Effects of Temperature on Gasoline Exhaust VOC speciation

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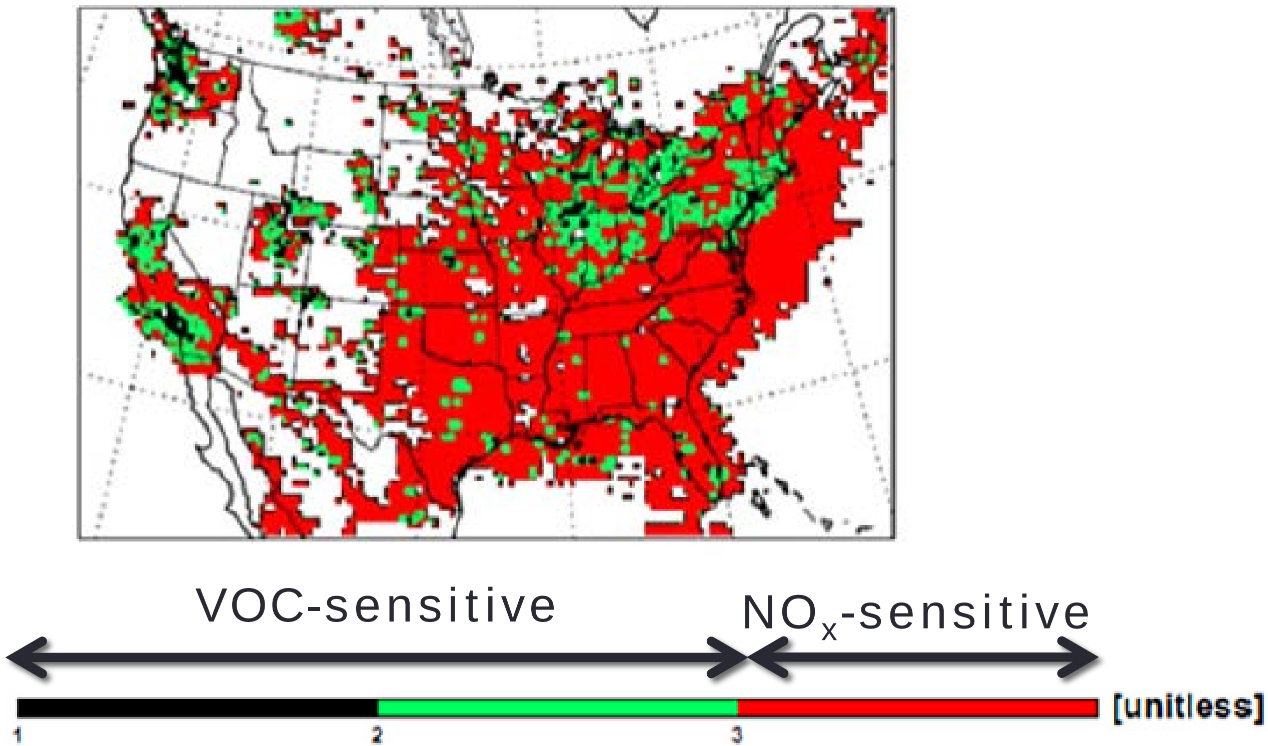
The VOC ozone problem

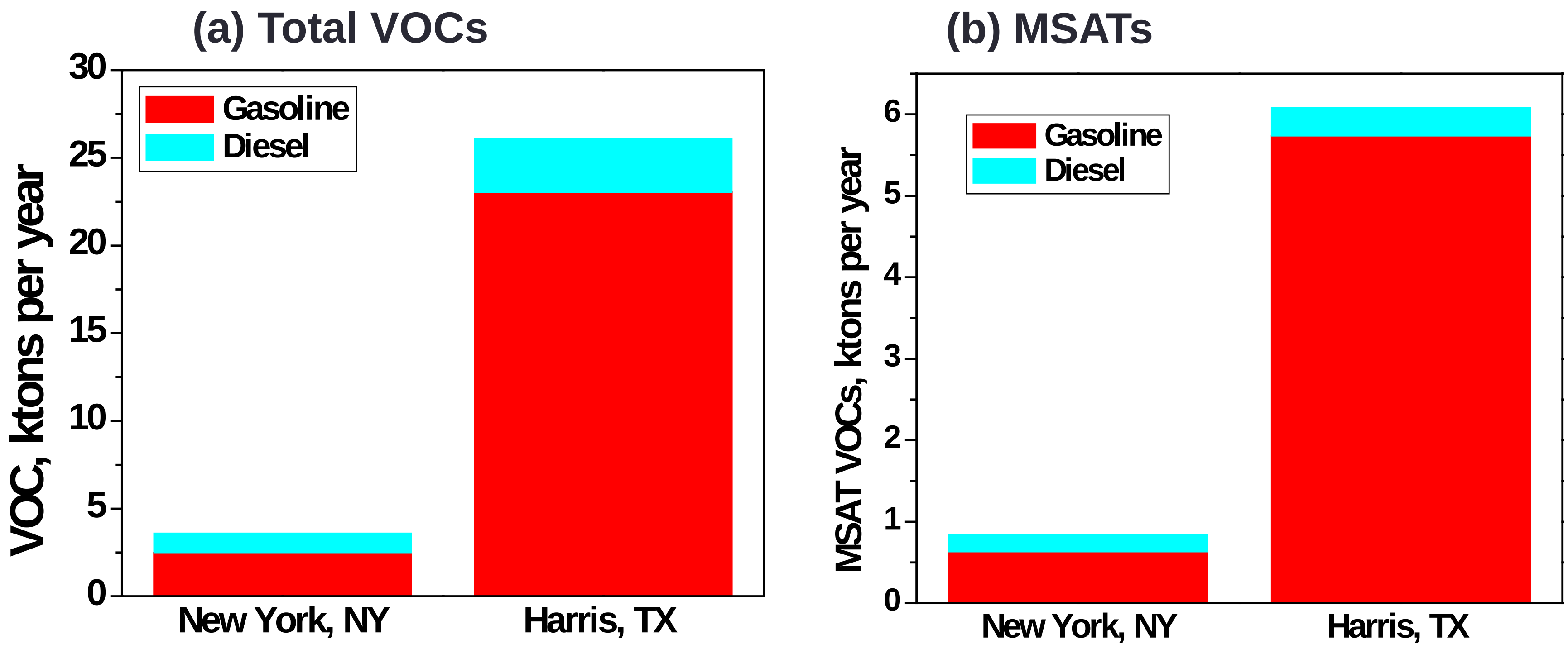
What drives ozone?



- VOC major contributor to ozone in urban regions, which are NO_x-saturated i.e. VOC sensitive.

Choi et al., 2012

Motor Vehicle VOC emissions

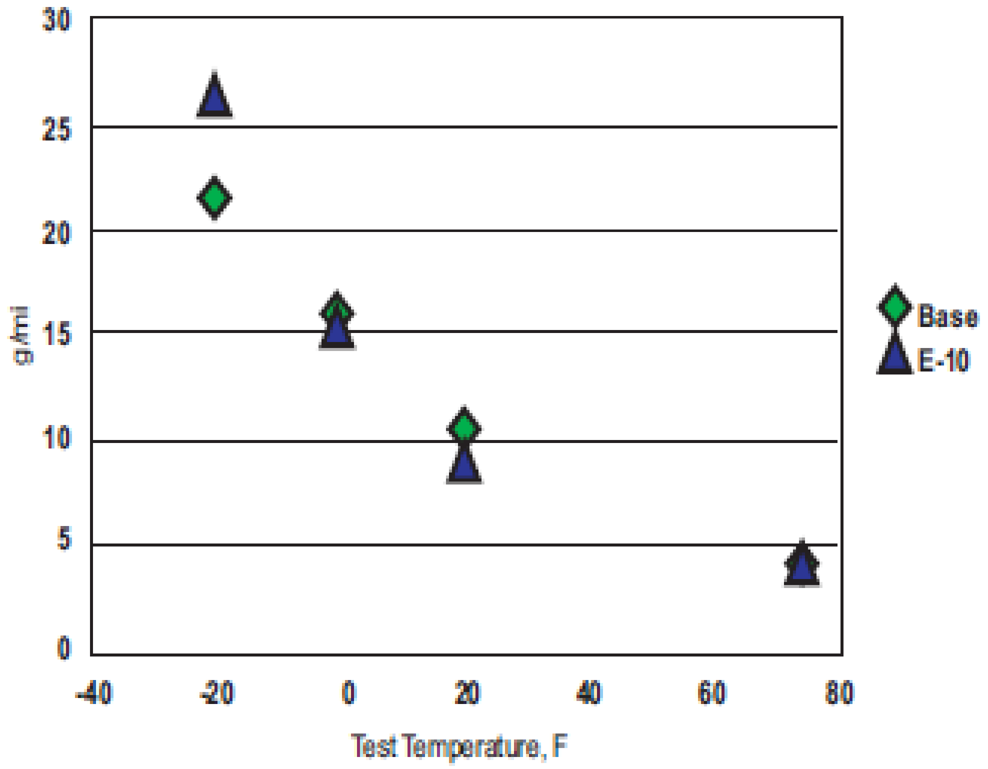


- Two urban counties – New York (NYC-Manhattan) and Harris (Houston)
- Major contributor to urban VOC emissions.
- Gasoline VOCs- comprise of **M**obile **S**ource **A**ir **T**oxics (**MSAT**s)
- Gasoline dominates the split for both emission cases.

USEPA NEI, 2011

Temperature dependence of VOC emissions

Total hydrocarbons vs. T



Temperature ↑ → **Catalytic efficiency** ↑ → **Emissions** ↓

***Stump et al*.**

Motivation for current work

- Previous studies focused on total hydrocarbons and MSATS at different temperatures.
- Little quantification of uncertainty in emission factors
- No comprehensive evaluation of speciation profiles - imperative for air quality modeling.
- This work intends to build on previous work to develop comprehensive temperature dependent speciation profiles.

Key questions

- How do the speciation profiles for gasoline exhaust vary under temperature?
- What is the uncertainty in the emission factors for species classes?
- How does the MSAT content (both species and total) in VOCs vary with temperature?
- What implications do the results have for air quality modeling?

Vehicle fleet

Name	Year	Technology	Standard	Mileage	Configuration
Buick Lucerne	**2010**	**MPFI**	**Tier 2/Bin 4**	**22000**	**3.9L V-6**
Honda Accord	**2010**	**MPFI**	**Tier 2/Bin 5**	**24000**	**2.4L I-4**
Jeep Patriot	**2010**	**MPFI**	**Tier 2/Bin 5**	**22000**	**2.0L I-4**
Kia Forte EX	**2010**	**MPFI**	**Tier 2/Bin 5**	**25000**	**2.0L I-4**
Mazda 6	**2010**	**MPFI**	**Tier 2/Bin 5**	**24000**	**2.5L I-4**
Mitsubishi Galant	**2010**	**MPFI**	**Tier 2/Bin 5**	**38000**	**2.4L I-4**

Temperatures

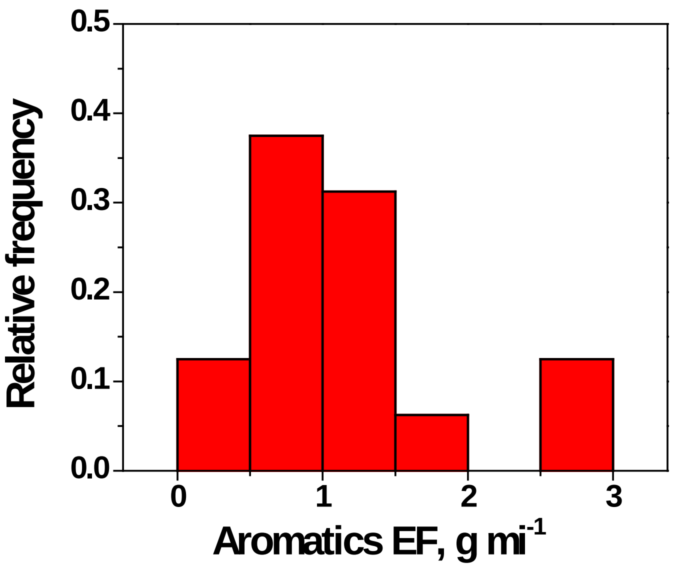
- 0 ^{o}F
- 20^{o}F
- 75^{o}F

- Driving conditions
  - FTP (urban conditions)
  - US-06 (aggressive highway)

Additional details

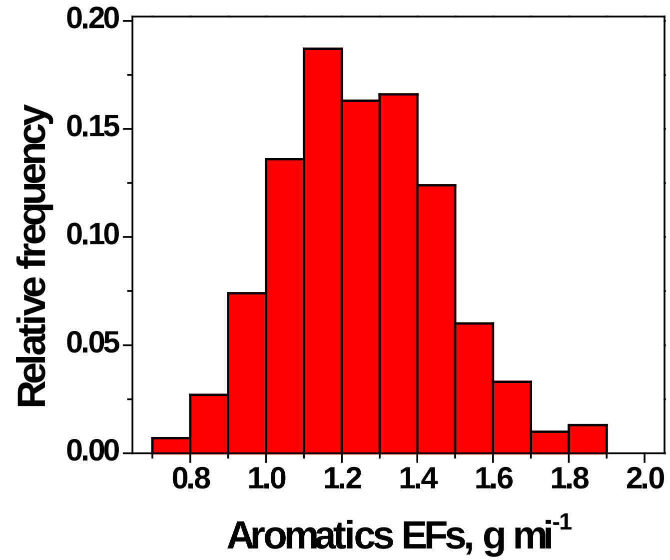
- Testing done at the USEPA's OTAQ premises.
- All vehicles used 10% ethanol by volume.
- 160 compounds, grouped into following species classes
  - Aromatics
  - Alkanes
  - Cyclic Alkanes
  - Alkenes
  - Alkynes
  - Ethers
  - Aldehydes
  - Ketones
- Methane evaluated separately
- FTP – 3 phases: Cold Start, Running and Hot Start.
- Cold Start evaluated separately

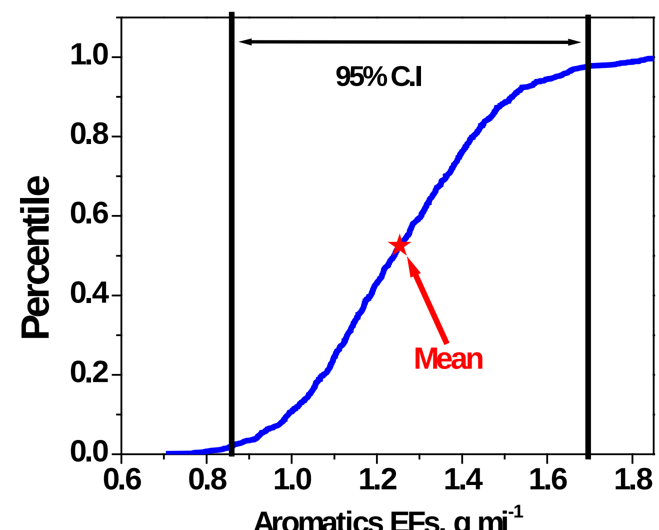
Bootstrap Method



Draw Sample
Calculate Mean

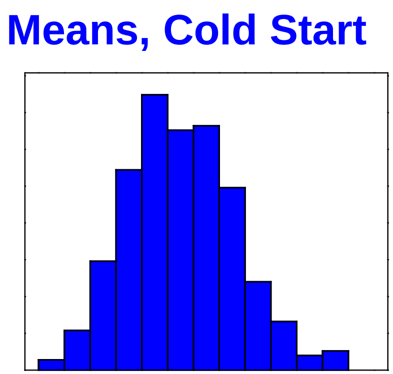
Repeat 1000 times

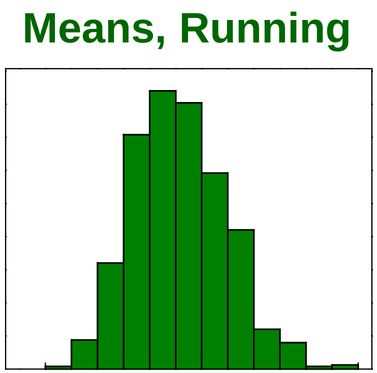


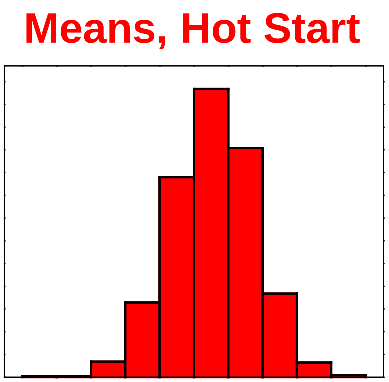


- Example with FTP Cold Start at 0°F.
- Distribution of means from random sampling.
- Uncertainty shown by 95% confidence interval.

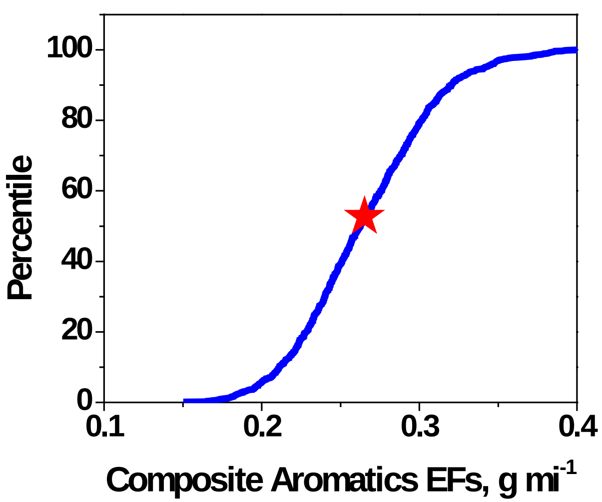
FTP Composite Emissions: Monte Carlo method



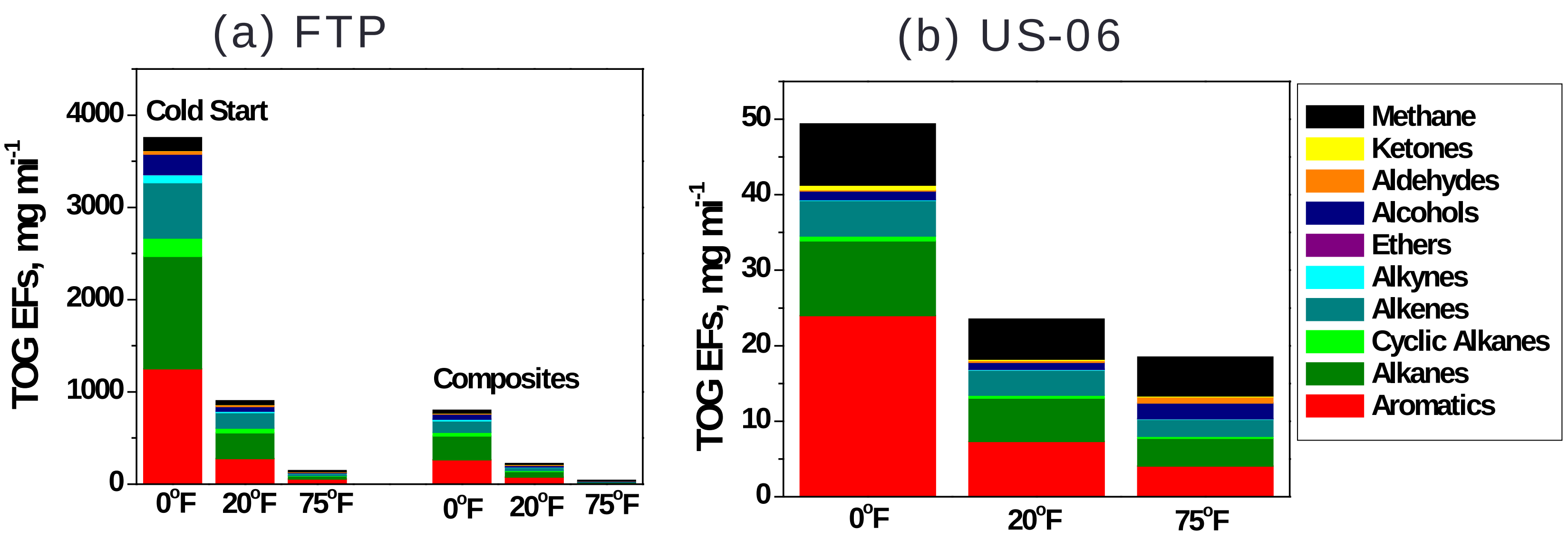




0.43*Cold Start+Running+0.57*Hot Start



Temperature dependence of mean emission factors



- Significant decrease with temperature due to increasing catalyst efficiency.
- US-06 emissions significantly lower than FTP-Composite.

Uncertainty in mean emission factors

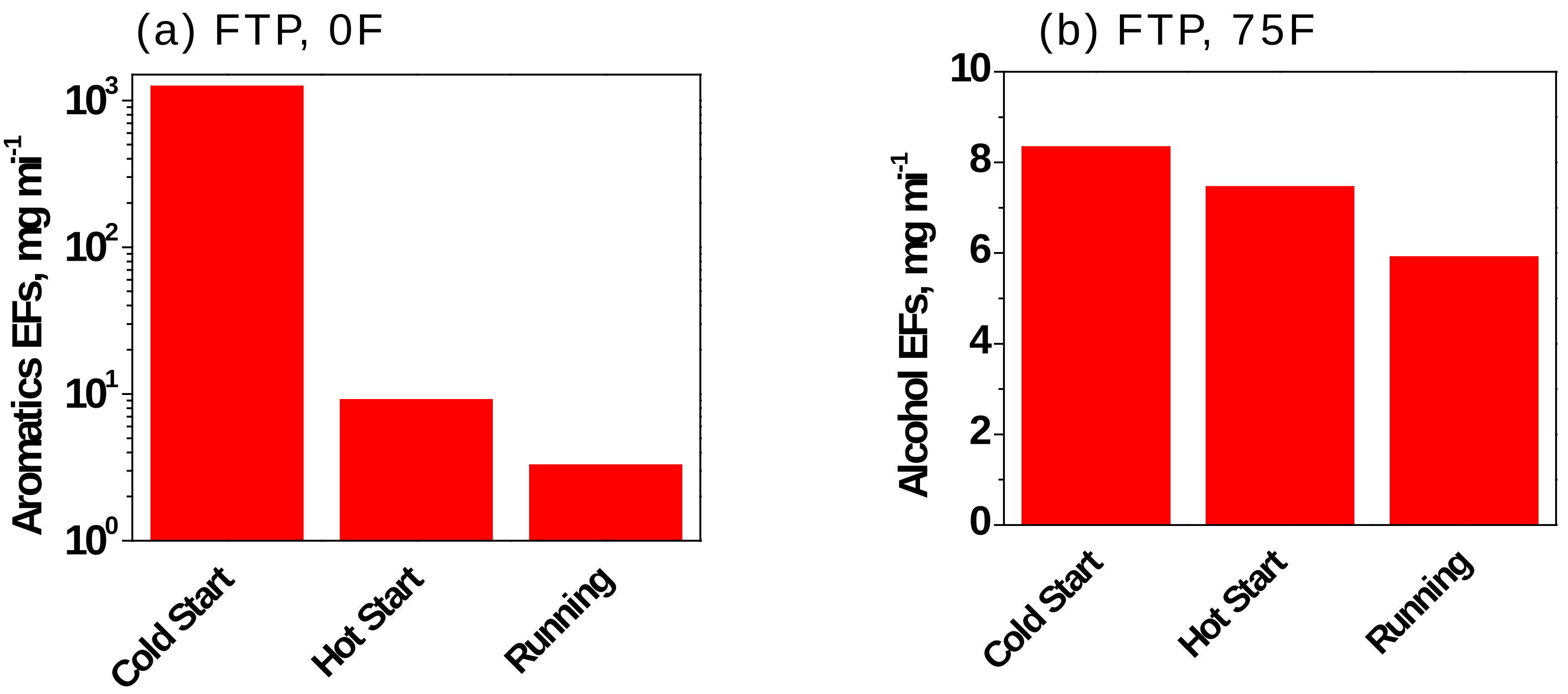
	0 ºF	20 ºF	75 ºF
Aromatics	265 (188-356)	51 (76-99)	12 (9-15)
Alkanes	256 (189-317)	61 (46-74)	8 (7-10)
Cyclic Alkanes	41 (25-59)	11 (7-14)	1.1 (0.8-1.3)
Alkenes	125 (100-150)	36 (26-46)	5 (4-6)
Alkynes	19 (14-24)	3.3 (2.3-4.3)	0.4 (0.2-0.6)
Alcohols	54 (39-69)	**18 (10-28)**	7 (2-13)
Aldehydes	9 (8-11)	7 (6-8)	3 (4-11)
Ketones	1.2 (1-1.3)	1.7 (1-2.5)	0.6 (0.5-0.7)
Methane	34 (29-39)	12 (9-14)	5 (3-7)

- Example with FTP composite emissions, units in mg mi^{-1}.
- Broadly factor of 2, uncertainty.

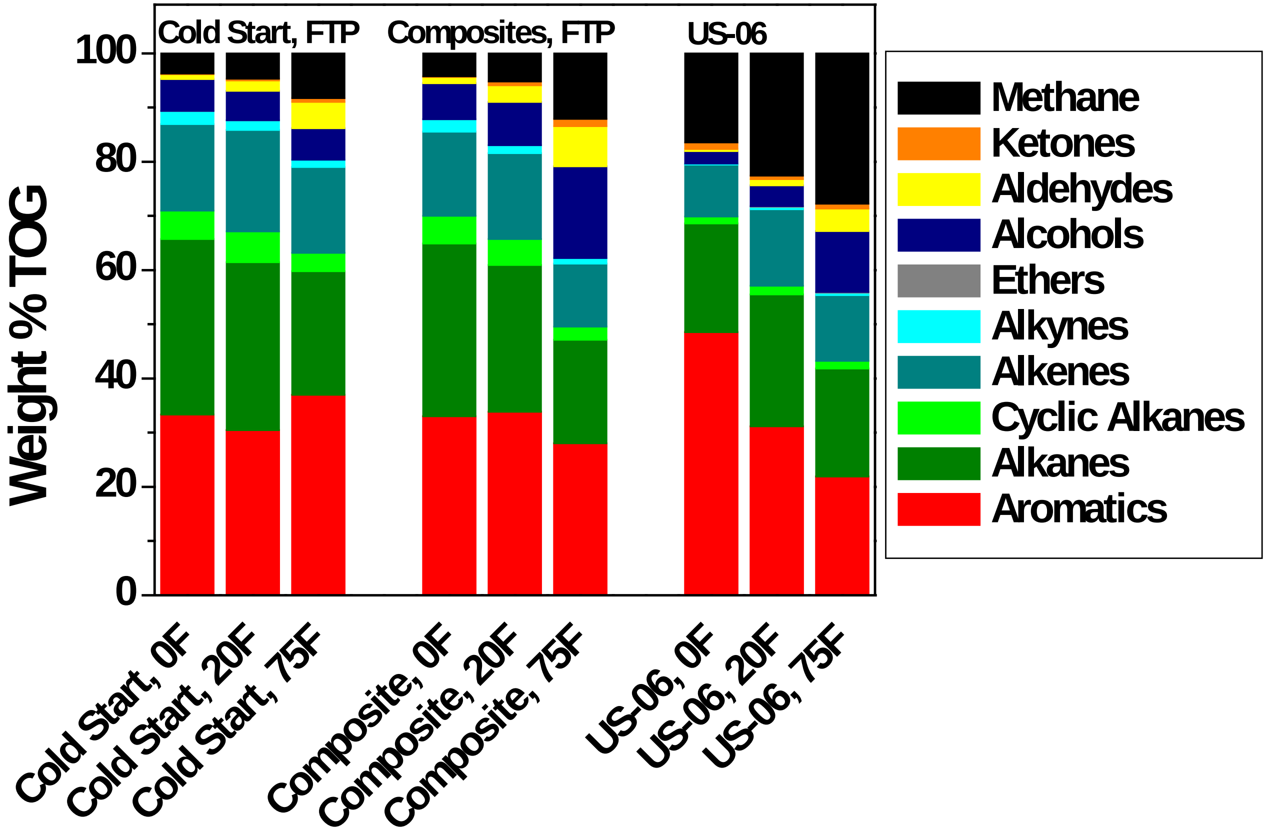
What influences composite emissions?

- Two scenarios:
- **CASE 1 :** Cold Start dominates by orders of magnitude.
- ***Applicable to most hydrocarbons at all temperatures*.**

- CASE 2: Hot Start and Running comparable to Cold Start.
- ***Applicable to all oxygenates - alcohols, aldehydes and ketones.***

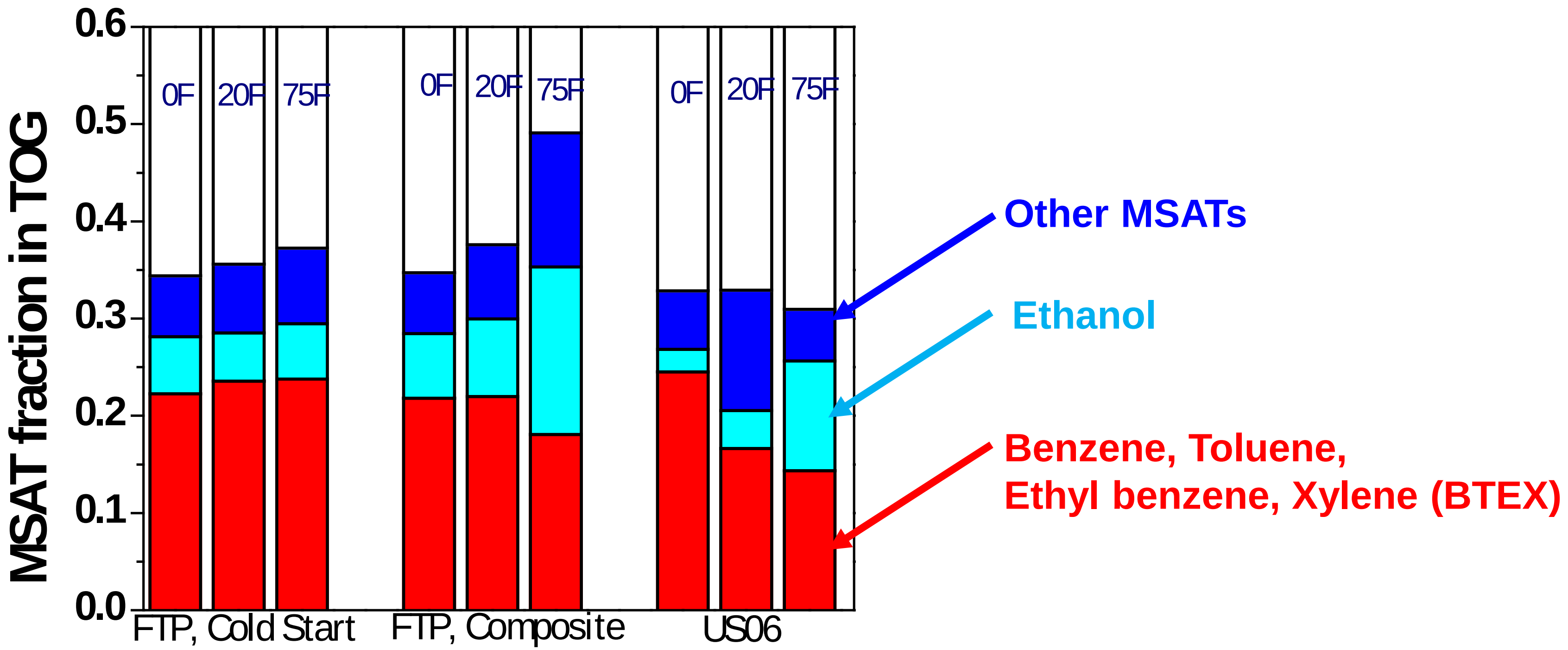


Speciation profiles



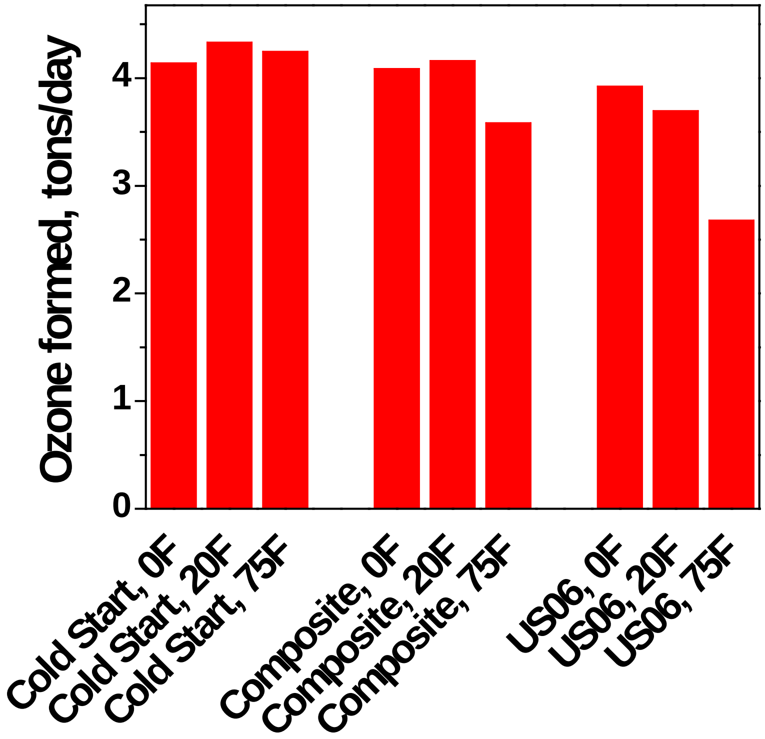
- Significant increases seen in speciation for alcohols, aldehydes and methane.
- Alkanes show definitive decrease with temperature for both Cold Start and composite phases of the FTP cycle.
- Aromatics significantly fall with temperature for the US-06 cycle.

MSAT fraction in TOG profile



- Three distinct patterns.
- FTP, Cold Start – MSAT fraction increases marginally with temperature. Speciation constant.
- FTP, Composite – Substantial change in MSAT fraction and speciation.
- US06- MSAT fraction unchanged, substantial change in speciation.

Ozone forming potential: the Carter MIR scale



Ozone potential = VOC mass fraction x MIR x emission rate (1 ton/day)

- US-06: definitive changes with temperature, especially at 75ºF.
- Weaker trends for FTP-Composite profiles.
- Need detailed air quality modeling representing varying NO_x conditions to accurately understand the impacts.

http://www.cert.ucr.edu/~carter/emitdb/

Conclusions

- Significant difference in speciation across temperatures and driving conditions.
- Cold Start emissions were the dominant FTP phase for most hydrocarbons, greater by at least 2 order of magnitude than Running and Hot Start emissions .
- For alcohols and carbonyls, Cold Start, Running and Hot Start emissions were comparable.
- Three distinct patterns for MSAT fractions with temperature.

  Cold Start: Marginal change in MSAT fraction, speciation unchanged
  Composite : Significant change in MSAT fraction and speciation
  US06: Marginal change in MSAT fraction, significant for speciation

- Ozone forming potential decreased at 75^{o}F for Composite and US-06 profiles.

Future directions

- Speciation results will be available at the USEPA's SPECIATE database for the next version.
- Use these profiles to inform and update MOVES model to build motor vehicle emissions inventories.

Acknowledgements

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