TEXAS COMMISSION ON ENVIRONMENTAL QUALITY

Emissions Modeling of Specific Highly Reactive Volatile Organic Compounds (HRVOC) in the Houston-Galveston-Brazoria Ozone Nonattainment Area

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Podium Presentation

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Abstract

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The 2006 Texas Air Quality Study (TexAQS II) confirmed many of the results from the 2000 Texas Air Quality Study (TexAQS 2000). Both of these studies rank among the most extensive and comprehensive studies of their kind undertaken to date. Chief among many important findings was the discovery of the role played by certain light olefins in the rapid, intense formation of ozone in the Houston-Galveston-Brazoria (HGB) ozone nonattainment area. Atmospheric concentrations of species such as ethylene and propylene were often found to be many times larger than could be explained by reported emissions inventories. Successfully modeling pollutant concentrations observed during the study necessitated adjustments to these reported emissions. As a consequence of these findings, in 2001, the Texas Natural Resource Conservation Commission (now Texas Commission on Environmental Quality) began developing regulations targeting specific highly-reactive VOCs (HRVOC). Adjusting the modeling inventories to account for unreported HRVOC emissions and later test-driving controls on emissions of these specific compounds presented a set of unique challenges to emissions modelers, since emission processing software typically is not designed to apply adjustments or controls to individual VOC species. This paper describes a set of procedures developed by TCEQ which allowed us to successfully adjust and control (in processing for the photochemical model) emissions of individual hydrocarbon species in the TexAQS 2000 modeling episode. This paper also provides an introduction to ongoing efforts to reconcile more recent inventories with ambient measurements made at twelve automatic gas chromatographs (auto-GCs) currently operating continuously in the HGB nonattainment area.

This Presentation:
A Compilation of 7 Years of Progress

- Background and Motivation
- Reactivity
- Speciation
- Developing and Defining HRVOC "Adjustment"
- Modeling the Adjustment
- HRVOC Controls
- HRVOC Rules
- Rethinking HRVOC Adjustments
- Recent Developments
- Conclusions

Background & Motivation

Background & Motivation

- TexAQS 2000 Field Study (Summer 2000)
  - Corroborating field studies (aircraft, monitoring) indicated that reported VOC EIs may be underestimated by 10-100x.
  - Highly-reactive species were found to be in larger proportion than expected, and found at locations not expected.
  - Ethylene and propylene are generally the most important contributors to total reactivity-weighted concentration in Houston.
  - Some classes of alkanes are often very important contributors as well.

Background & Motivation cont.

- TexAQS II Field Study (2005-06)
  - Used many experienced TexAQS 2000 participants/scientists
  - Leadership provided by NOAA, TCEQ, Universities, TERC, TARC, non-attainment areas, near non-attainment areas, and Industry.
  - Intensive field study campaign
    - August 1 – October 15, 2006
  - 2006 Special Inventory (SI) of HRVOC emissions
    - August 15 – September 15, 2006
    - Requested from 141 accounts (plants) in 24 counties.

Background & Motivation cont.

- TexAQS II Study Findings
  - Historically, reported emissions of VOCs have been insufficient to explain concentrations measured in the HGB area.
  - Specifically, Highly-Reactive VOCs (HRVOC – Ethene, Propene, Butenes, and 1,3-Butadiene) may have been under-reported by as much as an order of magnitude.
  - TexAQS II data suggest that the discrepancy between reported emissions and observed concentrations of ethene is smaller than was the case in 2000. The discrepancy for propene appears to have changed little.


NOAA
R 104
UNITED STATES DEPT. OF COMMERCE
2005
2006
The Texas Air Quality Study II
N48RF

Background & Motivation cont.

- More TexAQS II Study Findings
  - Large emissions of HRVOC found by Solar Occultation Flux (SOF) measurements; the large temporally-variable emissions observed appear to be much larger than the emissions reported in the 2004 EI. [Melqvist]
  - NO_X emissions from power plants have decreased, with WA Parish having the largest observed decrease. CEMS-based NO_X EIs appear to be accurate. [Ryerson]
- All this, despite the fact that TCEQ has some of the most thorough and detailed EI reporting requirements of any state agency
  - Progress is continually made, as we discover and understand the causes (e.g., tank landing losses, oil and gas patches, flash) thanks to new technology and dedicated Emissions Assessment staff.
  - HGB is likely the most complex area in the US, with its large urban area and large concentrations of petrochemical complexes.

Solar Occultation Flux

Second TexAQS II data workshop held May 29-May 31, 2007

- Presentations can be found at TCEQ website: http://www.tceq.state.tx.us/implementation/air/airmod/texaqs-files/TexAQS_II.html#workshops

- Updates on preliminary analyses discussed in the Oct 31 Rapid Science Synthesis document: http://www.tceq.state.tx.us/assets/public/implementation/air/am/workshop/20061012-13/RSST_Preliminary_Findings_Report_20061031.pdf

Reactivity

- Definition: The potential of a given volatile organic compound to make ozone
- **"All VOCs are not created equal"**
  - If all VOCs were equally effective at making ozone, there would be no need to speciate the VOCs. However…

Some VOCs make ozone much more effectively than others.

Reactivity: Maximum Incremental Reactivity (MIR)

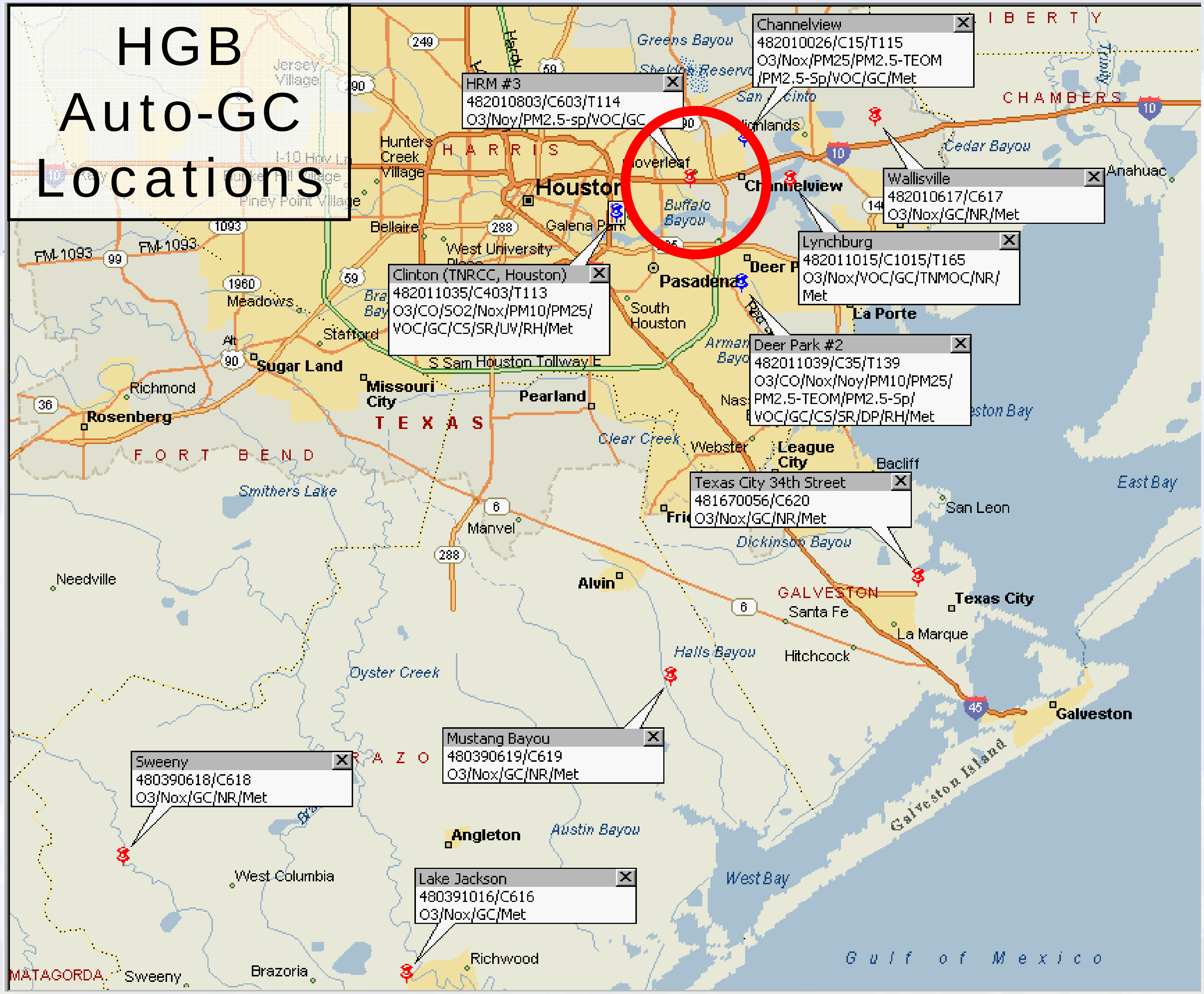
- MIR is the maximum amount of ozone that can be formed by adding an incremental amount of a particular VOC to a mixture of NO_X-rich air
  - Units are grams of ozone per gram of VOC
  - In urban core and Ship Channel, MIR is a suitable metric to use, given the huge amount of NO_X in those areas
  - Calculated from smog chamber experiments and photochemical modeling

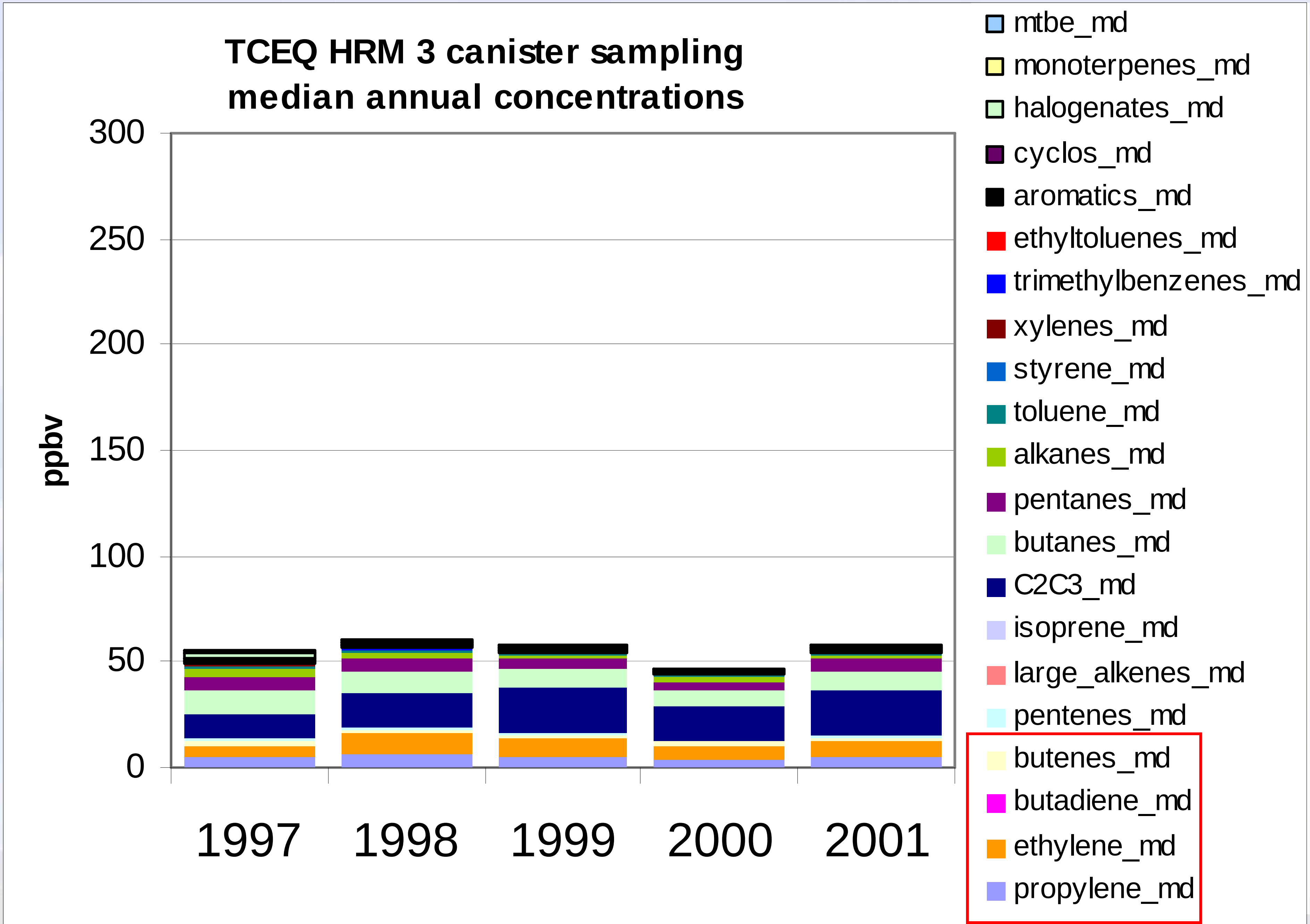
Reactivity - MIR

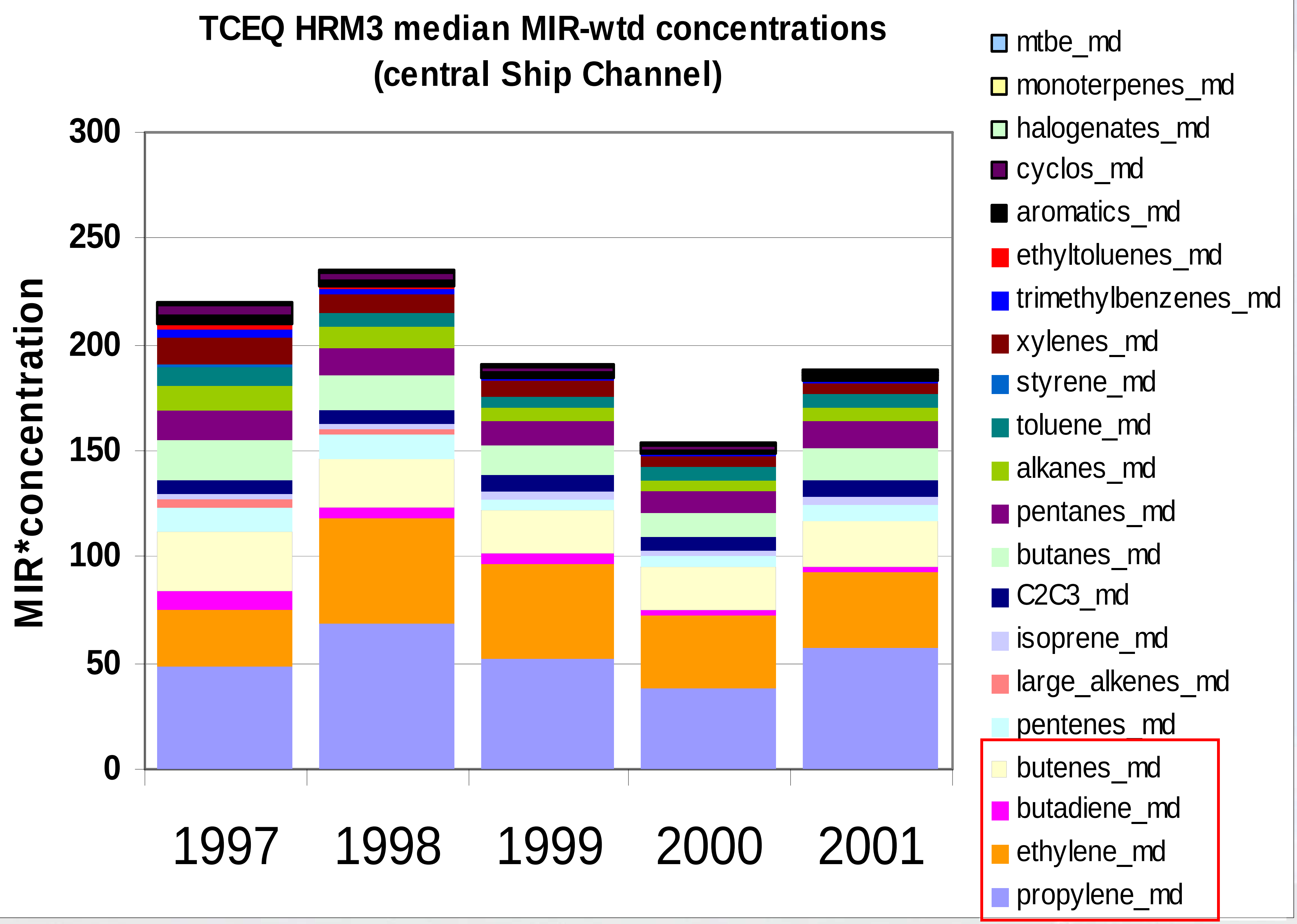
MIR Table excerpt from Carter's reactivity scales, 2002

2-Methyl-2-Butene	14.45
trans-2-Butene	13.91
1,3-Butadiene	13.58
cis-2-Butene	13.23
Propene	11.58
1,2,3-Trimethyl Benzene	11.26
1,3,5-Trimethyl Benzene	11.22
Isoprene	10.69
m-Xylene	10.61
1-Butene	10.29
cis-2-Pentene	10.24
trans-2-Pentene	10.23
Ethene	9.08
1-Pentene	7.79
o-Xylene	7.49
• • •	
Acetylene	1.25
2,3,4-Trimethyl Pentane	1.23
2-Methyl Heptane	1.20
2,3-Dimethyl Butane	1.14
n-Octane	1.11
n-Nonane	0.96
n-Decane	0.83
Benzene	0.82
Propane	0.56
Methane	0.0139

HGB Auto-GC Locations




TCEQ HRM 3 canister sampling
median annual concentrations
ppbv
300
250
200
150
100
50
0
1997
1998
1999
2000
2001
mtbe_md
monoterpenes_md
halogenates_md
cyclos_md
aromatics_md
ethyltoluenes_md
trimethylbenzenes_md
xylenes_md
styrene_md
toluene_md
alkanes_md
pentanes_md
butanes_md
C2C3_md
isoprene_md
large_alkenes_md
pentenes_md
butenes_md
butadiene_md
ethylene_md
propylene_md


TCEQ HRM3 median MIR-wtd concentrations
(central Ship Channel)
MIR*concentration
300
250
200
150
100
50
0
1997
1998
1999
2000
2001
mtbe_md
monoterpenes_md
halogenates_md
cyclos_md
aromatics_md
ethyltoluenes_md
trimethylbenzenes_md
xylenes_md
styrene_md
toluene_md
alkanes_md
pentanes_md
butanes_md
C2C3_md
isoprene_md
large_alkenes_md
pentenes_md
butenes_md
butadiene_md
ethylene_md
propylene_md

Speciation

- Historically: improvements upon EPA-default profiles
  - Texas SCC-average, COAST Special Inventory, 1993
  - Specific contracts to update specific categories
- Dec. 2002 SIP: if a source reported >75% speciated, use that speciation for all of that source's emissions
  - Otherwise, use Texas SCC-average or EPA default speciation
- Dec. 2004 SIP: use compound-specific emissions <u>as reported</u> for all sources
  - For unspeciated portion, apply default profile, after removing non-VOC and common species from the profiles
- Current Work:
  - Where there's hourly speciated data, perform the Dec. 2004 process for every hour
  - Speciation is much improved now (e.g., more than 83% of the reported Harris County VOC is speciated by the companies)

Speciation - TCEQ Procedure

1. Extract STARS (State of Texas Air Reporting System) Report
2. Remove non-VOC compounds
3. Replace mixtures (crude oil, gasoline, naphtha, stoddard solvent, and "refinery") with refined profiles
4. Import EPA Default SCC Profiles
   - After Deletion of non-VOC/non-Reactives
   - And Re-normalization of this dataset
   - Check for profiles composed of only one compound after removal of non-VOC/non-Reactives
     - Replace such profile with a more appropriate profile (SPECIATE, CARB, TCEQ); e.g., EPA 0007 is replaced with CARB 0719

Speciation - TCEQ Procedure

5. Assign profile to each point that had unspeciated VOC
6. Compare reported speciated emissions with profile assigned to each point
   - Retain reported speciated emissions and remove common species from assigned profile for each emission point
   - Normalize resulting profile for each point, thereby creating a unique speciation profile (for each point) to be assigned to each emission point's unspeciated VOC
   - Apply to unspeciated VOC on a point-by-point basis
7. Substitute resulting speciation in place of unspeciated VOC in reported emissions
8. Create a point-specific profile for each path in STARS

Speciation - Sample Process

Sample Point

Account: XY3456Z

FIN: A-1

EPN: B234

SCC: 12345678

Reported Species

Nonmethane VOC-U	80.0 %
Pentane	10.0 %
Propane	4.0 %
N-Butane	2.0 %
Benzene	2.0 %
Ethylbenzene	2.0 %

Intermediate A-1/B234/9876 Profile

Isomers of Hexane	25.0 %
Isomers of Heptane	31.4 %
Isomers of Octane	25.0 %
C7 Cycloparaffins	5.0 %
C8 Cycloparaffins	1.5 %
Isomers of Pentane	11.0 %
Isobutane	1.1 %

SCC Profile Assignment: 9876

Isomers of Hexane	5.0 %
Isomers of Heptane	6.0 %
Isomers of Octane	5.0 %
C7 Cycloparaffins	1.0 %
C8 Cycloparaffins	0.3 %
Isomers of Pentane	2.1 %
Methane	61.3 %
Ethane	8.0 %
Propane	7.0 %
N-Butane	4.0 %
Isobutane	0.2 %
Benzene	0.1 %

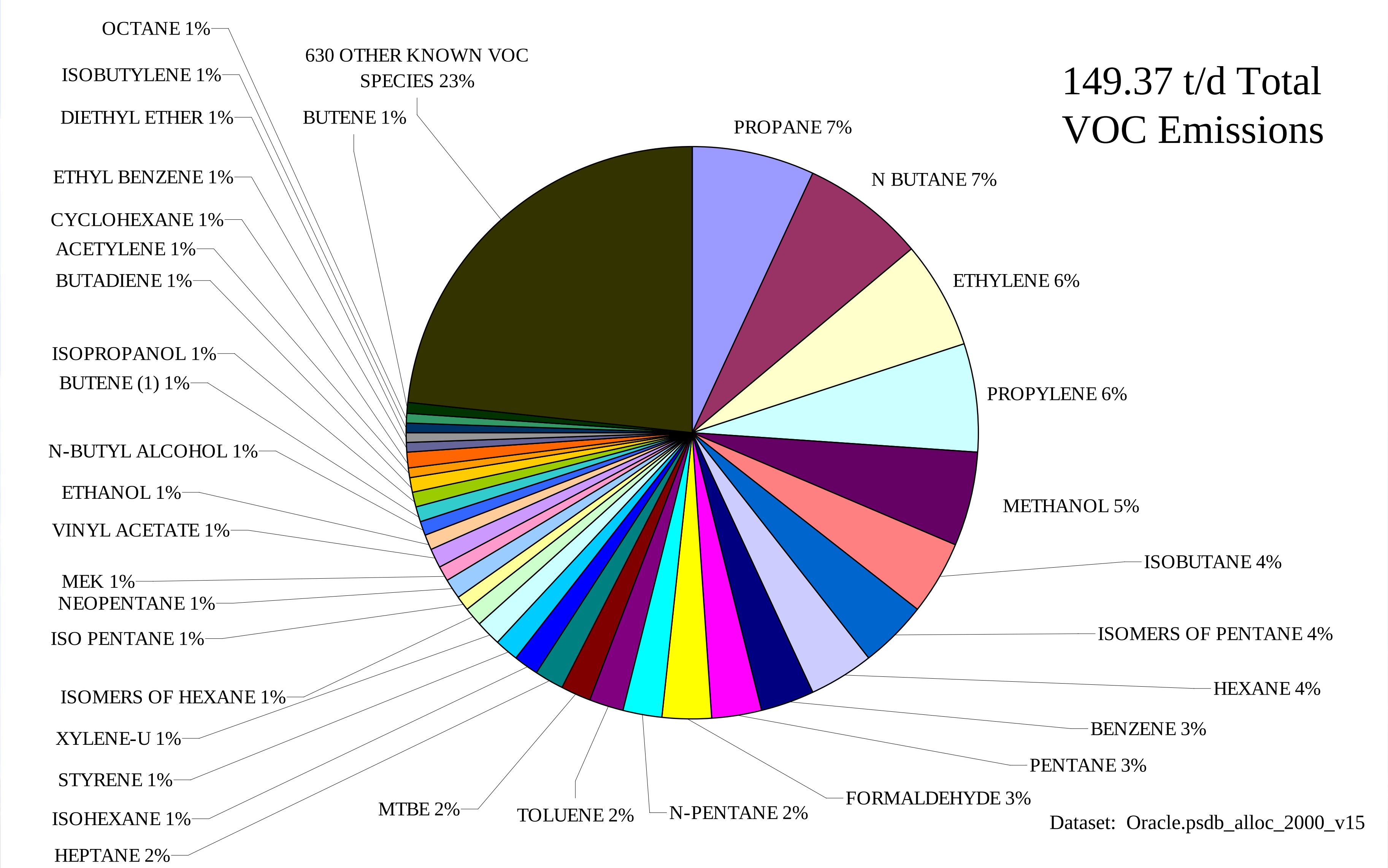
Augmented Profile 9876

Isomers of Hexane	16.0 %
Isomers of Heptane	20.0 %
Isomers of Octane	16.0 %
C7 Cycloparaffins	3.0 %
C8 Cycloparaffins	1.0 %
Isomers of Pentane	7.0 %
Propane	23.0 %
N-Butane	13.0 %
Isobutane	0.7 %
Benzene	0.3 %

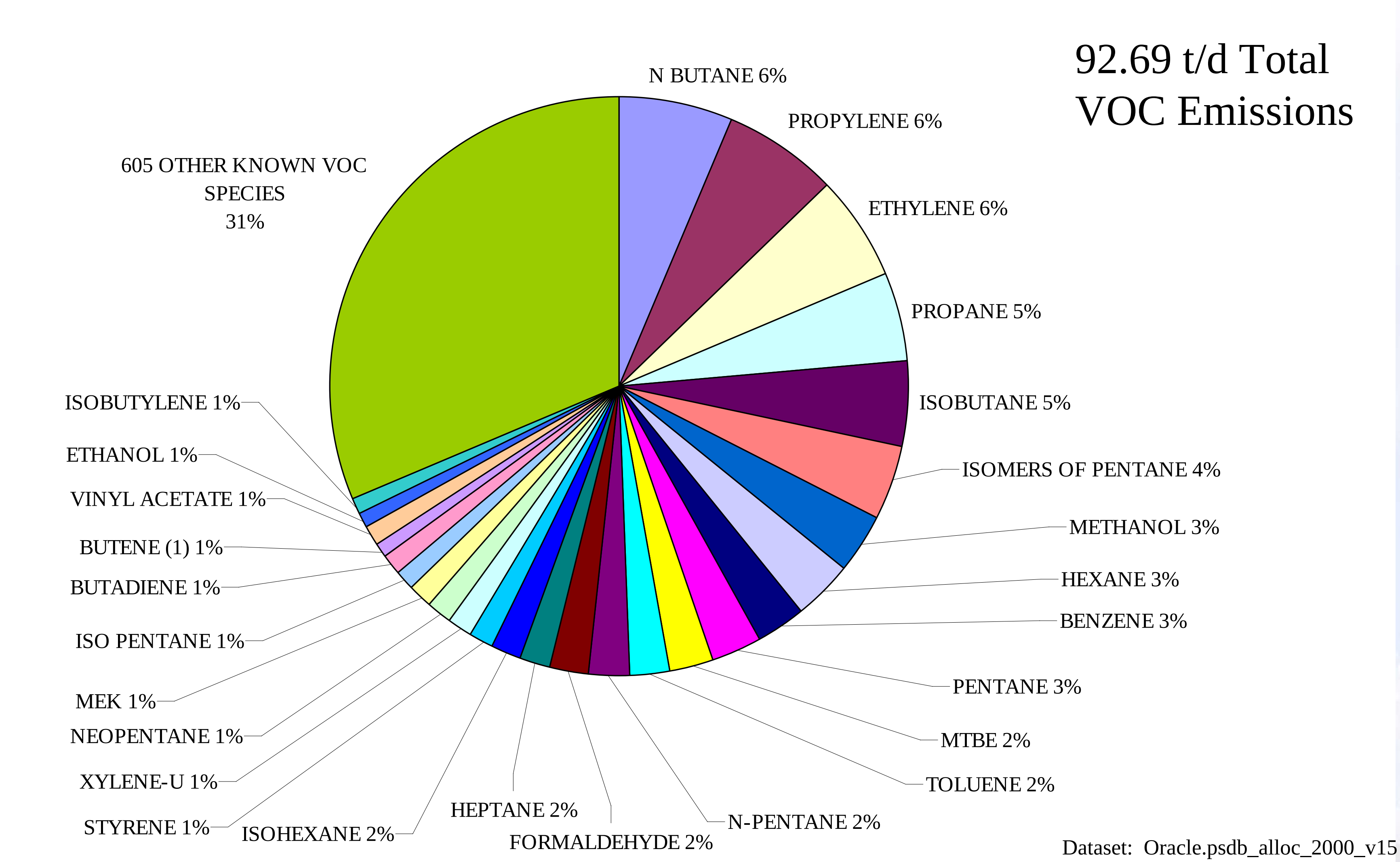
Resulting A-1/B234 Speciation

Isomers of Hexane	20.0 %	Pentane	10.0 %
Isomers of Heptane	25.0 %	Propane	4.0 %
Isomers of Octane	20.0 %	N-Butane	2.0 %
C7 Cycloparaffins	4.0 %	Benzene	2.0 %
C8 Cycloparaffins	1.0 %	Ethylbenzene	2.0 %
Isomers of Pentane	9.0 %		
Isobutane	1.0 %		

2000 HGB 8-County VOC Speciation



2000 Harris County VOC Speciation



Speciation as Modeled

- Air Quality Models (AQMs), such as CAMx, by necessity, use simplified photochemical reaction mechanisms
- The CB-IV and the more recent CB05 chemistry mechanisms, are based upon the molecular structure approach (i.e., carbon bonds)

Sample CB-IV Reported Species vs. Modeled Lumped

SPECIES	PAR	OLE	TOL	XYL	FORM	ALD2	ETH	ISOP	MEOH	ETOH
ETHYLENE	0.00	0.00	0.00	0.00	0.00	0.00	1.00	0.00	0.00	0.00
PROPENE	1.00	1.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
1-BUTENE	2.00	1.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
1,3-BUTADIENE	0.00	2.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
PENTENE	3.00	1.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
HEXENE	3.00	0.33	0.00	0.00	0.00	1.17	0.00	0.00	0.00	0.00
ISOPRENE	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1.00	0.00	0.00

Speciation - CB-IV MIR

CB-IV SPECIES	CB-IV MIR ($g\ O_3$ / g CB-IV ROG)
FORM	17.313
OLE	14.493
ISOP	13.125
ALD2	9.021
XYL	7.149
ETH	7.146
ETOH	1.995
TOL	1.5417
MEOH	1.2303
PAR	1.0374

Speciation - CB05

- CB05 is an update to CB-IV:
  - More reactions: 96 → 156
  - More species: 37 → 51
  - Chlorine, toxics
  - Updated reaction rate constants
  - Updated NO_x recycling
- Now available in CMAQ and CAMx
- TCEQ plans to use CB05 in current and future SIP modeling

HRVOC Adjustment

- TexAQS 2000 researchers agree that the reported EI under-estimates the amount of real-world industrial VOC concentrations compared to ambient measurements
  - Routine and special surface measurements
  - NOAA, DOE, Baylor aircraft flights
  - Olefin instrument measurements on Baylor aircraft data suggested emissions of olefins roughly equal to emissions of NO_X

HRVOC Adjustment

- Dec. 2002 SIP Revision
  - Olefin-to-NO_X ratio = 1, where Olefin = 12 HRVOC families
  - Applied to 27 selected accounts
  - Treated as generic Olefin mixture
  - Improved model performance
  - Time invariant adjustment only
  - Results supported by Environ's Inverse Modeling

HRVOC Adjustment

- Dec 2004 SIP Revision
  - Terminal Olefins (double bond at end of carbon chain)
    - Baylor Aircraft actually measured this
  - All accounts in HGB 8 County area with site-wide Terminal Olefin Emissions > 10 tpy
  - Species modeled individually (instead of generic olefin)
    - Comparable performance to earlier method
    - More flexibility in control strategy modeling
    - Daily and Hourly adjustments for SI sources

Modeling the HRVOC Adjustment

- The HRVOC adjustment was modeled by creating an “extra olefin” (“exole”) file, which was merged with the existing VOC file.
- In the Dec 2004 SIP Revision:
  - Added 155 tpd of HRVOC for daily records
  - Added 163-203 tpd of HRVOC for hourly Special Inventory (SI) records, depending on day

Refining HRVOC Definition

- Original "Big 12" (Dec 2002 SIP, 2000 EI)
  - Propylene, ethylene, formaldehyde, acetaldehyde, isoprene, butenes, 1,3-butadiene, toluene, pentenes, trimethylbenzenes, xylenes, ethyltoluenes
- Terminal olefins (Dec 2004 SIP, 2000 EI re-speciated)
  - Ethylene, propylene, 1-butene, 1,3-butadiene, 1,2-butadiene, pentene, 2-methyl-1-butene, 3-methyl-1-butene, hexene, isoprene, 1-decene, propadiene, 1,3-pentadiene
- 4 HRVOC compounds controlled and rules written
  - Ethylene (ethene)
  - Propylene (propene)
  - 1,3-Butadiene
  - Isomers of Butene

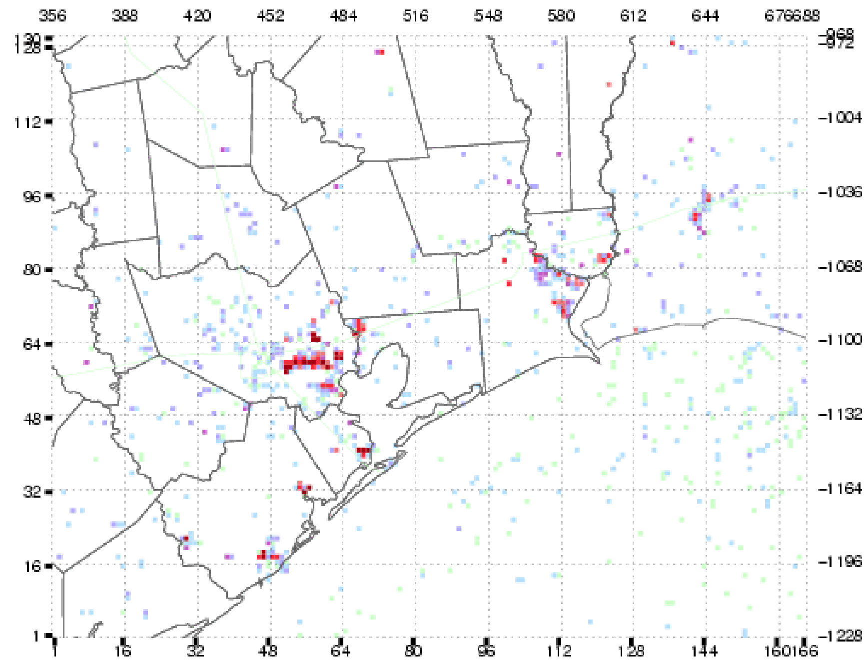
HRVOC Controls - History

- Dec 2000 SIP Revision reduced industrial NO_X in HGB by 90%
- 2001 industry coalition lawsuit claimed the last 10% of reduction were not cost effective
- Can we obtain the equivalent 10% with VOC controls?
  - Modeling estimated VOC reduction needed to offset last 10% of NO_X reduction:
    - NOx-VOC curves; equivalent reactivity
    - 36% overall reduction of HRVOC required in HGB
    - Approx 50% reduction of the 4 HRVOCs in Harris Co., with lesser reductions of ethene and propene in the 7 adjacent counties
    - Modeled as reduction from the “extra olefin” file
    - In addition to the 80% NOx reductions

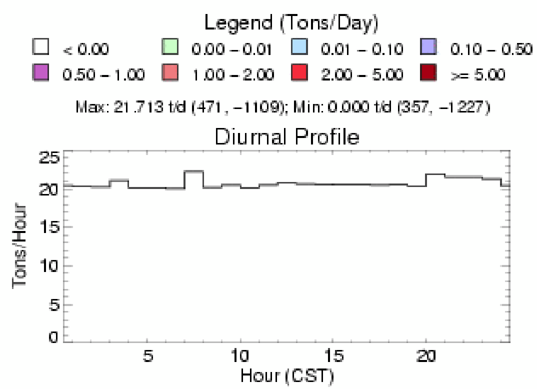
Modeling the HRVOC Controls

hg_02km.base5b Total Point CB–IV HC Emissions, 08/30/2000

Adjusted

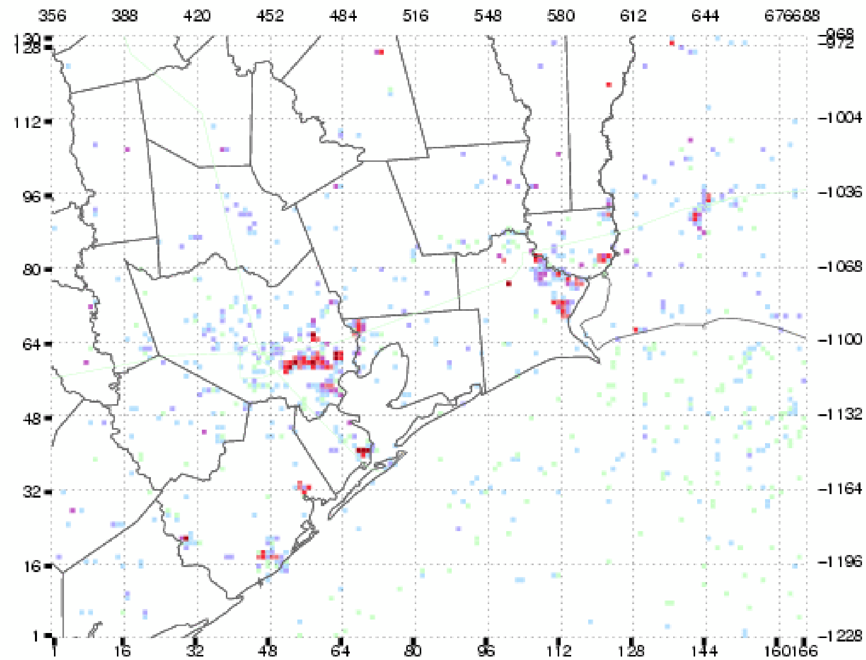


Emissions Plotted	
County	Tons/Day
Brazoria	61.07
Chambers	19.94
Fort Bend	3.55
Galveston	45.10
Harris	253.15
Liberty	2.64
Montgomery	2.39
Waller	1.07
HG SUBTOTAL:	388.91
Hardin	1.95
Jefferson	45.36
Orange	17.15
BPA SUBTOTAL:	64.46
MAP TOTAL:	496.74

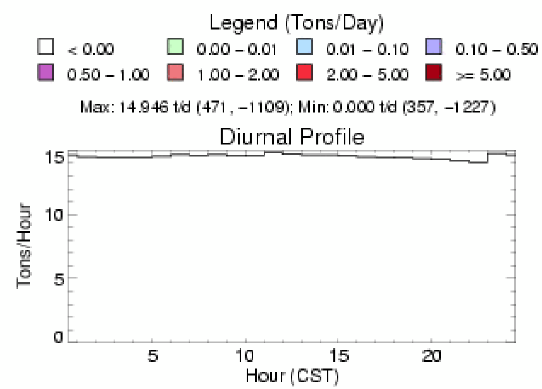


hg_02km.fy07l_harCap Total Point CB–IV HC Emissions, 08/30/2000

Controlled



Emissions Plotted	
County	Tons/Day
Brazoria	31.92
Chambers	12.34
Fort Bend	2.94
Galveston	38.25
Harris	140.43
Liberty	2.16
Montgomery	2.39
Waller	0.80
HG SUBTOTAL:	231.23
Hardin	1.96
Jefferson	50.14
Orange	17.29
BPA SUBTOTAL:	69.38
MAP TOTAL:	348.68



HRVOC Rules Development

- TCEQ adopted rules in Dec 2002, revised in 2004, addressing the two concerns:
  - Rapid formation of ozone and short-term variability:
    - Short-term HRVOC emissions cap
    - 1200 lb/hr site-wide limit on total HRVOC emissions
  - Steady-state and routine emissions:
    - Long-term HRVOC emissions cap
    - Site-wide annual cap
    - Trading allowed under TCEQ Chapter 101 Rules (HECT – HRVOC Emissions Cap and Trade program)

HRVOC Rules Development cont.

- The following units in HRVOC service are subject to the rule and some sort of monitoring:
  - Flares
  - Cooling tower heat exchangers
  - Vent gas streams
- Fugitives are not subject to the HRVOC caps since they are not easily monitored at the levels that would be required to be effective
- HRVOC process flow monitoring implemented in 2005

Collateral Benefits of HRVOC Rules

- Enhanced HRVOC monitoring (Ch. 115 rules) will shed additional light on which sources are most likely under-estimating emissions
- MSS Permitting to address short-term fluctuations

Rethinking HRVOC Adjustments: Recent Developments

- **How to reconcile reported emissions with ambient concentrations (to respond to TexAQS II findings)?**
  - Ambient monitored data is expressed as a mixing ratio (e.g. parts/billion carbon) while emissions are reported as mass rate (e.g. tons/day), so the two can't be directly compared.
  - Air Quality models input emissions and output concentrations: the Industrial Source Complex (ISC) model is a Gaussian plume model widely used in permitting applications.

Rethinking HRVOC Adjustments: Recent Developments

- PSCF "Potential Source Contribution Function" is a technique for locating source regions associated with high monitored pollutant concentrations.
- This next phase of emissions reconciliation marries ISC (estimates magnitude) with PSCF (estimates where) to provide an estimate of how much additional emissions are needed and where, in order to reconcile reported emissions with ambient concentrations.
- Best shown graphically
- Stayed tuned for presentations of this technique

Recent Developments: EI Improvement Projects

- Ever-improving EI Guidance Document (e.g., flares, equipment leak fugitives, cooling towers)
- Flares (minimization, DRE, speciation, design, alternatives)
- Tank Landing Losses (>7000 tpy increase HGB)
- Flash from upstream oil & gas area sources (>80,000 tpy increase HGB; >750,000 tpy statewide)
- Remote sensing
  - Differential Absorption LIDAR (DIAL)
  - HAWK infrared video camera flyovers
  - GasFindIR cameras onsite
- Coast Guard records of barge activity


08/27/2007 10


NPL
National Physical Laboratory
Environmental Remote Sensing System


N74767


Hawk

Conclusions

Modelers can take advantage of higher resolution data

- Better quantity of emissions
  - Greater confidence in modeling
  - Control the minimum amount necessary to achieve attainment
- Better quality of emissions
  - More precise modeling
  - More precise control strategies

Conclusions

Modelers can take advantage of higher resolution data

- Quality emissions
  - Better spatial precision
    - To target control strategies where
  - Better temporal precision
    - To target control strategies when
  - Better chemical precision (speciation)
    - To target which contaminants

Acknowledgments

- Coauthors
- TCEQ Emissions Assessment Section
- TCEQ Data Analysis/Field Study Team
- TCEQ Air Modeling Team
- TCEQ Air Quality Division Managers
- TexAQS participating researchers

Questions ?

References

- TexAQS documents, reports, webpages
- Other presentations
- EPA
- SIPs

Key Words

- TCEQ
- Texas Commission on Environmental Quality
- Highly Reactive VOC
- HRVOC
- TexAQS 2000
- TexAQS II
- Houston-Galveston-Brazoria nonattainment area
- HGB
- Ozone modeling
- Photochemical modeling
- TCEQ SIP
- Emissions Reconciliation
- HRVOC Adjustment
- Olefin emissions
- Terminal olefins
- Auto-GC
- Speciation
- Reactivity
- Maximum Incremental Reactivity
- MIR
- Underestimated emissions
- William Carter
- December 2000 SIP
- December 2002 SIP
- December 2004 SIP