

VOCs Measured Aboard the R/V Brown During TexAQS II and Their •OH Reactivity

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Introduction

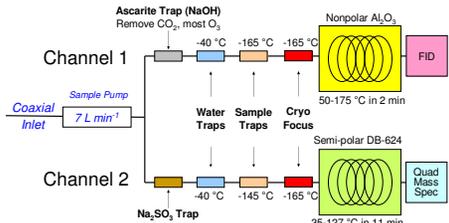
Volatile Organic Compounds (VOCs) and NO_x (= NO + NO₂) are vital components in the photochemical production of ozone (O₃). The first step in initiating the radical cycle responsible for O₃ production is the reaction between •OH (produced in situ during the daytime) and VOCs.

Along the Gulf coast of Texas there exists an immense variety of natural, urban, and industrial sources of VOCs. A wide spectrum of VOCs were measured aboard the NOAA R/V Ronald H. Brown during TexAQS/GoMACCS 2006 in an effort to fully characterize their sources and determine the key species responsible for the photochemical ozone production in the Houston/ Galveston area.



Instrumentation

Measurements were made with a custom dual channel gas chromatograph (GC) incorporating both a Flame Ionization Detector (FID) associated with an 18m Aluminum oxide column (Al₂O₃) for the light hydrocarbons and a quadrupole mass spectrometer (MS) associated with a 20m DB-624 column for the heavier VOCs.



Separate, parallel samples were cryogenically collected for 5 min at the start of every 1/2-hour at flow rates of 70 sccm (350cc sample size @STP). Buildup of CO₂-ice was prevented by using an Ascarite trap in CH1 and by using a slightly higher trapping temperature in CH2. Ozone was removed from CH1 with a Na₂SO₃ scrubber. Water was removed from both channels cryogenically.

The sensitivities of both the FID and MS detectors are somewhat species dependent and calibrations were performed for each measured species. FID detection limits for all species were ~5-10 pptv. By operating the mass spectrometer in selected ion mode detection limits of ~1-10 pptv were achieved.

The accuracy for all compounds is ± 20%.

Results

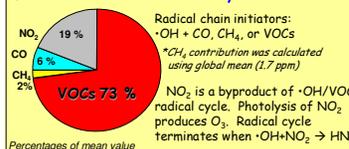
VOC OH Loss Rate: $\tau_{OH}^{-1} (s^{-1}) = k_{OH,VOC} \times [VOC]$

| | La Porte, Tx Aug 2000 | | Galveston Bay and Houston, 2006 Includes HSC and Barbour's Cut | | at 298 K and 1013 mbar KOH Median Max s ⁻¹ × 10 ¹⁴ | |
|---|--------------------------|--------|---|--------|---|--------------|
| | Median | Max | Median | Max | Median | Max |
| Alkanes | | | | | 0.52 | 128.8 |
| Ethane | 5.90 | 85.20 | 4.734 | 197.01 | 0.30 | 0.035 |
| Propane | 3.15 | 79.80 | 3.046 | 347.49 | 1.10 | 0.082 |
| n-Butane | 1.11 | 18.40 | 1.062 | 487.63 | 2.40 | 0.063 |
| i-Butane | 1.21 | 71.60 | 0.960 | 182.07 | 2.20 | 0.052 |
| n-Pentane | 0.37 | 17.10 | 0.389 | 183.10 | 4.00 | 0.038 |
| i-Pentane | 0.91 | 30.70 | 0.771 | 183.10 | 3.70 | 0.070 |
| n-Hexane | 0.29 | 7.46 | 0.208 | 80.85 | 5.50 | 0.028 |
| 2,2-Dimethylbutane | --- | --- | 0.032 | 4.84 | 2.30 | 0.002 |
| 3-Methylpentane | 0.16 | 3.29 | 0.132 | 33.21 | 5.40 | 0.018 |
| Sum 2,3-Dimethylbutane and 2-methylpentane | 0.26 | 3.85 | 0.215 | 60.53 | 5.60 | 0.030 |
| Cyclohexane | 0.09 | 2.51 | 0.071 | 22.56 | 7.20 | 0.012 |
| Methylcyclopentane | --- | --- | 0.101 | 31.37 | 5.70 | 0.014 |
| Methylcyclohexane | --- | --- | 0.050 | 23.62 | 10.00 | 0.012 |
| n-Heptane | 0.08 | 0.86 | 0.055 | 29.30 | 7.00 | 0.009 |
| n-Octane | 0.04 | 0.51 | 0.016 | 9.36 | 8.70 | 0.002 |
| n-Decane | 0.03 | 0.74 | 0.011 | 3.43 | 11.20 | 0.003 |
| Alkenes | | | | | 0.88 | 161.6 |
| Ethene | 1.83 | 566.00 | 0.897 | 54.54 | 9.00 | 0.199 |
| Propene | 0.45 | 111.00 | 0.257 | 55.58 | 26.00 | 0.164 |
| 2-Methylpropene | 0.06 | 3.01 | 0.064 | 11.37 | 51.00 | 0.080 |
| 1-Butene | 0.06 | 41.70 | 0.033 | 23.54 | 31.00 | 0.025 |
| cis-2-butene | 0.01 | 1.18 | 0.006 | 10.75 | 56.00 | 0.008 |
| trans-2-butene | 0.01 | 0.89 | 0.006 | 14.58 | 64.00 | 0.009 |
| 2-methyl-1-butene | 0.02 | 1.52 | 0.056 | 5.79 | 61.00 | 0.084 |
| 3-methyl-1-butene | --- | --- | 0.003 | 0.31 | 32.00 | 0.002 |
| 2-methyl-2-butene | --- | --- | 0.014 | 11.35 | 87.00 | 0.030 |
| 1-Pentene | 0.02 | 2.09 | 0.014 | 2.84 | 31.00 | 0.011 |
| cis-2-pentene | 0.01 | 1.43 | 0.007 | 4.24 | 65.00 | 0.011 |
| trans-2-pentene | 0.01 | 2.36 | 0.013 | 8.36 | 67.00 | 0.021 |
| cis-2-hexene | --- | --- | 0.003 | 4.33 | 62.00 | 0.005 |
| trans-2-hexene | --- | --- | 0.001 | 2.53 | 62.00 | 0.002 |
| cis-3-hexene | --- | --- | 0.002 | 1.78 | 62.00 | 0.003 |
| Ethene (Acetylene) | 0.41 | 13.20 | 0.323 | 5.79 | 0.90 | 0.007 |
| Terpenes and Oxidation Products | | | | | 0.30 | 4.4 |
| Isoprene | 0.18 | 33.90 | 0.055 | 1.58 | 101.00 | 0.137 |
| alpha-Pinene | 0.10 | 0.25 | 0.014 | 0.25 | 53.70 | 0.018 |
| beta-Pinene | --- | --- | 0.008 | 0.21 | 78.90 | 0.016 |
| Limonene | --- | --- | 0.003 | 0.85 | 171.00 | 0.013 |
| Methacrolein (MACR) | 0.08 | 1.16 | 0.024 | 0.55 | 33.50 | 0.020 |
| Methyl Vinyl Ketone (MVK) | 0.13 | 2.26 | 0.028 | 0.73 | 18.80 | 0.013 |
| Other Alkenes/Monomers | | | | | 0.09 | 92.0 |
| 1-Octene | --- | --- | 0.006 | 5.31 | 38.00 | 0.006 |
| Styrene | 0.01 | 14.70 | 0.004 | 3.27 | 58.00 | 0.006 |
| 1,3-Butadiene | 0.09 | 16.70 | 0.018 | 2.89 | 67.00 | 0.030 |
| Propylene Oxide | --- | --- | 0.026 | 21.59 | 0.50 | 0.000 |
| Methyl Acrylate | --- | --- | 0.001 | 18.16 | 25.10 | 0.001 |
| Methyl Methacrylate | --- | --- | <0.001 | 1.14 | 26.10 | 0.001 |
| Vinyl Acetate | --- | --- | 0.007 | 76.13 | 49.00 | 0.008 |
| Acrylonitrile (2-propenenitrile) | --- | --- | 0.018 | 17.20 | 8.50 | 0.004 |
| Aromatics | | | | | 0.10 | 11.2 |
| Benzene | 0.34 | 32.10 | 0.206 | 56.68 | 1.20 | 0.006 |
| Toluene | 0.40 | 13.30 | 0.170 | 15.86 | 6.00 | 0.025 |
| m,p-Xylenes | 0.16 | 11.20 | 0.055 | 10.99 | 19.00 | 0.026 |
| o-Xylene | 0.06 | 5.82 | 0.024 | 3.87 | 13.70 | 0.008 |
| Ethylbenzene | 0.06 | 2.32 | 0.027 | 3.07 | 7.10 | 0.005 |
| 1,2,3-Trimethylbenzene | 0.09 | 0.35 | 0.003 | 1.23 | 33.00 | 0.002 |
| 1,2,4-Trimethylbenzene | 0.05 | 1.85 | 0.014 | 3.81 | 33.00 | 0.011 |
| 1,3,5-Trimethylbenzene | 0.01 | 0.44 | 0.003 | 1.10 | 58.00 | 0.004 |
| 1-Ethyl-2-methylbenzene | --- | --- | 0.003 | 1.04 | 12.30 | 0.001 |
| 1-Ethyl-3,4-methylbenzene | --- | --- | 0.011 | 5.27 | 15.60 | 0.004 |
| n-Propylbenzene | --- | --- | 0.003 | 0.83 | 6.00 | 0.000 |
| i-Propylbenzene | 0.01 | 0.76 | 0.002 | 1.07 | 6.50 | 0.000 |
| Oxygenates | | | | | 0.84 | 6.4 |
| Formaldehyde | 3.90 | 35.50 | 1.732 | 31.60 | 8.00 | 0.041 |
| Acetaldehyde | 1.94 | 66.30 | 0.629 | 5.10 | 16.00 | 0.248 |
| Propanal | 0.21 | 4.19 | 0.177 | 2.03 | 20.00 | 0.087 |
| Acetone | 3.25 | 68.80 | 2.852 | 43.05 | 0.23 | 0.016 |
| 2-Butanone (MEK) | 0.28 | 7.75 | 0.218 | 22.90 | 1.15 | 0.065 |
| Methanol | 3.90 | 574.00 | 2.780 | 144.23 | 0.93 | 0.064 |
| Ethanol | --- | --- | 0.593 | 26.63 | 3.27 | 0.048 |
| i-Propanol | --- | --- | 0.175 | 7.06 | 4.20 | 0.018 |
| Methyl-tert-butyl-ether (MTBE) | 0.35 | 7.11 | 0.021 | 13.75 | 3.10 | 0.002 |
| Methyl Formate | --- | --- | 0.048 | 0.24 | 0.17 | 0.000 |
| Others: Nitrogen, Sulfur, Chlorine, and Fluorine containing compounds are not shown here | | | | | 0.05 | |

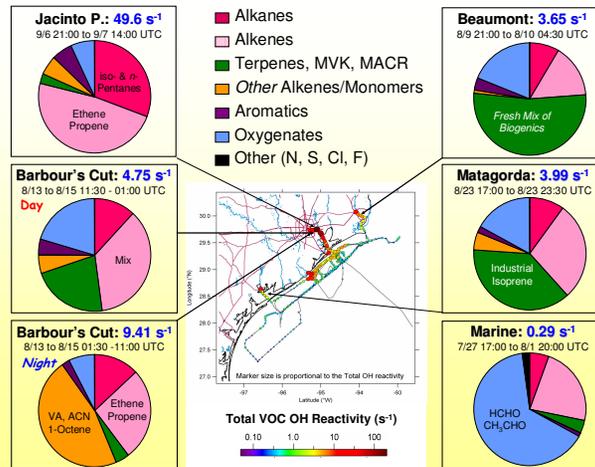
Ref for 2000 data: Jobson, B.T., et al. (2004), *J. Geophys. Res.*, 109, D24305. Karl, T. (2003), *J. Geophys. Res.*, 108(D16), 4508.

Ref for kOH data: Atkinson, R. (1997), *J. Phys. Chem. Ref. Data*, 26, 215-290. Atkinson, R., *Gas-Phase Tropospheric Chemistry of Organic Compounds, 1994*. DeMore, W.B., et al., *Chemical Kinetics and Photochemical Data for use in Stratospheric Modeling, 1997*.

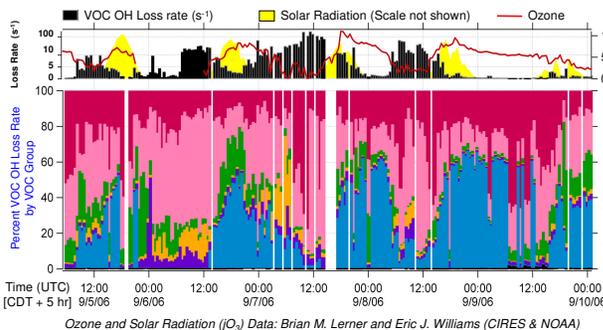
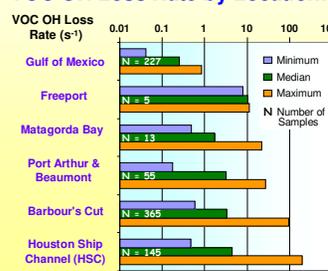
How much do VOCs contribute to possible O₃ formation in the Galveston Bay/Houston Area?



Mean OH Loss Rate by VOC Groups:



VOC OH Loss Rate by Location:



VOC and O₃ Time Series in HSC:

VOC mixing ratios were typically highest during the nighttime hours leading to a corresponding increase in the VOC •OH loss rate. This is related to many factors including meteorology (lower PBLs and wind speeds), emission sources, and VOC chemistry. Nighttime VOC plumes show strong indications of industrial sources (monomers—used in plastics production). There were large quantities of highly reactive VOCs present (alkenes, terpenes, monomers) through early morning which quickly reacted away as ozone production began. Late afternoon air mass were composed mainly of aldehydes (secondary formation).

Summary and Conclusions:

- Ethene, Propene, Isoprene, Formaldehyde, and Acetaldehyde were the largest contributors (based on median values) to possible ozone production in the Galveston Bay/Houston area during TexAQS 2006.
- Large emissions of highly reactive VOCs in the area contribute strongly to the photochemical production of O₃.
- The magnitude and variability of the VOC •OH loss rate (s⁻¹) was dependent upon:
 - Location – Houston Ship Channel and Barbour's Cut were strongly affected by industrial emissions
 - Chemistry – Highly reactive VOCs can accumulate during evening (slower loss rates) and react away during day (shorter chemical lifetimes)
 - Time of day – Meteorology and emission source rates (biogenic, urban, industrial) may vary over 24-hours

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