Eagle Ford shale air quality

Gunnar W. Schade and Geoffrey Roest
San Antonio, 18 November 2014
Hydrocarbon air pollution

• some basics
  – “fugitives”
  – flaring
• Eagle Ford long term changes
• Floresville monitor data
  – overview, comparative HC reactivity
    • emissions estimate using ethane
    • source factors
  – case study
• Some Conclusions
1. Fugitives

Unburned hydrocarbons

→ major source of pollutant exposure (e.g. workers)

• alkanes
• BTEX (benzene, toluene, ethylbenzene, xylenes)
A “leaky” industry

• heavy hydrocarbon pollution in Utah
  – record winter ozone values
  – special issue of ACP: http://www.atmos-chem-phys-discuss.net/special_issue217.html

• heavy hydrocarbon pollution in Colorado
  – large emissions, controlling atmospheric reactivity (Petrón et al., 2012, 2014; Gilman et al., 2013)
  – ppm levels near oil and gas sources (Warneke et al., 2014); O(100) background enhancements in rural communities (Thompson et al., 2014)
2. Flaring

Uncontrolled flaring leads to incomplete combustion
→ major source of reactive hydrocarbons and soot
• ethylene, formaldehyde
• soot, PAHs
Eagle Ford shale area with landmarks
Production, Ozone, Emissions

(a) Oil production
+ Gas production
× Max 4th highest 8-hr Ozone

(b) Coastal 1
+ Coastal 2
+ San Antonio
+ Floresville *

kBOE per day vs. Ozone (ppb)

Ethane conc. (ppb)

2007 2008 2009 2010 2011 2012 2013

Schade and Roest, submitted to EOS
Median = 9.6 ppb
2-5 times background
Boundary layer height effects

SE trajectory days - ethane concentration vs. time

Day Avg

Night Avg

Time (LST)
Basis for estimating total emissions

Ethane enhancement over background concentration

Enhancement = 8.1 ppb

Corpus Christi

Floresville

Ethane concentration (ppb)
## Fingerprinting: factor analysis

<table>
<thead>
<tr>
<th>Component</th>
<th>Factor1</th>
<th>Factor2</th>
<th>Factor3</th>
<th>Component</th>
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<th>Factor2</th>
<th>Factor3</th>
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<td>2,2-Dimethylbutane</td>
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<td>Ethylene</td>
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<td>Cyclohexane</td>
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<td>0.29</td>
<td>-0.21</td>
<td>3-Methylhexane</td>
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<td></td>
<td>Methylcyclohexane</td>
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<td>0.28</td>
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<td>-0.19</td>
<td>Methylcyclopentane</td>
<td>0.90</td>
<td>0.35</td>
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<td>t-2-Butene</td>
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<td>0.51</td>
<td></td>
<td>2-Methylhexane</td>
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<td>c-2-Butene</td>
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<td>0.50</td>
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<td>Benzene</td>
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<td>n-Heptane</td>
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<td>0.21</td>
<td>Ethyl-Benzene</td>
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<td>0.80</td>
<td>0.28</td>
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<td>1,3,5-Trimethylbenzene</td>
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<td>1,2,4-Trimethylbenzene</td>
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<tr>
<td>Cyclopentane</td>
<td>0.91</td>
<td>0.32</td>
<td></td>
<td>1,2,3-Trimethylbenzene</td>
<td>0.35</td>
<td>0.58</td>
<td>0.25</td>
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</tbody>
</table>
79% of benzene explained by the 2 factors from the shale area.
Butadiene only related to combustion

highest butadiene levels from urban Floresville
Comparing the factors

long trajectories over shale area

Floresville itself
VOC reactivity, $R$

$\rightarrow$ “fuel” to produce ozone ($P_{O3} \sim R_{VOC} \times [VOC]$)

<table>
<thead>
<tr>
<th></th>
<th>all median</th>
<th>“shale” median</th>
<th>“shale” median summer</th>
<th>“shale” percent</th>
<th>SC median</th>
<th>SC percent</th>
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<tbody>
<tr>
<td>$CH_4$</td>
<td>0.315</td>
<td>0.315</td>
<td>0.315</td>
<td>8.5</td>
<td>0.27</td>
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<td>$CO$</td>
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<td>sumVOCs</td>
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<td>1.94</td>
<td>1.75</td>
<td>55</td>
<td>2.1</td>
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<tr>
<td>$NO_2$</td>
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<td>0.81</td>
<td>0.57</td>
<td>22.5</td>
<td>1.26</td>
<td>25</td>
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<tr>
<td>$R_{tot}$</td>
<td>2.615</td>
<td>3.565</td>
<td>3.135</td>
<td>100</td>
<td>4.25</td>
<td>82</td>
</tr>
</tbody>
</table>

**median data columns in units of s$^{-1}$**

SC = Houston “ship channel” (Gilman et al., JGR, 2009), excludes “oxygenates”

“shale” numbers calculated from one year of Floresville monitor data, 2013/14
VOC reactivity comparison
relative composition

Source: Gilman et al., J. Geophys. Res. VOL. 114, D00F06, doi:10.1029/2008JD011525, 2009 and own data analysis using Floresville monitor data
Median = 9.6 ppb
2-5 times background

Floresville - ethane vs time

case study
Pollution plumes, 5/6 March 2014

- not an upset emission
- source identified
  - flaring/venting
  - west of Karnes City
  - 20 miles (!) upwind
- meteorological conditions conducive of pollutant accumulation
  - inversion layer
  - strong onsite smell
  - impact was observed at Calaveras Lake monitor
NOAA HYSPLIT MODEL
Concentration (mass/m3) averaged between 0 m and 100 m
Integrated from 1800 05 Mar to 1830 05 Mar 14 (UTC)
Mass Release started at 1800 05 Mar 14 (UTC)

Source: 28.870 N 97.930 W

SA

>1.0E-08 mass/m3
>1.0E-09 mass/m3
>1.0E-10 mass/m3
>1.0E-11 mass/m3

Maximum: 2.3E-08 mass/m3
Minimum: 5.6E-14 mass/m3

NAM METEOROLOGICAL DATA
Release: lat.: 28.870000  lon.: -97.930000  hgt: 5 to 20 m
Pollutant: Mass - Unspecified
Release Quantity: 1000 mass  Start: 14 03 05 18 0  Duration: 24 hrs, 10 min
Pollutant Averaging/Integration Period: 0 hrs and 30 min
Dry Deposition rate: 0 cm/s  Wet Removal: None  #Part: 70000
Meteorology: 0000Z 5 Mar 2014 - NAM12
This is not a NOAA product. It was produced by: unknown
NOAA HYSPLIT MODEL

Concentration (mg/m³) averaged between 0 m and 200 m
Integrated from 2000 06 Mar to 2100 06 Mar 14 (UTC)
Mass Release started at 2000 06 Mar 14 (UTC)

SA

NAM METEOROLOGICAL DATA

Job ID: 2754     Job Start: Tue Oct 21 23:14:04 UTC 2014
Release: lat.: 28.870000    lon.: -97.930000    Hgt: 0 to 50 m
Pollutant: Mass - Unspecified
Release Quantity: 1000 kg    Start: 14 03 06 20 0    Duration: 24 hrs, 0 min
Pollutant Averaging/Integration Period: 1 hrs and 0 min
Dry Deposition Rate: 0 cm/s    Wet Removal: None    #Part: 70000
Meteorology: 0000Z 6 Mar 2014 - NAM12
This is not a NOAA product. It was produced by: unknown
Some Conclusions

• very large hydrocarbon pollution
  – $O(10^{-100})$ above background, downwind
  – not upset emissions, but “business as usual”
  – similar reactivity than most polluted Houston
    • effects on regional ozone are unequivocal

• regular pollution “plumes”
  – emissions are widespread
  – inversions are common
  – health/nuisance effects are documented
Reactivity comparison detail

- Houston data includes formaldehyde, acetaldehyde, ethanol, methanol, etc.
  - adds another $\sim 1 \text{ s}^{-1}$ to the distribution
- formaldehyde and acetaldehyde could be quite abundant in the shale area due to the flares
- distribution moves to higher reactivity for SE winds
SE vs. NE winds

Floresville data

reactivity (s^-1), w/o 'oxygenates'

frequency

0.0 0.2 0.4 0.6 0.8 1.0

0.01 0.1 1 10 100

reactivity (s^-1), w/o 'oxygenates'