Volatile Organic Compounds (VOCs) Measured Aboard the *Ronald H. Brown*

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**(GC)-PIT-MS:** D. Welsh-Bon, C. Warneke, and J.A. de Gouw

**QCL-TILDAS:** S.C. Herndon and M.S. Zahnisner *(Aerodyne)*

Other Data: H. Osthoff, B.M. Lerner, and E.J. Williams

1. Overview of instruments and VOCs reported
2. •OH loss chemistry and total air mass •OH reactivity
3. VOC contribution to •OH loss during TexAQS 2006
1. VOC Instruments on RHB

**GC-FID; GC-MS**
- 5 min sample acquisition
- 30 minute sample cycle
- Full speciation of VOCs
- Lowest detection limit (~1 ppt)
- 80 compounds reported

**QCL-TILDAS**
- Spectroscopic technique
- Continuous sampling
- <1 second duty cycle
- Formaldehyde (HCHO)
  - LOD ~75 ppt
- 4 compounds reported

**(GC)-PIT-MS**
- Continuous sampling
- 10 second duty cycle
- VOCs are not fully resolved
- Detection limits (~1 ppb)
- 15 masses reported
1. Overview of VOCs Reported

**Alkanes:**
C$_2$-C$_{10}$ linear, branched, and cyclic

**Alkenes:**
Ethene, Propene, C$_4$-C$_6$ linear & branched
*-- Used in plastics production*

**Terpenes and Ox. Prod:**
Isoprene -- *Used in rubber production*
a-Pinene, β-Pinene, Limonene
Methacrolein
Methylvinylketone

**Oxy:** Aldehydes, Alcohols, Ketones, etc.

**Aromatics:** C$_6$-C$_9$

**Other Alkenes/Monomers:**
1,3-Butadiene, 1-Octene
Styrene, Acrylonitrile,
Vinyl Acetate, Methyl Acrylate
Methyl Methacrylate

**Oxidation Products of Isoprene**

*Mixing ratios and OH loss rates for all compounds from 2000 and 2006 appear on Gilman et al. poster*
1. Overview of GC-FID/MS Data

- 200+ compounds monitored
- Few unknown compounds
- 80 compounds reported

>85-95% of VOC reactivity by C₂-C₁₀ hydrocarbons measured by GC-FID/MS
R/V Brown Cruise Track for TexAQS 2006
2. •OH Loss Chemistry

•OH + VOCs, CO, CH₄ → O₃

•OH Loss chemistry can lead to ozone formation
  – OH reaction with VOCs, CO, CH₄ initiates radical chain reaction
  – Net result is formation of ozone and regeneration of •OH
  – OH + VOC reaction products (i.e. HCHO) are also reactive with •OH
  – Cycle is terminated when •OH + NO₂ → HNO₃

Calculation of •OH Loss Rate

\[ \tau_{OH}^{-1} (s^{-1}) = k_{OH,VOC} \times [VOC] \]

“OH loss frequency”
2. Total Air Mass • OH Reactivity

Eastern Coast and Gulf Crossing

Total OH Loss Rate (s^{-1})

- CH₄ (Global Mean)
- CO
- VOCs
- NO₂

Ship plumes

Time (UTC)

7/29/06 7/30/06 7/31/06 8/1/06
2. Total Air Mass • OH Reactivity

Galveston Bay and Houston

- CH₄ (Global Mean)
- CO
- VOCs
- NO₂

Time (UTC)

00:00 00:00 00:00 00:00 00:00 00:00 00:00 00:00
8/11/06 8/12/06 8/13/06 8/14/06 8/15/06 8/16/06 8/17/06 8/18/06

Total OH Loss Rate (s⁻¹)

0 20 40 60 80 100

Barbour’s Cut

HSC

Gulf
2. Mean Air Mass •OH Reactivity

East Coast & Gulf Crossing

- NO₂: 9%
- CO: 26%
- CH₄: 39%
- VOCs: 26%

All Galv. Bay and Houston

- NO₂: 19%
- CO: 6%
- CH₄: 2%
- VOCs: 73%
2. Mean Air Mass •OH Reactivity

### Total Air Mass •OH Reactivity:

- **Mean:** 1.0 s\(^{-1}\)
- **Median:** 1.0 s\(^{-1}\)
- **Maximum:** 2.4 s\(^{-1}\)
- **Minimum:** 0.7 s\(^{-1}\)

*Number of Points: 130*

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**East Coast & Gulf Crossing**

- **NO\(_2\):** 9%
- **VOCs:** 26%
- **CO:** 39%
- **CH\(_4\):** 26%

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**All Galv. Bay and Houston**

- **VOCs:** 73%
- **NO\(_2\):** 19%
- **CO:** 6%
- **CH\(_4\):** 2%

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### Total Air Mass •OH Reactivity:

- **Mean:** 12.3 s\(^{-1}\)
- **Median:** 6.3 s\(^{-1}\)
- **Maximum:** 207 s\(^{-1}\)
- **Minimum:** 0.8 s\(^{-1}\)

*Number of Points: 435*
3. VOC Reactivity by Location

**Total VOC •OH Loss Rate (s⁻¹)**

Size and color of marker is proportional to Log (OH loss rate with all VOCs)
3. VOC Reactivity by Location

**Yellow**: $> 12 \text{ s}^{-1}$

**Marine**: $0.29 \text{ s}^{-1}$

**Beaumont**: $3.65 \text{ s}^{-1}$

**Barbour’s**: $7.0 \text{ s}^{-1}$

### Mean $\cdot$OH loss by VOC Groups:
- Alkanes
- Alkenes
- Terpenes & Prod.
- Other Alkenes/Monomers
- Aromatics
- Oxygenates
- Other (N, S, Cl, F)

### Mean $\cdot$OH loss by VOC Groups:

- **Jacinto P.** $49.6 \text{ s}^{-1}$
  - 9/6 21:00 to 9/7 14:00 UTC
- **Beaumont** $3.65 \text{ s}^{-1}$
  - 8/9 21:00 to 8/10 04:30 UTC
- **Barbour’s** $7.0 \text{ s}^{-1}$
  - 8/13 01:00 to 8/15 06:00 UTC
- **Marine** $0.29 \text{ s}^{-1}$
  - 7/27 17:00 to 8/1 20:00 UTC
3. VOC Reactivity by Location

**Mean •OH loss by VOC Groups:**
- Alkanes
- Alkenes
- Terpenes & Prod.
- Other Alkenes/Monomers
- Aromatics
- Oxygenates
- Other (N, S, Cl, F)

**1st O₃ Event: 4.2 s⁻¹**
8/17 17:00 to 8/18 00:30 UTC
- 8 hr Day Avg.
- 90 ppb Ozone

**Beaumont: 3.65 s⁻¹**
8/9 21:00 to 8/10 04:30 UTC
- Fresh Mix of Biogenics

**Jacinto P.: 49.6 s⁻¹**
9/6 21:00 to 9/7 14:00 UTC

**Barbour’s: 7.0 s⁻¹**
8/13 01:00 to 8/15 06:00 UTC
- VA, ACN
- 1-Octene
- C2-C4

**Marine: 0.29 s⁻¹**
7/27 17:00 to 8/1 20:00 UTC
- HCHO
- CH₃CHO
- Mix
3. VOC Reactivity -- Diurnal

Diurnal Mean VOC •OH Loss for G.B. and Houston

**VOC Groups:**
- Alkanes
- Alkenes
- Terpenes, MVK, MCR
- *Other Alkenes/Monomers*
- Aromatics
- Oxygenates
- Other (N, S, Cl, F)

**Other Data:**
- Ozone
- Solar Radiation

Local Time (CDT) → 7 p.m.  1 a.m.  7 a.m.  1 p.m.  6:59 p.m.
3. VOC Reactivity -- Diurnal

- OH Loss Rate for VOCs ($s^{-1}$)

- SE Coast and Gulf Crossing
- Galveston Bay and Houston

Cumulative Probability (100%)

- Daytime (12:00 - 00:30 UTC)
- Nighttime (01:00 - 11:30 UTC)
Benzene Sources
PITPIT--MS MS
1 min avg.1 min avg.
PIT-PIT-MS of [Benzene] in HSC transects
PIT-MS of [Benzene] in HSC transects
See Welsh-Bon et al. poster for more details on PIT-MS
1. VOCs reported represent a vast majority of all VOC •OH reactivity for the >200 compounds observed by GC-FID/MS
   • Full Speciation with GC-FID/MS and GC-PIT-MS
   • Fast Response with PIT-MS and QCL-TILDAS
2. VOCs dominated •OH chemistry in all inland locations
3. The magnitude and variability of the VOC •OH Loss rate was dependent upon:
   • Location (emission sources)
   • VOC composition (primary/fresh vs. secondary/processed)
   • Time of day (meteorology and emission sources/rates)

High levels of HRVOCs during **day or night** could contribute to ozone exceedances