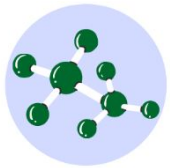


Atmospheric Chemical Mechanisms Conference

Chemistry of Reactive Organic Gases in Mega-cities of China: Insights from Vertical Gradient and Eddy Covariance Flux Measurements

Bin Yuan

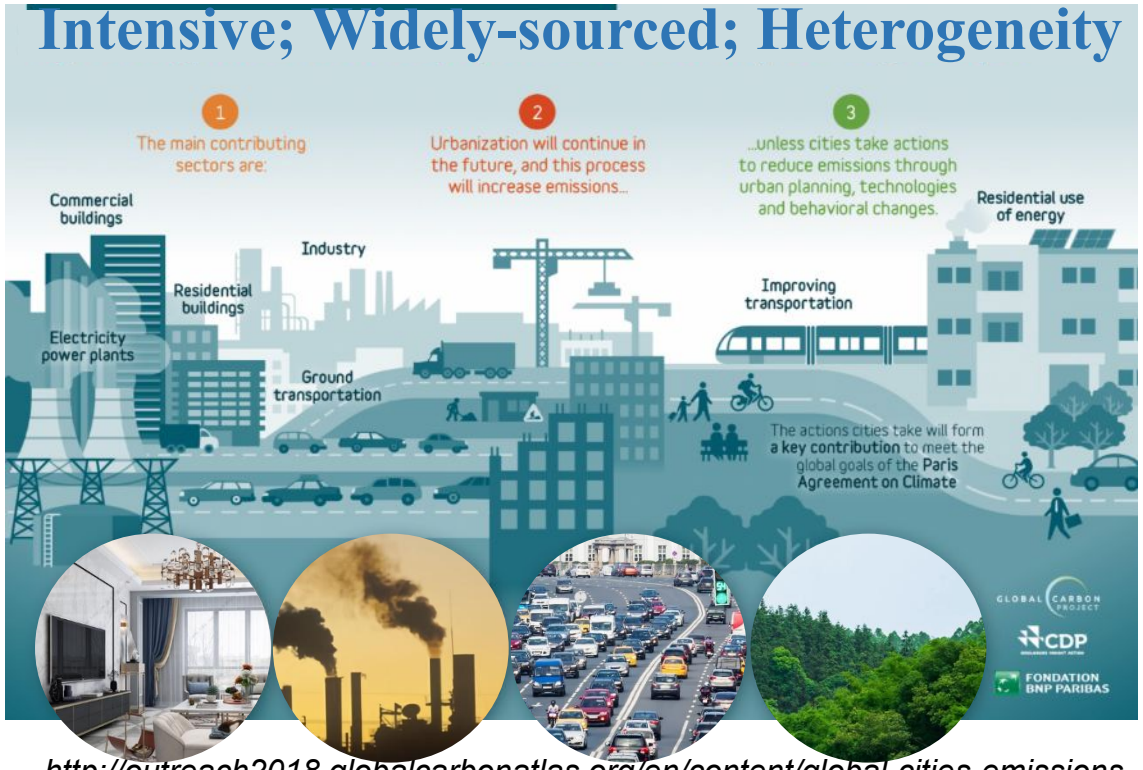
Institute for Environmental and Climate Research
Jinan University

暨南大學
JINAN UNIVERSITY

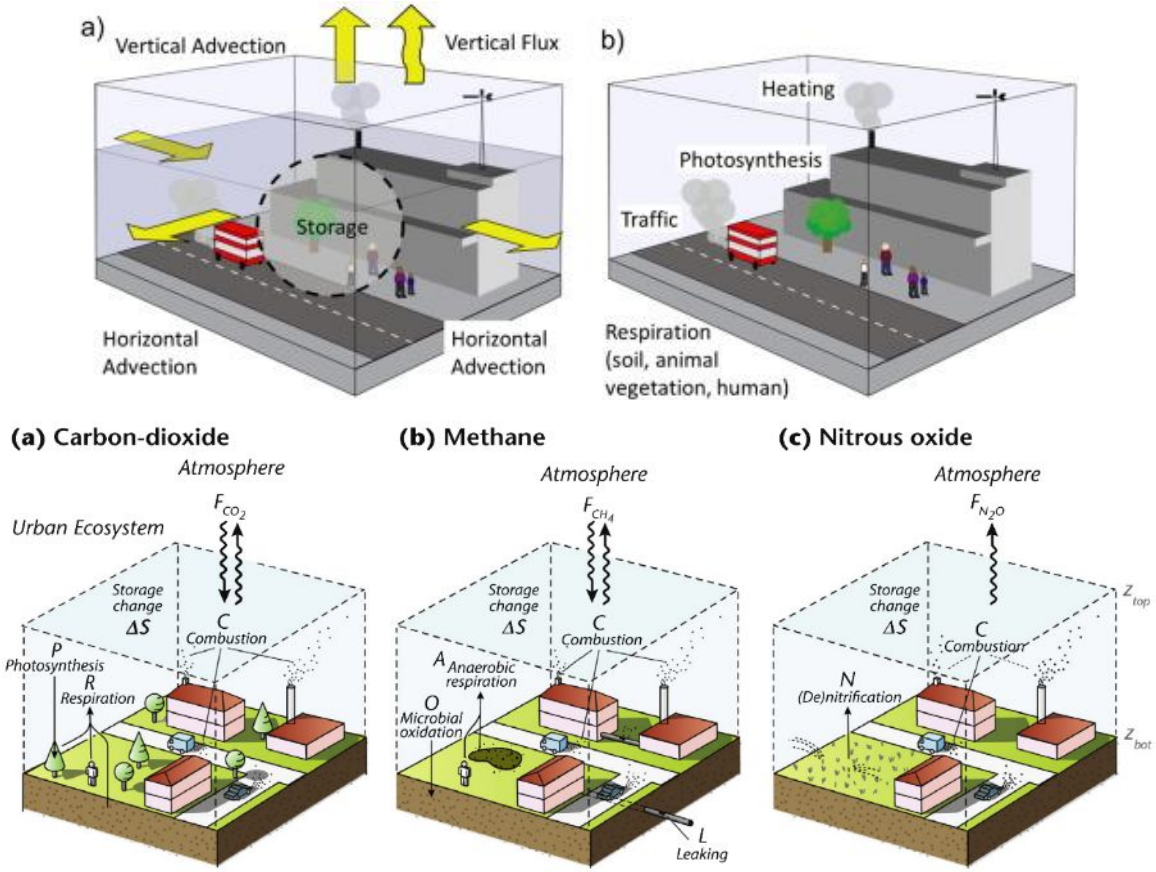
2022-12-7

Urban is one of the main components of ecosystem

- Urban ecosystem is the highest form of human settlement
- High energy use + Intensive human activities=Large GHG & air pollutant emissior

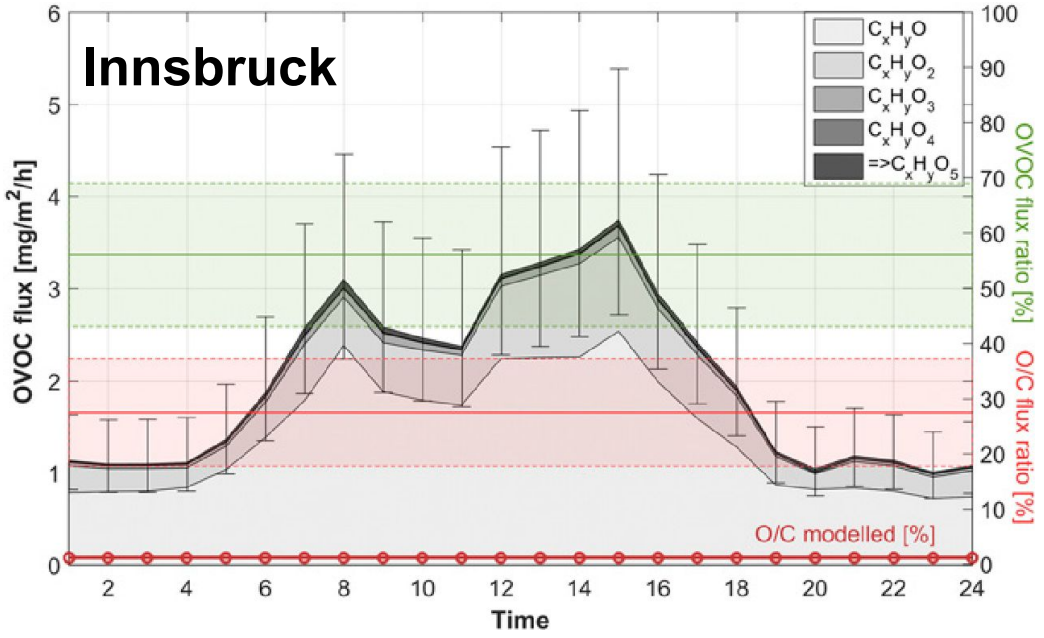


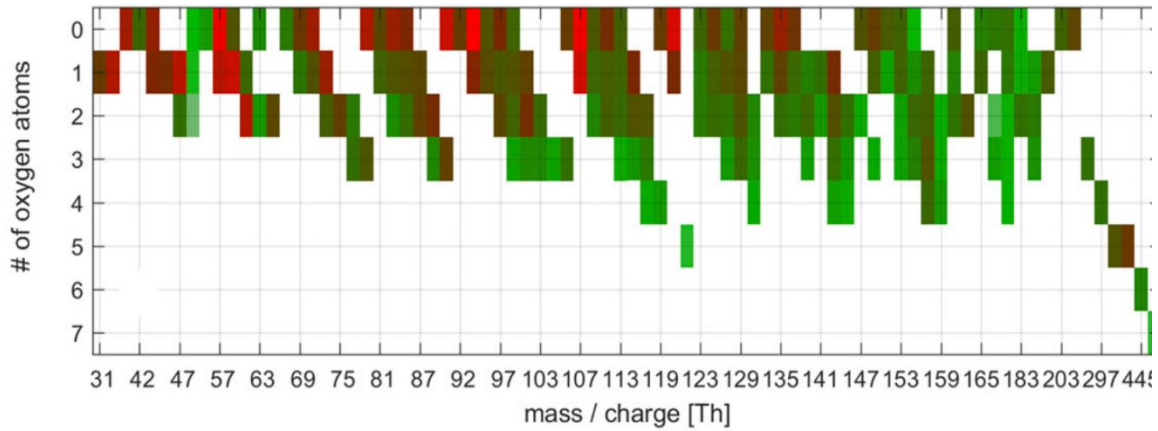
http://outreach2018.globalcarbonatlas.org/en/content/global-cities-emissions

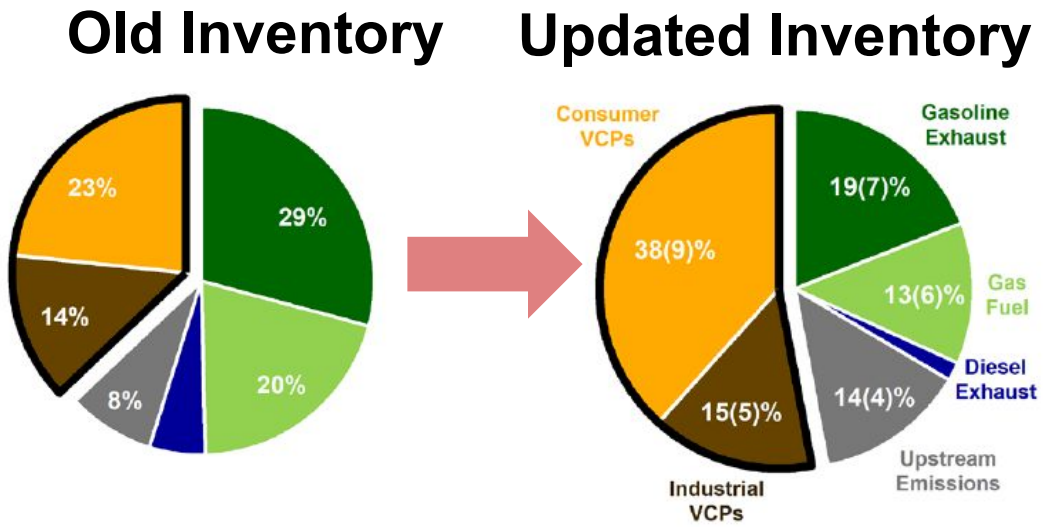


Urban flux study enhances the knowledge of emission and environmental impact

Significant “new” emissions of reactive organics in urban region







190 Gg

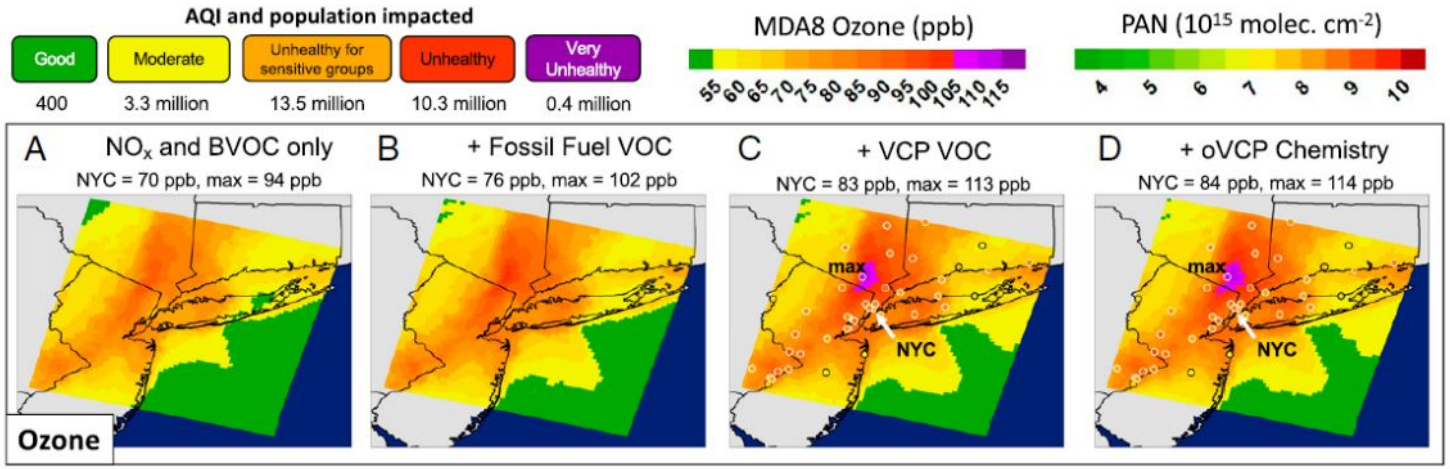
350±50 Gg

Urban oxygenated VOCs emission was significantly underestimated

Karl et al., 2018 PNAS; McDonald et al., 2018 Science

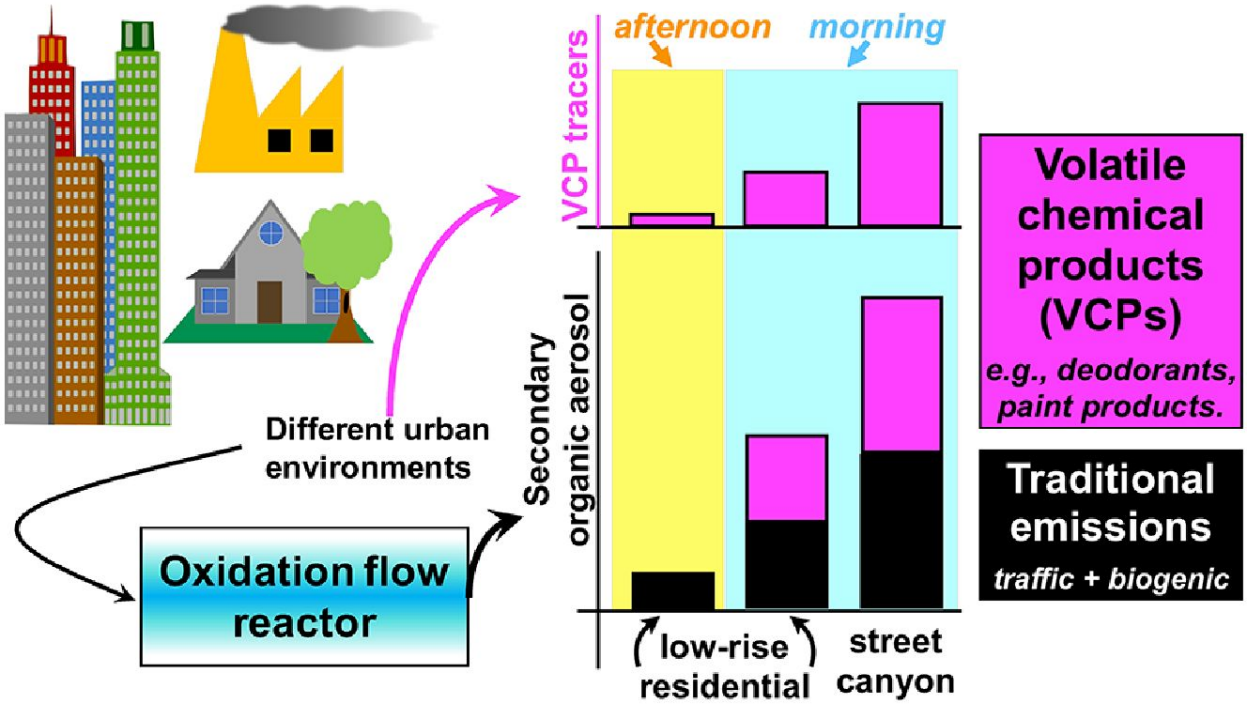
“New” emissions of reactive organic gases affect air quality

Coggon et al., 2021



Ozone formation

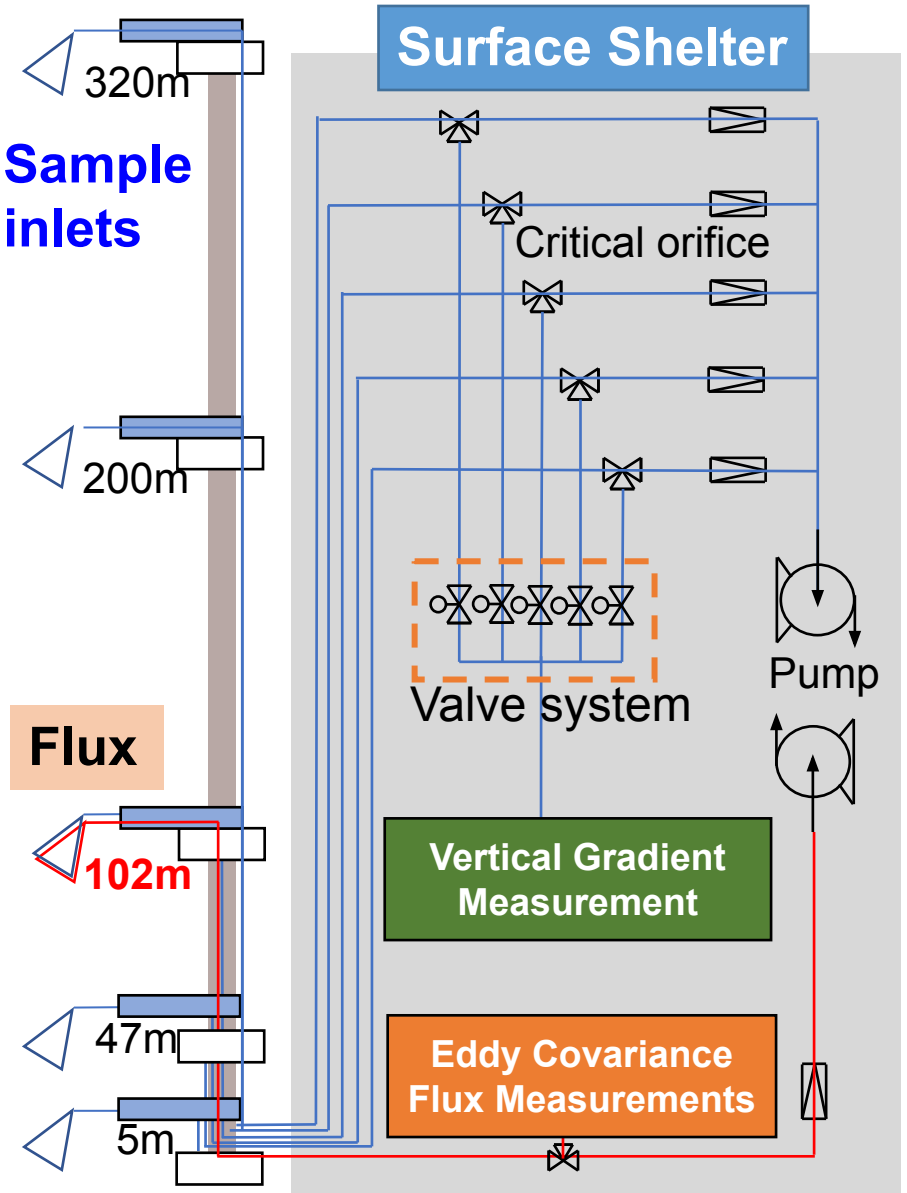
Shah et al., 2020



SOA formation

Flux and gradient measurements in urban of Beijing

Tower

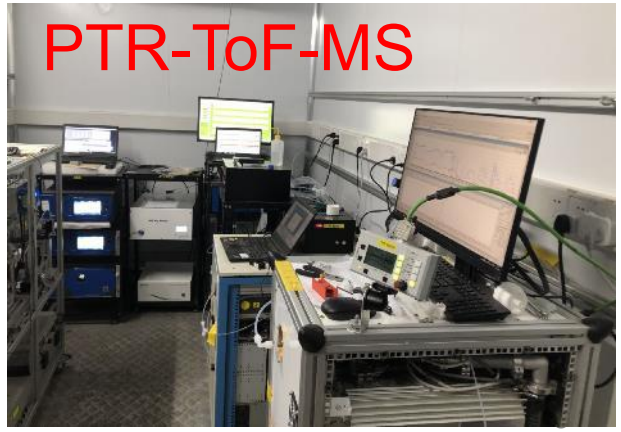


Tower site and surrounding buildings

Flux

Gradient

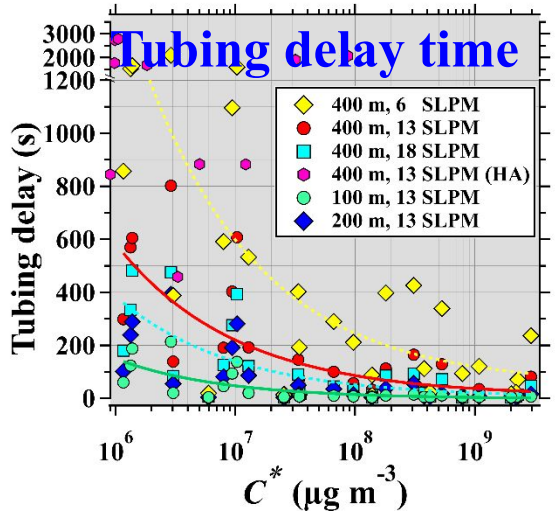
Instrumentation

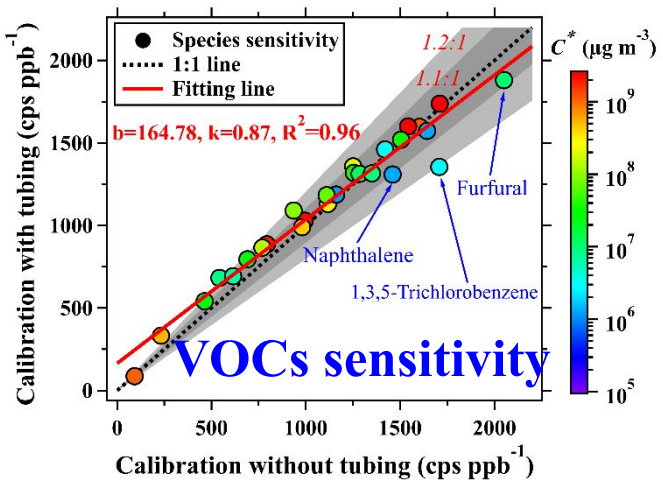


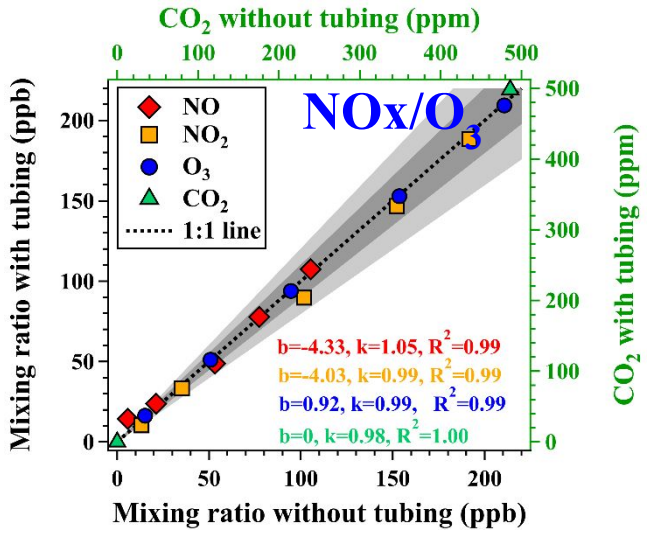
Long tubing assessment for gas measurements

- **Negligible loss for most gas species, except for very reactive ones (NO, monoterpenes) in the daytime**

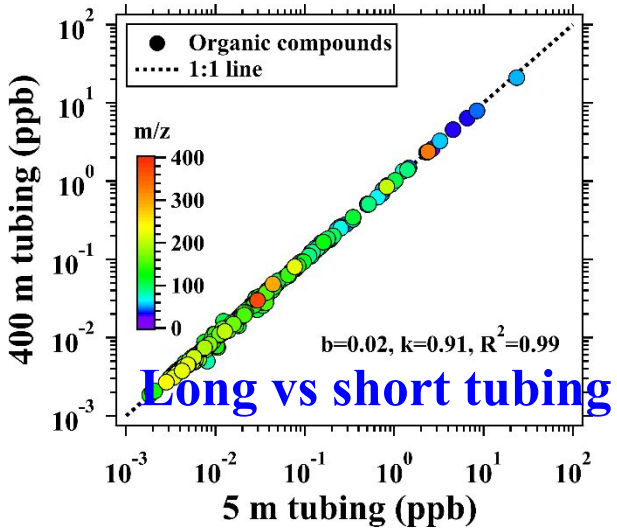
Laboratory assessment

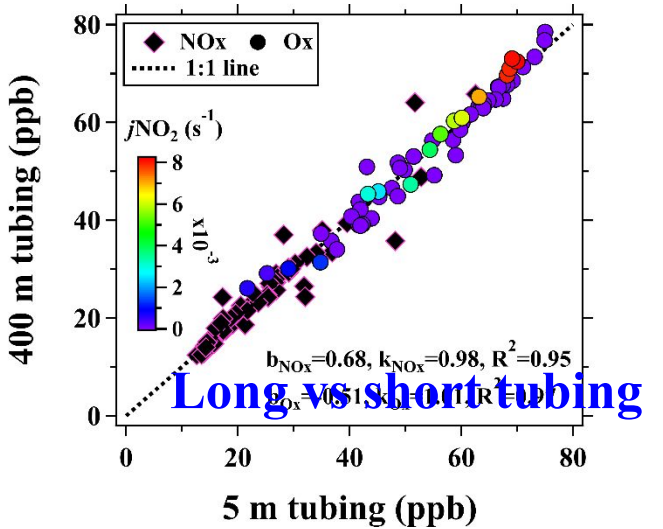


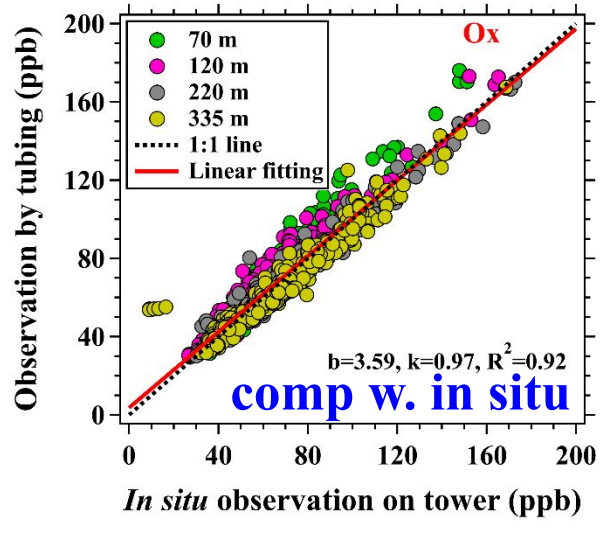




Field evaluation

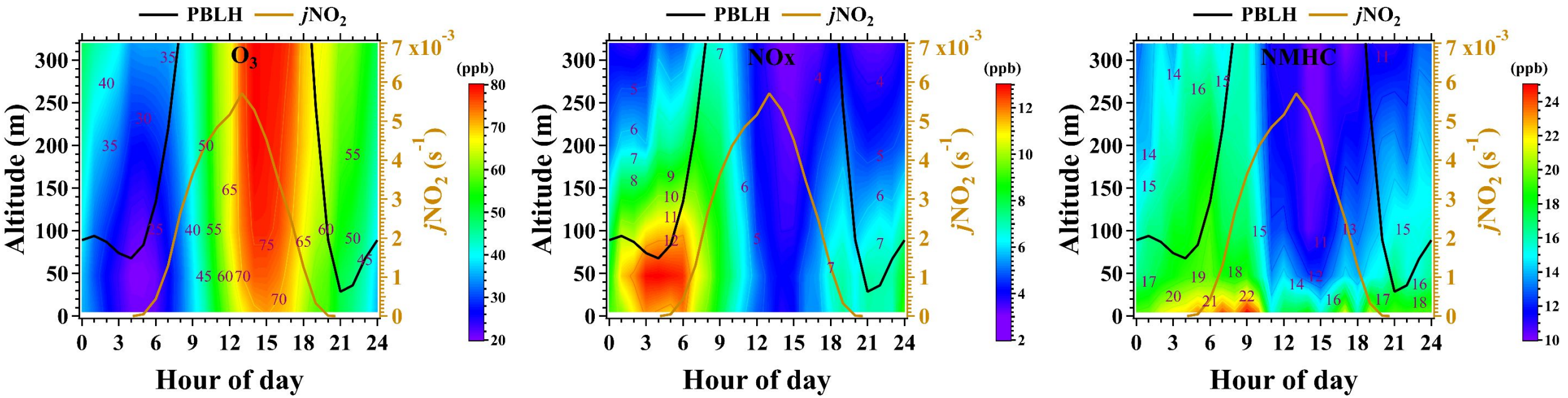






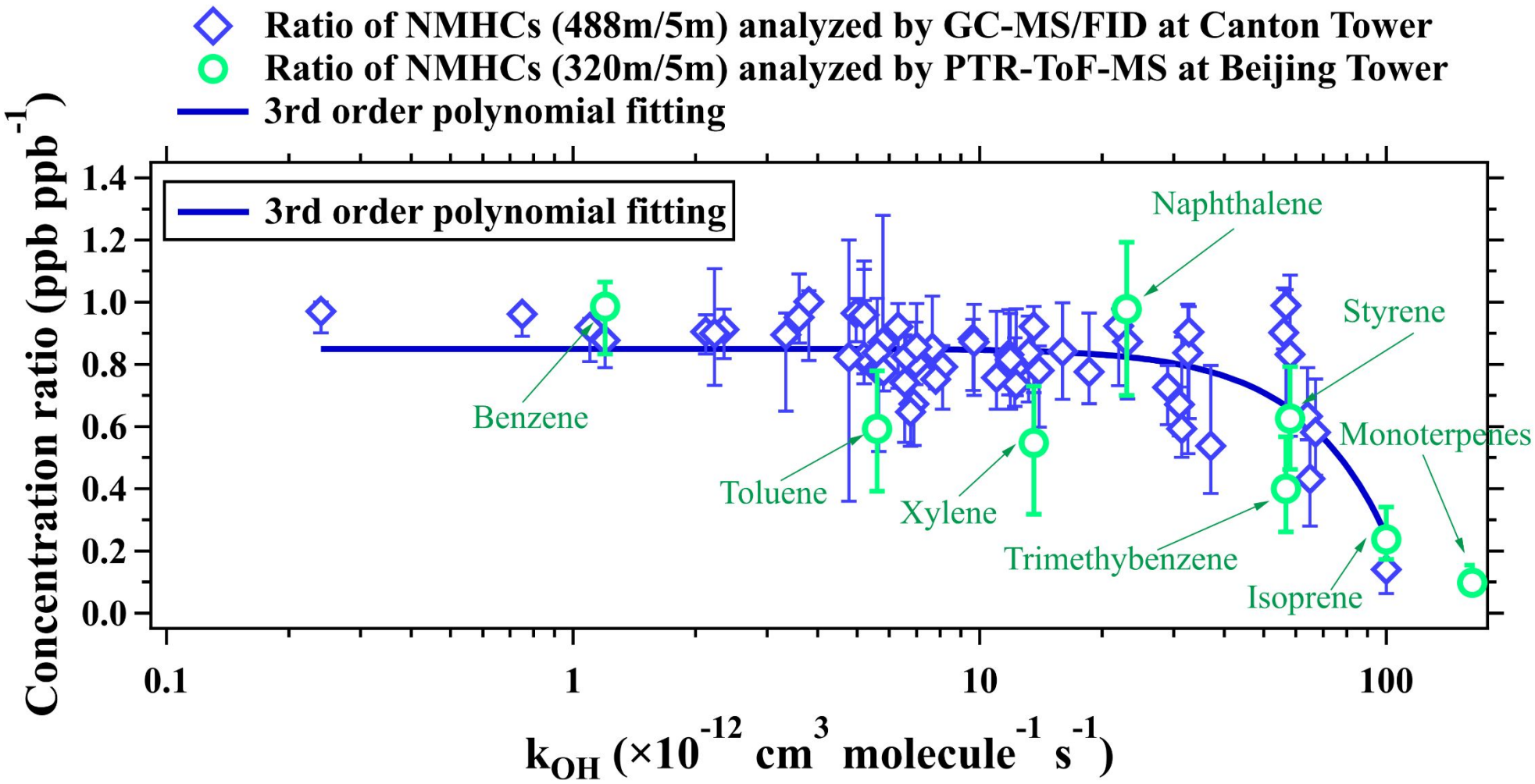
Li et al., in review

Vertical gradients of ozone and precursors are significant



- Strong gradient were observed at night
- Air pollutants are generally well mixed during the daytime

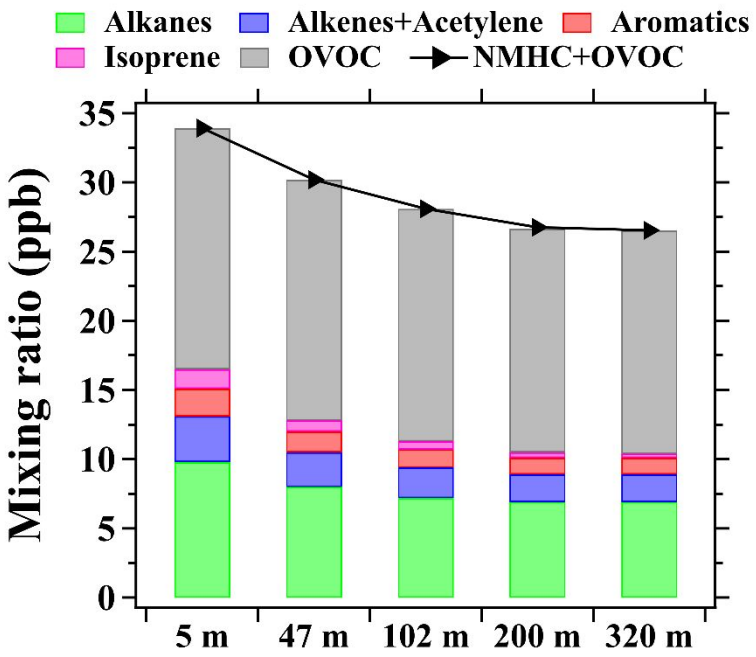
Reactive species decline more rapidly with height



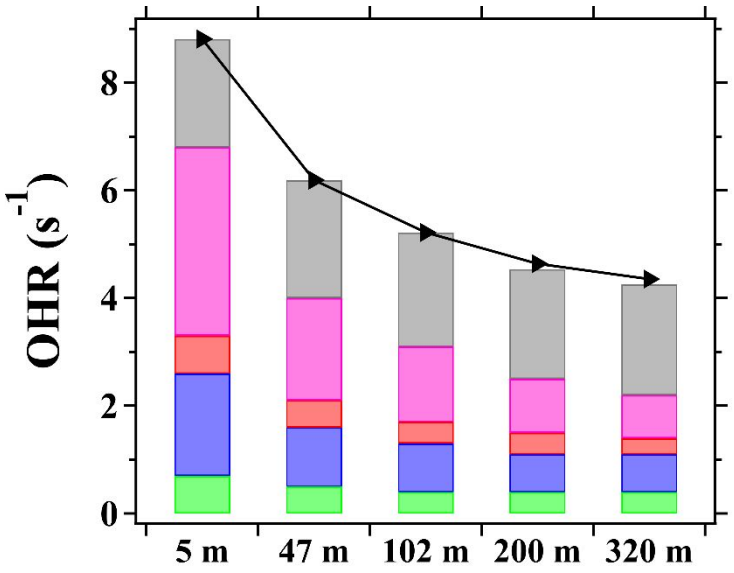
- Stronger gradient is observed for more reactive species

OVOC are more important in aloft atmosphere

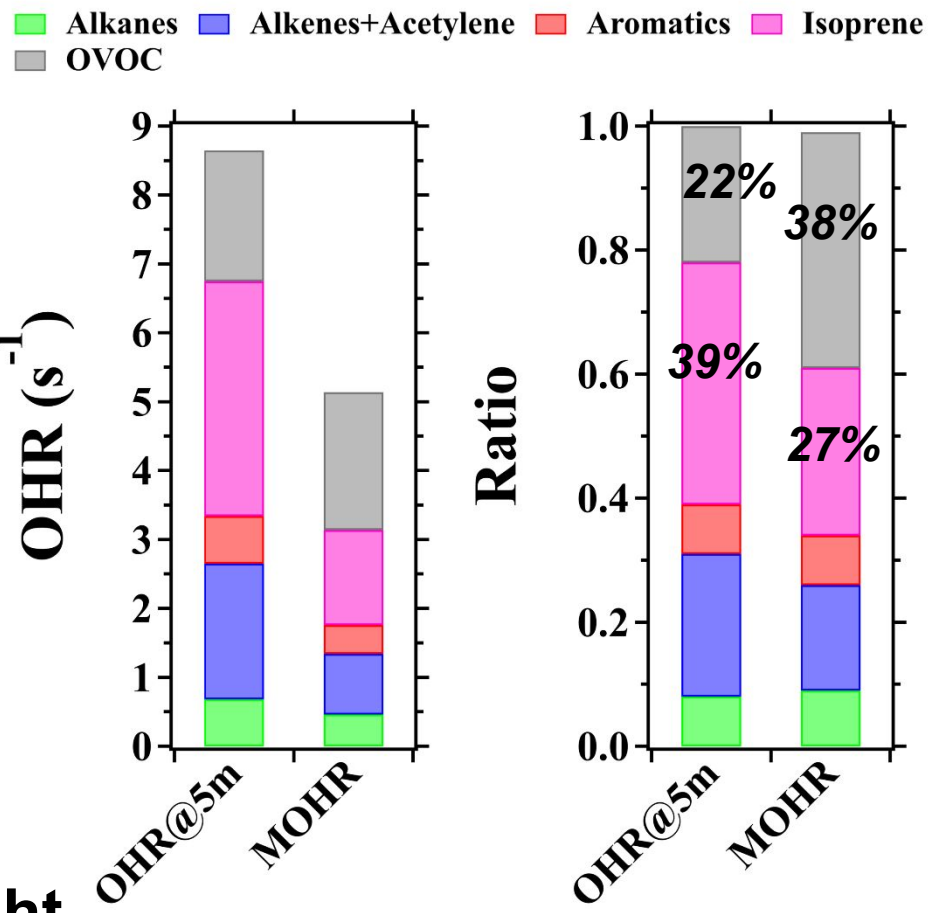
LT 11:00-16:00



OHR: OH reactivity



MOHR: Mean OHR between 5-320 m

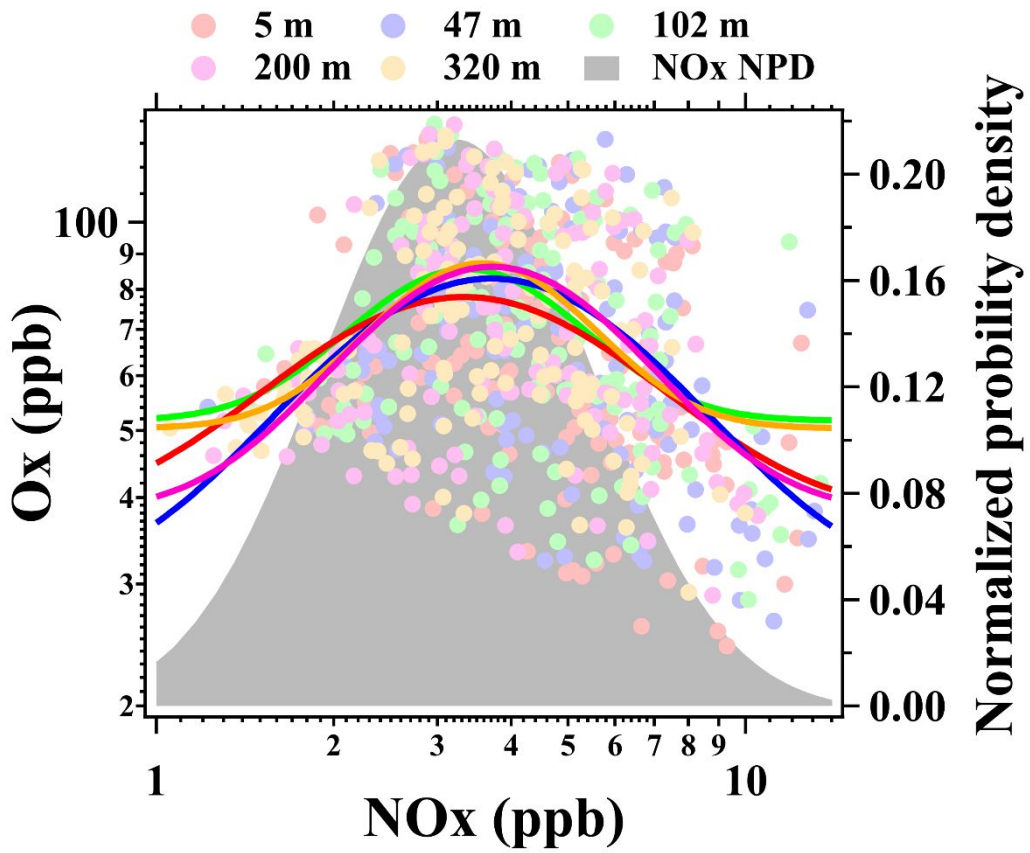


- Contributions of reactive VOCs to the total concentration and OHR rapidly decline with height
- OVOCs account for larger fractions in OHR in higher altitudes

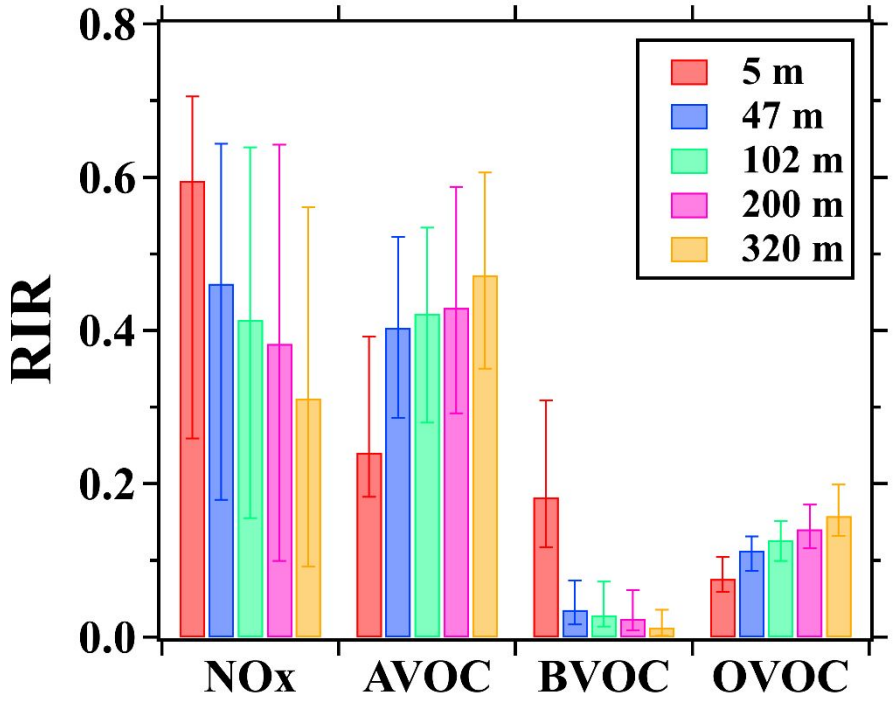
Vertical distributions of ozone formation sensitivity

Statistical method

LT 11:00-16:00

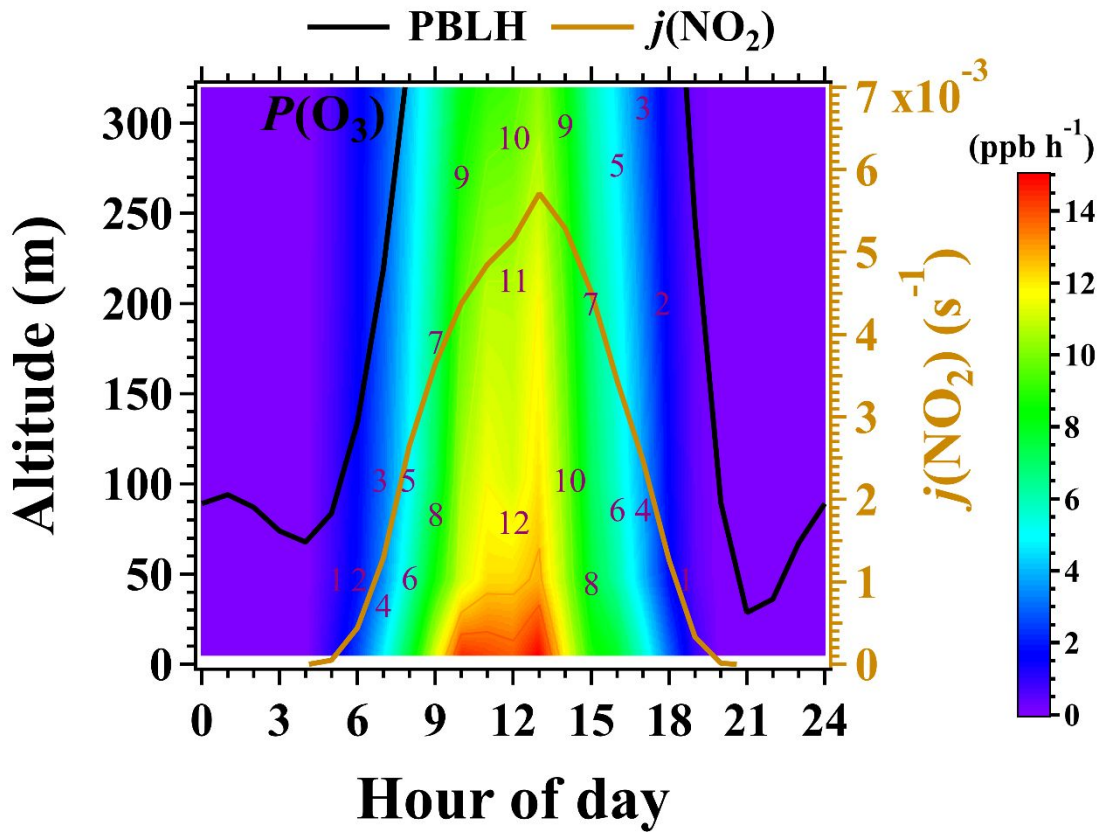


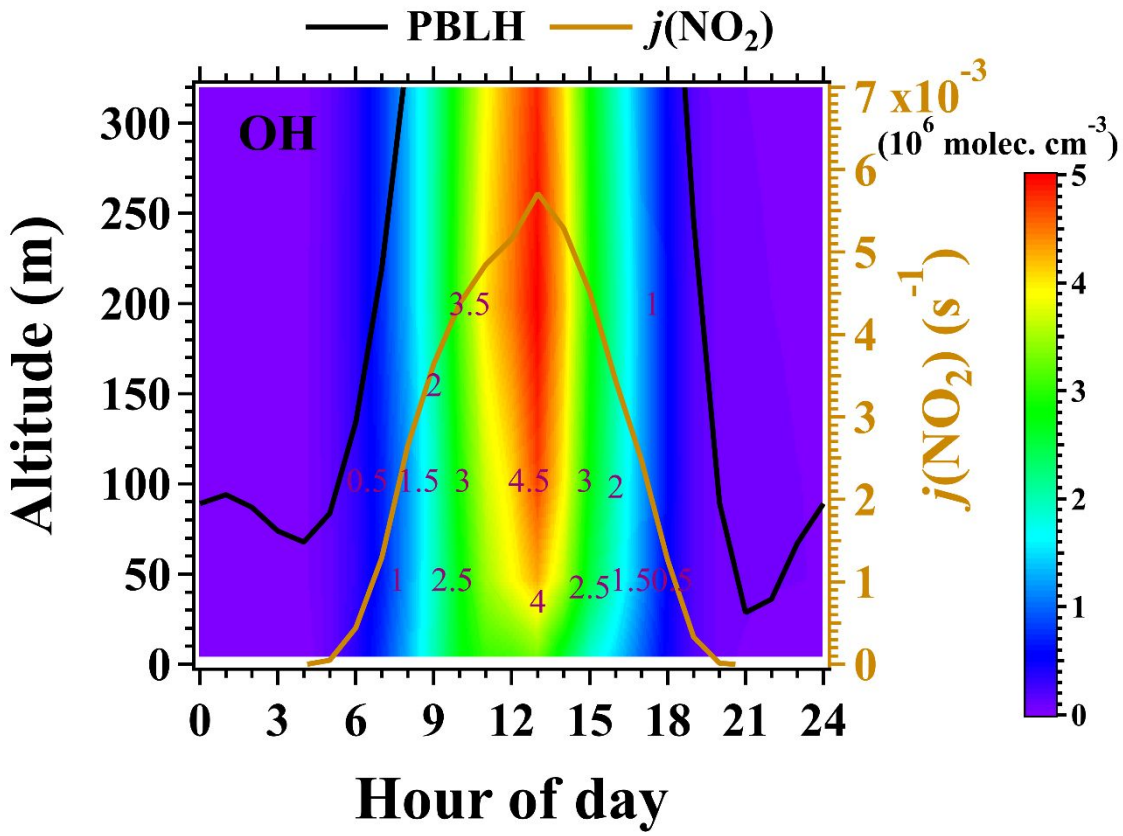
Box model simulations



- Ozone formation exhibits insignificant vertical discrepancy in the lower BL
- Ozone formation is more sensitive to changes in AVOC and OVOC in higher altitudes

Strong aloft photochemical formation of ozone

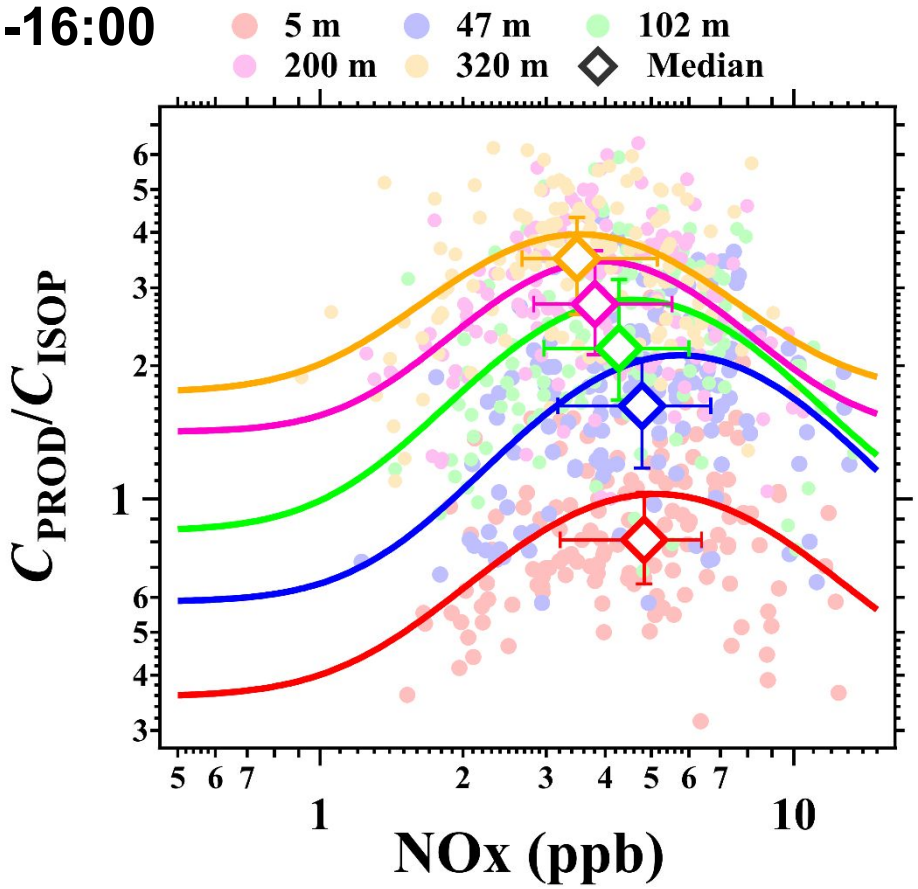


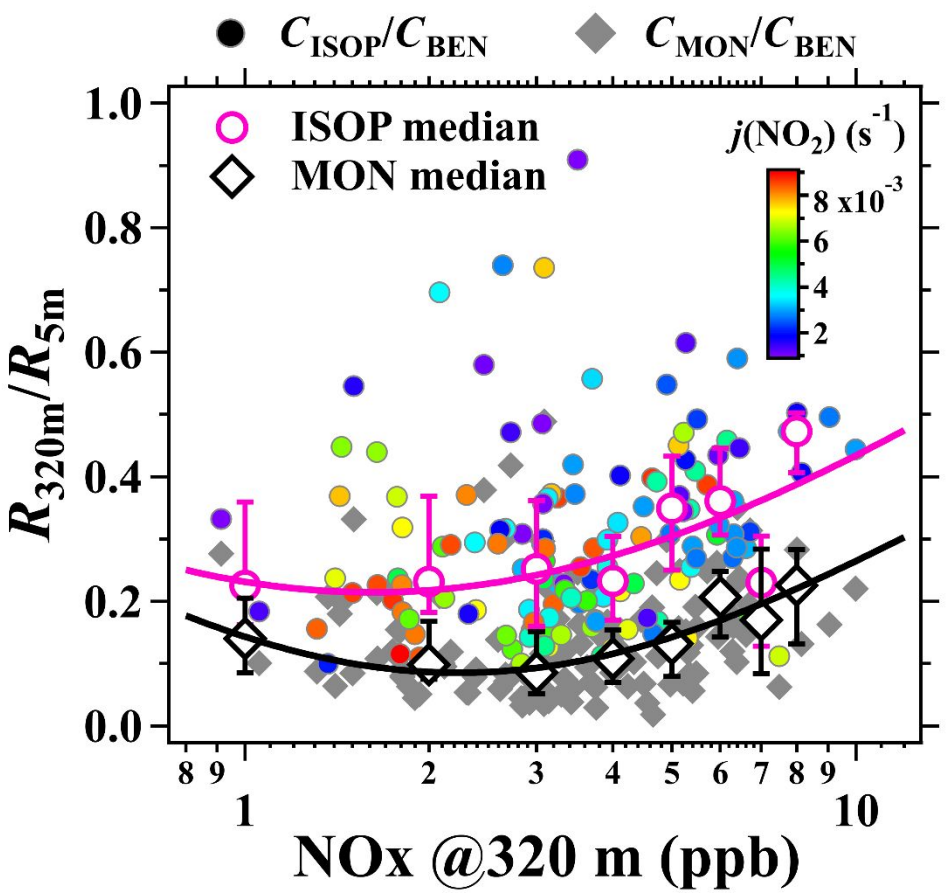


- Ozone production rates decline with height but is still large in aloft
- OH concentrations increase with height

Vertical gradient indicates NOx-dependence of oxidation capacity

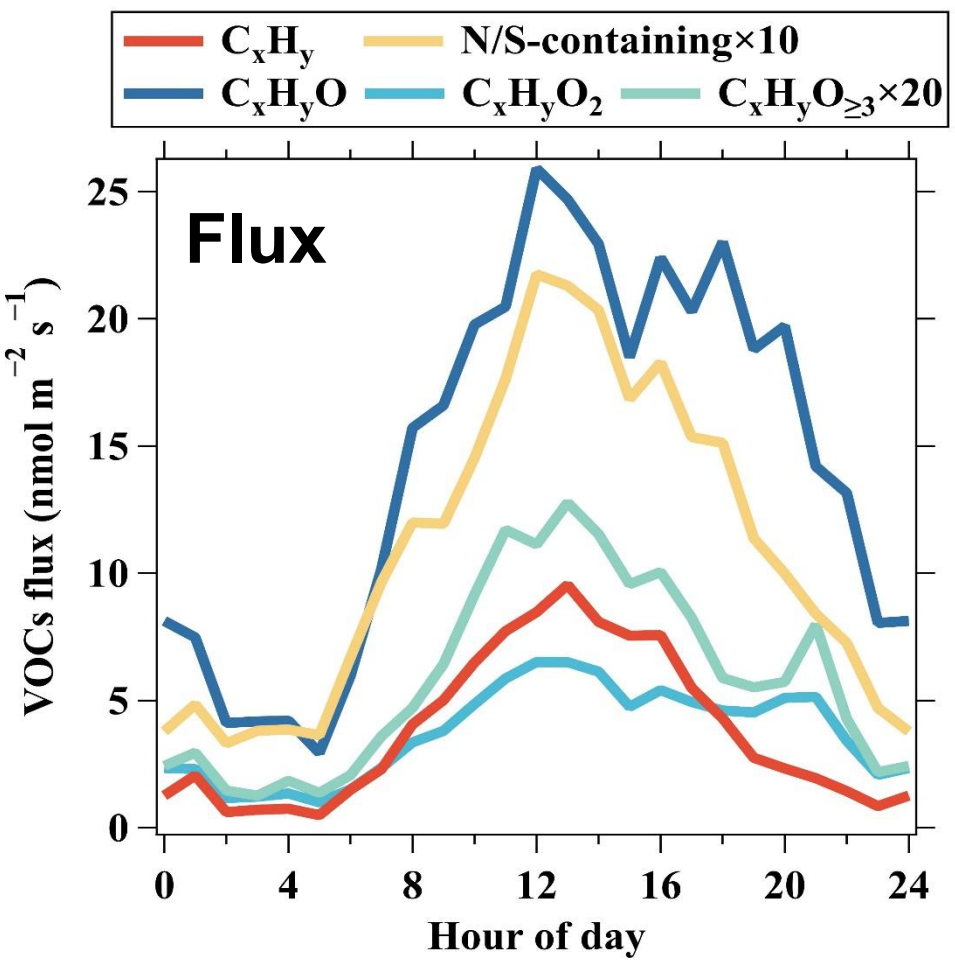
LT 11:00-16:00

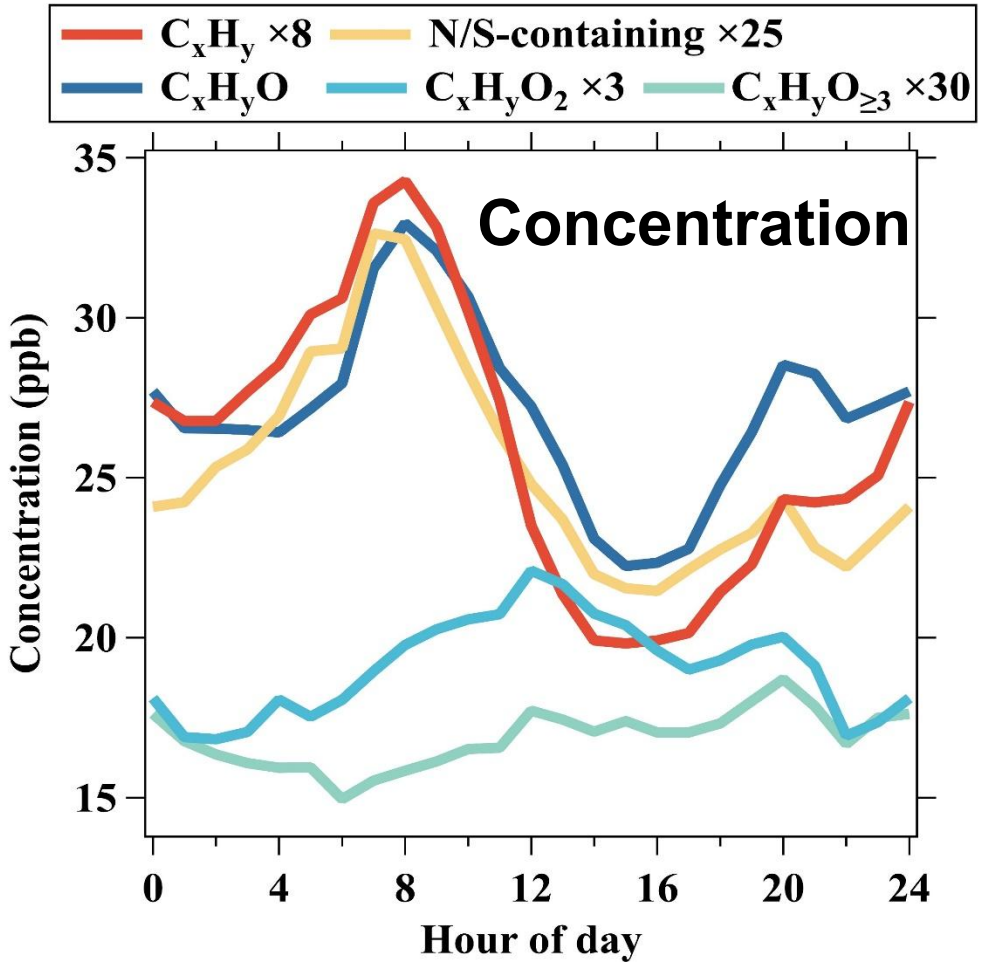




- The tuning points of oxidation capacity decrease with height.
- Significant fraction of time for chemistry is in the low-NOx regime for urban Beijing

VOCs fluxes and concentrations: different diurnal variations



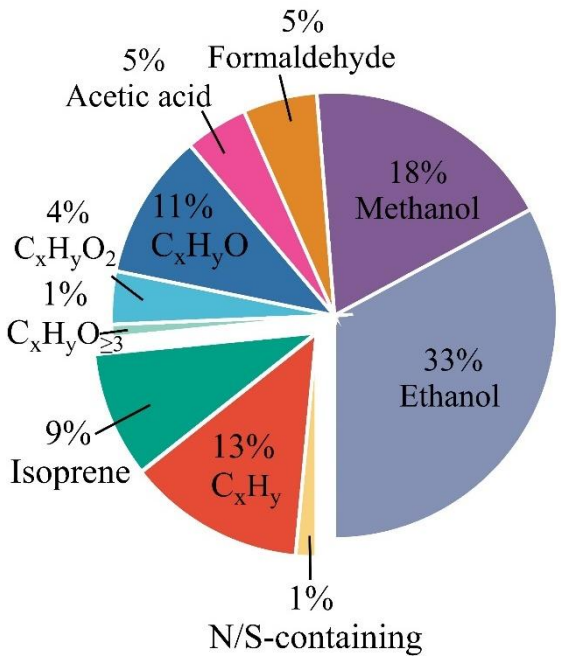


VOCs fluxes were higher in the day and lower at night, decoupling with boundary layer

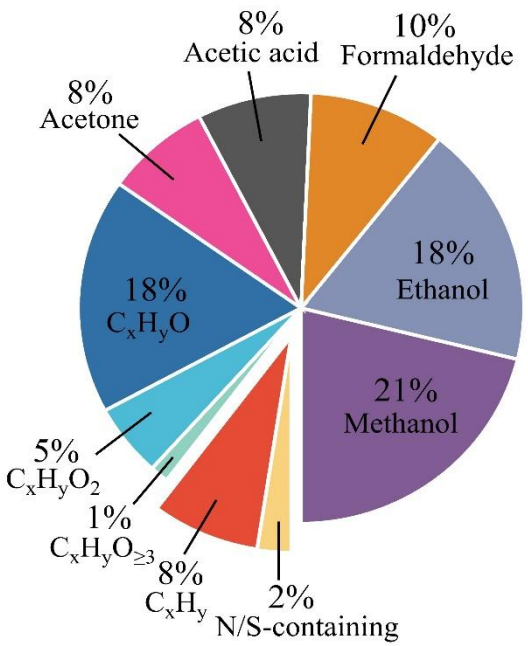
VOCs fluxes and concentrations: different compositions

VOCs fluxes (fresh emission) → **VOCs concentrations (aged air)**

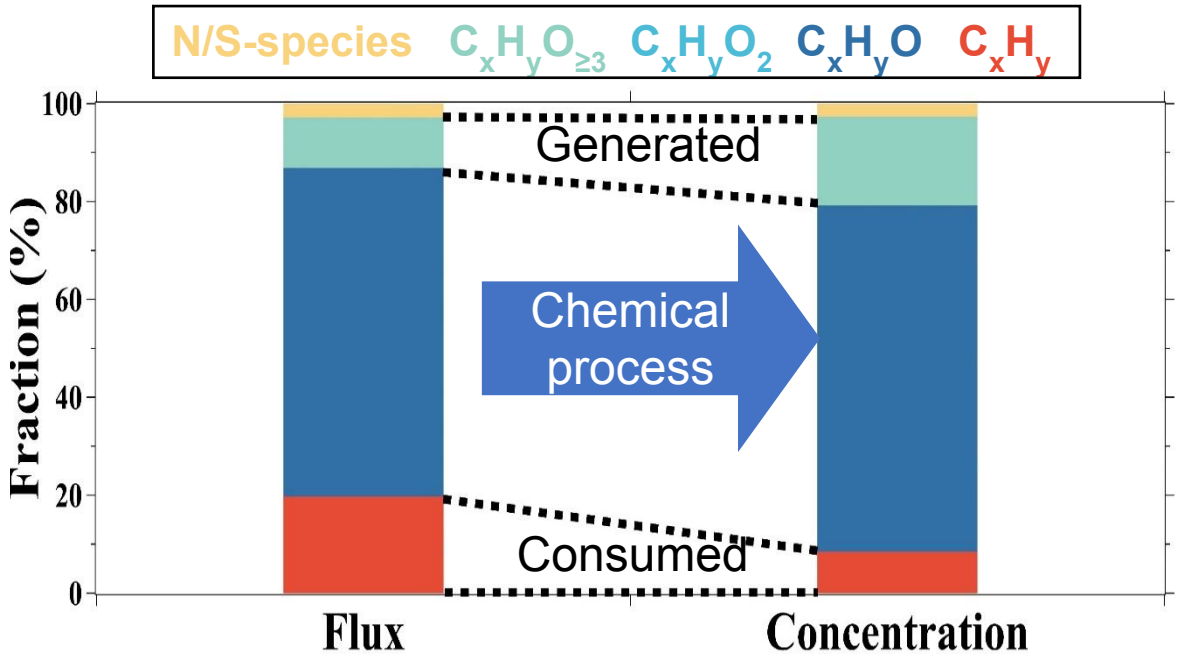
Flux



Concentration



Evolution from fluxes to concentrations



OVOCs dominated VOCs fluxes (77%)

Hydrocarbons ↓ OVOCs ↑

The composition differences indicates chemical processes of VOCs in the air

Source apportionment of VOCs based on flux data

❑ VOCs species screen

VOCs No.

PTR-TOF-MS data

Peak fitting evaluation

1872

Ion signal strength

Conc. detection limits

1538

VOC concentrations

Flux detection limits

215

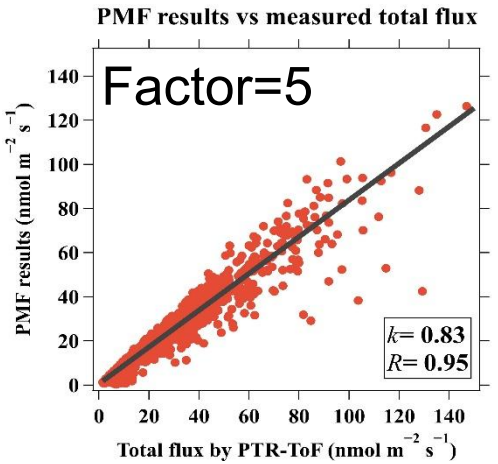
VOC fluxes

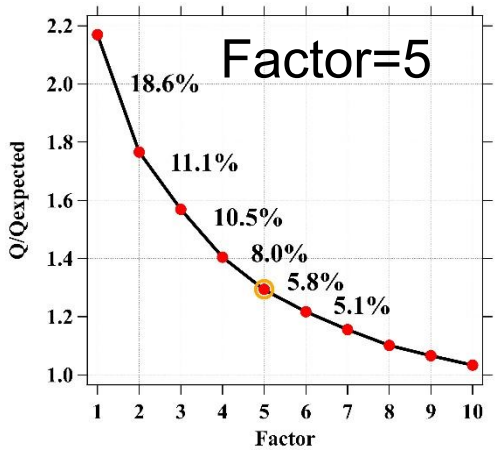
Positive flux screen

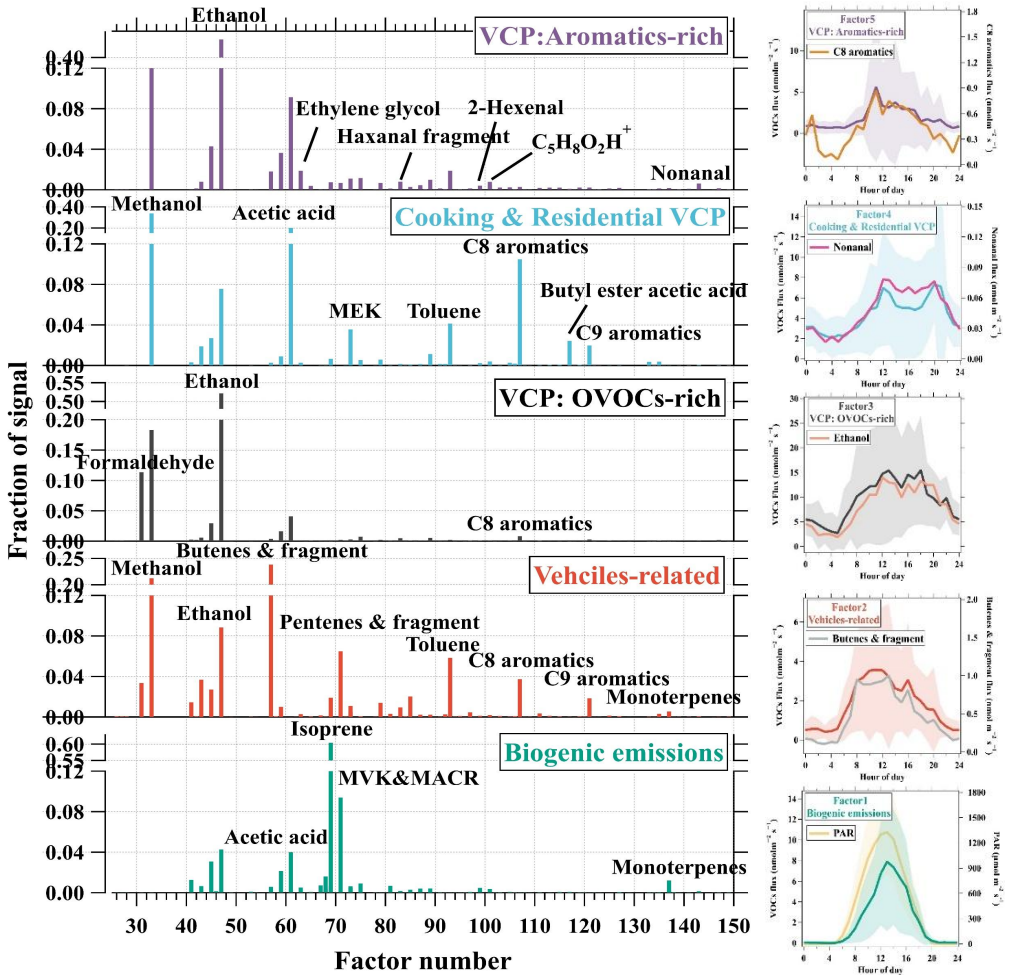
195

Species for PMF

❑ Determine factor No. based on the expected residual
❑ Identify factors according to tracer and spectrum



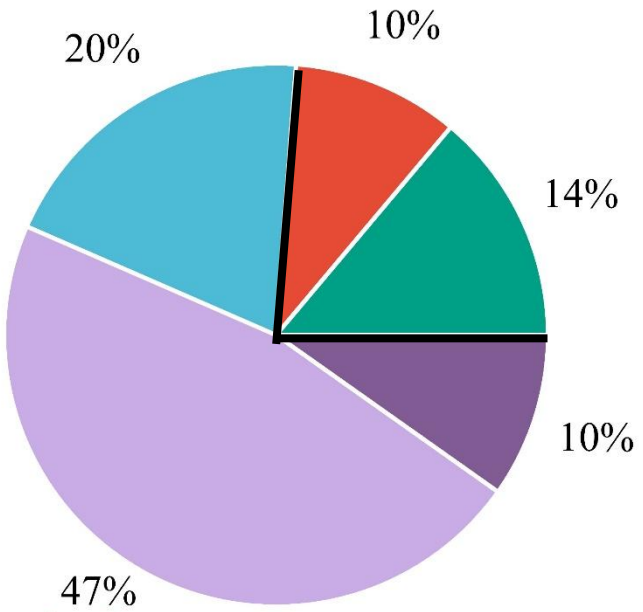




Urban VOCs source structure has changed quietly

❑ Flux-based PMF analysis revealed current VOCs source structure

PMF results of VOCs fluxes

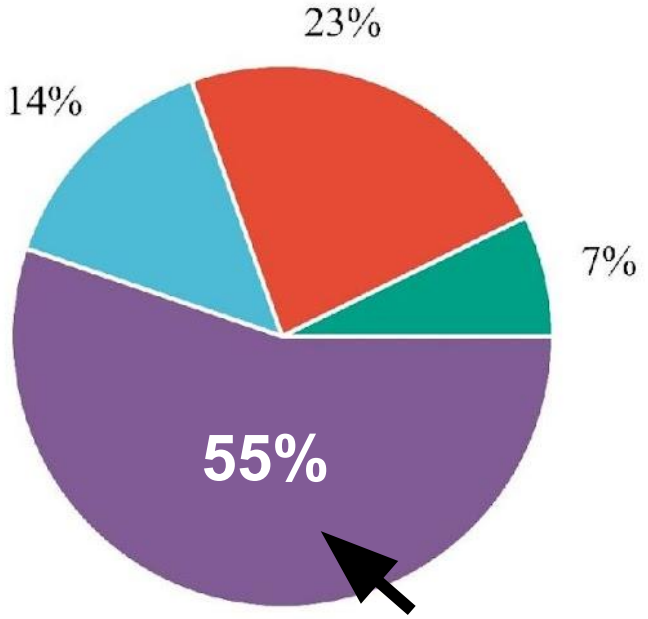


Integration of similar source profiles

Fill out the unmeasured key VOCs species

Vehicles-related
Biogenic emissions
Cooking & Residential VCP
VCP: OVOCs-rich
VCP: Aromatics-rich

Source contribution after integration

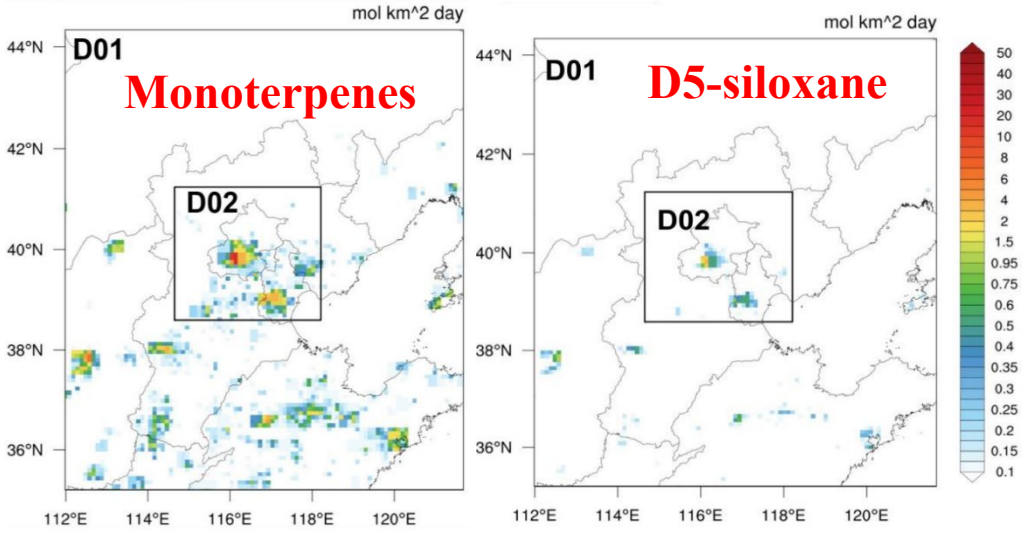


Volatile chemical products

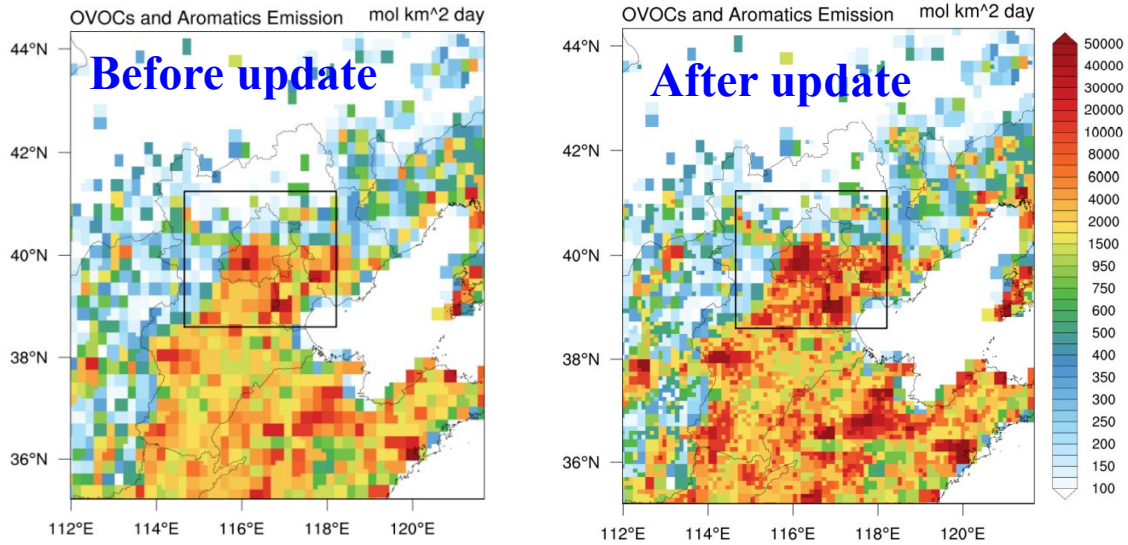
Volatile chemical products (VCPs) dominate VOCs emission in urban Beijing

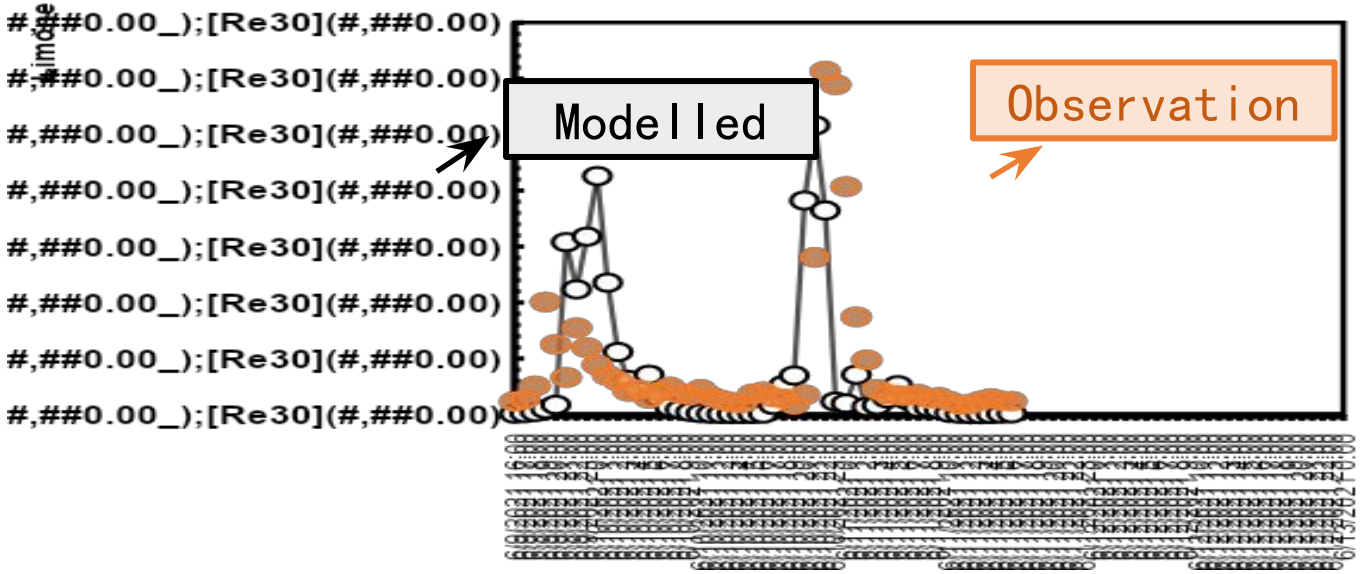
Validation of key VOCs concentration in the model

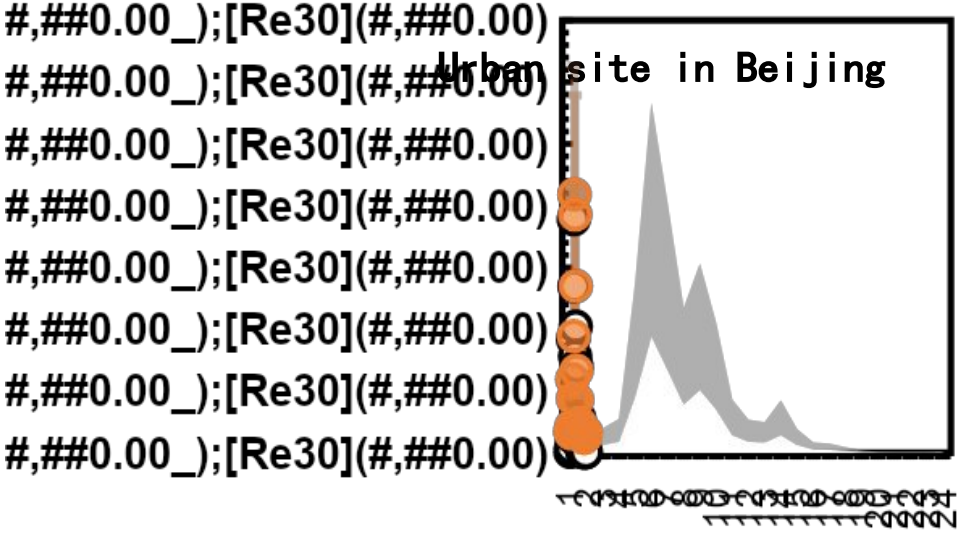
Add new VOCs species and their mechanisms



Update VOCs emission inventory

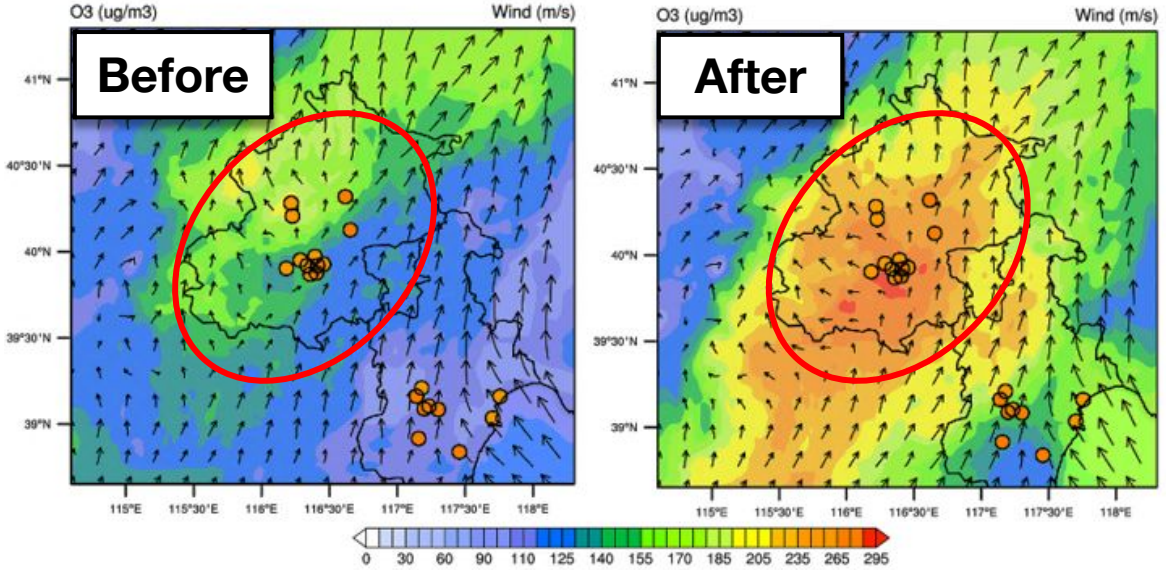


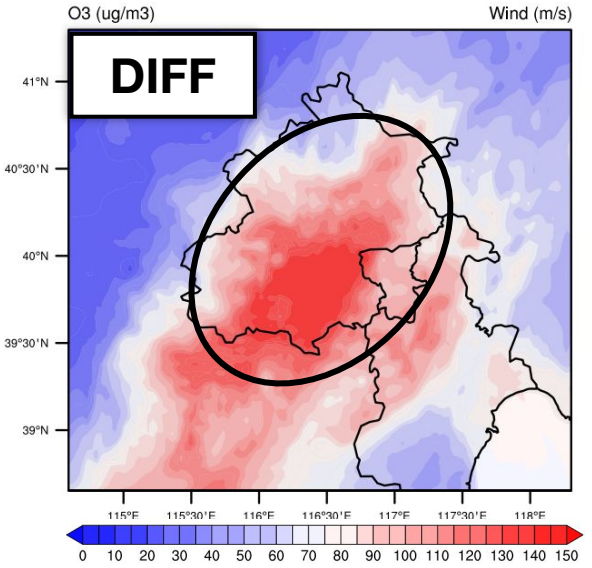


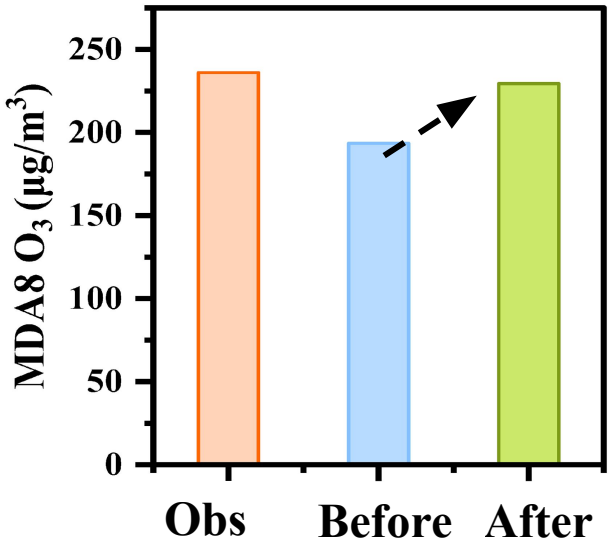


Inventory update improved O_3 simulation performance

- **Update anthropogenic emission inventory in the regional air quality model**







Summary

- Reactive species are consumed rapidly with the increase of height
- OVOCs play more important roles in sustaining atmospheric oxidation capacity aloft
- Source analysis of VOCs based on flux data provides new insights into VOCs emissions
- Regional air quality simulation can be improved with measured VOC flux information

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Xianjun He

Thank you for your time！

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