Extension of the MOZART mechanism

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Motivation

- Include more species that are measured so as to more rigorously evaluate the model
- Take advantage of online MEGAN in CLM to include speciated terpenes needed for SOA
- More accurately represent lumped aromatics and alkanes
- Attempt to represent observed isoprene oxidation products and OH recycling

Speciated Terpenes
needed for SOA

Instead of C10H16 (lumped monoterpenes):

- APIN (alpha-pinene)
- BPIN (beta-pinene)
- LIMON (limonene)
- MYRC (myrcene)
- BCARY (C15H24 -> beta-caryophyllene)
- And some new intermediates (TERPROD1, TERP2O2, TERPROD2, TERP2OOH, NTERPO2)

MEGAN emissions

MEGAN-v2.1 incorporated in CLM, calculates biogenic emissions for 150 compounds

- APIN: a-pinene, d-3-carene, a-thujene
- BPIN: b-pinene, sabinene, camphene
- LIMON: limonene, a-phellandrene, g-terpinene, a-terpinene, b-phellandrene
- MYRC: myrcene, b-ocimene (cis and trans)
- BCARY: all sesquiterpenes (but b-caryophyllene has a remarkably fast O3 rate coefficient)

MBO

emitted from western forests, instead of isoprene
observed at Manitou Forest (BEACHON)

MBO -> C5H10O

MBOO2 -> C5H11O4

HMPROP -> C4H8O2

HMPROPO2 -> C4H7O4

MBOOOH -> C5H12O4

MBONO3O2 -> C5H10NO6

Aromatics

Original MOZART-4:
TOLUENE = lumped aromatic (Benzene + Toluene + Xylenes)
(some emissions files now call this 'AROMATICS')

Split for Colette's SOA scheme: BENZENE, TOLUENE, XYLENE
With very simplified chemistry - accounts only for loss of BENZENE, XYLENE;
Nothing done with BENNO3, XYLNO3 – thus loss of NOx from the model
BENZENE + OH -> BENO2
BENO2 + HO2 -> BENOOH
BENO2 + NO -> BENNO3
XYLENE + OH -> XYLO2
XYLO2 + HO2 -> XYLOOH
XYLO2 + NO -> XYLNO3

Updated Feb 2013 (to recycle NOx):
BENO2 + NO -> 0.9*GLYOXAL + 0.9*BIGALD + 0.9*NO2 + 0.9*HO2
XYLO2 + NO -> 0.62*BIGALD + 0.34*GLYOXAL + 0.54*CH3COCHO
+ 0.9*NO2 + 0.9*HO2

New Aromatic Species

Observations are available of Benzene, Toluene, Xylenes
Have different lifetimes so better to represent separately

BENZENE -> C6H6
PHENOL -> C6H6O
BEPOMUC -> C6H6O3
BENZO2 -> C6H7O5
PHENO2 -> C6H7O6
PHENO -> C6H7O5
PHENOOH -> C6H8O6
C6H5O2 -> C6H5O2
C6H5OOH -> C6H6O2
BENZOOH -> C6H8O5
BIGALD1 -> C4H4O2
BIGALD2 -> C5H6O2
BIGALD3 -> C5H6O2
BIGALD4 -> C6H8O2

MALO2 -> C4H3O4
CRESOL -> C7H8O
TEPOMUC -> C7H8O3
BZOO -> C7H7O2
BZOOH -> C7H8O2
BZALD -> C7H6O
ACBZO2 -> C7H5O3
DICARBO2 -> C5H5O4
MDIALO2 -> C4H5O4
XYLENES -> C8H10
XYLOL -> C8H10O
XYLOLO2 -> C8H11O6
XYLOLOOH -> C8H12O6
XYLENO2 -> C8H11O5
XYLENOOH -> C8H12O5

Split BIGALK

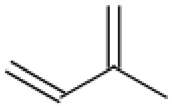
Goal: improved representation of oxidation products such as CH_3CHO and CH_3COCH_3

Plan to treat n-butane, isobutane, isopentane pseudo-explicitly, then have a lumped n-alkane of larger stuff (pentane, hexane...)

… in progress

Isoprene Oxidation

implementation of MIM2 by Martin Schultz



ISOP
(C_5H_8)

- new isoprene scheme has **78 C5 reactions**
  (old scheme had 21 C5 reactions)
- more detailed treatment of C4 and C3 products, too
- added epoxide formation and OH recycling from isoprene ROOH+OH (Paulot et al., 2012)
- Also, expansion of MVK and MACR oxidation

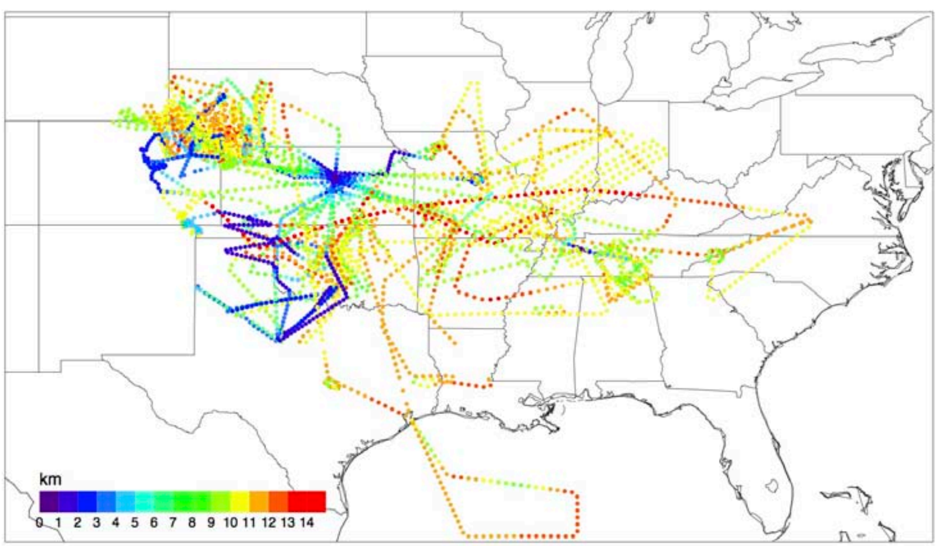
John Orlando & Geoff Tyndall are reviewing these updates
May be desired for particular studies, but not likely desired for standard simulations

Example of Emissions Evaluation

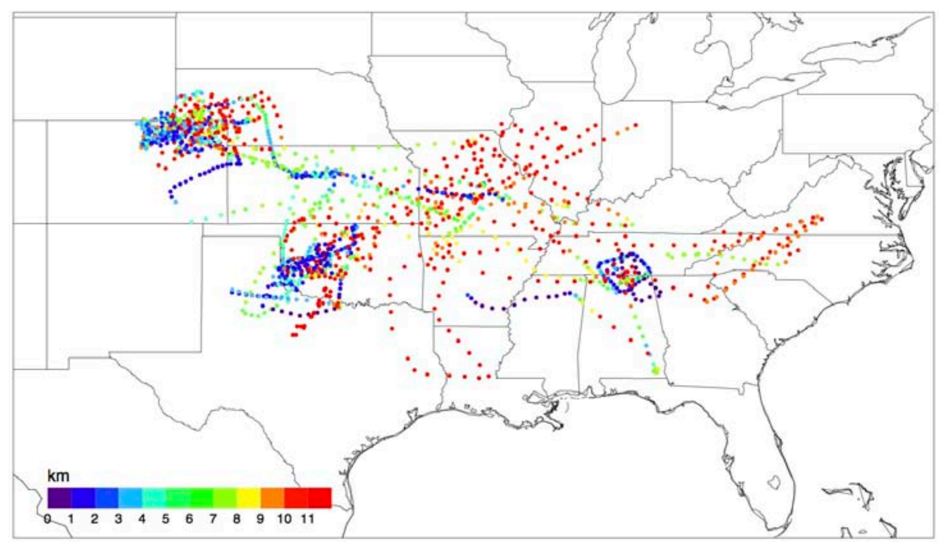
Observations during DC3 (Deep Convective Clouds and Chemistry, May-June 2012) and NASA/SEAC4RS (Aug-Sep 2013) show extensive evidence of emissions from oil & natural gas exploration in central US – indicated by specific ratios of alkanes:
i-pentane/n-pentane, i-butane/n-butane

To test the emissions inventories, these alkanes were added as tracers to MOZART-4 (reacted with OH, but ignored products)

DC3 GV flights



DC3 DC-8 flights



Alkane tracers in MOZART-4

MOZART-4 simulation of ethane, propane, butanes and pentanes using specified OH

Driven with GEOS-5 meteorology, 1.9°x2.5° horizontal resolution

Oil & gas extraction emissions estimated from EDGAR 4.2 methane inventory

Anthropogenic emissions from ACCMIP

Fire emissions from FINN

Reaction	Reaction rate	Rate at 298K	Lifetime (days)
C2H6 + OH	8.70E-12 exp(-1070/T)	2.40E-13	48
C3H8 + OH	1.00E-11 exp(-665/T)	1.07E-12	11
n-C4H10 + OH	1.40E-11 exp(-520/T)	2.45E-12	4.7
i-C4H10 + OH	7.00E-12 exp(-350/T)	2.16E-12	5.4
n-C5H12 + OH	1.81E-11 exp(-452/T)	3.97E-12	2.9
i-C5H12 + OH	1.01E-11 exp(-296/T)	3.74E-12	3.1

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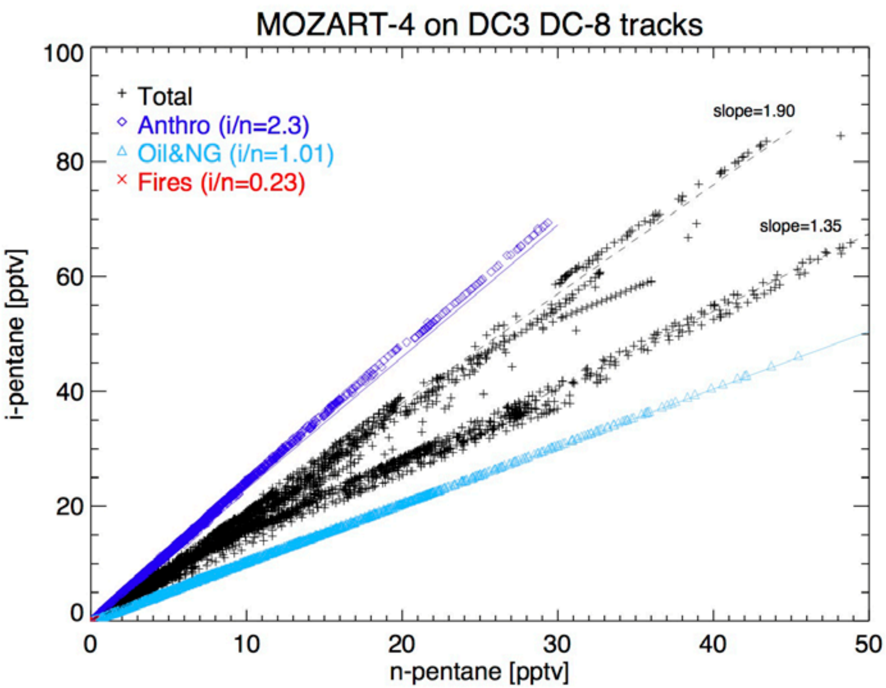
i-pentane vs n-pentane for all DC3 DC-8 flights

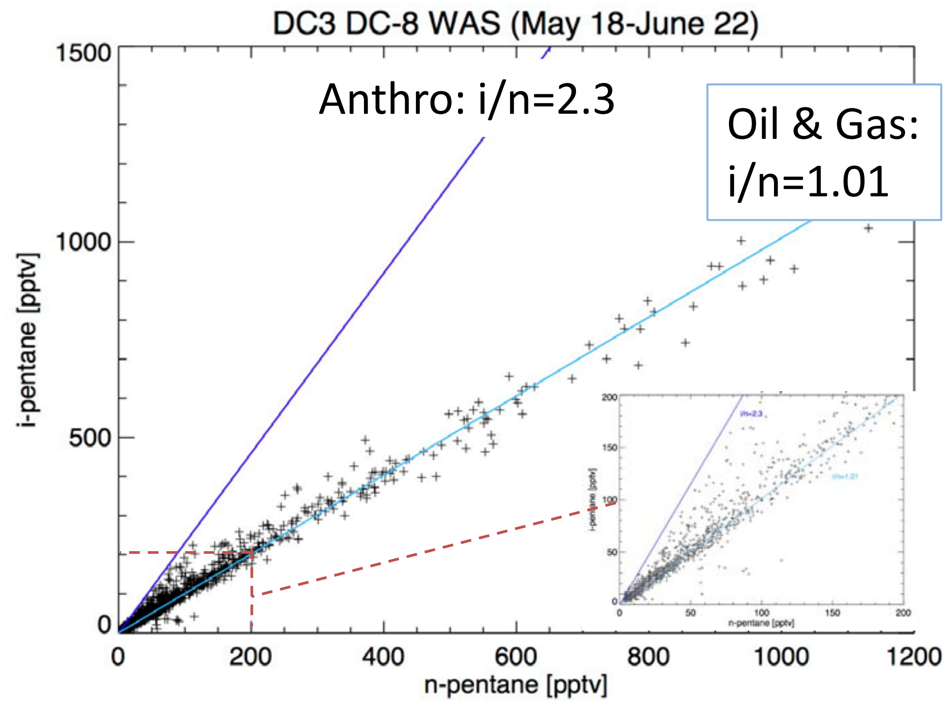
MOZART interpolated to the flight tracks



Model shows 2 groupings of data – slightly different mixtures of anthropogenic and oil-gas

Mixing ratios much lower than observations

Observations from WAS-merge



WAS data shows that the highest mixing ratios are from oil-gas sources

Lower mixing ratios have some anthro. signature

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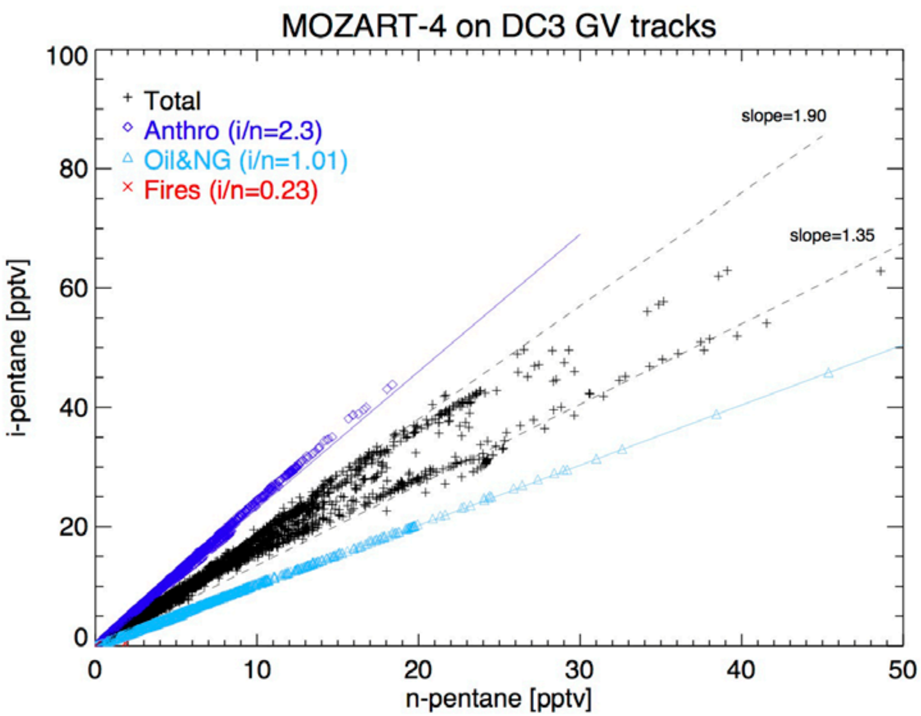
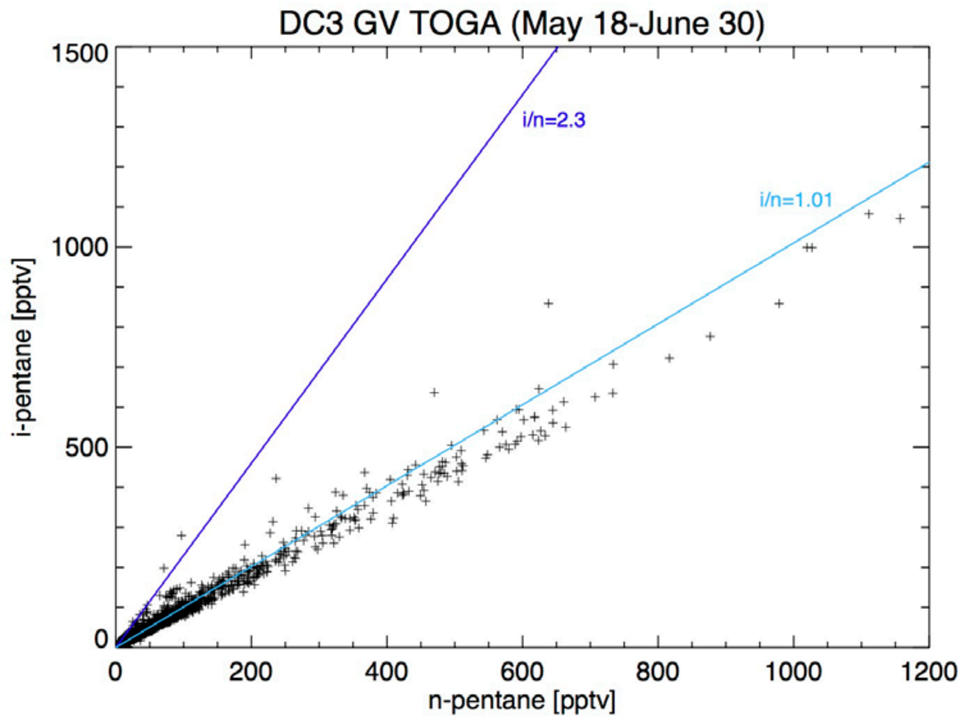
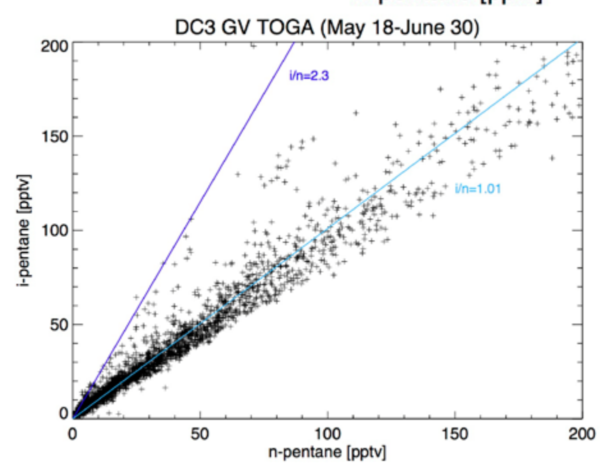
i-pentane vs n-pentane for all DC3 G-V flights

MOZART interpolated to the flight tracks

Observations from TOGA-merge (R4)







GV data have higher proportion of observations at high altitude

Primary signature from oil-gas even at low mixing ratios

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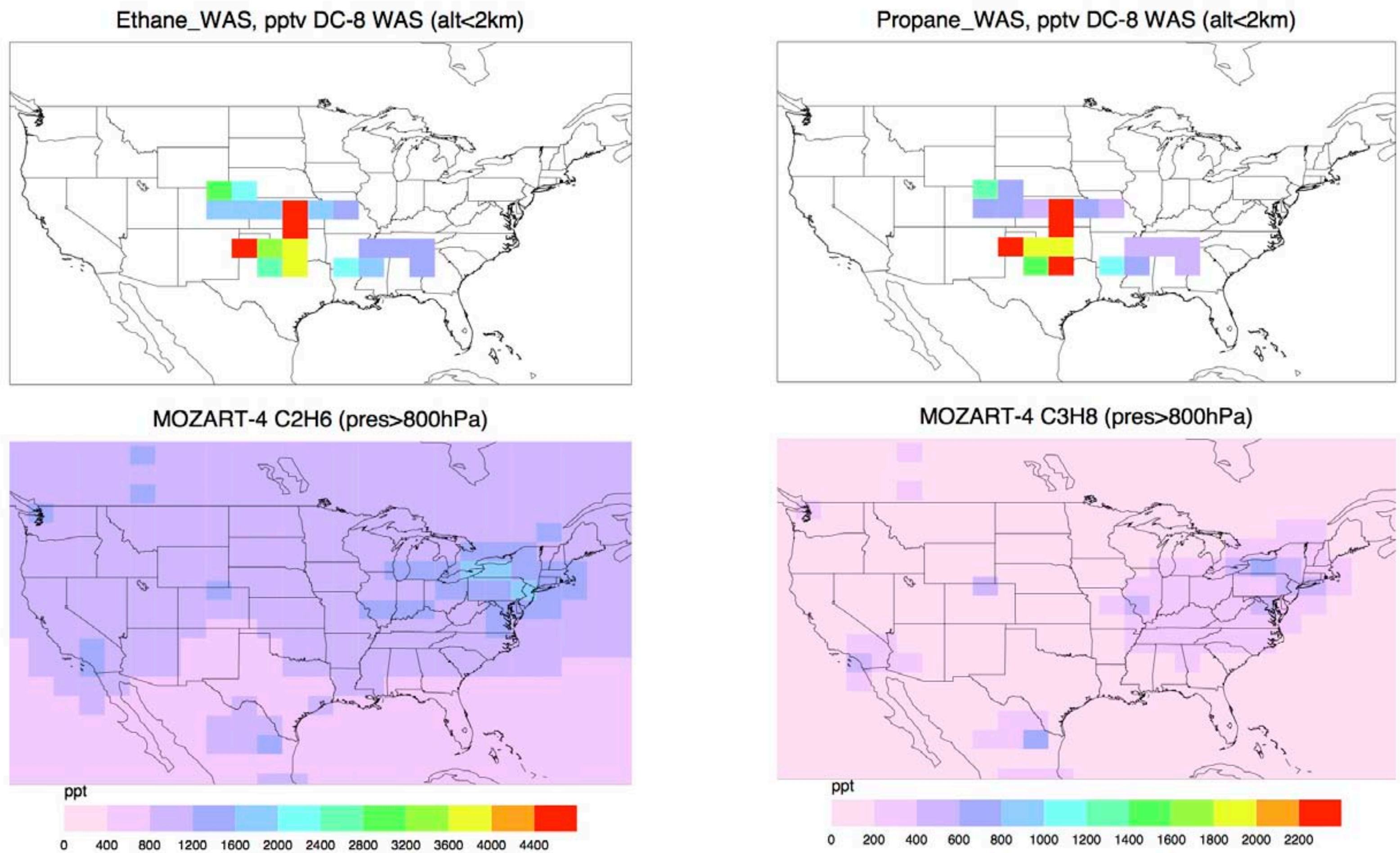
Model evaluation for Boundary Layer

DC-8 WAS observations averaged to model grid – all flights, for altitudes < 2km
Model monthly mean for June averaged over altitudes below 800 hPa

→ **Model is clearly missing sources in Texas-Oklahoma-Kansas**

→ **Ethane and propane come from many sources, but the coincident i-/n- pentane ratios indicate O&NG sources are missing**



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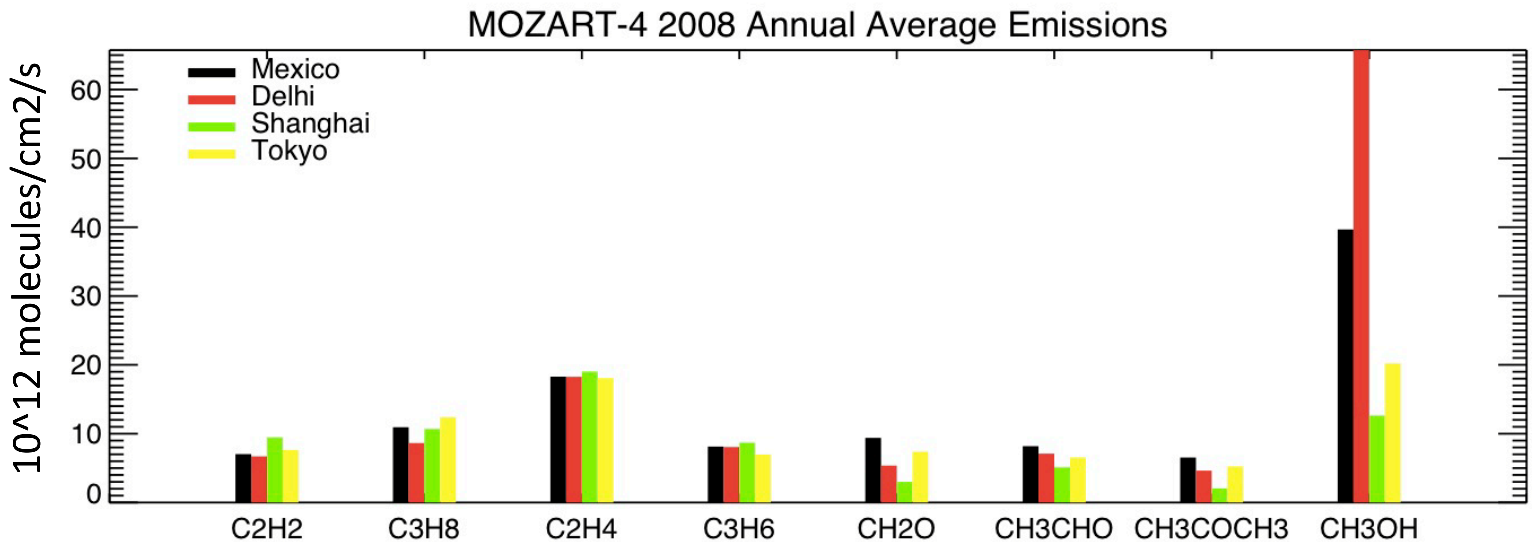
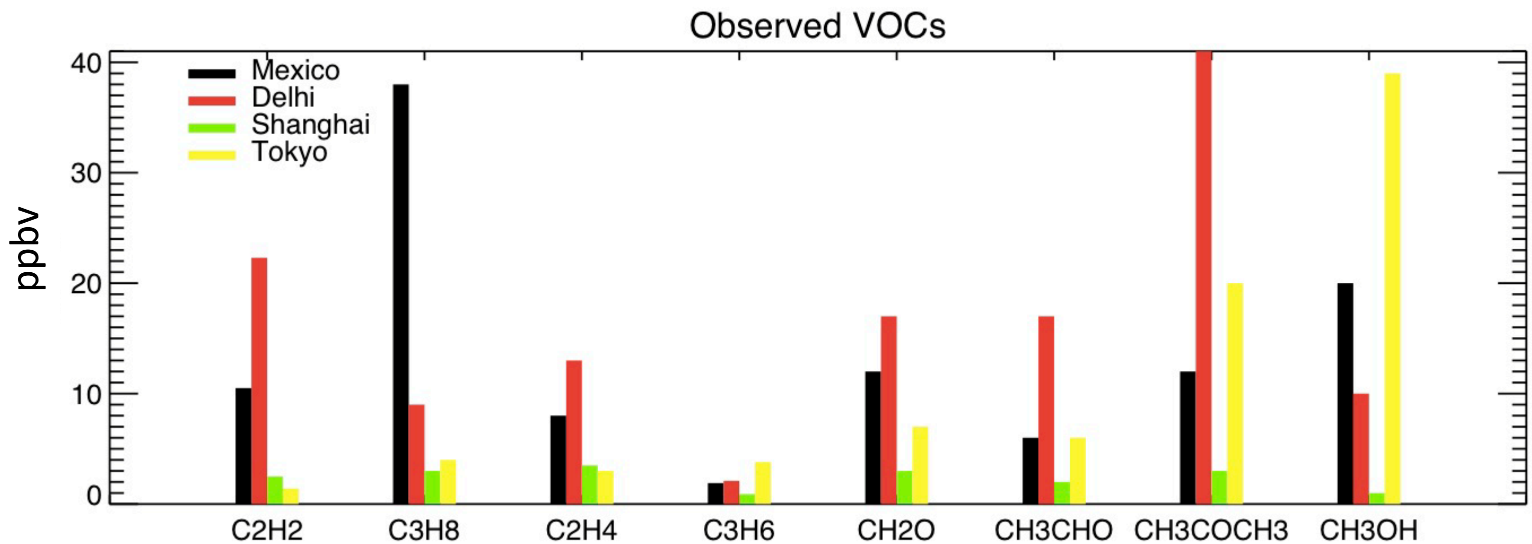
Emissions VOC profiles for various cities –

Emissions inventory speciation does not show the differences between cities that is seen in the observations





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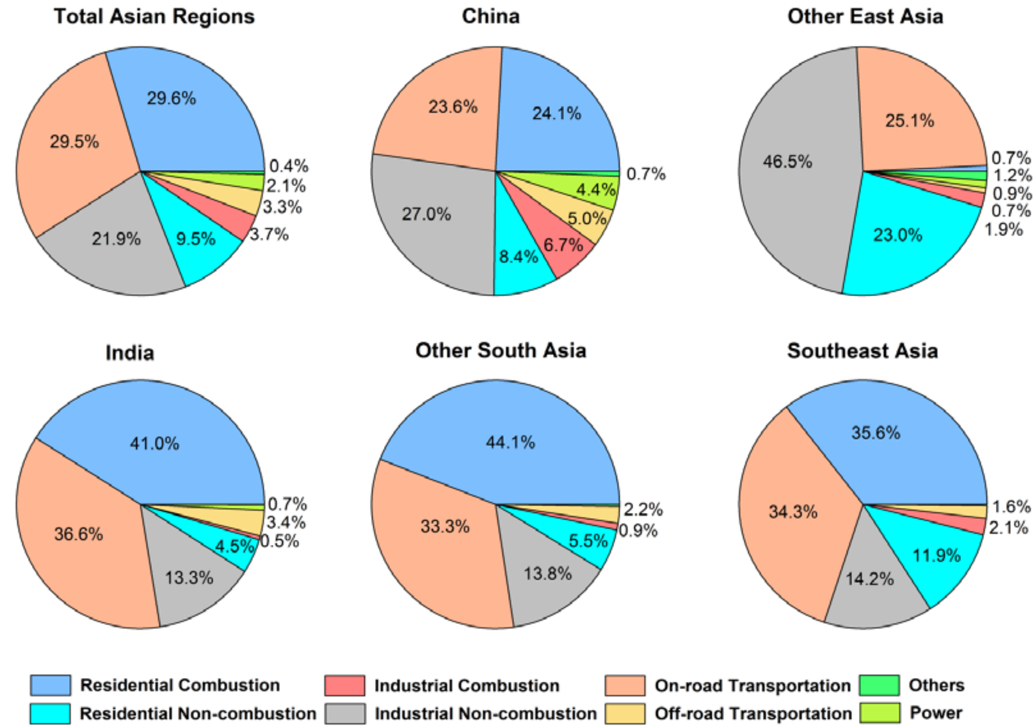
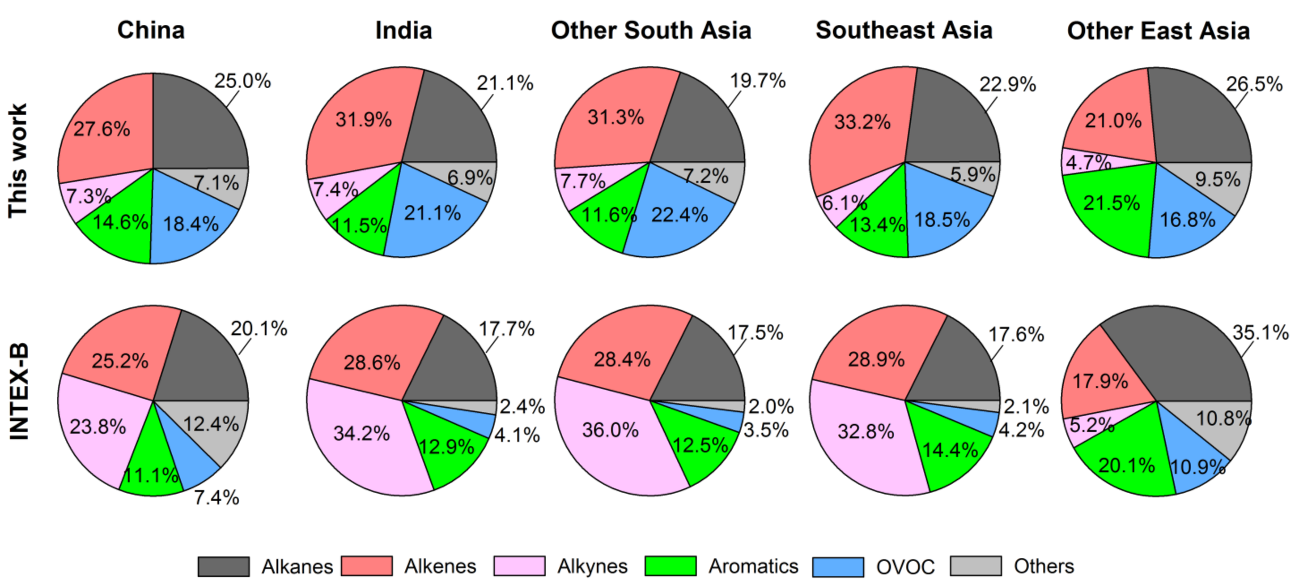
VOC speciation for Asian emissions



Each region of Asia has different contributions of sources
→ Leading to differences in relative amounts of types of VOCs

New inventory has greater contribution of oxygenated VOCs and reduced alkynes



M. Li, Q. Zhang et al., Mapping Asian anthropogenic NMVOC emissions to multiple model chemical mechanisms, Atmos. Chem Phys Disc., 13, 32649, 2013.
Poster: A33G-0309

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