Sesquiterpene emissions and secondary organic aerosol formation potentials for southeast Texas

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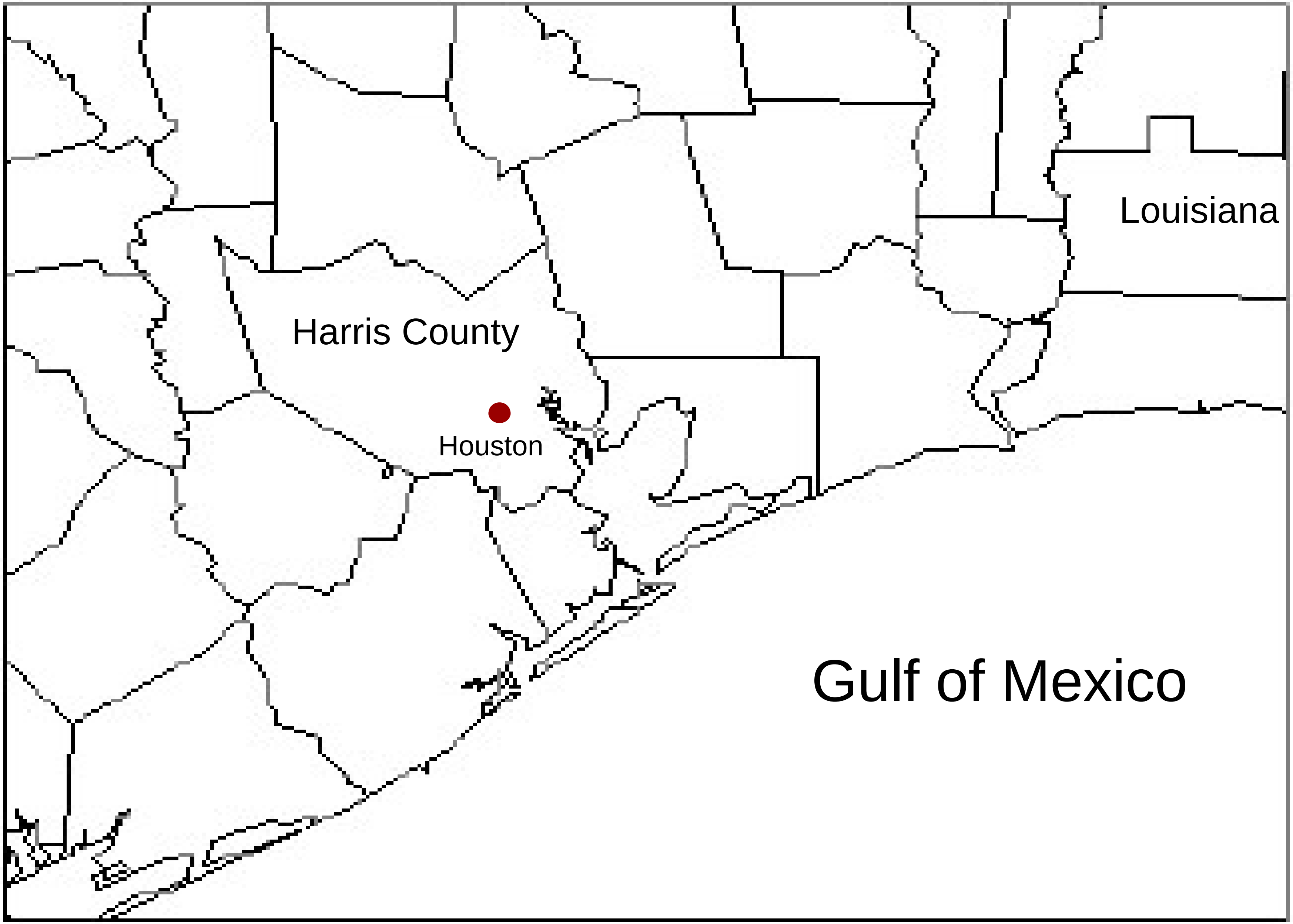
goals

- Estimate sesquiterpene emissions from vegetation in Houston-Galveston area (HGA)
- Assess potential contribution to Secondary Organic Aerosol (SOA)

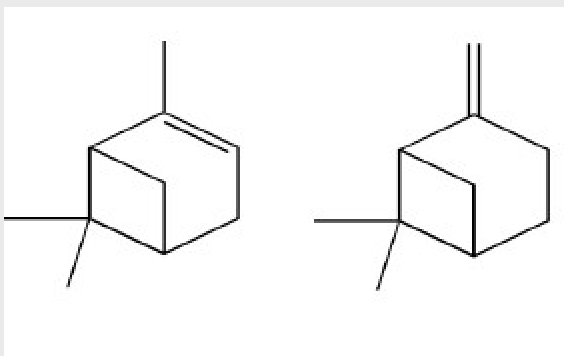


69,440 square kilometer domain for biogenic emission modeling.

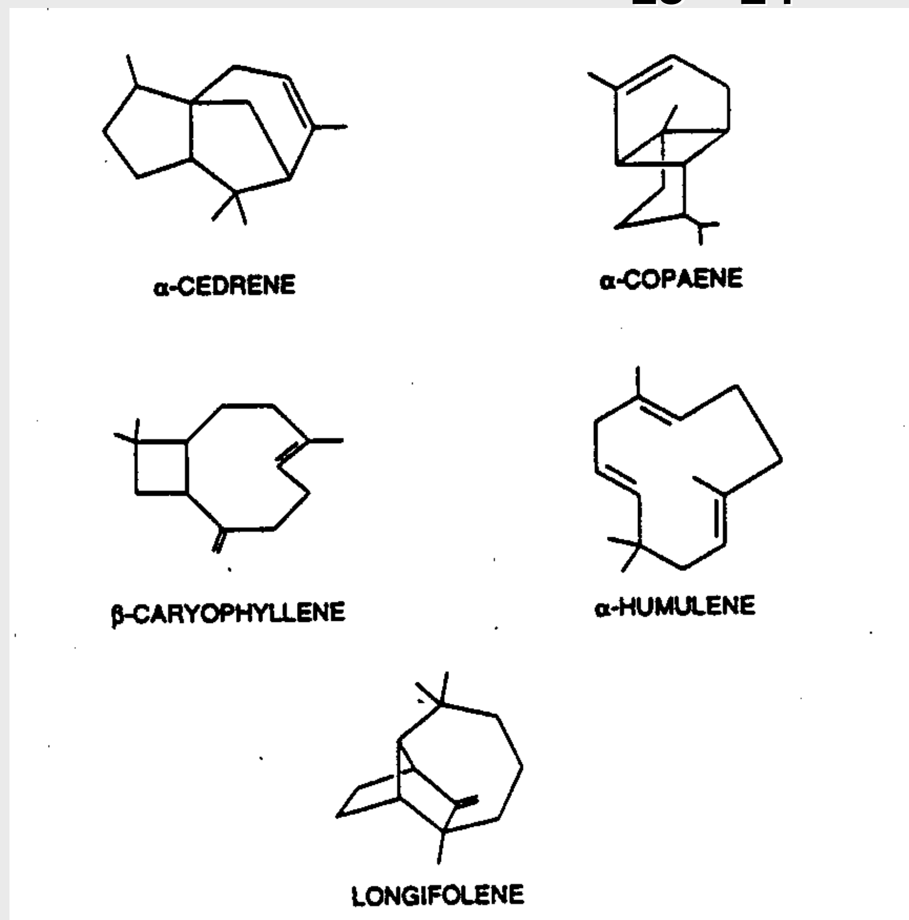
TERPENES: isoprene (C_5H_8) building blocks

MONOTERPENES: 2 blocks → $C_{10}H_{16}$

SESQUITERPENES: 3 blocks → $C_{15}H_{24}$

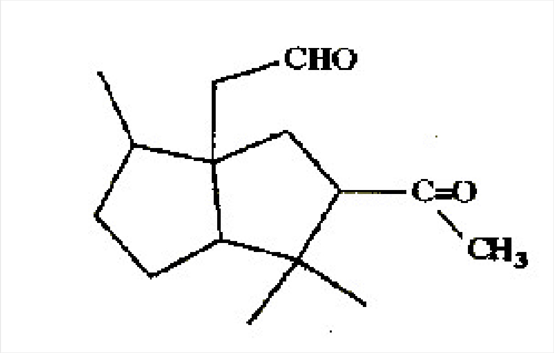


a-pinene ß -pinene

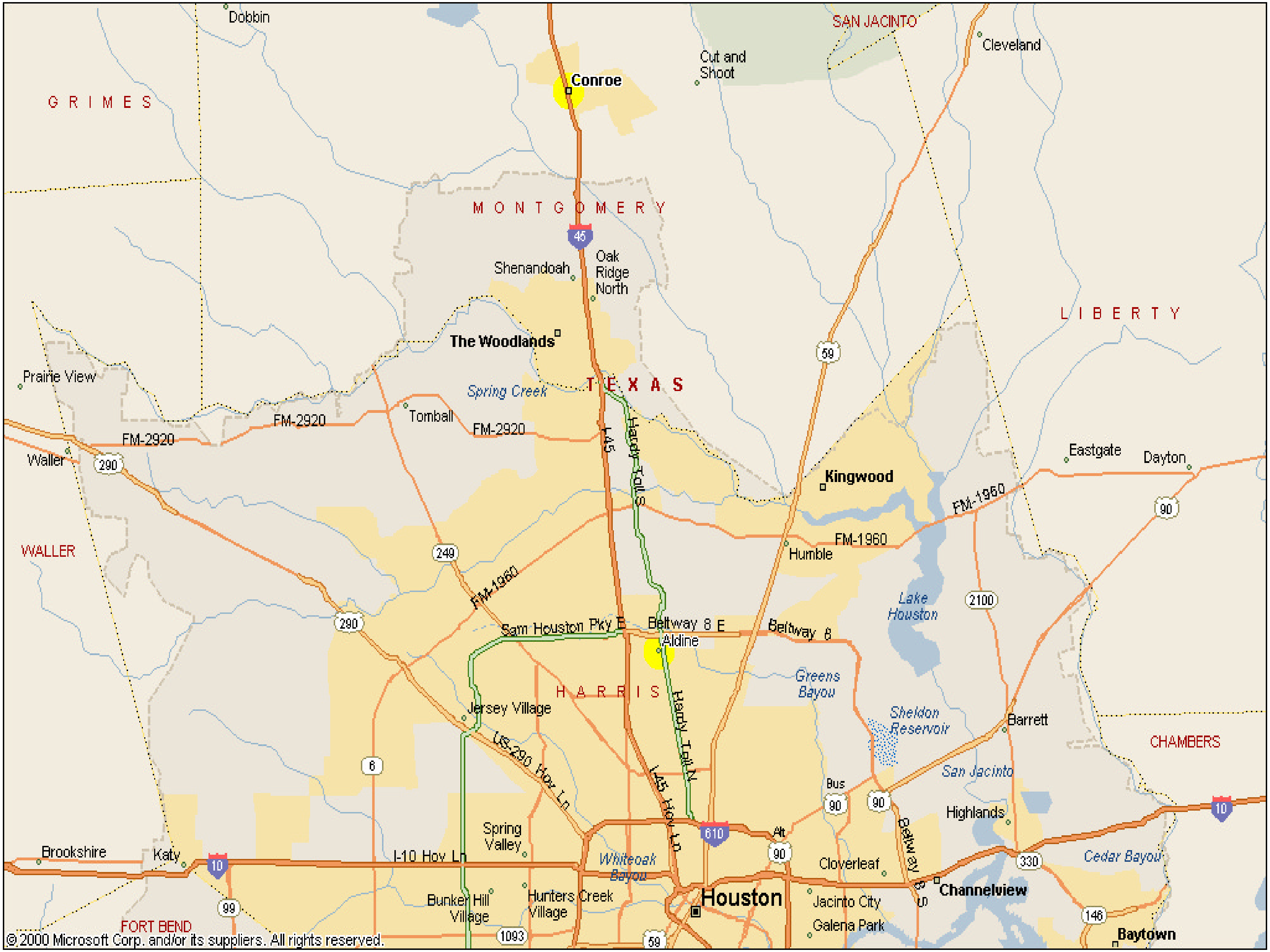


- Atmospheric reactions with O_3, NO_3, and OH radicals
- Less volatile reaction products condense onto atmospheric particles resulting in aerosol formation
- BVOCs are significant SOA precursors

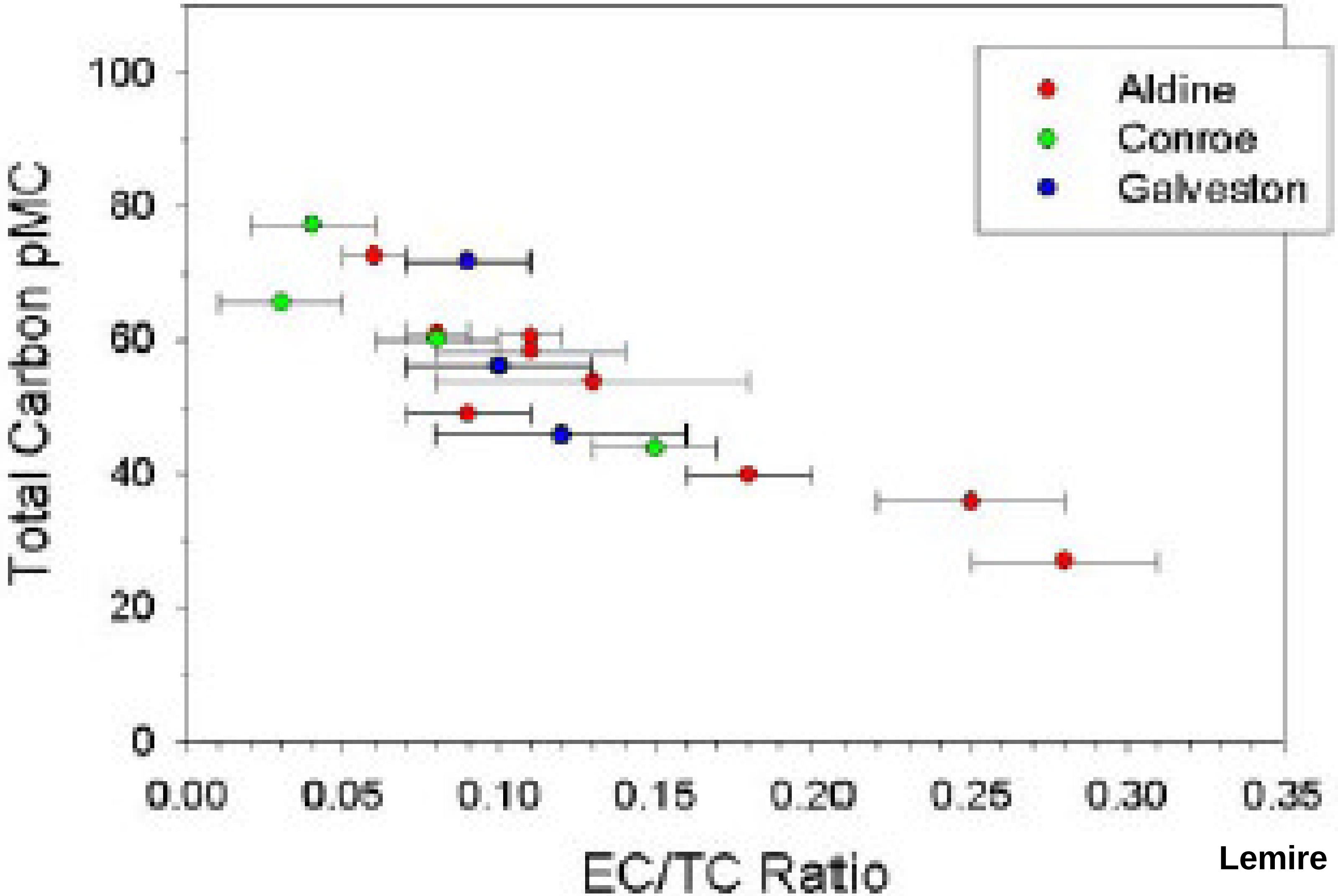
Product of α-cedrene reaction with O_3 →



keto-aldehyde.


Dobbin
SAN JACINTO
Cleveland
Cut and Shoot
Conroe
GRIMES
MONTGOMERY
45
Oak Ridge North
Shenandoah
LIBERTY
The Woodlands
59
Prairie View
Spring Creek
TEXAS
Tomball
FM-2920
FM-2920
FM-2920
Waller
290
I-45
Hardy Toll S
Eastgate
Dayton
Kingwood
FM-1960
90
FM-1960
WALLER
249
Humble
FM-1960
Lake Houston
2100
290
Sam Houston Pky E
Beltway 8 E
Beltway 8
Aldine
Greens Bayou
HARRIS
Jersey Village
Sheldon Reservoir
Barrett
US-290 Hov Ln
Hardy Toll N
CHAMBERS
6
I-45 Hov Ln
San Jacinto
Bus 90
90
Spring Valley
Highlands
Beltway 8
10
Brookshire
Katy
10
I-10 Hov Ln
610
Alt 90
Cloverleaf
Whiteoak Bayou
330
Cedar Bayou
Bunker Hill Village
Hunters Creek Village
Houston
Channelview
99
Jacinto City
146
FORT BEND
Galena Park
1093
59
Baytown

pMC vs. EC/TC Ratio



Lemire 2001

Importance of precursors to SOA formation

1. Overall aerosol potential

2. Atmospheric emissions

3. Presence of other initiating reactants (O_3, OH, NO_3, sunlight, acid catalysts)

Gas-phase reaction with ozone

BVOC concentration = 100 ppb

BVOC	Yield
Sesquiterpenes	~100%
Cyclic Monoterpenes with two double bonds	~40%
Monounsaturated cyclic monoterpenes	5-25%
Open Chain Hydrocarbons	~5%

Source: Hoffmann *et al*. (1997)

South east Texas Biogenic Mixture (Modeling Results)

	Initial	With St Emissions
Isoprene	81%	66%
Monoterpenes	11%	9%
OVC	9%	7%
Sesquiterpenes	0%	17% (-30%)

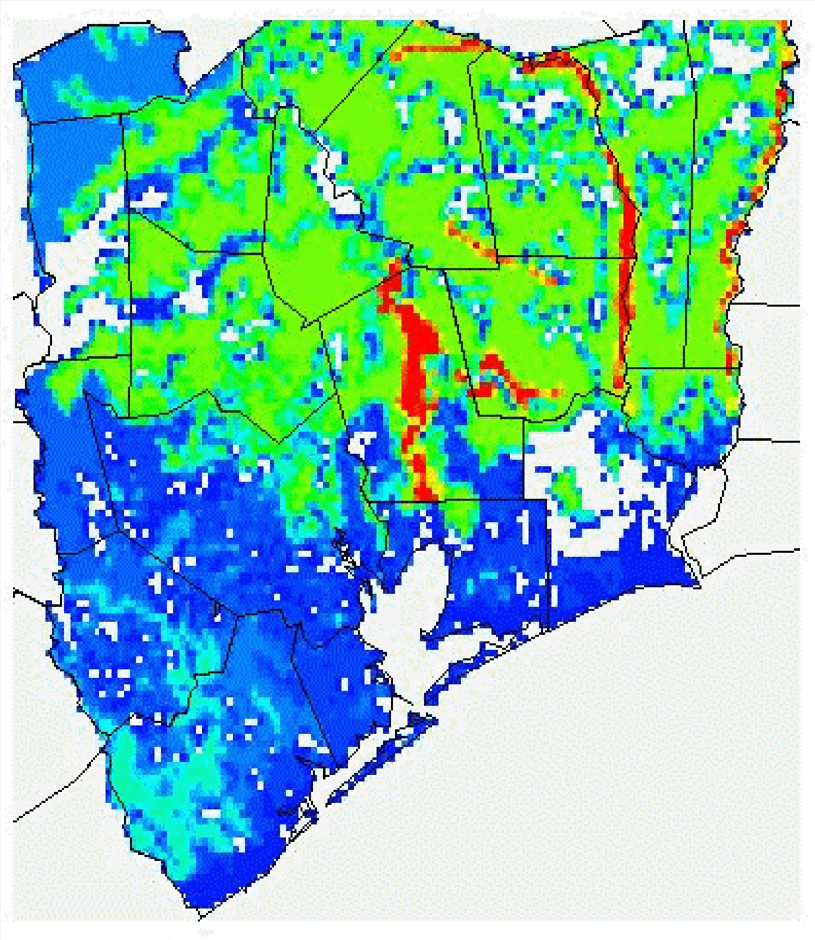
g l o b e i s

Global Biosphere Emissions and Interaction System

- Microsoft Access Based Model

- Estimates Biogenic Emissions
    - Plant species
    - Plant biomass
    - Soil type
    - Ambient temperature
    - Solar radiation

- Design to use in combination with photochemical modeling systems for ozone and particulate matter



Previous GloBEIS simulations

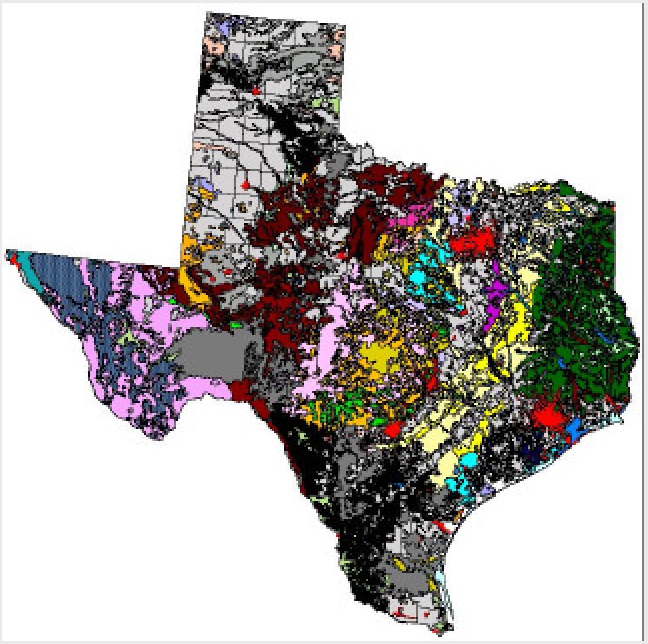
- Isoprene predictions in eastern Texas
  - Magnitude - Less than a factor of two (Allen *et al.*, 2002)
  - Spatial distribution - Confirmed by aircraft observations (TexAQS 2000)
  - “Comparison of Biogenic Isoprene Emission Estimates with Aircraft Measurements during the Texas Air Quality Study,” Jihee Song UT-Austin.

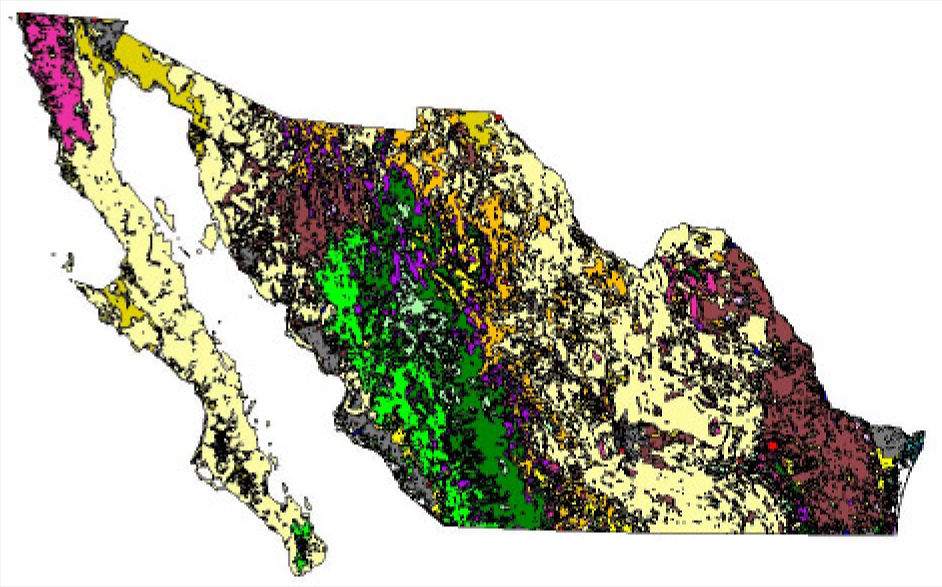
- Same calculation procedures for sesquiterpene
  - Rough estimate of magnitude
  - Spatial distribution

land cover input

UT GIS landuse/landcover database

- Describes land coverage/ Emission factor
- Developed by UT-Austin/ENVIRON for TCEQ study
- Texas and Mexico - 1 kilometer resolution
- Formatted for direct compatibility with GloBEIS





Source: Yarwood et al., 1999b; Wiedinmyer et al., 2000

Family	Genus	Species (Botanical Name)	Species (Common Name)	Emission per species (µg/gdl-hr)	Emission per family (µg/gdl-hr)	Emission per genus (µg/gdl-hr)
Asteraceae	Baccharis	B. halimifolia	Bush (Salt)	15.00	5.51	15.00
	Carthamus	C. tinctoreus	Safflower	0.24		0.24
	Artemesia	A. tridentata	Sagebrush (Big)	1.30		1.30
Betulaceae	Alnus	A. incana	Alder (Speckled)	0.30	0.29	0.30
	Betula	N/A	Birch	0.03		0.03
	Carpinus	C. betulus	Hornbeam	0.02		0.41
		C. caroliniana	Ironwood	0.80		
Ericaceae	Ledum	L. groenlandicum	Tea (Labrador)	14.00	14.00	14.00
Fabaceae	Medicago	M. sativa	Alfalfa	0.06	0.06	0.06
Fagaceae	Quercus	Q. velutina	Oak (Black)	8.50	22.65	22.65
		Q. gambelii	Oak (Gamble)	1.50		
		Q. stellata	Oak (Post)	78.00		
		Q. alba	Oak (White)	2.60		
Juglandaceae	Juglans	J. regia	Walnut (Hartley)	0.19	0.19	0.19
Malvaceae	Gossupium	G. hirsutum	Cotton (Pima)	0.09	0.09	0.09
Myrtaceae	Callistemon	C. nauseosus	Brush (Rabbit)	3.20	3.20	3.20
Oleaceae	Olea	O. europea	Olive (Manzanillo)	0.05	0.05	0.05
Pinaceae	Abies	A. lasiocarpa	Fir (Subalpine)	0.80	0.56	0.80
	Tsuga	T. canadensis	Hemlock (Eastern)	0.10		0.10
	Pinus	P. contorta	Pine (Lodgepole)	0.30		0.30
	Picea	P. egelmanii	Spruce (Eaglemann)	0.10		0.80
	Picea	P. glauca	Spruce (White)	1.50		
Rosaceae	Prunus	P. avium	Cherry (Bing)	0.10	19.43	1.57
		P. serotina	Cherry (Black)	3.80		
		P. persica	Peach (Halford)	0.80		
	Rubus	R. idaeus	Raspberry (Red)	73.00		73.00
Rhamnaceae	Ceanothus	C. leucodermis	Whitehorn	0.25	0.25	0.25
Solanaceae	Lyconpersicon	L. lycopersicum	Tomato (Sunny)	0.41	0.44	0.44
		L. lycopersicum	Tomato (Canning)	0.47		
Vitaceae	Vitis	V. vinifera	Grape (Columbard)	0.16	0.16	0.16

Source: Winer et al. 1992, König et al. 1995, Helmig et al.1999

30 species 14 families 22 genera

- Sesquiterpene emission factors were assigned based on taxonomic relationships

- Emission factor of zero assigned if no data
  - 45% of land cover types
  - Sensitivity analysis - Median value family level emission factors reassigned to each land cover

- EF Normalized to a standard temperature with dependence model based on monoterpene
- No PAR Dependence

u n c e r t a i n t y

- Experimental emission factors
  - Winer et al., (1992) - factor of five
  - Helmig *et al.* (1999) – factor of two
  - König *et al.* (1995) – author did not characterize uncertainty

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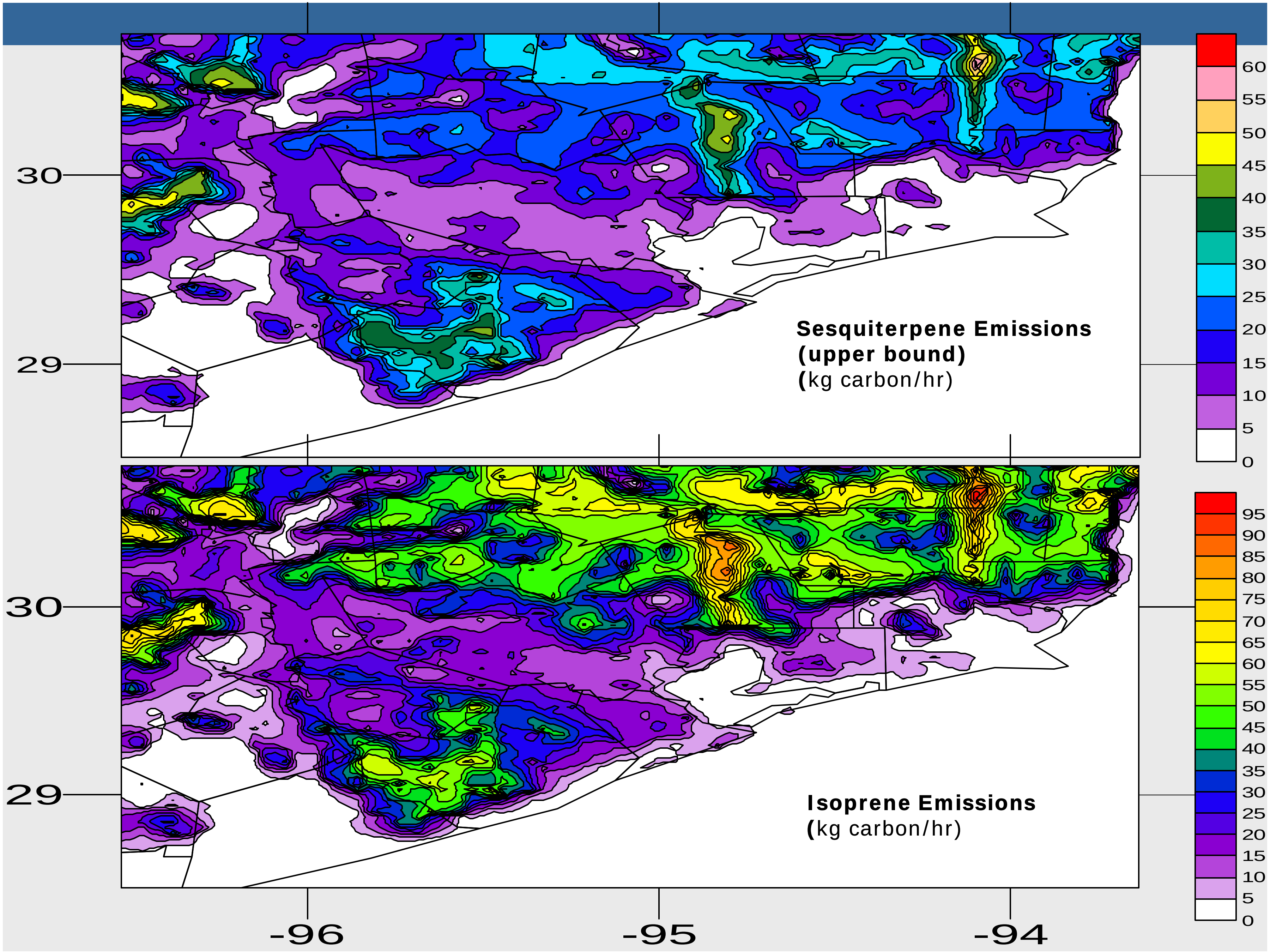
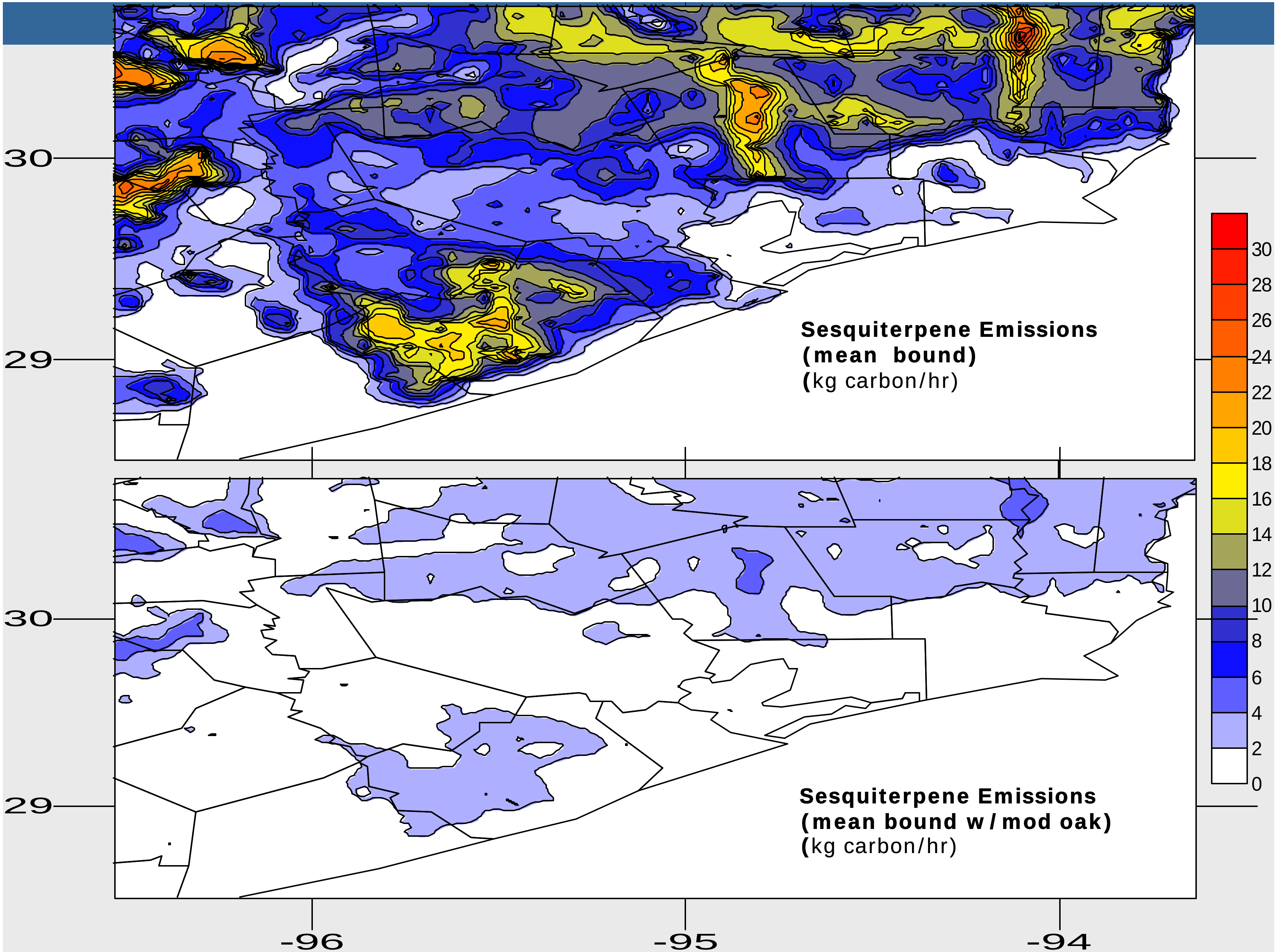
		Q. gambelii	Oak (Gamble)	1.50		
		Q. stellata	Oak (Post)	78.00		
		Q. alba	Oak (White)	2.60		

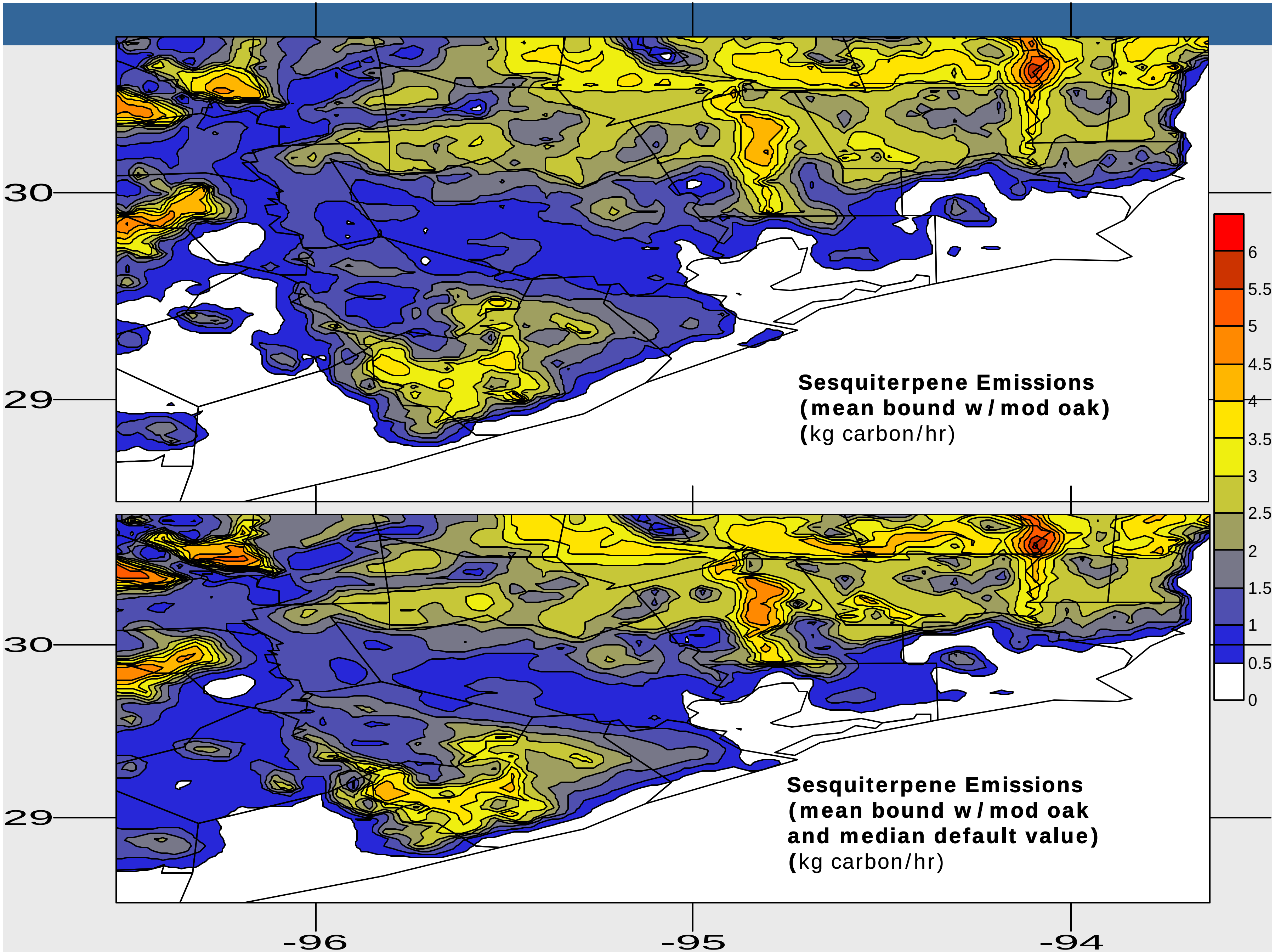
- Average emission factor values
  - *Quercus velutina*
  - *Quercus gambelii*
  - *Quercus alba*
- Average family emission value: 4.2 µg-C/gdl-hr

Scenario	Total sesquiterpene emissions in domain (kg C/hr)	Average sesquiterpene emissions flux (kg C/km^2-hr)
Total Sesquiterpenes (upper bound emission factor)	$4.5*10^4$	0.65 (0 – 4.4)
Total Sesquiterpenes (mean bound emission factor)	$2.3*10^4$	0.32 (0 – 2.2)
Total Sesquiterpenes (lower bound emission factor)	$1.1*10^4$	0.16 (0 – 1.1)
Total Sesquiterpenes (mean bound emission factor with modified oak)	$4.9*10^3$	0.07 (0 – 0.4)

September 8, 1993 12-1 pm
T= 30 °C with a cloudless sky at noon for a 69,440 square kilometer region


Sesquiterpene Emissions
(upper bound)
(kg carbon/hr)
60
55
50
45
40
35
30
25
20
15
10
5
0
30
29
Isoprene Emissions
(kg carbon/hr)
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
30
29
-96
-95
-94

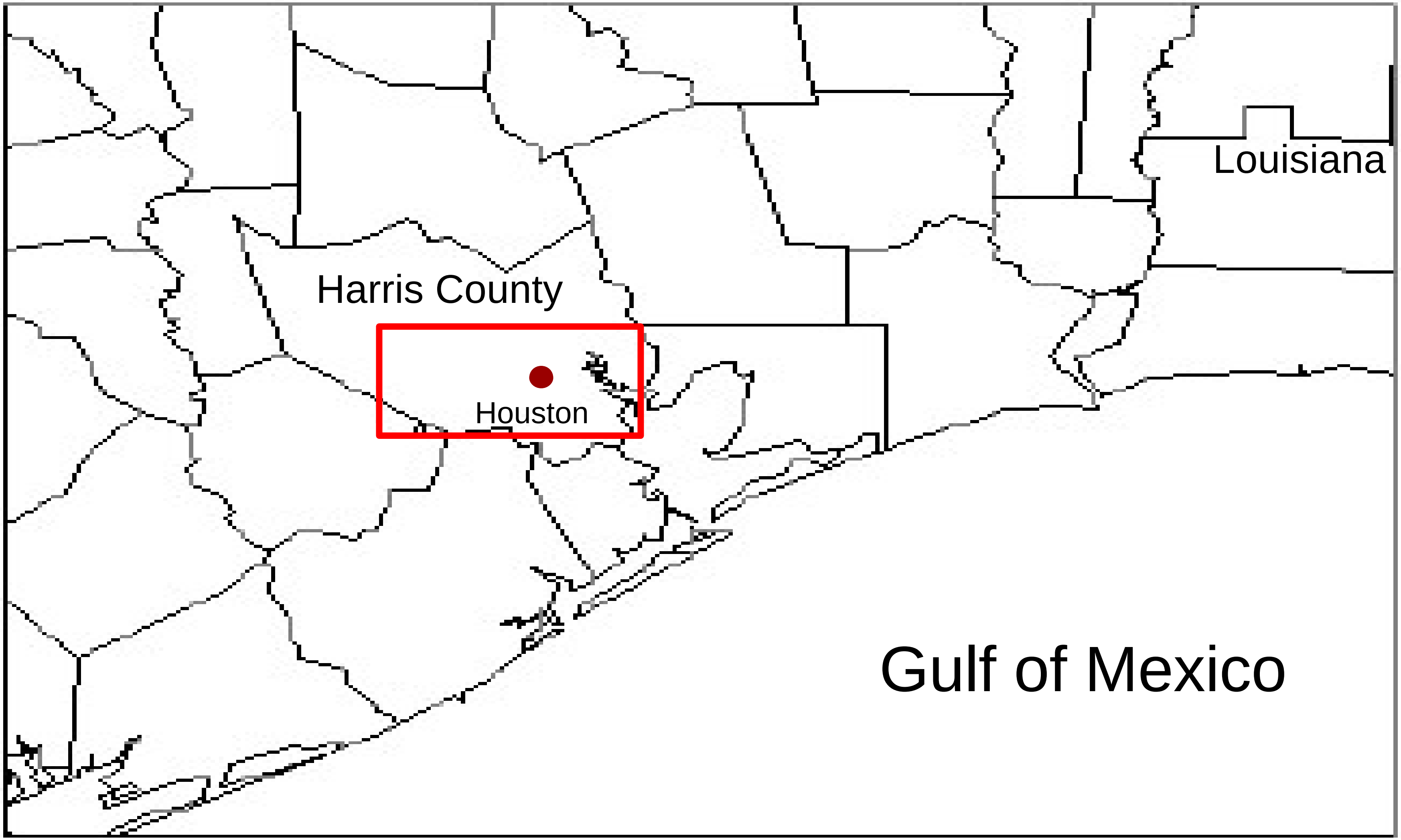

Sesquiterpene Emissions
(mean bound)
(kg carbon/hr)
Sesquiterpene Emissions
(mean bound w/mod oak)
(kg carbon/hr)
30
29
30
29
-96
-95
-94
0
2
4
6
8
10
12
14
16
18
20
22
24
26
28
30



Sesquiterpene Emissions
(mean bound w/ mod oak)
(kg carbon/hr)
Sesquiterpene Emissions
(mean bound w/ mod oak
and median default value)
(kg carbon/hr)
30
29
30
29
-96
-95
-94
6
5.5
5
4.5
4
3.5
3
2.5
2
1.5
1
0.5
0

Simulation	Biogenic SOA formation rates (kg C/day)		Biogenic SOA formation flux (kg C/km^2-day)	
	sesquiterpene	monoterpene	sesquiterpene	monoterpene
1. Upper bound emission factor	$8.7*10^3$	23.6	4.5	$1.2*10^{-2}$
2. Reported emission factor	$4.3*10^3$	23.6	2.3	$1.2*10^{-2}$
3. Lower bound emission factor	$2.2*10^3$	23.6	1.1	$1.2*10^{-2}$
4. Reported emission factor with modified oak	$8.7*10^2$	23.6	0.46	$1.2*10^{-2}$

- **1,920 square kilometer region**
- **Effective emission period of 8 hours**
- **All formation potential from other BVOC was neglected**
- **Conversion from sesquiterpenes to SOA 100 percent**



Red square indicates 1,920 square kilometer domain for biogenic SOA calculations

observed aerosol data

- Diesel fuel consumption and elemental carbon emissions from combustion in Houston area
  - 600 kg-elemental carbon/day
  - Annual average concentration of elemental carbon 1.6 µg-Carbon/m³

$$\text{SOA emissions}\,[\text{kg-C/day}]\left[\frac{1.6\,m\text{g-C/m}^3}{600\,\text{kg-C/day}}\right] = \text{SOA concentration}\,[m\text{g-C m}^3]$$

Source: Tropp et al., 1998, Dennis *et al.*, 2000

Biogenic SOA Concentration (mg-C/m^3) (Lower Bound)	**5.8**
Biogenic SOA Concentration (mg-C/m^3) (Normal Bound)	**11.5**
Biogenic SOA Concentration (mg-C/m^3) (Upper Bound)	**23.2**
Biogenic SOA Concentration (mg-C/m^3) (Normal Bound with Modified Oak)	**2.3**

Average above-canopy concentration of geologically modern SOA (Lemire 2001)

Aldine: 2.1 mg/m^3

Conroe: 2.7 mg/m^3

conclusions

- Emission peaks coincided for sesquiterpenes and isoprene

- High uncertainty for post oak (*quercus stellata)*
  - More than a factor of ten larger other oak species
  - Recalculated without value for post oak sesquiterpene emissions dropped by a factor of five for entire modeling domain

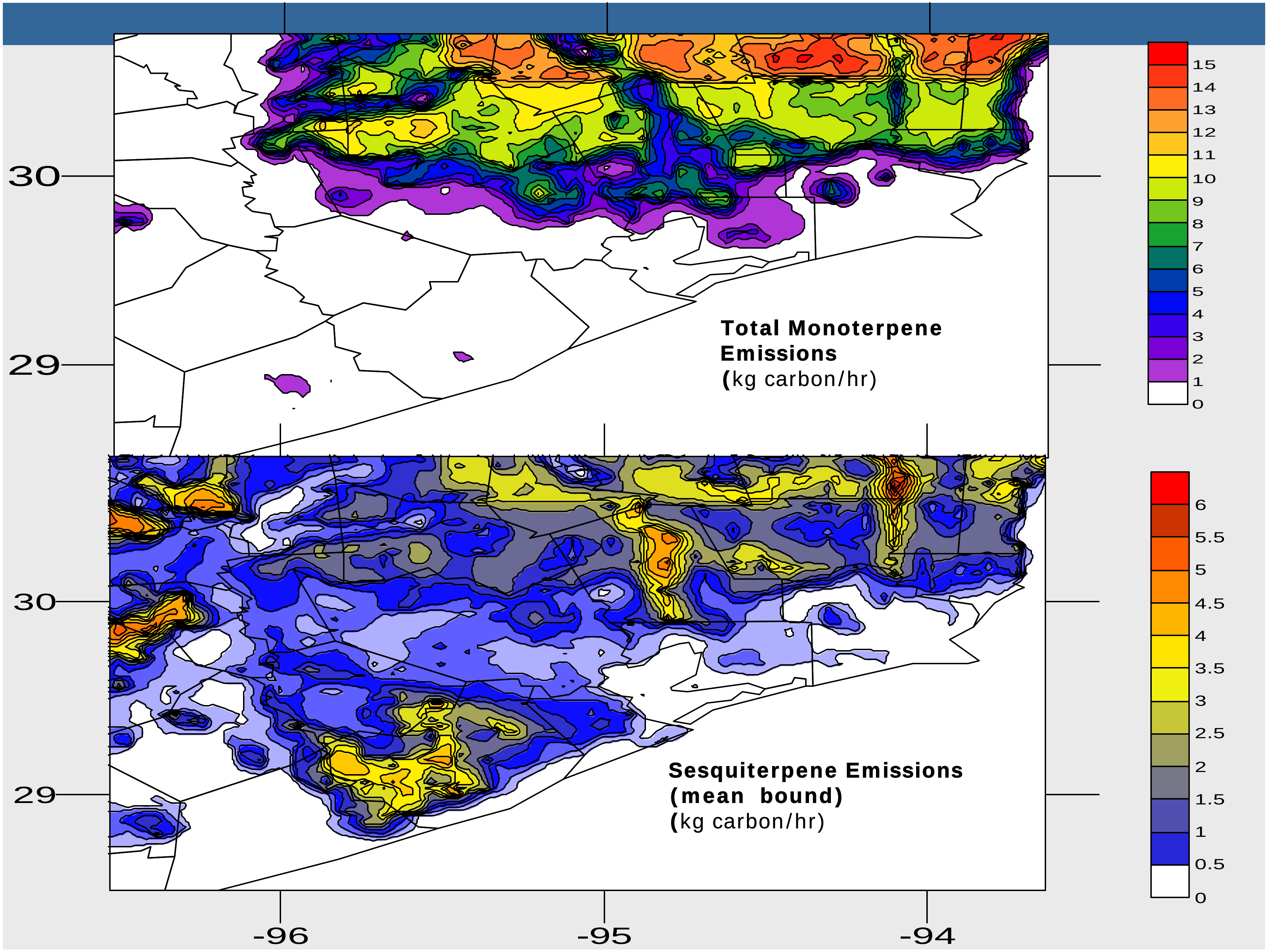
- Sesquiterpene emissions predicted using mod. oak were reasonably consistent with measurements of geologically modern carbon in ambient aerosol

conclusions

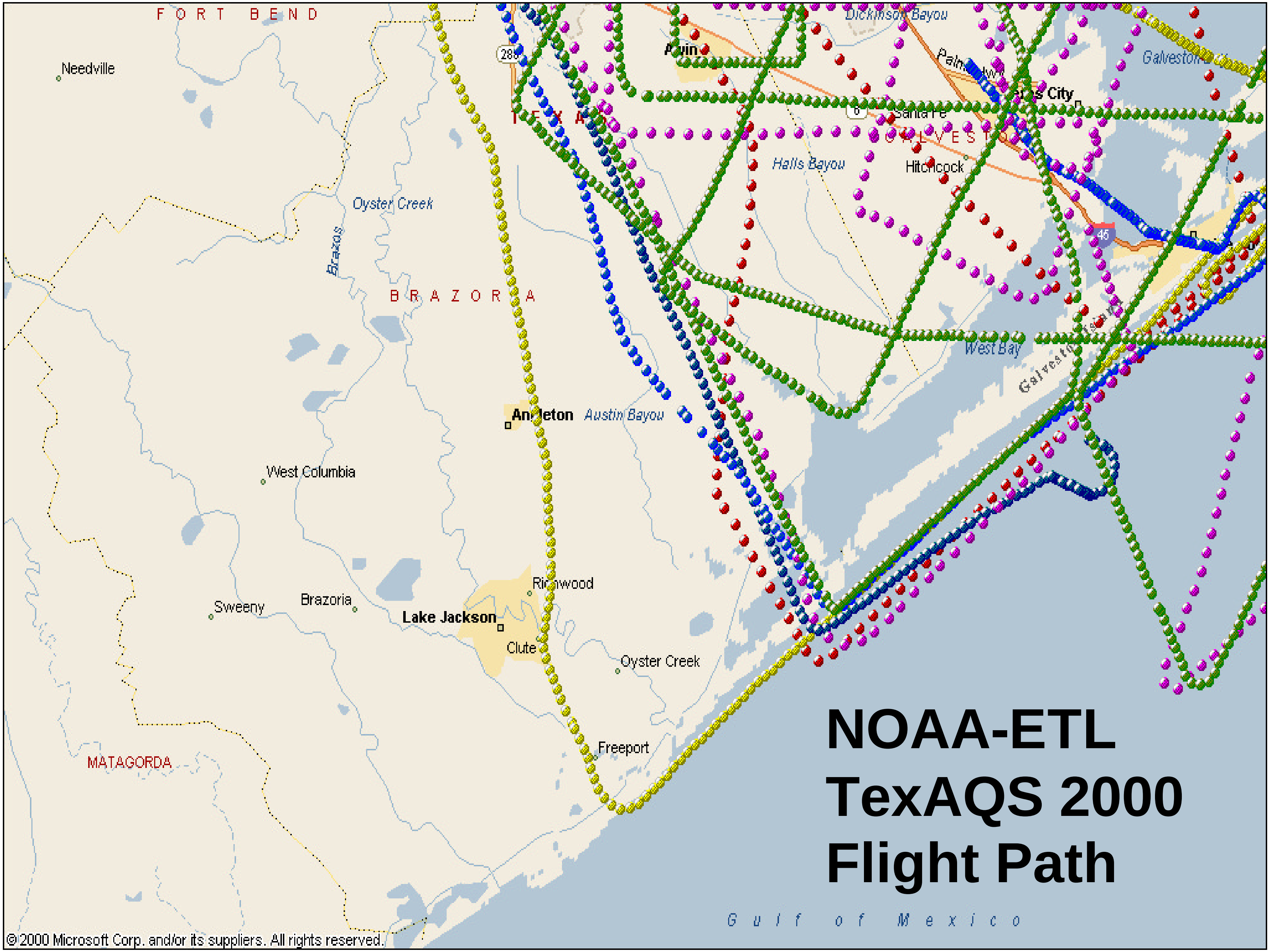
• Sesquiterpenes exceed monoterpenes in emission strength and yield suggesting that ST are important contributor to aerosol rates in southeast Texas

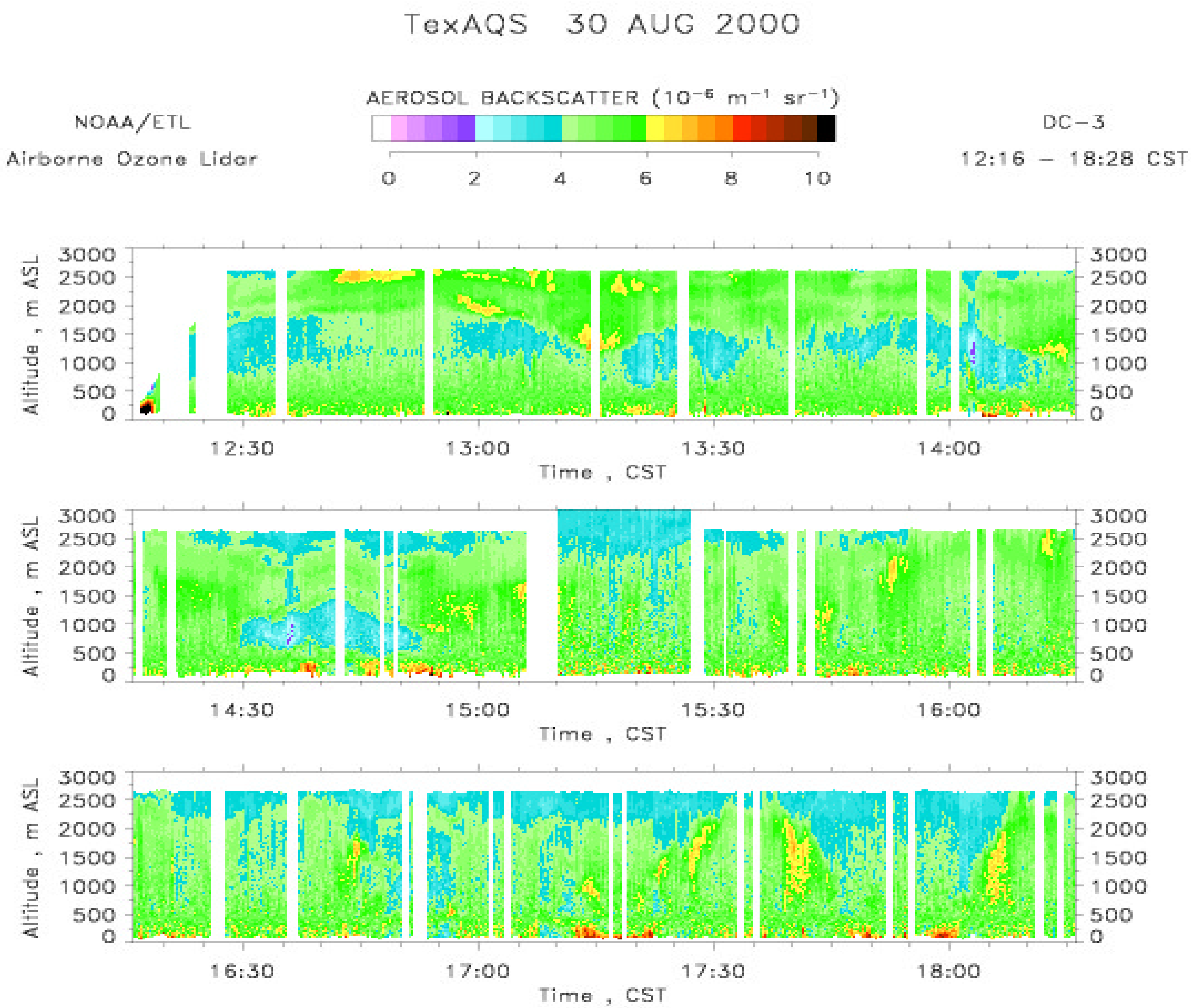
• ST emission factor data

• Confirm model predictions with aircraft aerosol data


Total Monoterpene Emissions
(kg carbon/hr)
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
30
29
Sesquiterpene Emissions (mean bound)
(kg carbon/hr)
6
5.5
5
4.5
4
3.5
3
2.5
2
1.5
1
0.5
0
30
29
-96
-95
-94

NOAA-ETL TexAQS 2000 Flight Path




TexAQS 30 AUG 2000
AEROSOL BACKSCATTER (10^{-6} m^{-1} sr^{-1})
0 2 4 6 8 10
NOAA/ETL
Airborne Ozone Lidar
DC-3
12:16 – 18:28 CST
Altitude , m ASL
0 500 1000 1500 2000 2500 3000
12:30 13:00 13:30 14:00
14:30 15:00 15:30 16:00
16:30 17:00 17:30 18:00
Time , CST

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