VOC Source Signatures and Source Apportionment Studies from Auto-GC Data in Houston, TX

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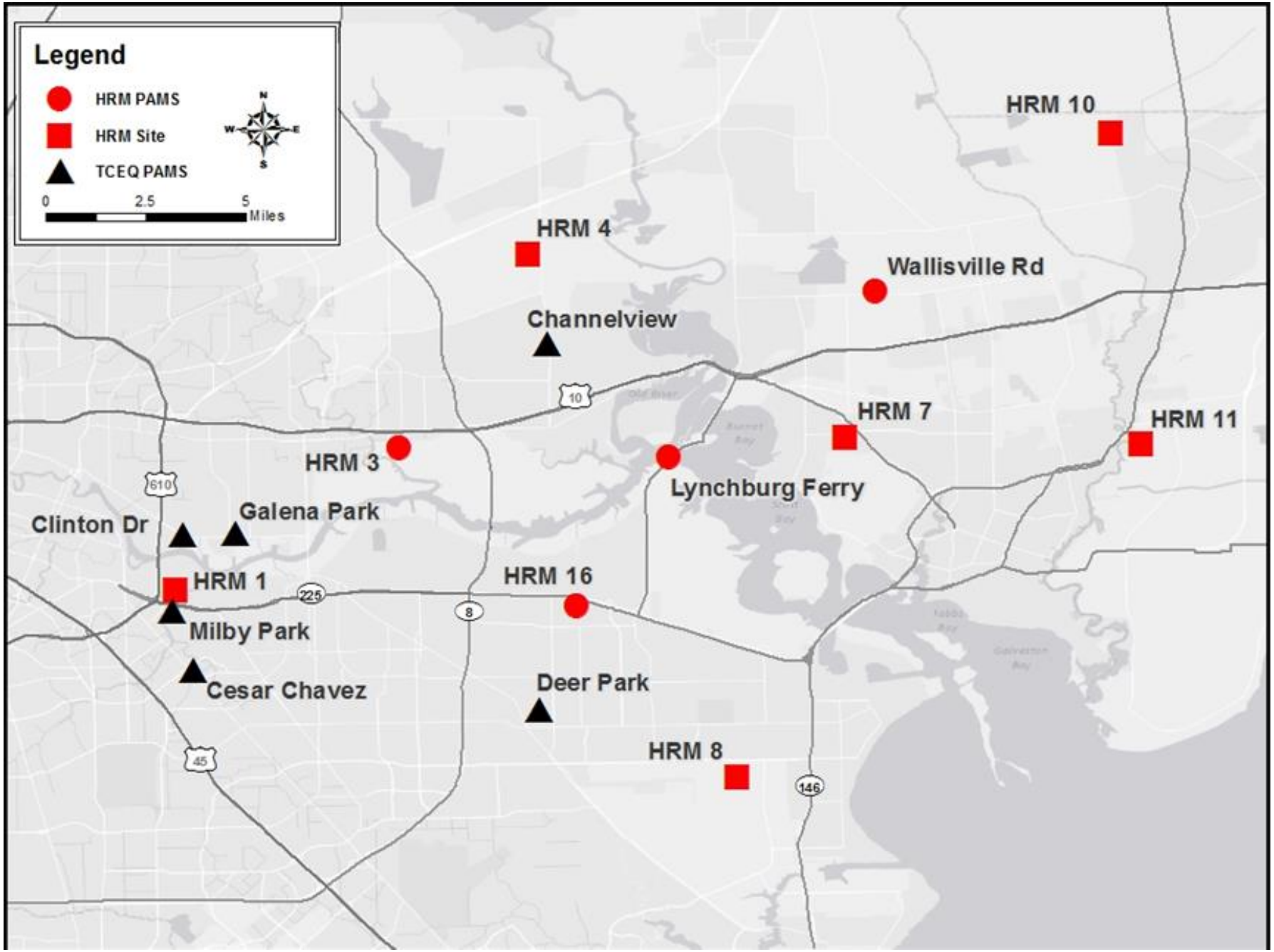
Overview

– Recent Trends in Ozone, NOx, and VOC Ambient Concentrations in Houston, TX

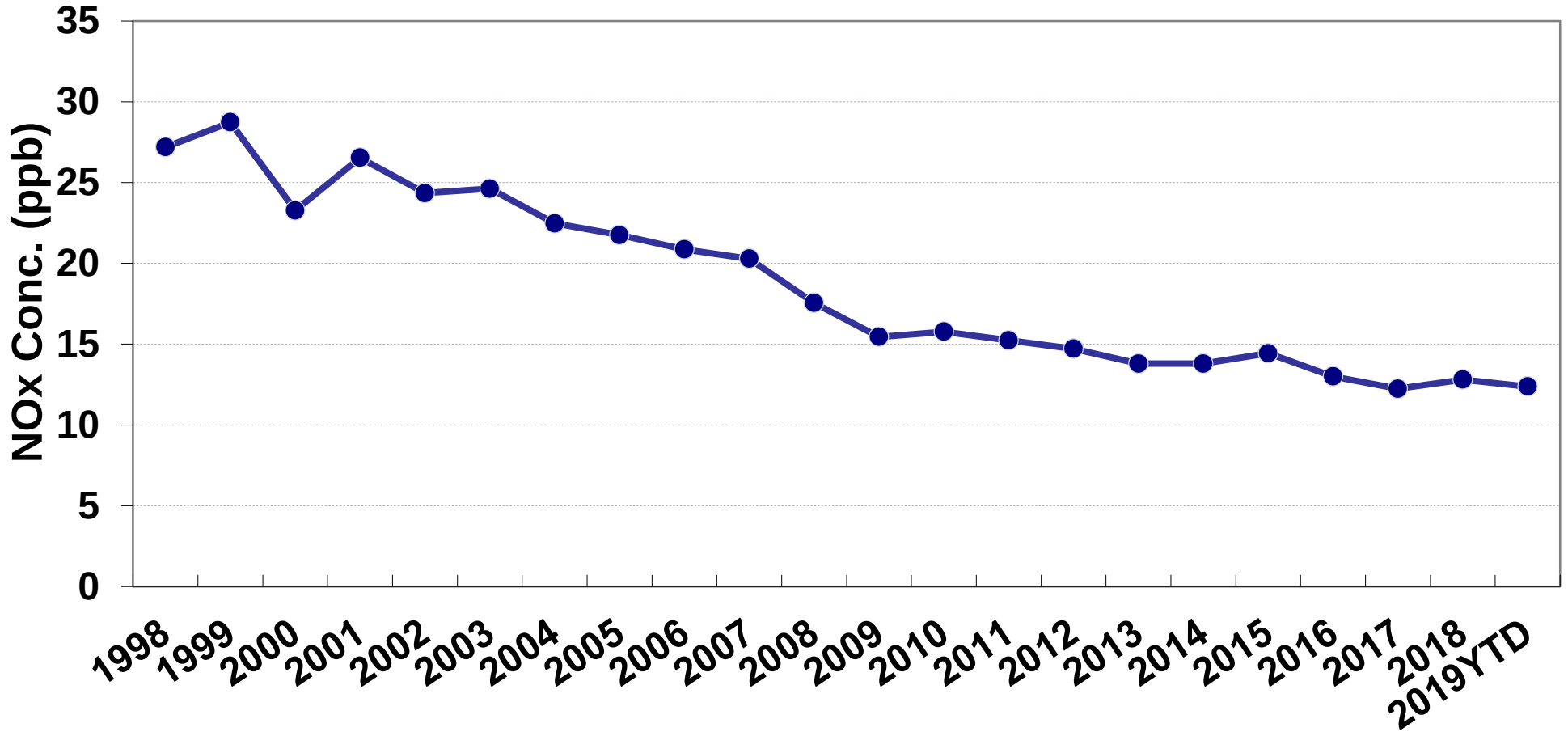
– VOC Source Apportionment Studies

– VOC Source Signatures

– Summary and Next Steps

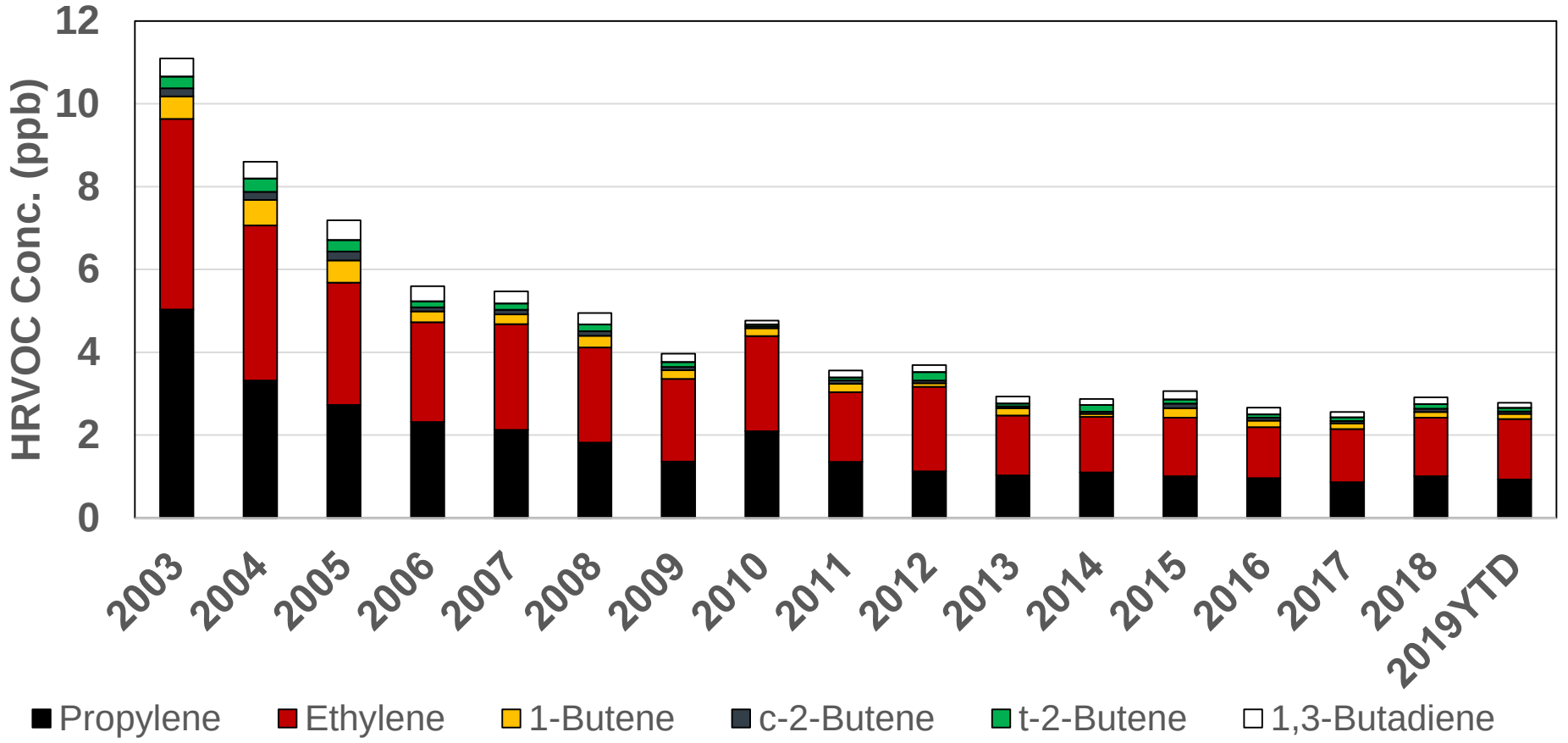

Legend
HRM PAMS
HRM Site
TCEQ PAMS
0
2.5
5
Miles
N
W
E
S
HRM 10
HRM 4
Wallisville Rd
Channelview
10
HRM 7
HRM 11
HRM 3
Lynchburg Ferry
610
Clinton Dr
Galena Park
HRM 1
HRM 16
225
8
Milby Park
Cesar Chavez
Deer Park
HRM 8
45
146

Houston Area NOx Concentration Trends, 1988 - 2019



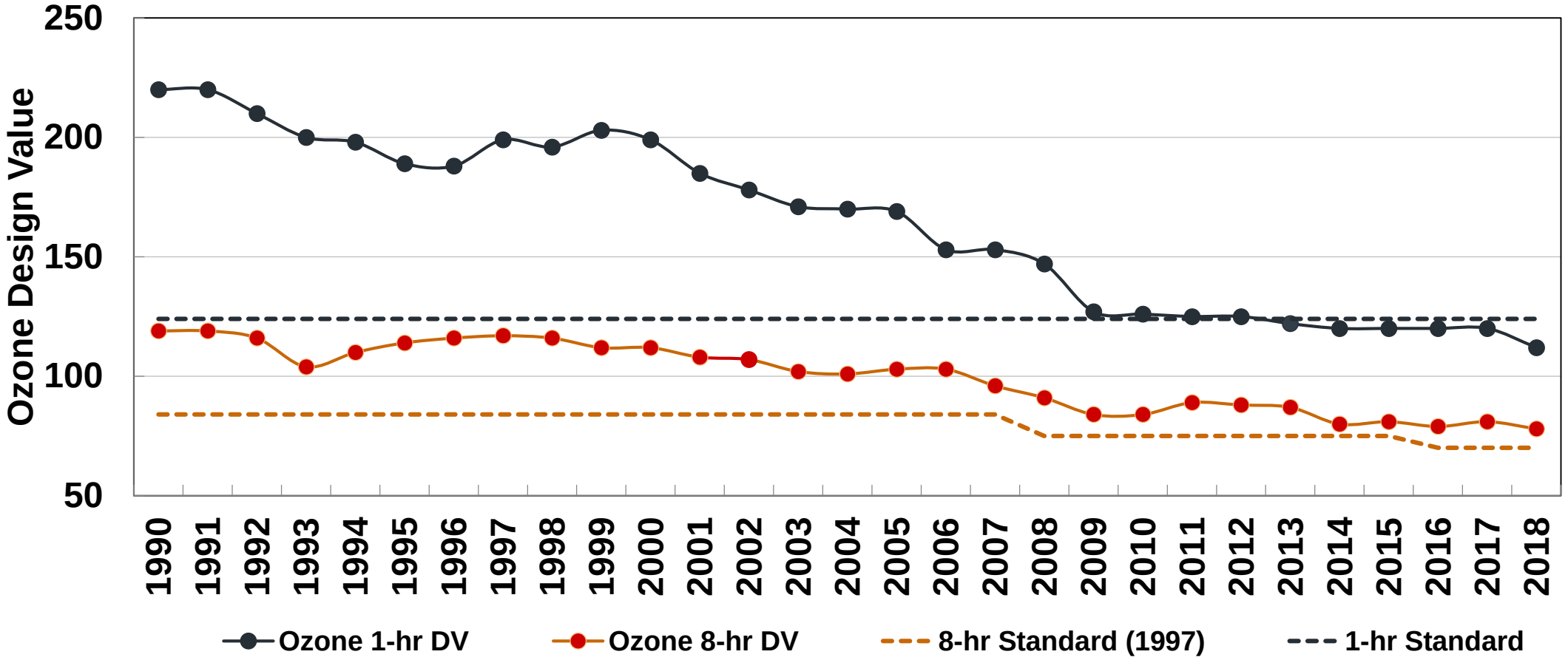
Annual Average Ambient NOx Levels from Long Term Monitors Texas Ave., Clinton Dr., Lang, Aldine, HRM 1 - 11

Houston Area HRVOC Trends, 2003 - 2019



Annual Average Ambient HROVC Levels from all Houston Area Auto-GC Monitoring Sites

Houston Area Ozone Design Value



1. Population data before 2007 from US Census Bureau. Population data after 2007 from Texas Department of State health Services. Ozone data from TCEQ.
2. 1-Hour NAAQS 124 ppb. 1997 8-Hour NAAQS 84 ppb. 2008 8-Hour NAAQS 75ppb 2015 8-hour NAAQS 70 ppb.

VOC in Houston

- Houston major sources of VOCs
  - Biogenic emissions
  - Vehicular emissions (combustion and gasoline evaporation)
  - Industrial processes, including refining, petrochemical, and natural gas processes

- Houston Ship Channel area is a concentrated source of highly reactive VOCs (HRVOCs).

- Recent work shows reduced influence of HRVOC on ozone exceedance days in Houston
  - Ozone Production Efficiency monitored at HRM 1, 3, and 7 beginning in 2017
  - OPE< 8 on all ozone exceedance days at HRM 1,3 in 2018, OPE > 8 on 1 ozone exceedance day at HRM 7 in 2018

VOC Source Apportionment

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VOC Source Apportionment Analysis

– Source Receptor Modeling performed using Positive Matrix Factorization (PMF)
  - EPA version 5.0, for
  - 2016 - 2018 Houston area Auto-GC hourly data

– 2016 - 2018 PMF analysis compared with previous analysis from 2003

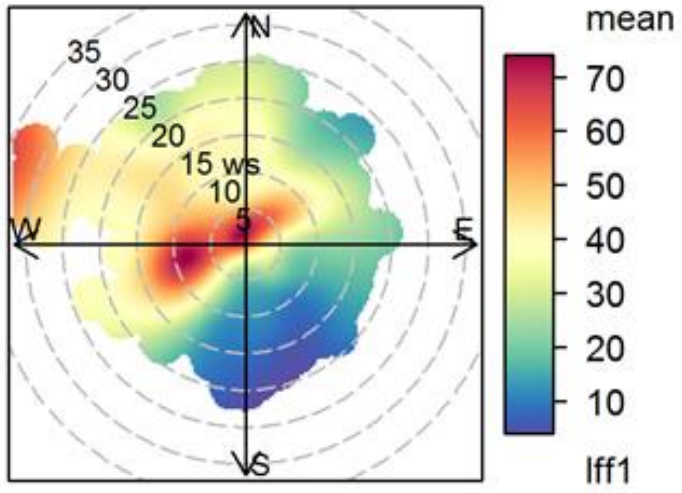
– 2016 - 2018 PMF analysis identified 8 source factors across
  - Refinery + natural gas (C2 – C4 alkanes)
  - Traffic (light alkanes + aromatics)
  - Gasoline Vapor (light alkanes)
  - Gasoline (heavy alkanes + aromatics)
  - Biogenic (isoprene)
  - Industrial (1,3-butadiene)
  - Petrochemical (C2 – C4 alkenes)
  - Refinery + Urban (mix of alkanes

VOC Source Apportionment Distribution, 2016 - 2018

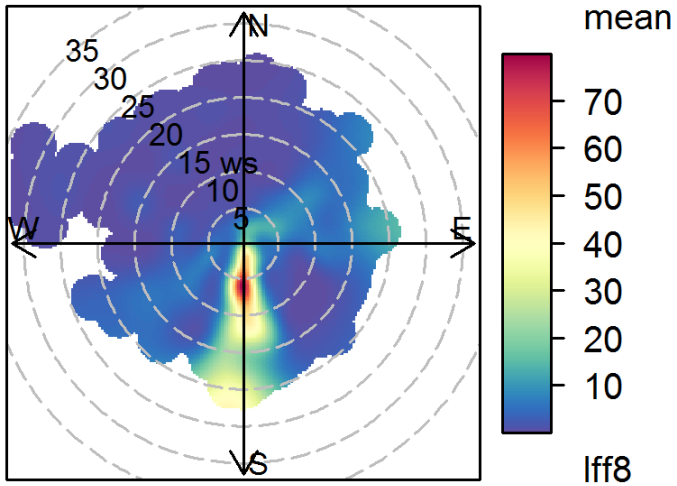
PMF Factors Summarized by Source	Milby Park	Cesar Chavez	Clinton Drive	HRM3	Deer Park	Lynchburg Ferry
Refinery + NG (C2-C4 alkanes)	45%	32%	25%	28%		39%
Traffic (light alkanes + aromatics)	3%	17%	22%	21%	22%	
Gasoline evaporative (light alkanes)			26%		4%	14%
Gasoline liquid (aromatics + heavy alkanes)	18%			24%	2%	30%
Biogenic (isoprene)		3%	1%	3%		2%
Industrial (1,3-butadiene)	20%	34%	22%	14%		3%
Petrochem (C2 – C4 alkene)	10%	11%	4%	12%		13%
Mix Refinery + Urban (mix of alkanes, etc)					72%	

Wind Direction & Wind Speed for VOC Factors at Lynchburg Ferry

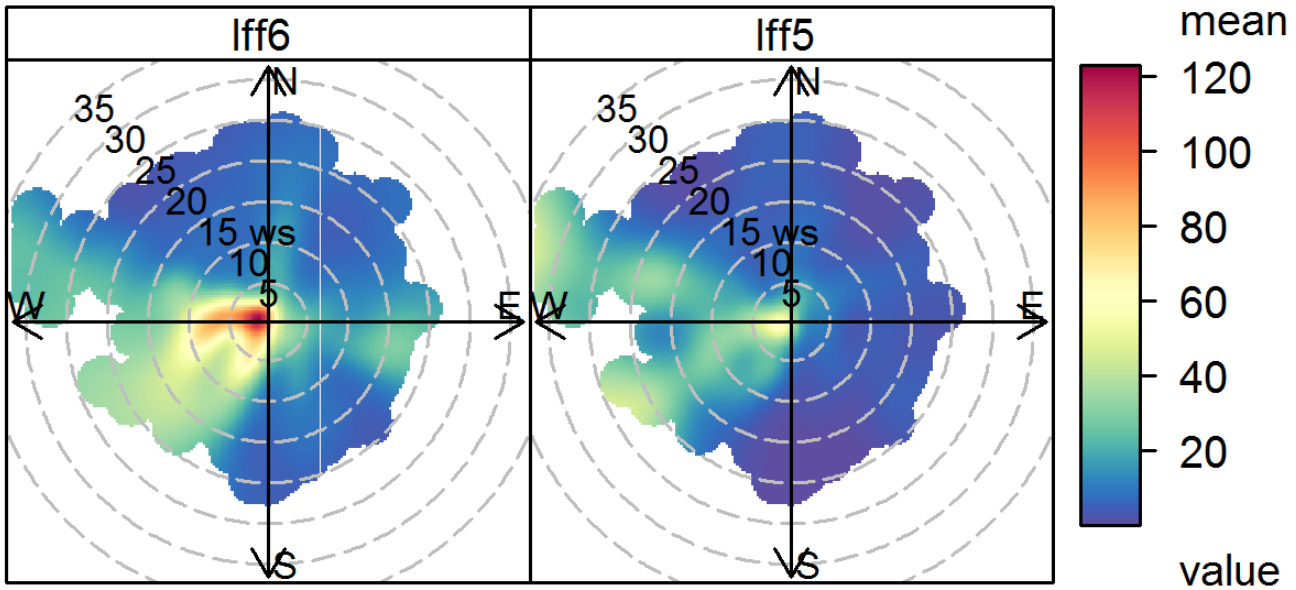
Refinery + Nat. Gas



Petrochemical



Gasoline (evap) **Gasoline (liquid)**



VOC Source Factors at Lynchburg Ferry exhibit Wind direction / speed dependence depending on distance from monitor and distribution of sources in the area

Changes in VOC Source % Composition, 2003 – 2016-2018

PMF Factors Summarized by Source	HRM-3 2003	HRM-3 2016-2018	Lynchburg 2003	Lynchburg 2016-2018
Vehicle Exhaust	-	15%	-	-
Biogenic	-	3%	-	1.7%
Aromatics	2%	-	15%	
Gasoline (liquid)	-	24%	-	30%
Refinery + Natural Gas	43%	27%	45%	39%
Petrochem Production	6%	12%	20%	13%
Industrial	10%	11%	3%	3%
Gasoline (evaporative)	29%		17%	14%

2016 – 2018 VOC Source Apportionment Analysis Summary

– Auto GC data used to identify major VOC source profiles in Houston 2016 – 2018.

– Refinery & Natural Gas factors were combined in 2016 – 2018 analysis

– Traffic & Gasoline related factors increase contribution in 2016 - 2018

VOC Source Signatures

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VOC Ratio: Source Signatures

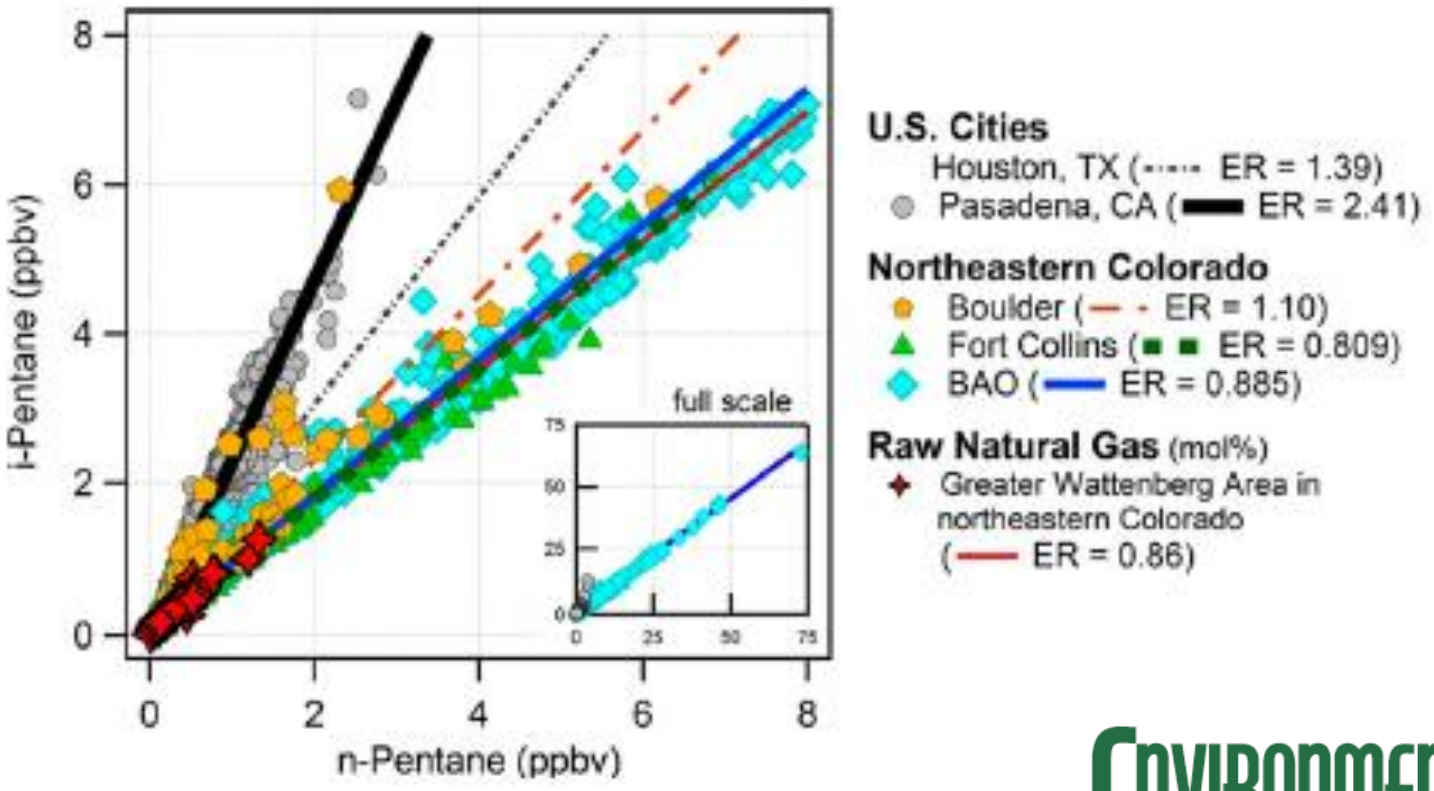
– Concentrations of various VOCs continue to decline in Houston area

– Alkane VOC contribution to ozone reactivity now more important than alkene (HROVC) contribution

– Same alkanes emitted from several sources
  • Benzene from refinery processes, chemical storage, gasoline combustion, etc

– Potential exists to use Auto-GC data to identify plume origins using ratios of observed concentrations

iso/normal pentane ratio as VOC source signature



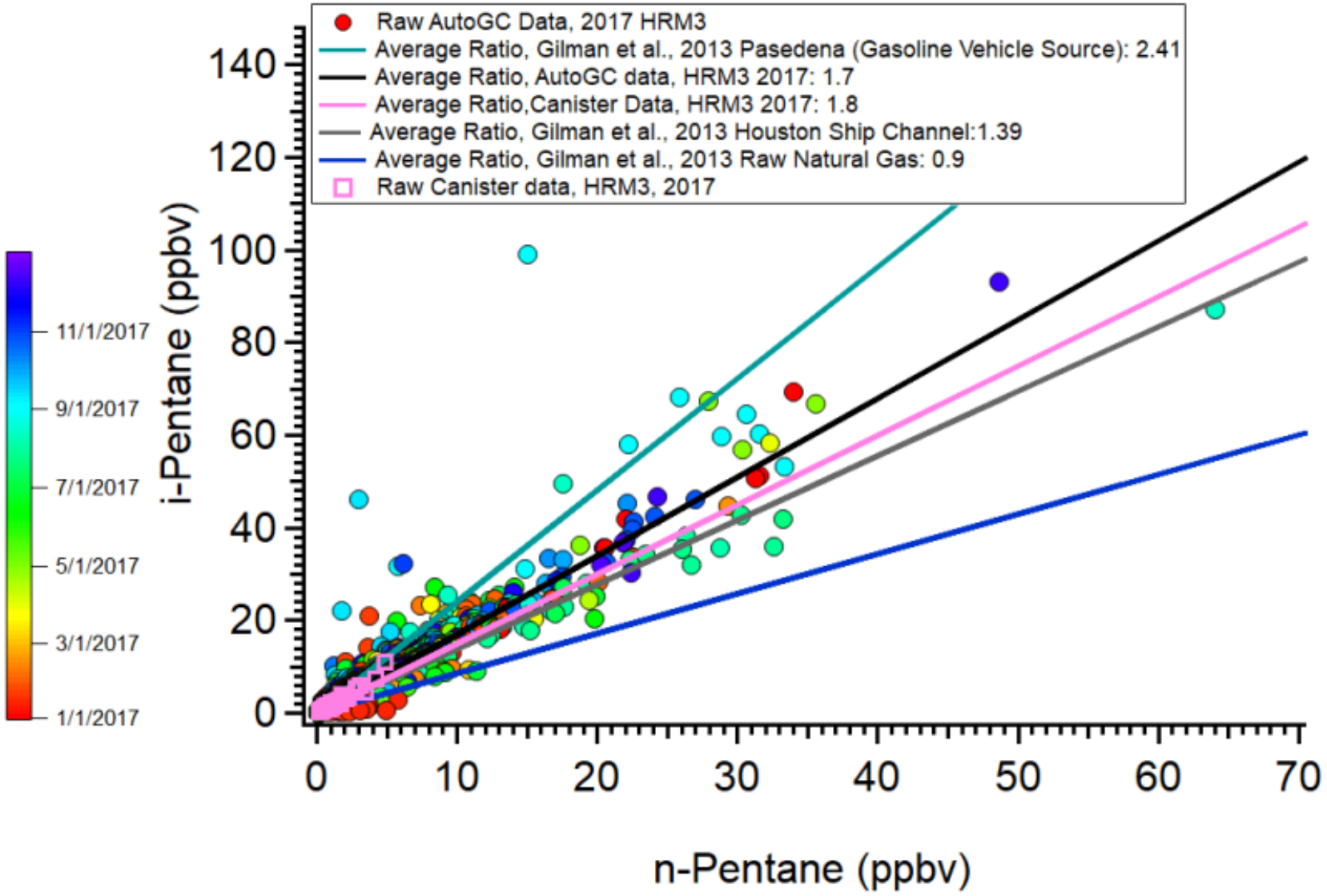
Iso/n- pentane ~ 1.4 for urban sources
Iso/n- pentane ~ 0.9 for raw natural gas

Environmental Science & Technology
Article
pubs.acs.org/est

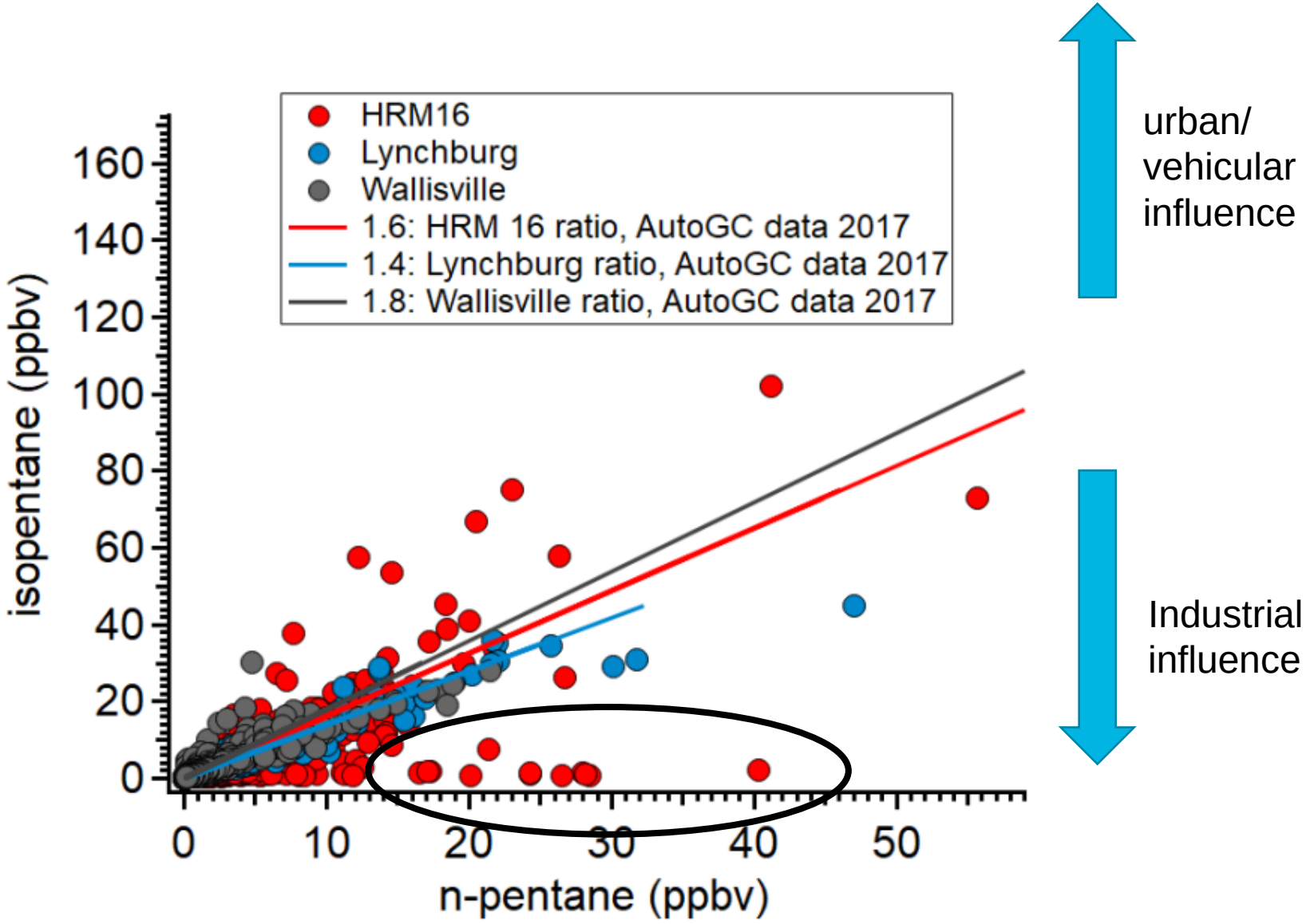
Source Signature of Volatile Organic Compounds from Oil and Natural Gas Operations in Northeastern Colorado

J. B. Gilman,* B. M. Lerner, W. C. Kuster, and J. A. de Gouw

iso/normal pentane ratios in Houston



iso/normal pentane ratios in Houston



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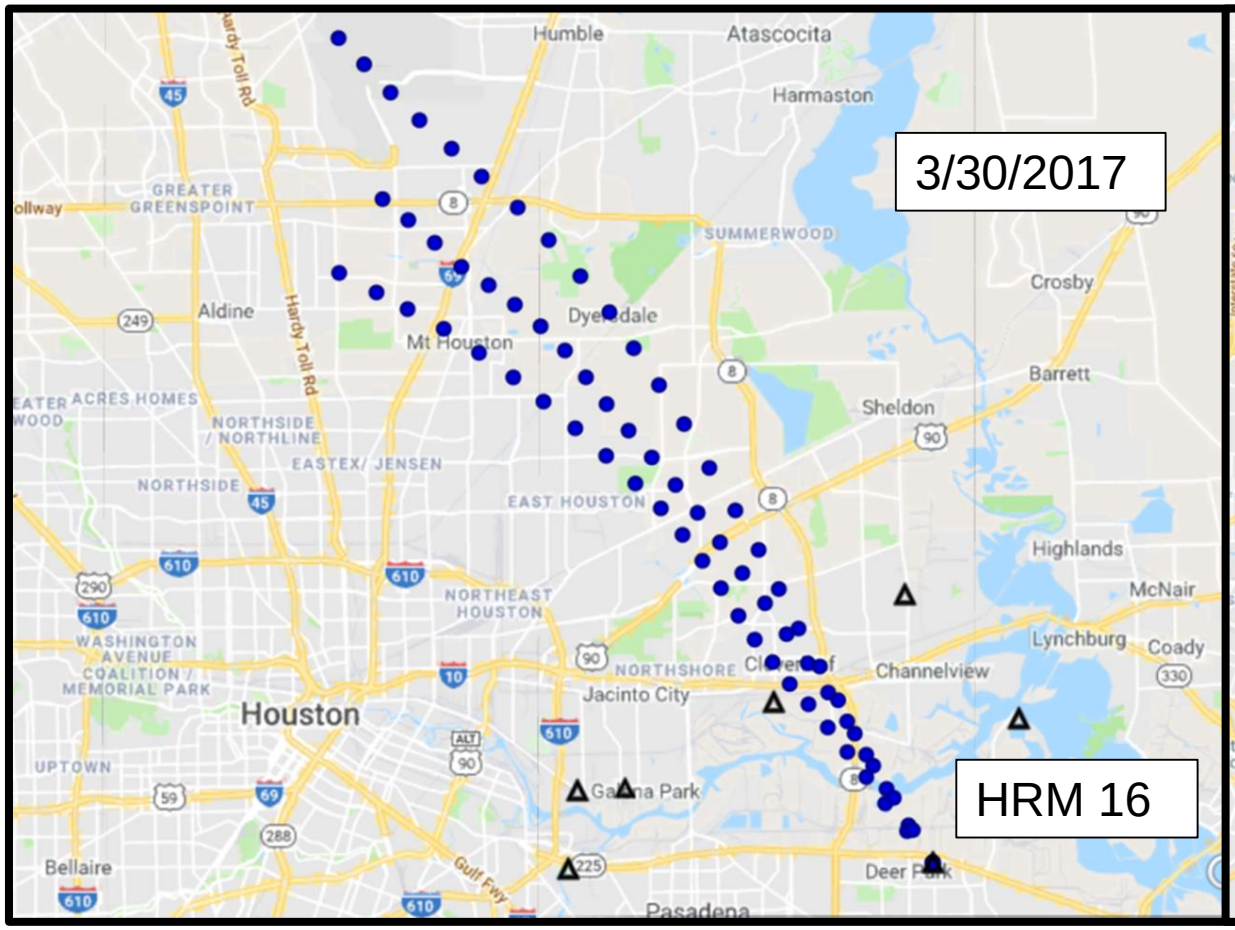
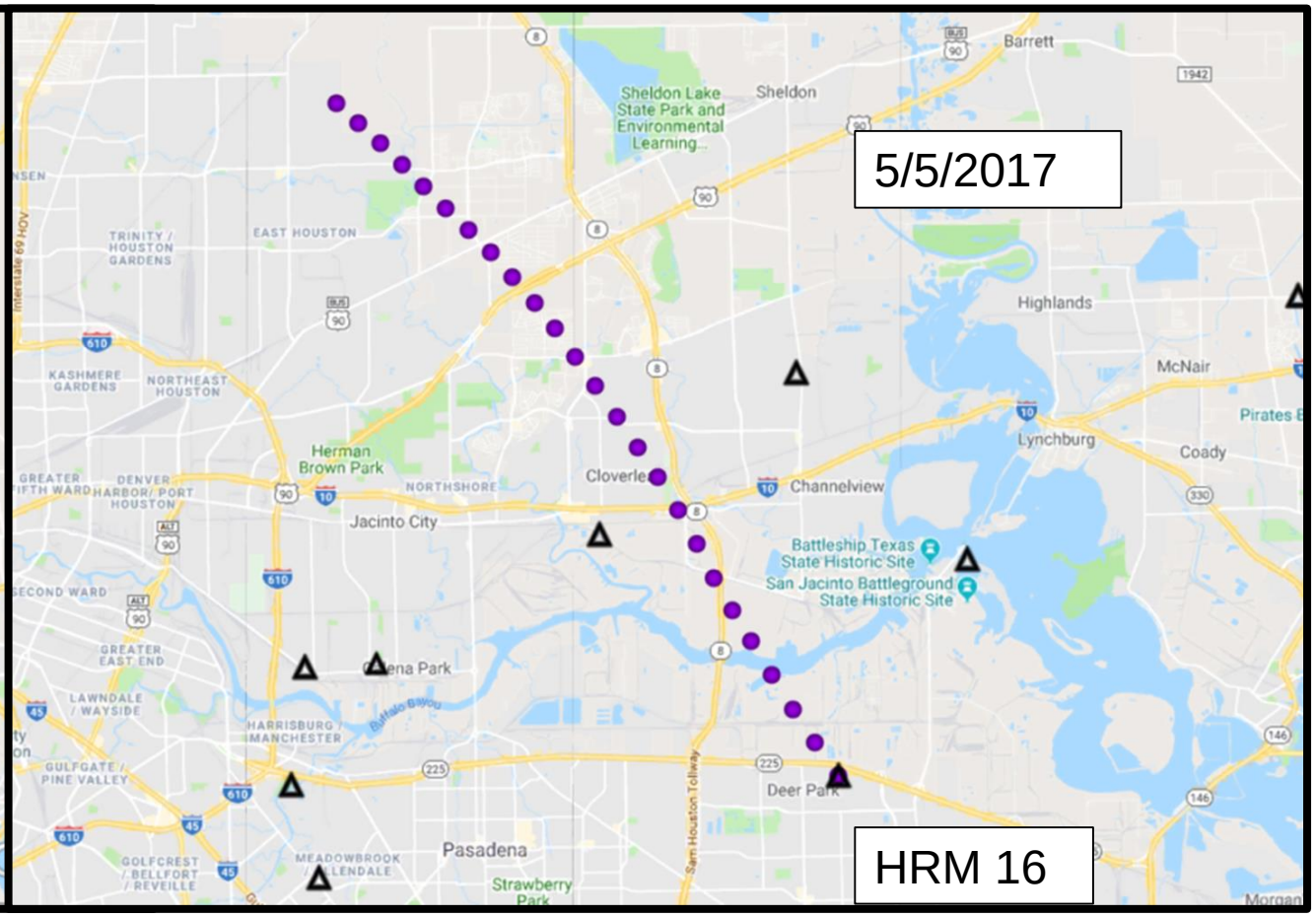
Back Trajectories for low iso-/n-pentane ratio events in 2017





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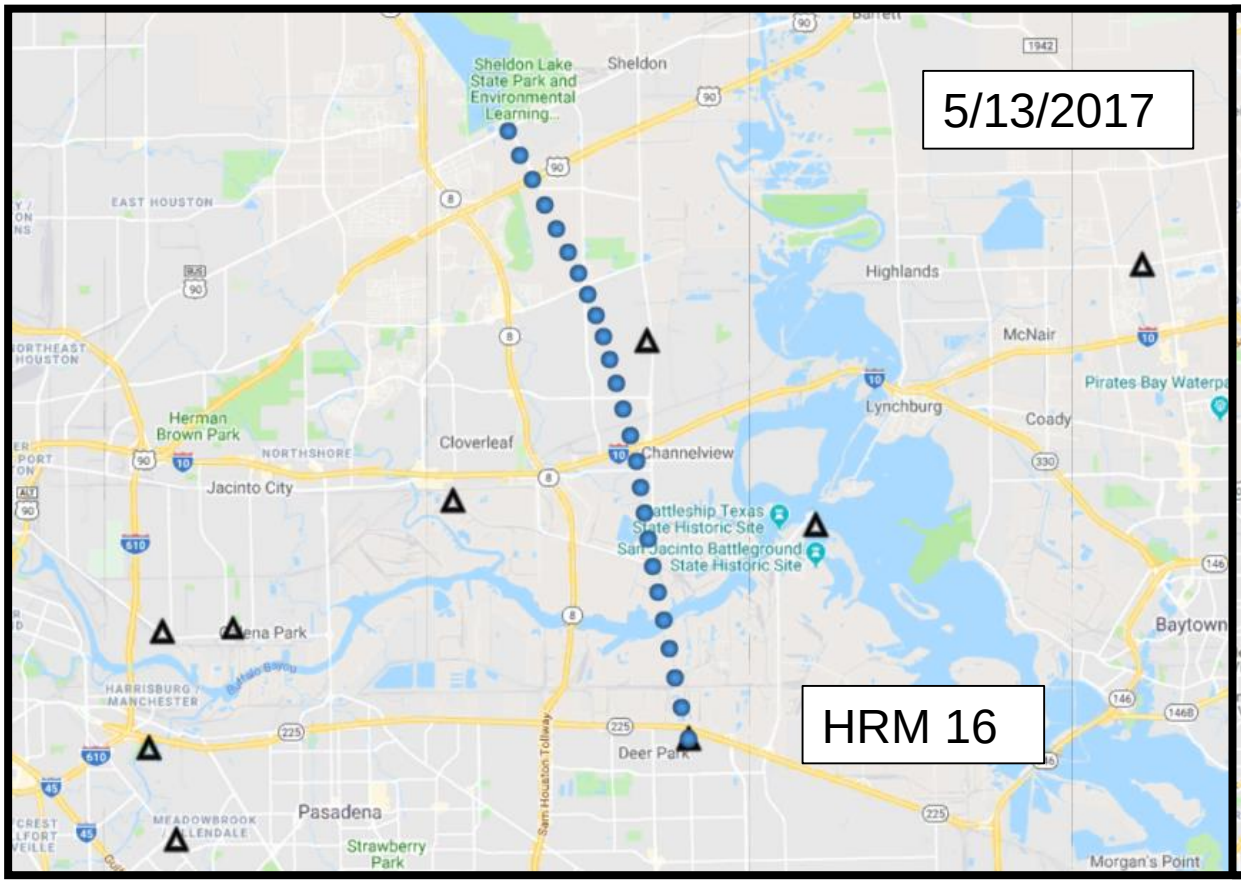
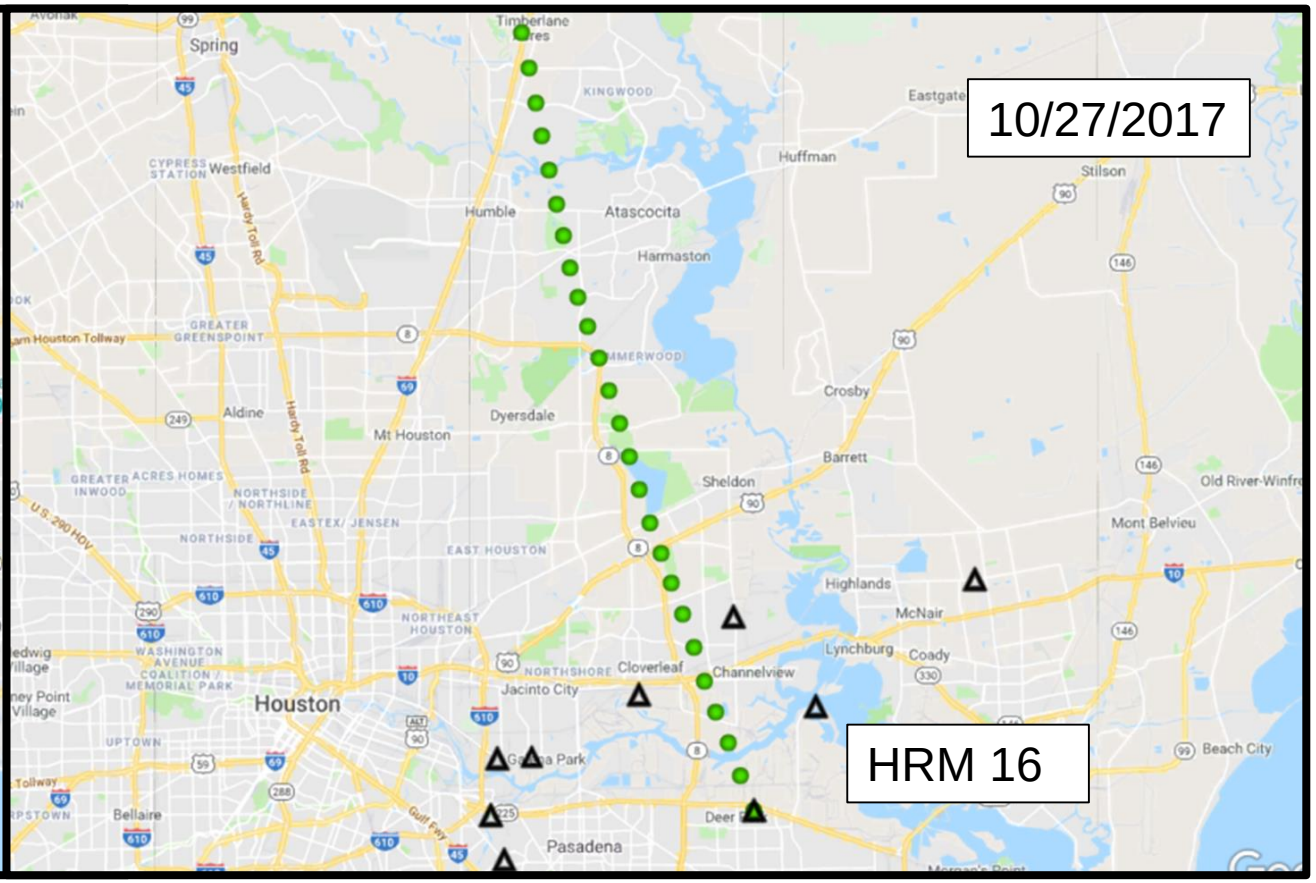


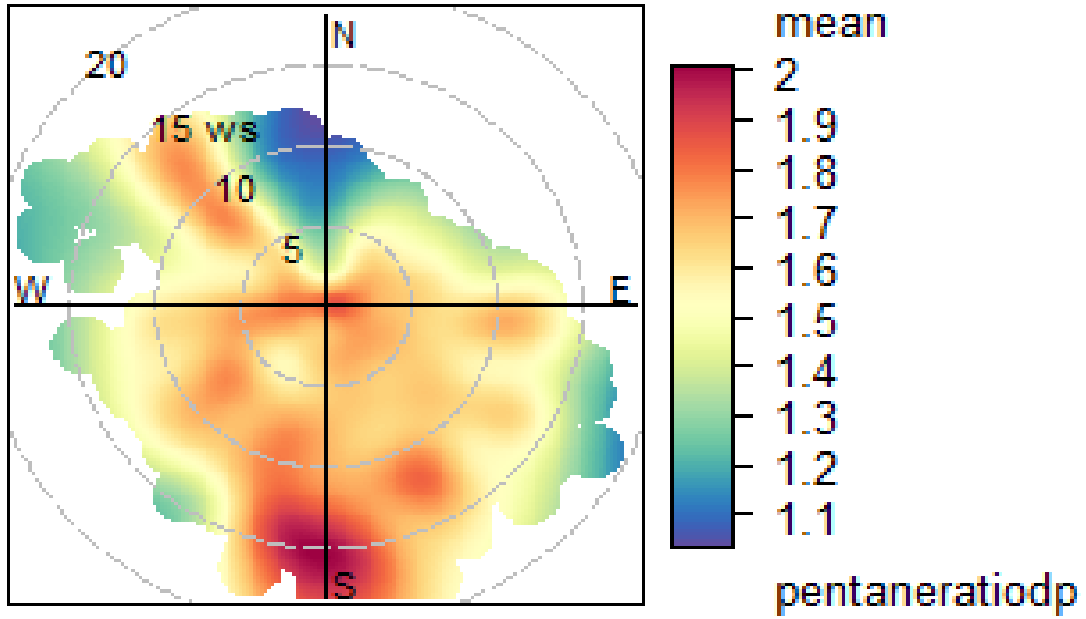


VOC Source Signatures Summary

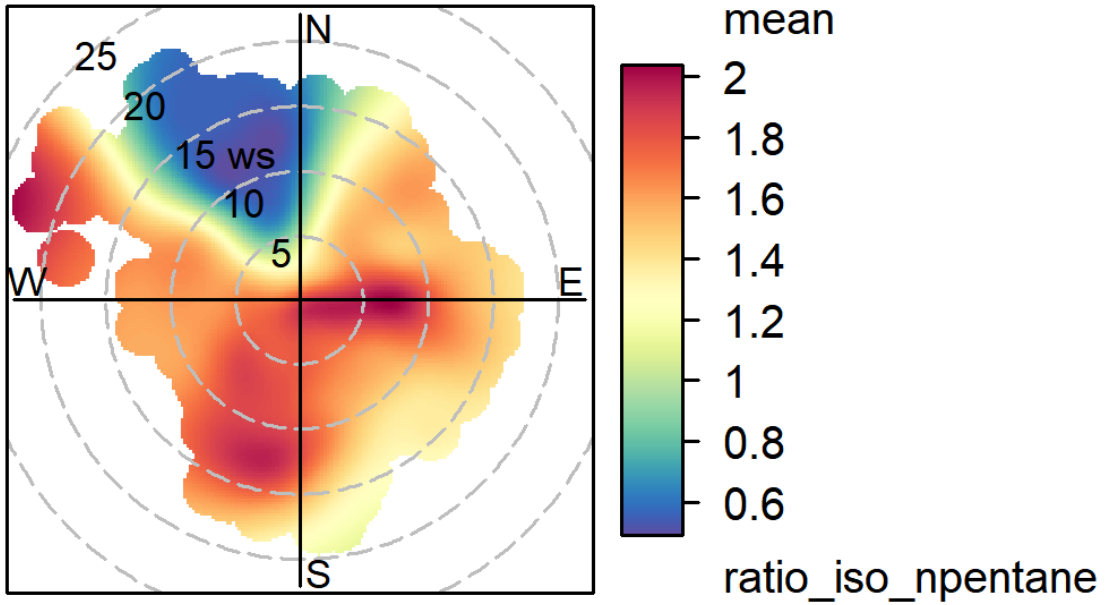
– Iso / n-pentane ratio an effective marker for industrial emission at HRM-16 in 2017

– Ratios of species with similar reactivities can be used to identify potential sources of VOC

Deer Park



HRM 16



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