# The U.S. Gulf region air toxicants (Styrene and BTEX) study: Emission estimate result by source types and concentration estimate

Chi-tsan Wang[1], William Vizuete[2], Marc Serre[2], Richard Strott[2], Jaime Green[2],Jared Bowden[4],Larry Engle[3], and Bok Haeng Baek[*1]

[1]Center for Spatial Information Science and Systems (CSISS), George Mason University, U.S.
[2]Department of Environmental Sciences & Engineering, University of North Carolina, Chapel Hill, NC. US
[3]Department of Epidemiology, University of North Carolina, Chapel Hill, NC. US
[4]Department of Marine, Earth, and Atmospheric Science, North Carolina State University, NC, U.S.

2

# Outline

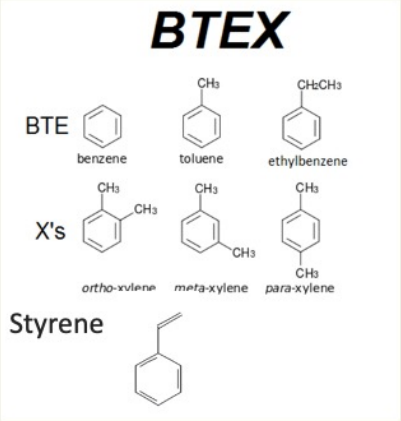
1. Research Background
2. Research scheme
3. Emission
4. CTM Model
5. Preliminary result

3

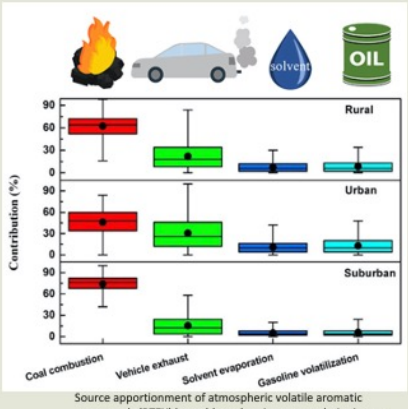
# Background

## The Styrene and BTEX

**S**tyrene, **B**enzene, **T**oluene, **E**thylbenzene, and **X**ylenes **(SBTEX)** are Hazardous Air Pollutants **(HAPs)**.
Source: coal combustion, vehicle, solvent, petrochemical industry.




http://www.gcesystems.com/what-is-btex/




Source apportionment of atmospheric volatile aromatic compounds (BTEX) by stable carbon isotope analysis: A case study during heating period in Taiyuan, northern China Yinghui Li , Yulong Yan , Dongmei Hu , Zhisheng Li , Aisheng Hao , Rumei Li , Cheng Wang a, Yang Xu a, Jingyuan Cao a, Zhuocheng Liu a, Lin Peng a 2020

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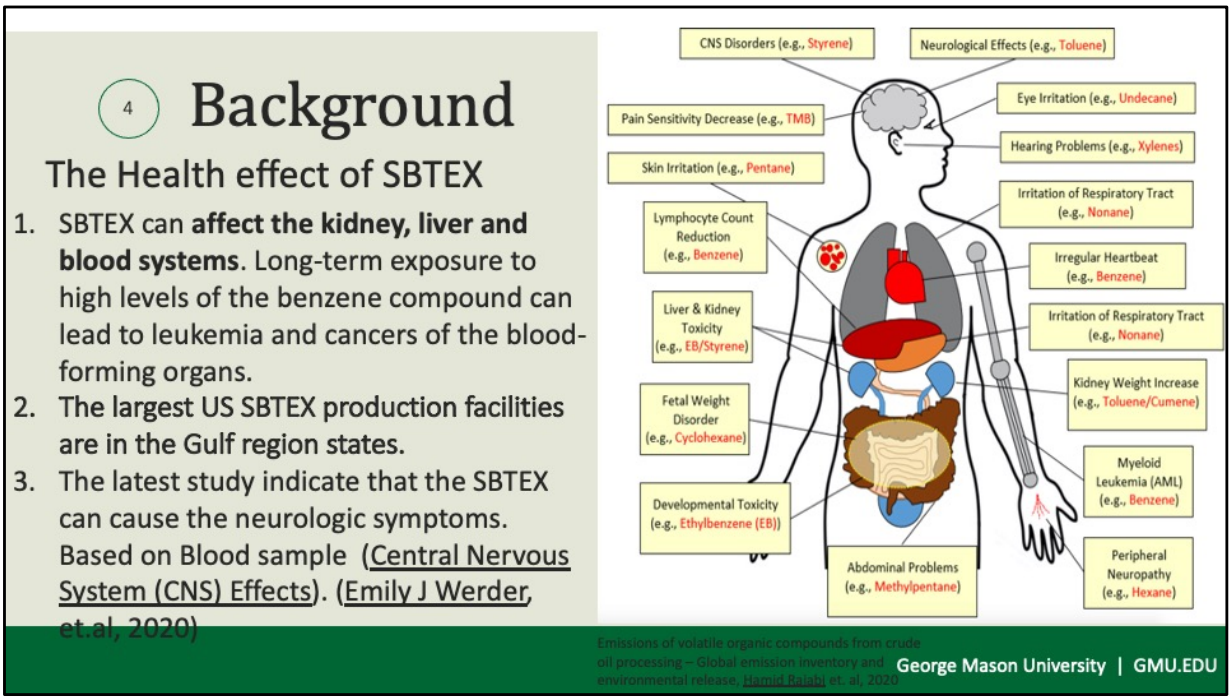
1. SBTEX are Hazardous Air Pollutants (HAPS)
2. The Source of SBTEX are from coal combustion, vehicle, solvent, and petrochemical industry.

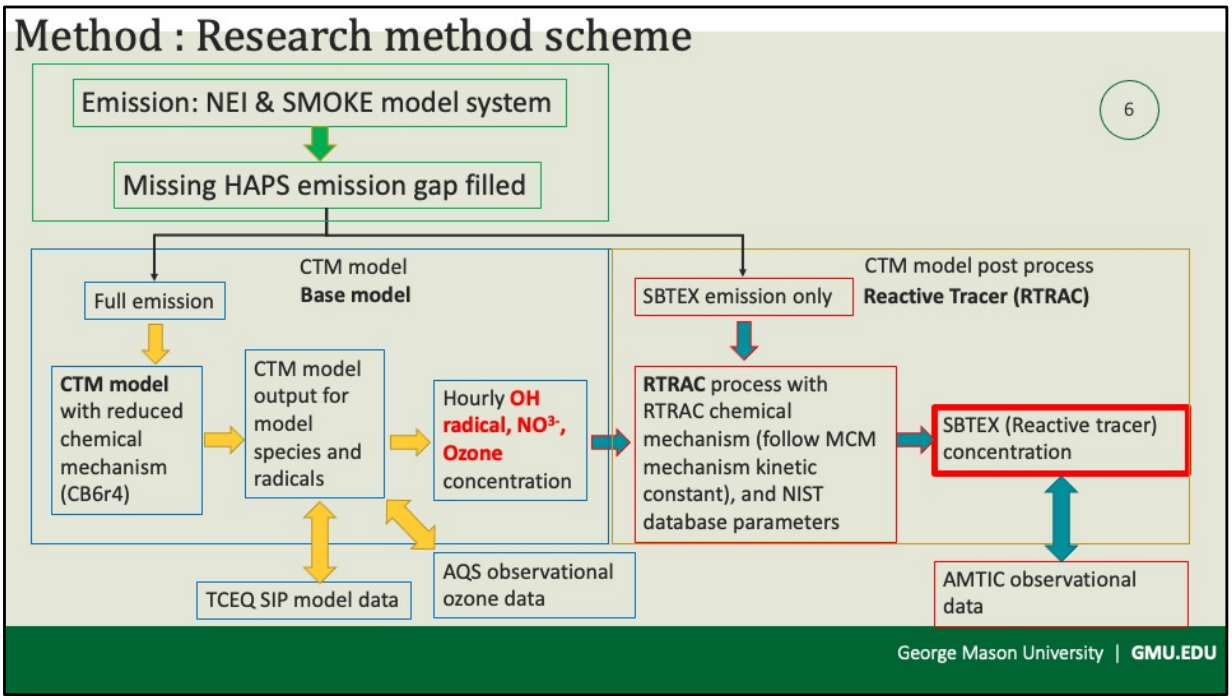



1. SBTEX are Hazardous air pollutants; cause the negative health impact in human organs. Such as Kidney, liver and blood system, CNS.
2. A study was published in 2020 shows the relationship between CNS symptoms outcome and SBTEX concentration in blood samples in GULF region.
3. Picture from: Emissions of volatile organic compounds from crude oil processing – Global emission inventory and environmental release, Hamid Rajabi et. al

5

# Background and research question

- **Can we estimate the SBTEX concentration in Gulf region?**
- **To study the human exposure of SBTEX, the Chemical Transport Model (CTM) can be used to simulate the concentration of SBTEX, But how?**
- The CTM usually used to simulate the Ozone and PM, but not for all HAPS species concentration.
- For example, the STEX species are not considered as the explicit species in current reduced chemical mechanism in CTM (CB6, SAPRC07…etc). The STEX species are surrogate to TOL and XYL.
- Therefore, we apply the USEPA National Emission Inventory (NEI) with SMOKE model to calculate the individual SBTEX emission data, and we introduce the **Reactive Tracer method** to simulate the individual SBTEX.




1. Introduce the HAPS emission from NEI HAPS inventory. The NEI may not consider all emission source.
2. Gap filled the missing HAPS by SCC and county level.
3. We made the emission input for CTM model and reactive tracer process
4. CTM base model simulate the hourly ozone and other oxidizing agent. (OH, NO3)
5. The model species and ozone are compared with TCEQ SIP model result including ozone, BENZ, TOL, XYL, FORM, and O3. The EPA AQS data are used to evaluate the ozone concentration.
6. The Reactive Tracer consider the chemical loss and deposition.
7. The ambient VOC measurement data are used to compare the model SBTEX concentration.

## Emission [1]: The total SBTEX emission data in the 2011 NEI by emission sectors in the model domain. (I: inventory species, m: model species)

7

| ton/ year | agfire | cmv | nonpt | nonroad | np_oilgas | onroad | othpt | ptegu | ptfire3D | ptnonipm | pt_oilgas | rail | rwc | Total |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| BENZENE (I) | 1,243 | 113 | 2,118 | 4,965 | 3,047 | 8,644 | 0 | 121 | **23,804** | 1,326 | 334 | 11 | 435 | 46,161 |
| BENZ (m) | 1,243 | 113 | 3,384 | 5,238 | 5,976 | 8,644 | 162 | 305 | **50,764** | 8,052 | 562 | 11 | 435 | 84,888 |
| XYLENES (I) | 0 | 27 | 5,683 | 15,724 | 3,414 | **22,534** | 0 | 64 | 4,801 | 2,592 | 186 | 22 | 29 | 39,351 |
| XYL (m) | 110 | 1,016 | 36,944 | 34,034 | 3,866 | 57,029 | 342 | 1,885 | 8,261 | 8,143 | 465 | 130 | 479 | 152,702 |
| TOLUENE (I) | 821 | 18 | 18,664 | 14,888 | 1,759 | **35,871** | 0 | 142 | 12,025 | 2,460 | 278 | 15 | 101 | 87,042 |
| TOL (m) | 296 | 970 | 49,737 | 34,037 | 7,063 | 44,754 | 337 | 681 | 36,616 | 17,122 | 945 | 147 | 1,170 | 193,874 |
| ETHYLBENZ(I) | 0 | 11 | 1,310 | 2,956 | 251 | **6,178** | 0 | 38 | 0 | 655 | 32 | 9 | 0 | 11,440 |
| STYRENE (I) | 0 | 12 | 856 | 188 | 1 | 253 | 0 | 8 | 0 | **2,392** | 1 | 10 | 0 | 3,721 |
| Total (I) | 2,064 | 180 | 29,897 | 38,994 | 11,400 | **73,481** | 162 | 557 | 67,589 | 16,151 | 1,060 | 67 | 565 | 226,442 |

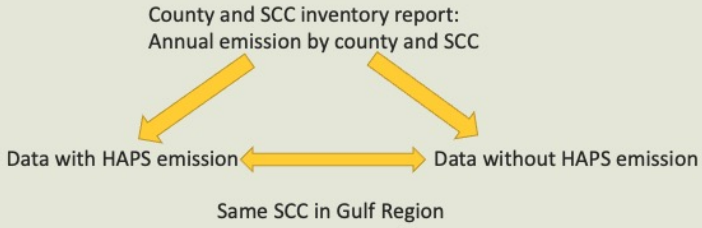


1. The Rows are different species, (I) is inventory species, (M) is model species. Columns are different emission sectors.
2. The largest SBTEX emission sector is “onroad”, the ptfire is the second.
3. The benzene is not equal to Benz which indicate the missing report of HAPS.
4. We picked 5 sectors that can be checked the SCC&County level emission to do gap fill for mission HAPs.

8

# Emission [2]: the NEI, SMOKE model and missing data gap filled process in county&SCC level

- Source Classification Code (SCC).
- Find the missing STEX data and gap filled the missing emission by the ratio of individual HAPs (i) and total VOC (VOC_INV) which have the same SCCs.
- Benzene is adjusted to BENZ directly.




$$\frac{HAPs_{i,SCC}}{VOC\_INV\_wHAPs_{i,SCC}} = \frac{HAPs\_missing_{i,scc}}{VOC\_INV\_wo\_HAPs_{i,SCC}}$$

$$HAPs\_missing_{i,scc} = VOC\_INV\_wo\_HAPs_{i,SCC} \times \frac{HAPs_{i,SCC}}{VOC\_INV\_wHAPs_{i,SCC}}$$

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1. We applied the annual emission by each county and SCC for those 5 emission missing sectors.
2. The data are separated into two group “with STEX” and “without STEX”.
3. We assumed the same SCC code have similar emission process, so the ratio of STEX and VOC should be similar in the same SCC in Gulf region.
5. Therefore, we can use the ratio for with STEX emission group to estimate the missing data for without STEX group.

## Emission [3]: The missing STEX emission data

| Missing STEX (tons/year) | | Alabama | Florida | Georgia | Louisiana | Mississippi | **Texas** | Species Total | Sector Total |
|---|---|---|---|---|---|---|---|---|---|
| | Toluene | 2.4 | 0.38 | 0.37 | 1.3 | 0.0072 | 4 | 8.46 | 14 |
| | Xylenes | 1.2 | 0.17 | 0.011 | 0.53 | 0.002 | 1.9 | 3.81 | |
| | Styrene | 0.0013 | 0.00033 | 0.0013 | 0.018 | 0 | 0.029 | 0.05 | |
| ptegu | Ethylbenz | 0.6 | 0.084 | 0.01 | 0.32 | 0.001 | 0.99 | 2.01 | |
| | Toluene | 7 | 1 | 0 | 47 | 2 | 49 | 105.8 | 189 |
| | Xylenes | 2.1 | 0.96 | 0.096 | 33 | 1.5 | 32 | 69.66 | |
| | Styrene | 0.011 | 0.0073 | 0 | 0.23 | 0.052 | 0.0091 | 0.31 | |
| pt_oilgas | Ethylbenz | 0.61 | 0.076 | 0.054 | 6.3 | 0.54 | 5.2 | 12.78 | |
| | Toluene | 56 | 139 | 183 | 213 | 53 | 97 | 741 | **2,544** |
| | Xylenes | 92 | 87 | 160 | 52 | 43 | 126 | 560 | |
| | Styrene | 26 | 53 | 134 | 462 | 39 | 398 | 1,112 | |
| **ptnonipm** | Ethylbenz | 13 | 21 | 29 | 15 | 16 | 37 | 131 | |
| | Toluene | 0 | 0 | 0 | 0 | 0 | 2,605 | 2,605 | **6,377** |
| | Xylenes | 0 | 0 | 0 | 0 | 0 | 3,229 | 3,229 | |
| | Styrene | 0 | 0 | 0 | 0 | 0 | 2 | 2 | |
| **np_oilgas** | Ethylbenz | 0 | 0 | 0 | 0 | 0 | 541 | 541 | |
| State Total | | 201 | 302 | 507 | **831** | 155 | **7128** | 9124 | 9124 |

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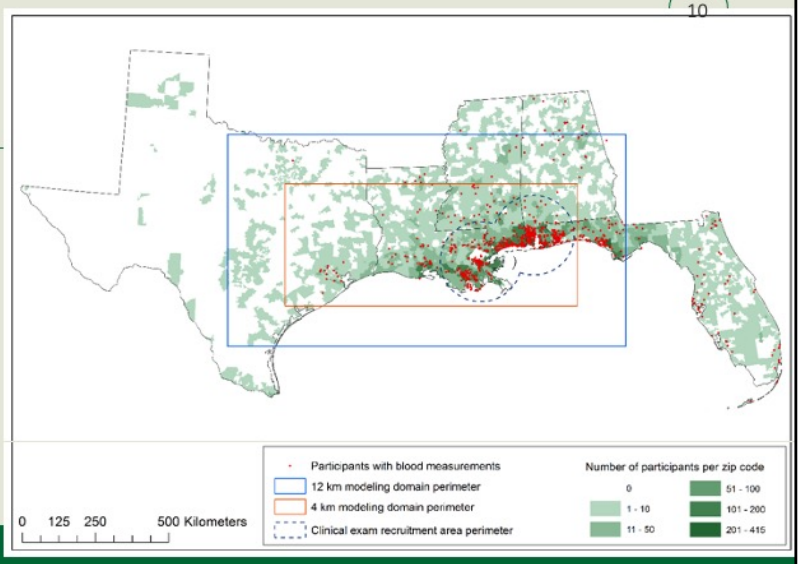
1. After we checked the annual emission report, there is no missing HAPs in nonpt sector.
2. Np_oilgas has largest missing HAPs (6377 ton/year), ptnonipm is the second largest missing (2544 ton/year). The np_oilgas missing happened in TX.
3. TX has largest missing 7123 ton/year.
4. We made the missing emission inventory by county and SCC. We used SMOKE to generate the adjust emission for RTRAC process usage.

## The CTM model

- CTM model : CAMx 7.0
- Period : 2012 May to Sep
- Met data: from USEPA, post processed by WRFCAMx and MCIP.
- Model domain: 12kmx12km flexi-nest to 4kmx4km
- Chemical mechanism: CB6r4




1. The CTM model is CAMx7.0
2. Simulation period, this time period is the same as TCEQ ozone SIP model
3. Met data:  All met data are from EPA
4. Model domain: 12KM resolution in blue rectangle  4Km resolution in red rectangle

# Reactive Tracer

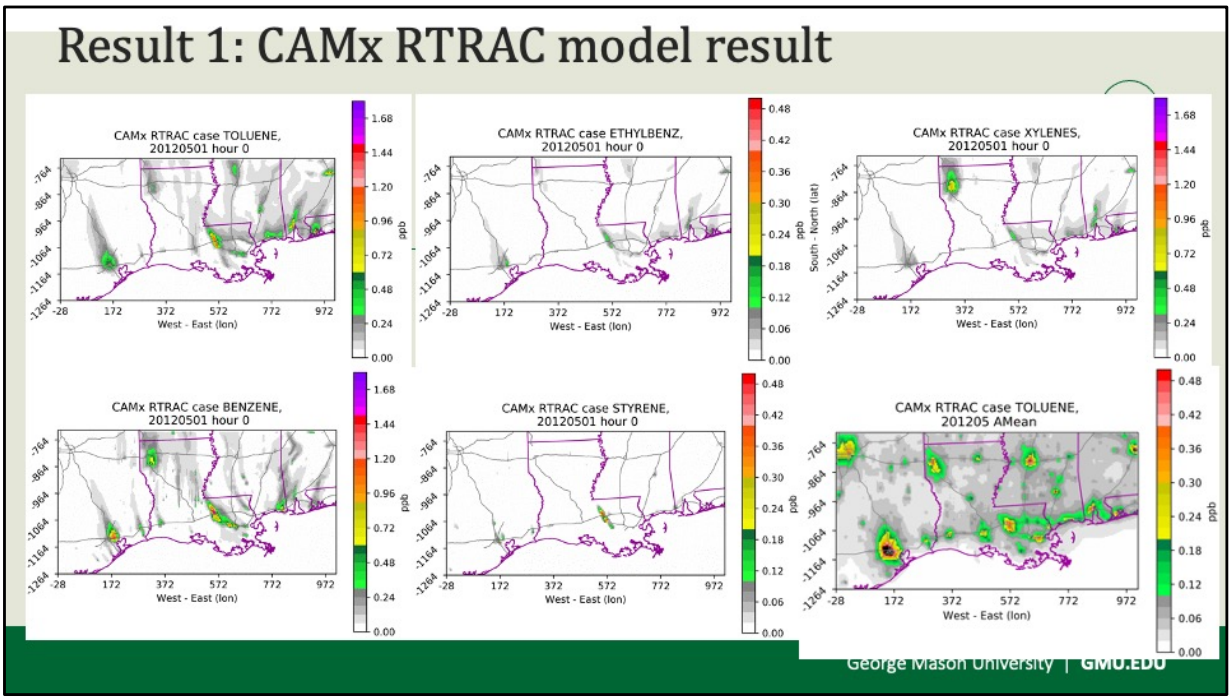
11

The tracer species simulation process considering chemical decay

**A + B --> X + Y $K_{298}$ Reaction Rate =[A][B]K**

| Reactants from SMOKE emission model | | Oxidizing agent from base model | Rate constant From Master Chemical Mechanism 3.3.1 |
|---|---|---|---|
| BENZENE | | | $K_{BENZENE, OH} = 2.3x10^{-12}$ EXP(-190/TEMP) |
| TOLUENE | | | $K_{TOLUENE, OH} = 1.8x10^{-12}$EXP(340/TEMP) |
| XYLENES | + | OH<br>Ozone<br>$NO_3$ | $K_{XYLENES, OH} = 1.36x10^{-11}$<br>$K_{XYLENES, NO3} = 4.1x10^{-16}$ |
| STYRENE | | | $K_{STYRENE, OH} = 5.8x10^{-11}$<br>$K_{STYRENE, NO3} = 1.5x10^{-12}$<br>$K_{STYRENE, O3} = 1.7x10^{-17}$ |
| ETHYLBENZ | | | $K_{ETHYLBENZ, OH} = 7x10^{-12}$<br>$K_{ETHYLBENZENE, NO3} = 1.2x10^{-16}$ |

1. The reactive Tracer is a method to simulate the tracer concentration with Chemical decay.
2. A+B are reactants, x+y are products, K is rate constant, the Chemical decay rate is [A][B]*K
3. The Reactants are from the SMOKE output.
4. The oxidants are from base model simulation.
5. The Rate constants are considered the MCM mechanism
6. The chemical reaction rate are used to calculate the HAPS chemical decay rate.
7. The Henry's law constants of HAPs are also considered for deposition process.




1. The RTRAC method generated the hourly concentration. The hourly plume direction pattern are affected by he wind direction, wind speed, PBL height and chemistry process effects.
2. Because the XYLENE and STYRENE have higher rate constant than B T E , the chemical decay of XYLENE and STYRENE are faster than others. The Styrene impact range is more local.
3. Those hourly data can be used to calculate the monthly average or diurnal pattern.

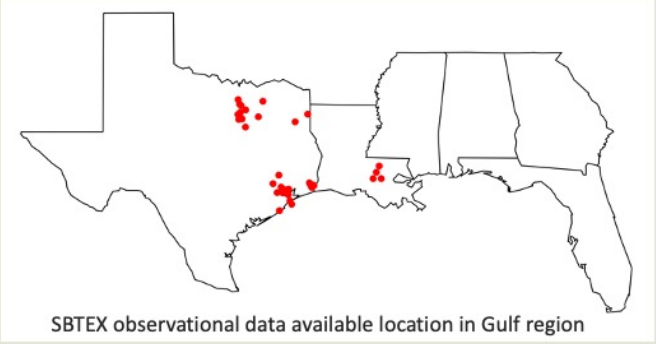
# The AMTIC observational data

https://www.epa.gov/amtic

13

## Ambient Monitoring Technology Information Center (USEPA)

1. The available data sites in 2012 and detect method by canister and GC-MS/FID,
2. The sample durations are 1 hour (TX), 3 hours (LA), or 24 hours (TX and LA)



SBTEX observational data available location in Gulf region

1. M/P Xylene
2. O Xylene
3. Toluene
4. Styrene
5. Ethylbenzene
6. Benzene

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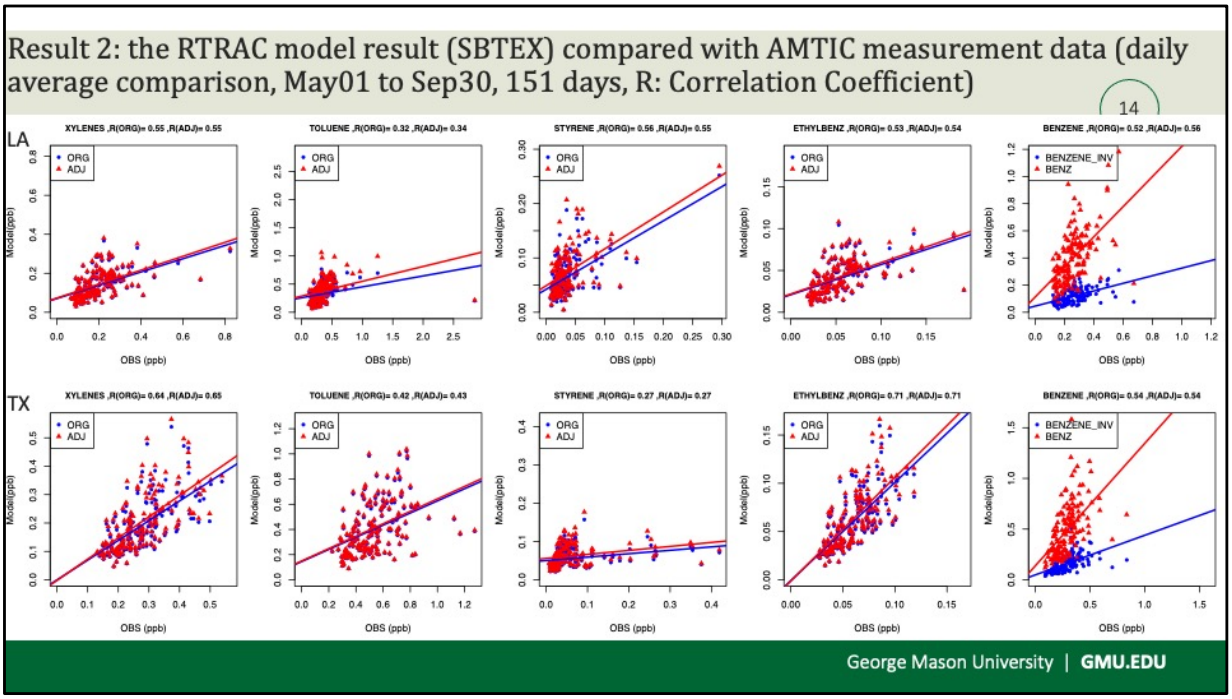
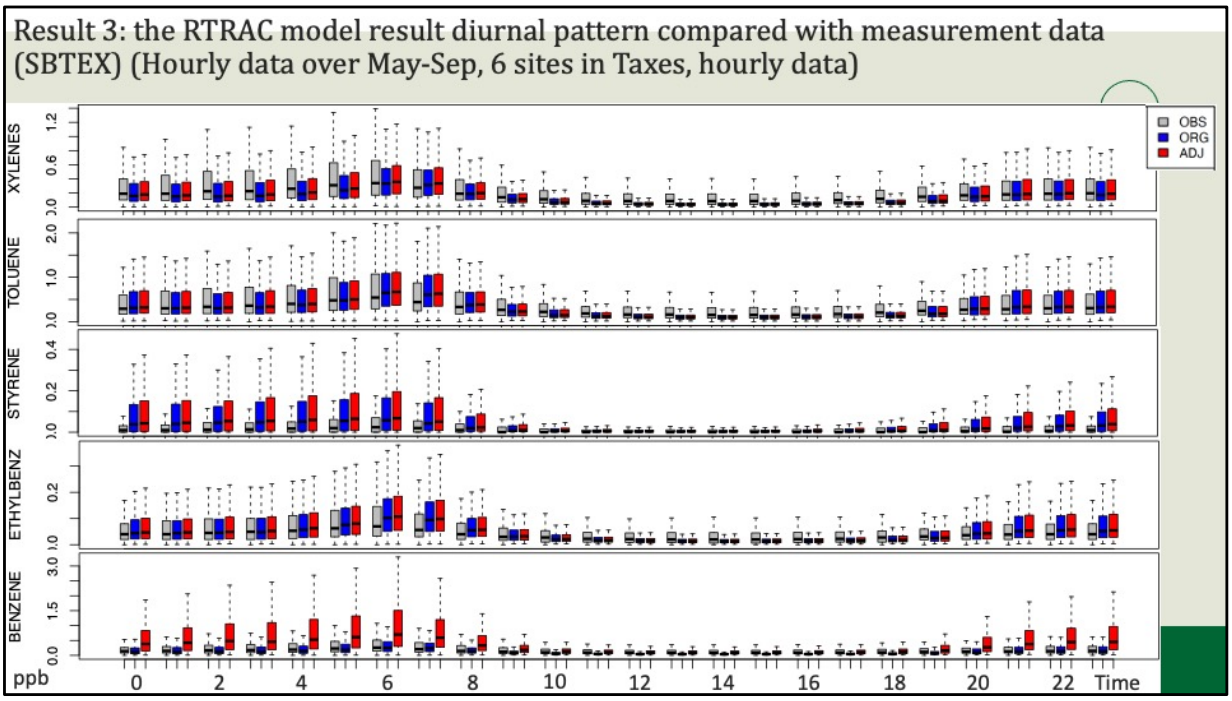
1. The AMTIC website has the HAPs measurement data, more than 50 different HAPs species data are available.
2. There are about 42 sites in TX and 4 sites in LA.
3. The sample durations are 1 hour (TX), 3 hours (LA), or 24 hours (TX and LA)
4. We apply those measurement data to verify our model RTRAC result.




1. These figures are the daily average comparison figures, the upper panels are LA ,and the lower panels are TX, Columns are for each SBTEX species.
2. The X axis is observational data, Y is model result.
3. The ORG is original emission inventory, the ADJ is the emission inventory after do the gap filled for the missing HAPS.
4. The ORG emission and ADJ emission of STEX don't show a lot difference. Benzene is overestimate when consider the Benzene is BENZ.
5. Xylenes and Ethylbenzene have better results.
6. Styrene is overestimate at the low concentration but underestimate at high concentration.




1. This the hourly data are from 6 sites in TX compared with model result at same grid cell.
2. The X-axis is Local time. The Y- axis is ppb
3. For Xylene, Toluene and Ethylbenzene, the outcomes are close at night.
4. The Styrene may over-estimate in the model.
5. The Benzene ORG is underestimate, but when we adjust it to the model species BENZ, it become over-estimate.

16

## Preliminary Results and Future plan

- The USEPA NEI data for SBTEX emission have some missing data for some SCC& county, but can be estimated by the ratio of individual HAPS and the total VOC.
- The AMTIC data compared with the model result are not excellent but close.
- The daily average results are good for xylenes, toluene, and ethylbenzene. The Styrene are overestimate at low concentration but underestimate at high concentration. Benzene are overestimate when Benz.
- There is no perfect way to estimate the real SBTEX concentration pattern, but this study shows a method to generate high resolution data that can be verified by observational data and support public health exposure study.
- Data fusion (Bayesian Maximum Entropy, BME) will be used to correct the error and develop high-resolution ambient concentration map of SBTEX over modeling domain

## Acknowledgement

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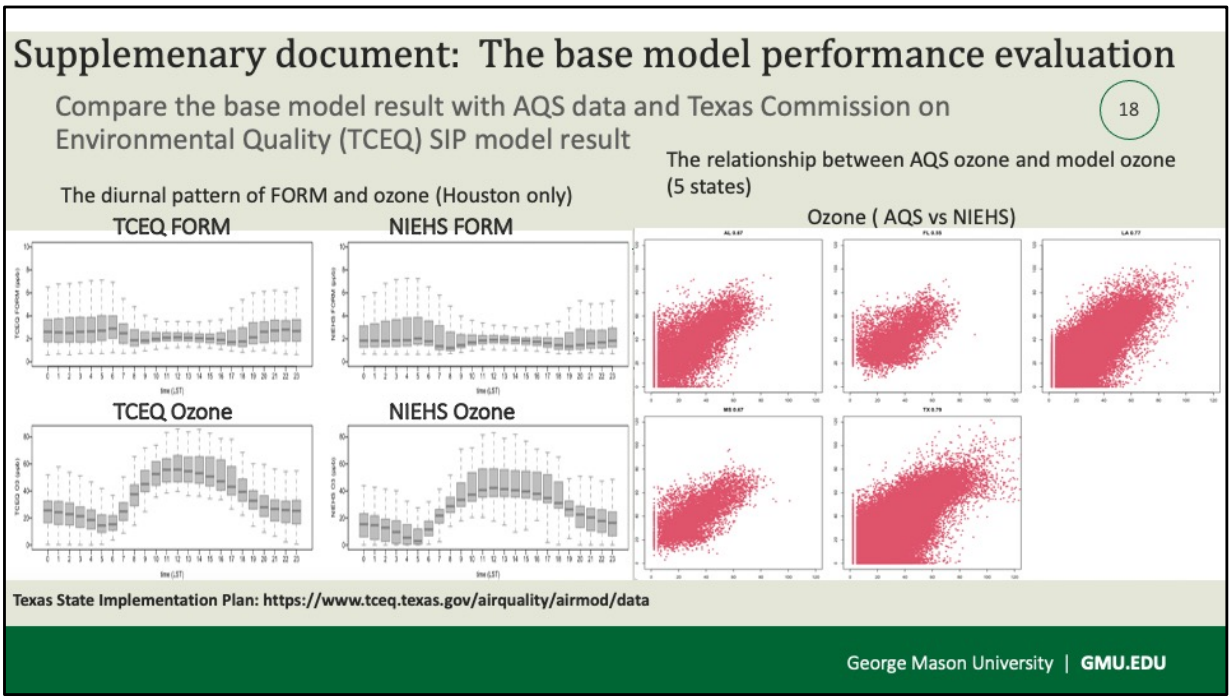
- Department of Marine, Earth, and Atmospheric Science, North Carolina State University
- Ramboll: CAMx model support
- Taxes Commission on environment Quality (TCEQ) : TCEQ SIP model output data
- California South Coast Air Quality Management District (SCAQMD): RTRAC method support.




1. The left-hand side is diurnal pattern comparison for TCEQ model data. FORM and Ozone. The Max ozone and the day / night FORM concentration are close.
2. The right-hand side is the comparison for AQS ozone and NIEHS ozone.
3. Those comparison indication that our base model output is in reasonable range and can be used to do RTRAC calculation.