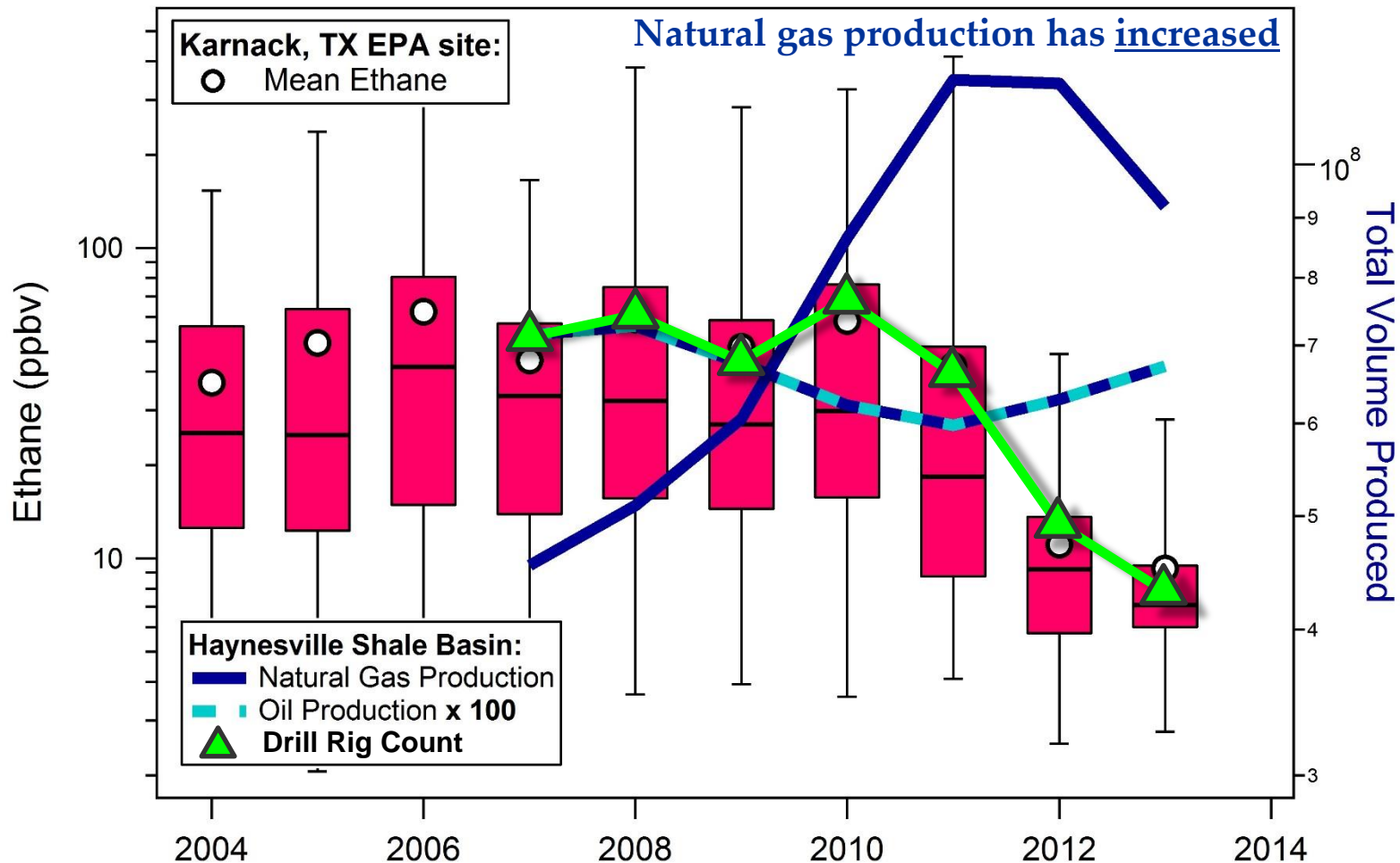
Significant decrease in ethane for 2012 - present



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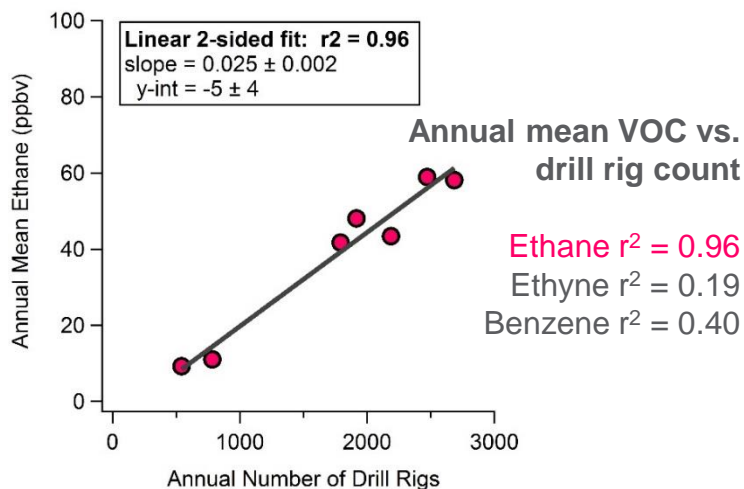
➤ Number of drilling rigs operating in Haynesville shale has decreased



III. EPA monitoring site at Karnack, TX in Haynesville Shale

Significant decrease in ethane for 2012 - present

Correlation plots



Annual Mean Ethane vs. ...	Fit Coef. (r^2)
Drill rig count Haynesville Shale and Harrison Co., TX	0.96
Casing Gas Prod. (Harrison Co. TX)	0.41
Natural Gas Prod. (Haynesville Shale)	0.31
Oil Production (Harrison Co. TX)	0.15
Condensate Production (Harrison Co.)	0.11
Oil Production (Haynesville Shale)	0.05

Drilling operations may be a significant emission source of light alkanes in Haynesville shale basin

- Karnack site is in Harrison Co., TX
- Harrison Co. data includes production from all reservoirs including Haynesville shale
- Haynesville shale data includes production and drill rig counts for Texas and Louisiana

Summary



- ❑ Detailed chemical analysis of emissions from oil and natural gas operations in 5 major U.S. shale basins
- ❑ VOC composition varied by basin
 - Enhancements in propane and other n-alkanes downwind of Haynesville shale basin
 - Karnack, TX ground site data agrees well with Haynesville flights F20130610 and F20060916
 - Marcellus appears to be the “driest” of the 5 shale basins
- ❑ Decrease in ambient concentrations of light alkanes at Karnack, TX ground site strongly correlates with number of drill rigs in operation