RECENT FIELD CAMPAIGNS IN CHINA

AQUARIUS Workshop

2. OKTOBER 2019 | HENDRIK FUCHS

Mitglied der Helmholtz-Gemeinschaft

北京大學
PEKING UNIVERSITY

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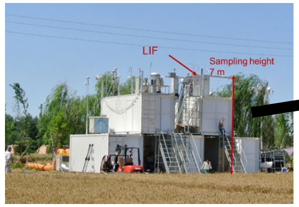
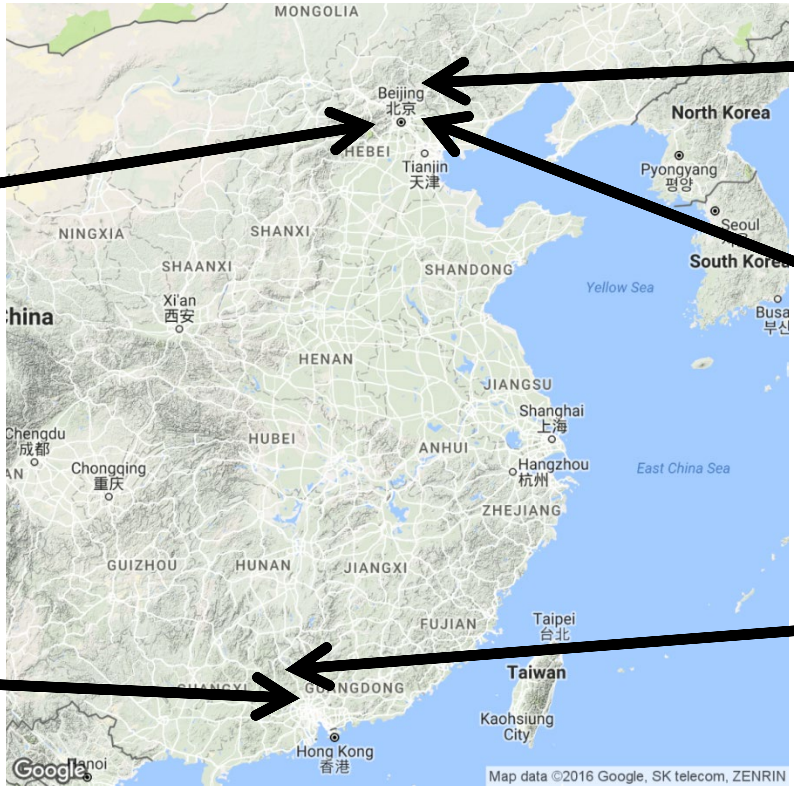
PHOTOCHEMISTY FIELD CAMPAIGNS IN CHINA

Goals:

- Understanding oxidation processes of pollutants and quantification of oxidation rates
- Understanding and quantification of ozone production

Wangdu Summer 2014





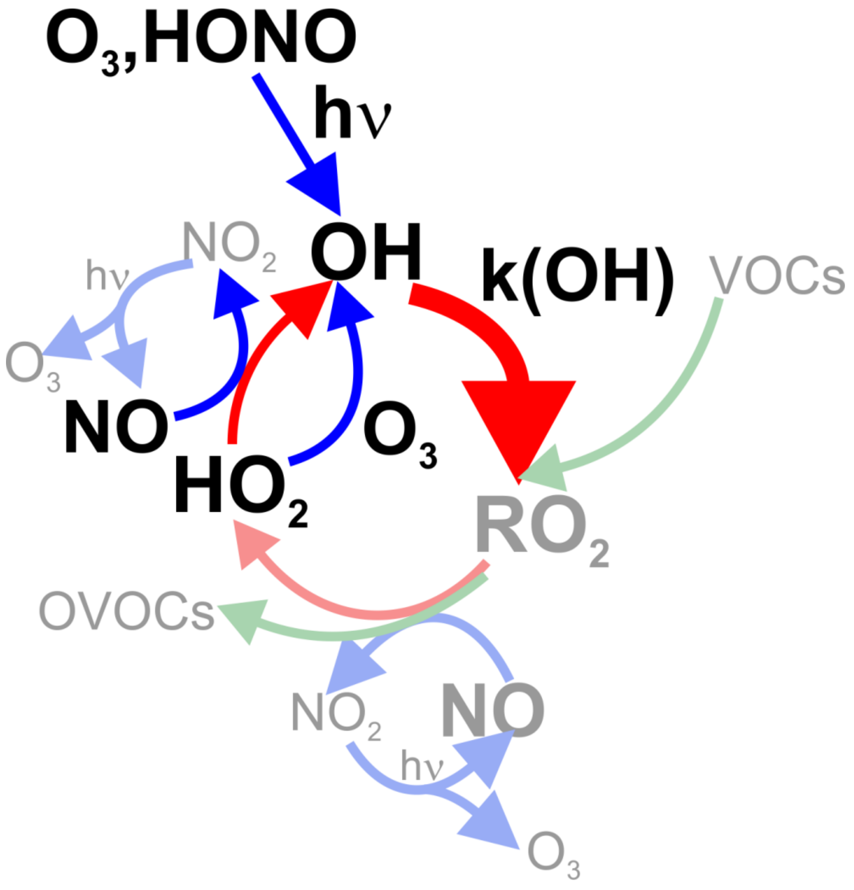
Heshan Fall 2014

Huairou Winter 2016

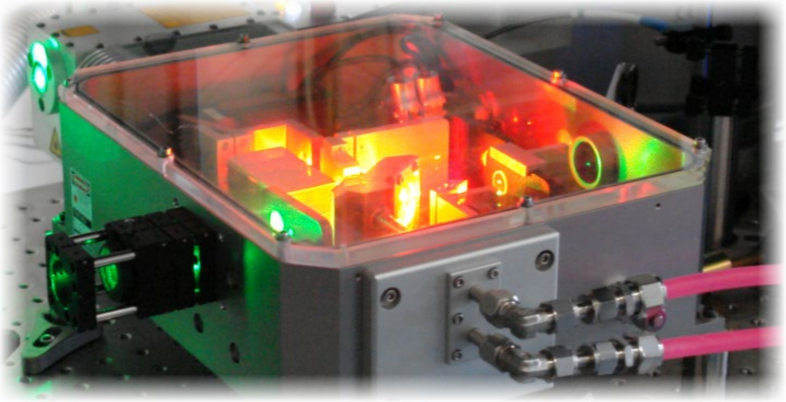
Yufa Summer 2006

Backgarden Summer 2006

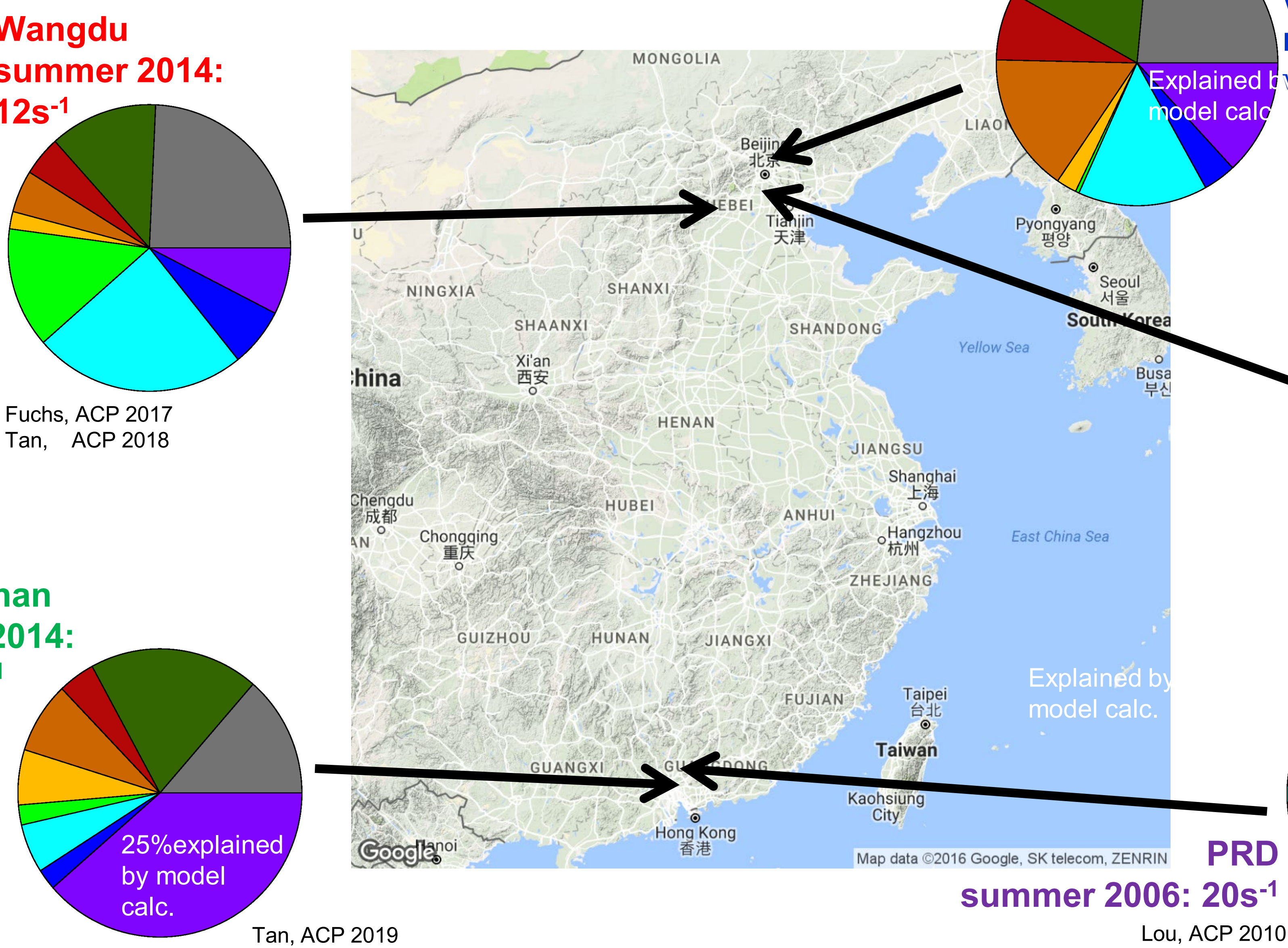
INSTRUMENTATION FOR INVESTIGATING RADICAL BUDGETS

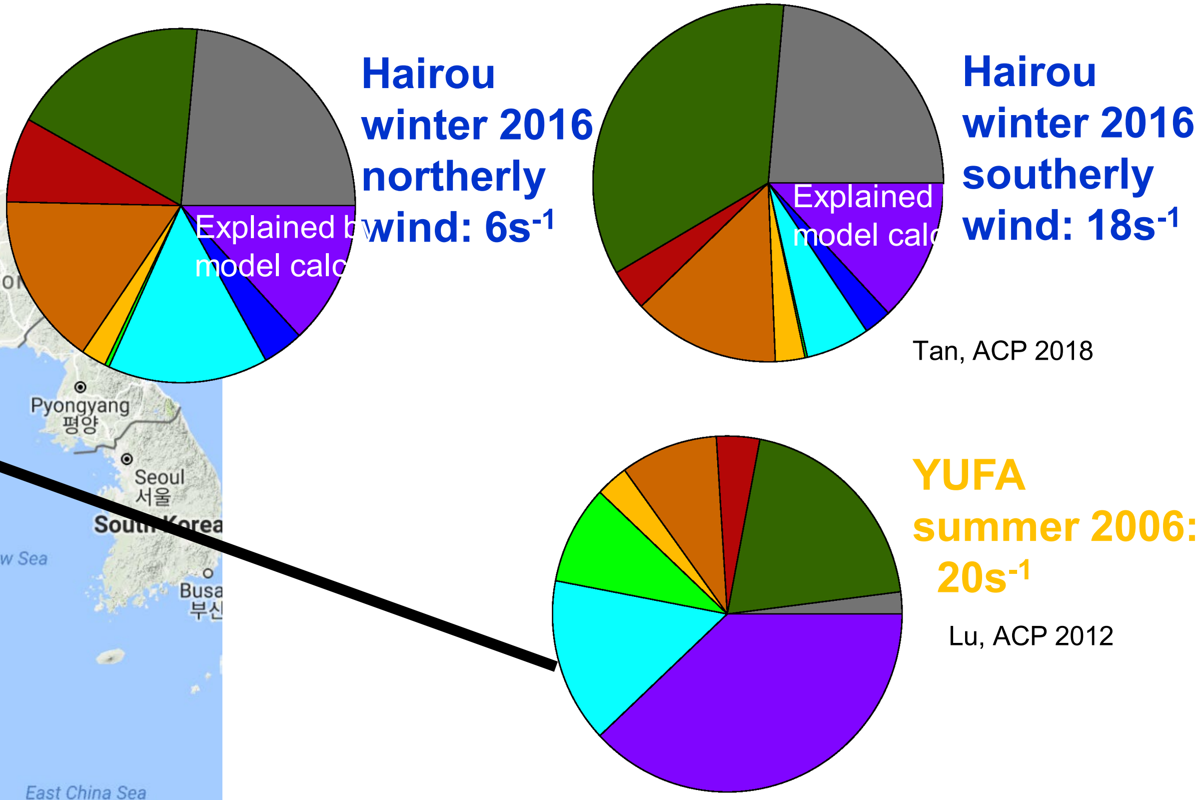


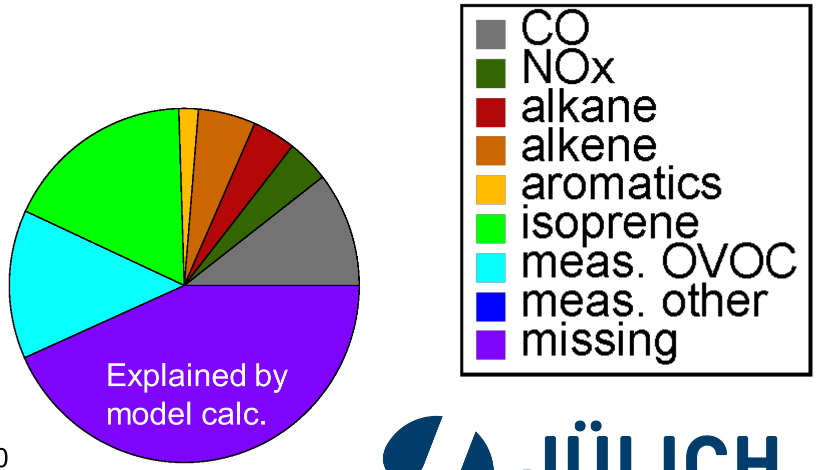
- Trace gas compounds:
  - NO, NO_2 (chemilumescence), O_3 (UV photometer)
  - HONO (long-path absorption, LOPAP)
  - Radicals (OH,HO_2,RO_2: laser-induced fluorescence)
  - Volatile organic compounds (gas-chromatography)
  - HCHO (Hantzsch-monitor)
  - OH reactivity (=inverse lifetime of OH, Laser flash photolysis + LIF)



OH REACTIVITY IN CHINA







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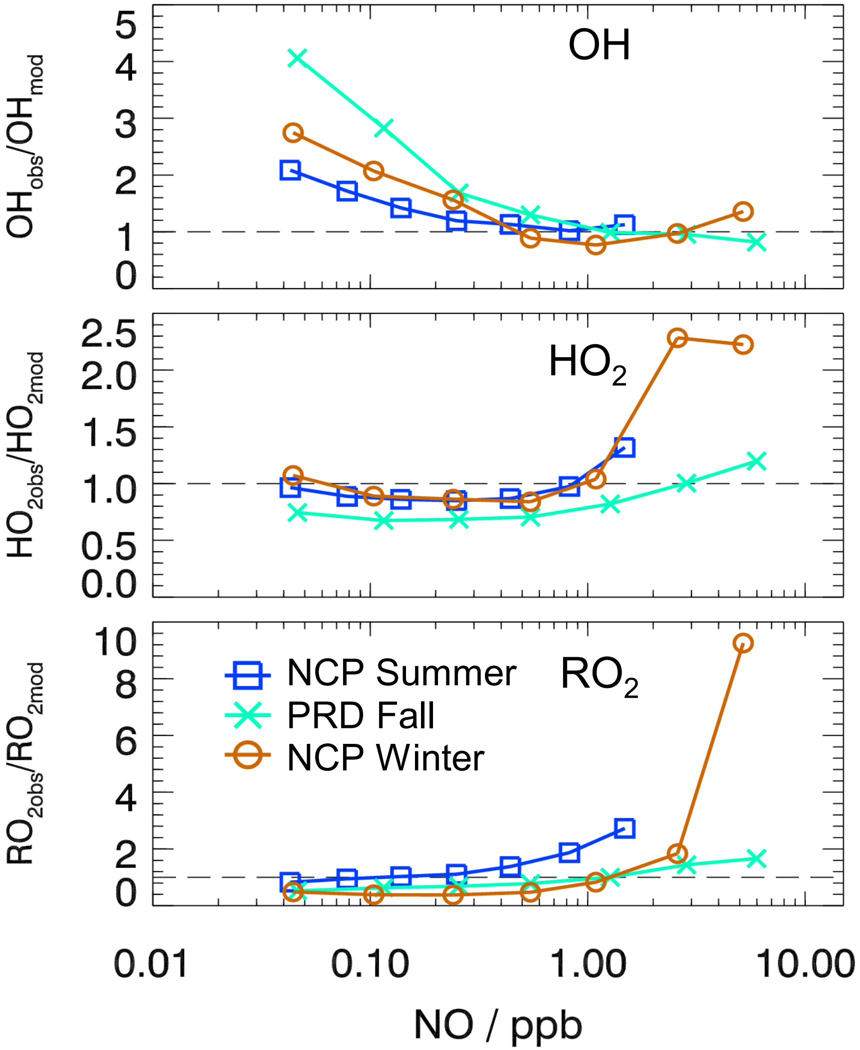
MODEL-MEASUREMENT COMPARISON



<u>Model:</u>

- RACM with updated isoprene mechanism
- Constraints: T, p, j, NOx, O_3, HONO, VOC

→Observed OH higher than model predictions with decreasing NO (NO<200pptv)

→Observed HO_2 / RO_2 higher than model predictions with increasing NO (NO>1ppbv)

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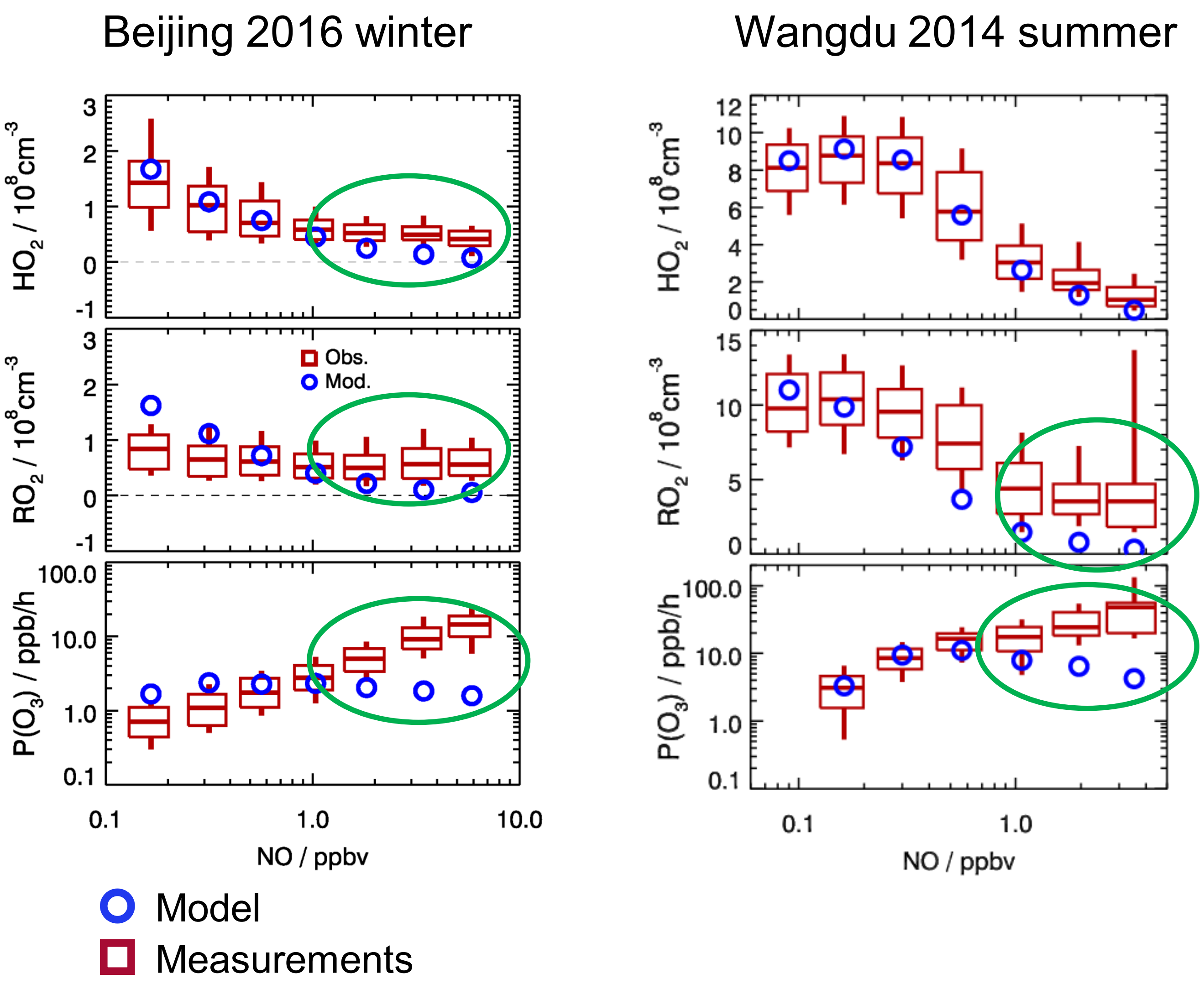
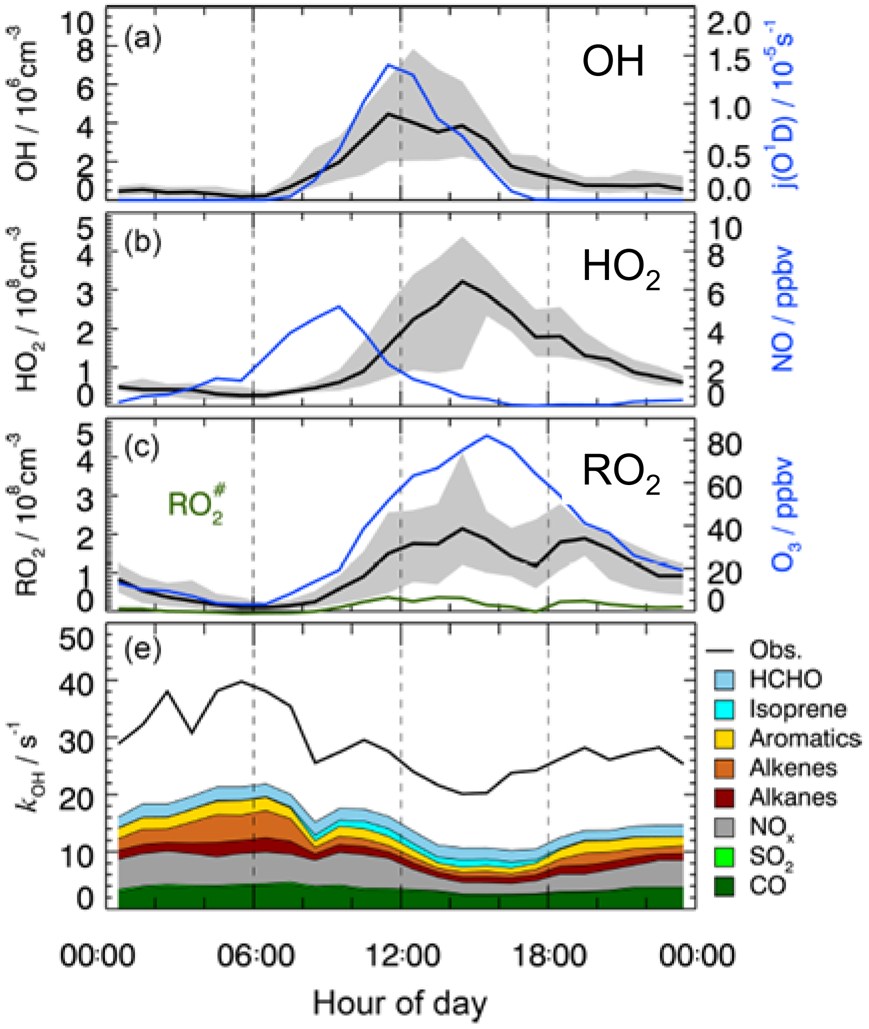
OZONE PRODUCTION RATES NORTH CHINA PLAIN



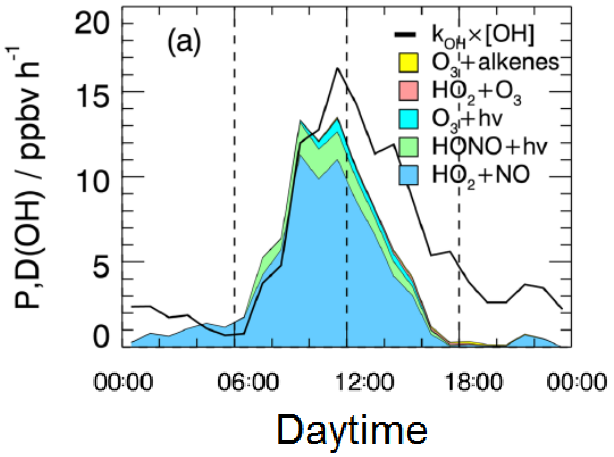
HO_2 / RO_2 concentrations higher than modelled concentrations

→Higher local ozone production rates than chemical models suggest

PEARL RIVER DELTA FALL 2014: MISSING OH REACTIVITY



OH Radical Budget



Using measured VOC concentrations
$\rightarrow \sum k_{OH+VOCi}\,[VOC_i] \times [OH]$

Using the measured OH reactivity (w/o CO, NOx)
$\rightarrow k_{OH}(VOC) \times [OH]$

- 50% of OH reactivity unexplained
- Missing OH reactivity due to unmeasured VOCs

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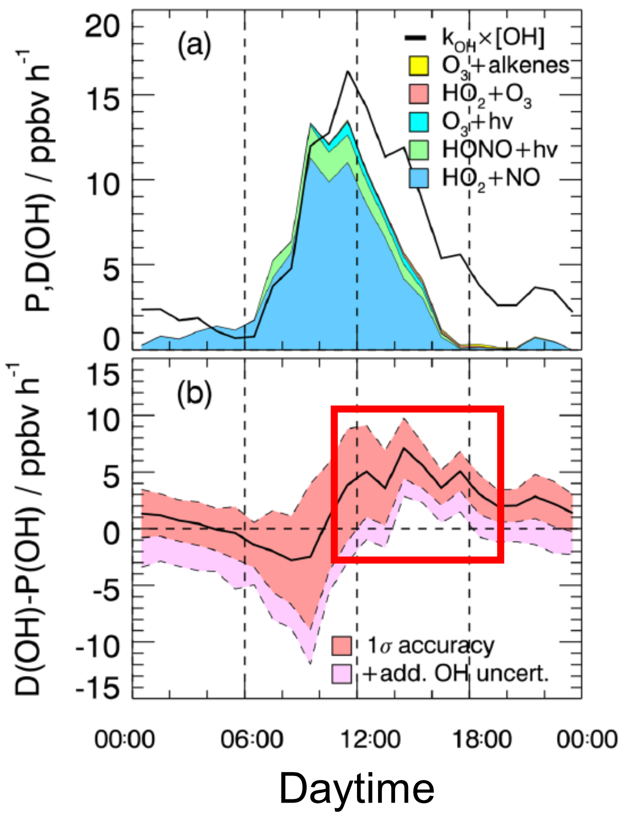
PEARL RIVER DELTA FALL 2014: MISSING OH SOURCE

OH Radical Budget

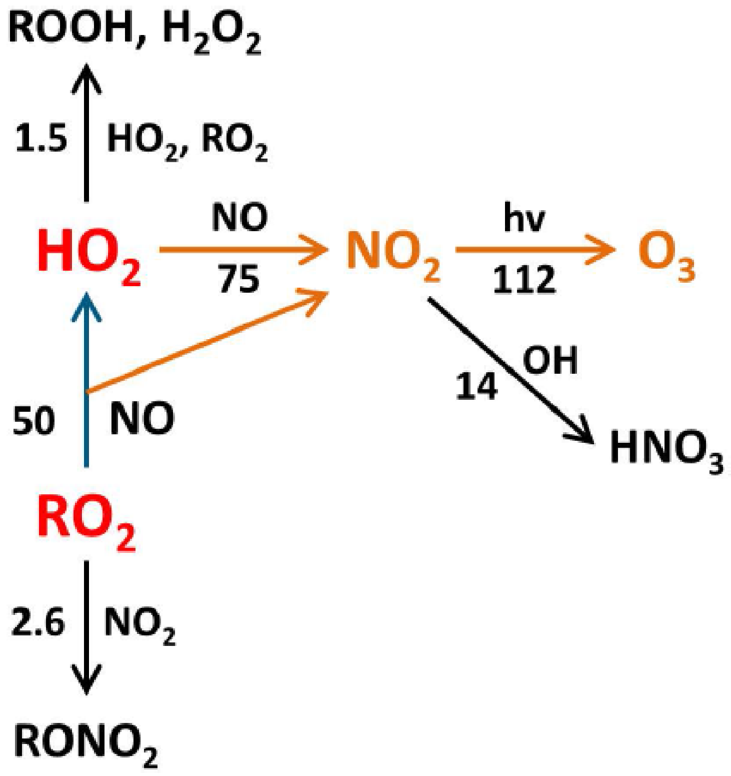


- Missing OH source (4-6 ppb/h) in the afternoon
- Missing RO_2 sink (2-5 ppb/h) in the afternoon
- HO_2 and total ROx budgets are closed

→Hypothesis: RO_2 regenerates OH without oxidation of NO

→No ozone production from this process

PEARL RIVER DELTA FALL 2014: OZONE PRODUCTION



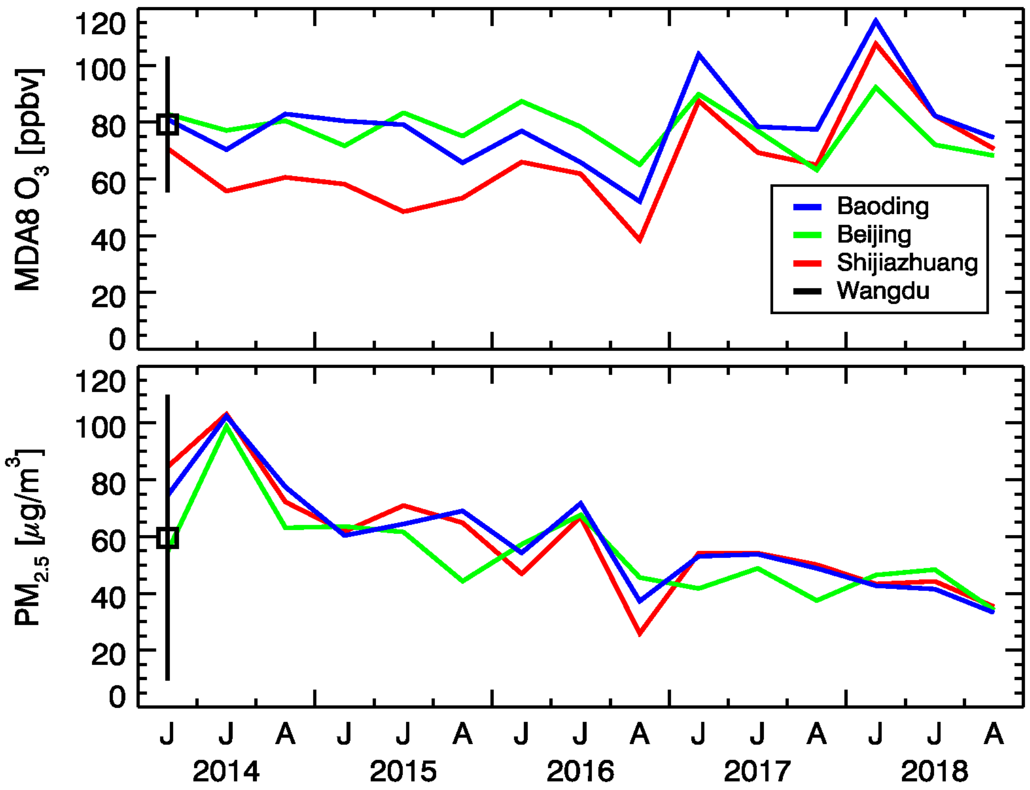
Integrated daily O_3 production (112ppbv):

- 14% from HCHO + OH/hν
- 8% from CO + OH
- 18% from measured VOCs
- 60% from unknown VOCs

If hypothesis of RO_2 → OH is correct

→25% RO_2 does not contribute to O_3 formation

OZONE AND PM2.5 TRENDS IN THE NORTH CHINA PLAIN



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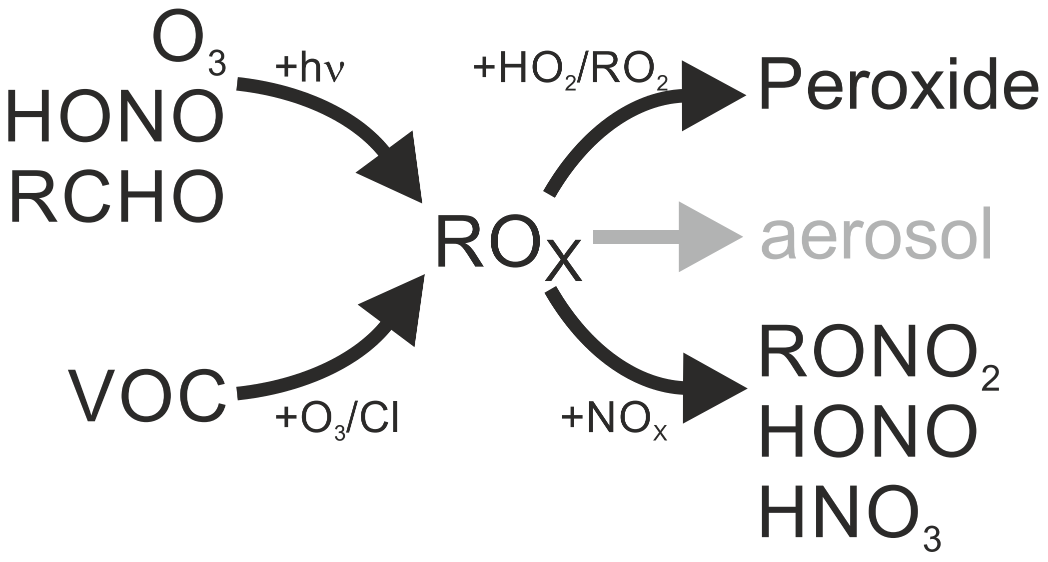
NCP SUMMER 2014: POTENTIAL IMPACT HO_2 UPTAKE

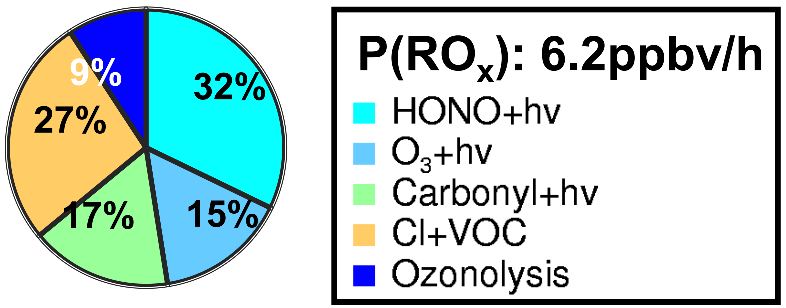


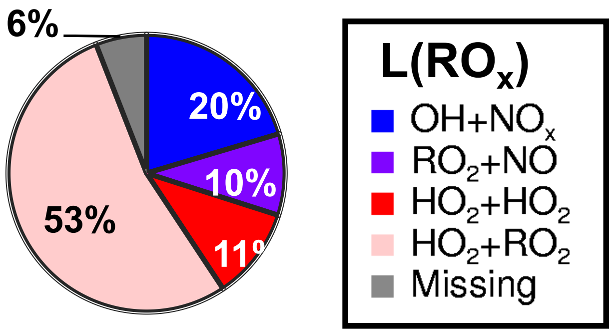
- HO_2 uptake on aerosol typically only important for liquid aerosol and catalyzed by transition metal ions
- Global models suggest that cleaning of air in China reduced HO_2 aerosol loss between in recent years

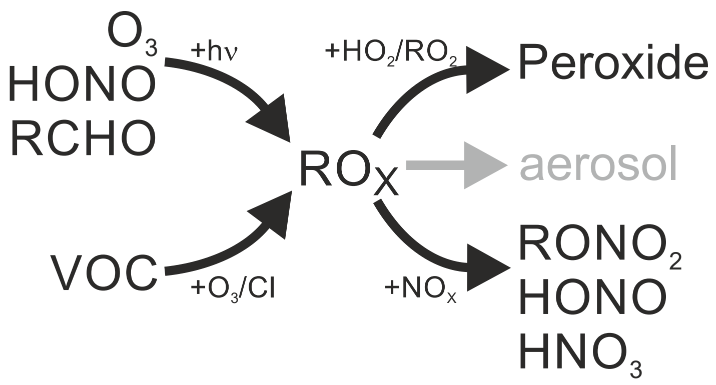
→Increase in peroxy radical concentrations

→Potential reason for observed increase in ozone pollution

NCP SUMMER 2014: POTENTIAL IMPACT HO_2 UPTAKE







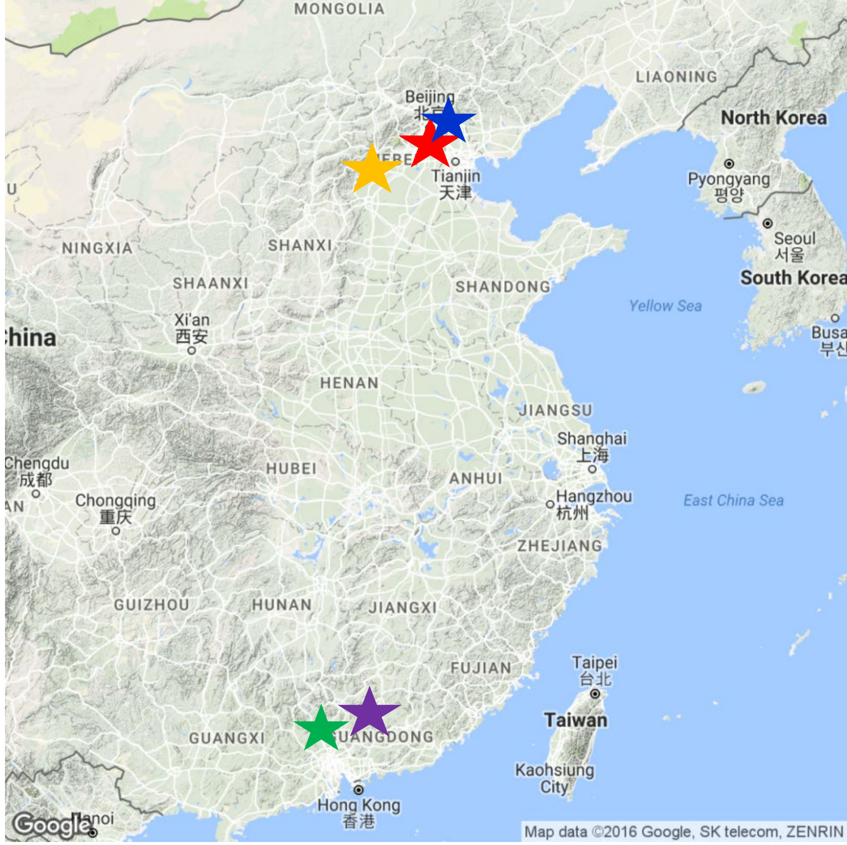
ROx budget is closed

→Additional radical loss are not required to explain observed radical concentrations

→HO_2 uptake does likely not explain ozone increase observed in China

SUMMARY OPEN QUESTIONS

- Which radical precursors contribute to radical production?
- How much do unmeasured organic compounds contribute to oxidation processes and which compounds are these?
- What is the imortance of RO_2 → OH conversion that does not lead to ozone production and what are the organic species behind?
- Could HO_2 uptake be of importantance for radical loss / ozone production?

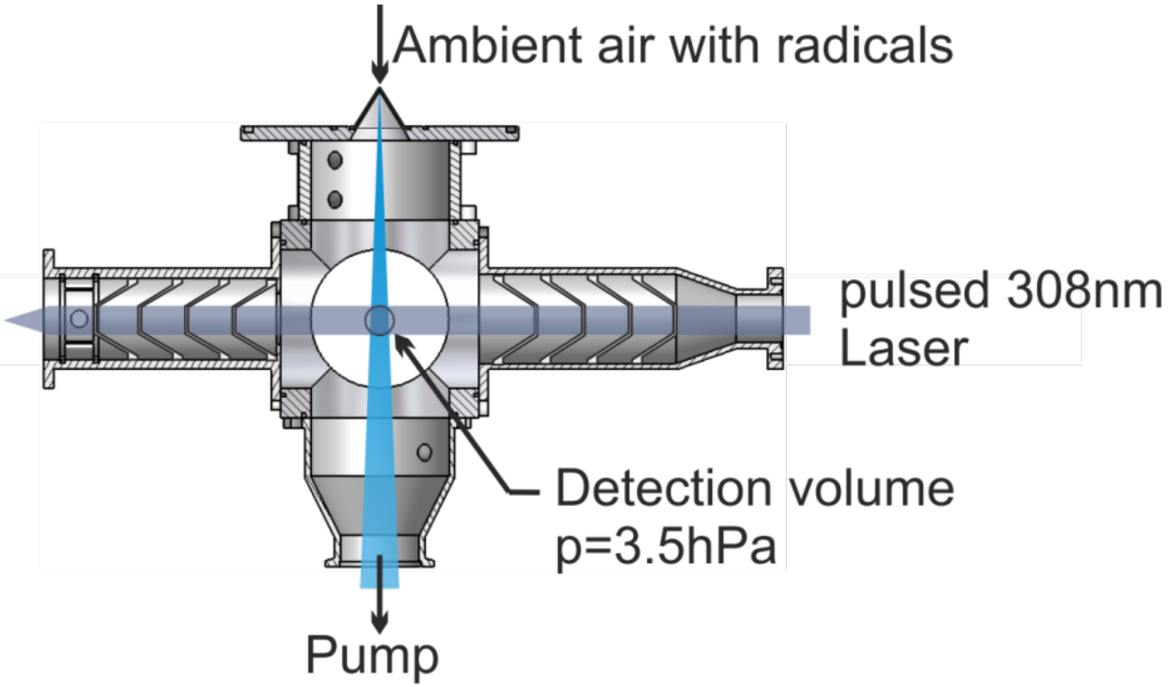


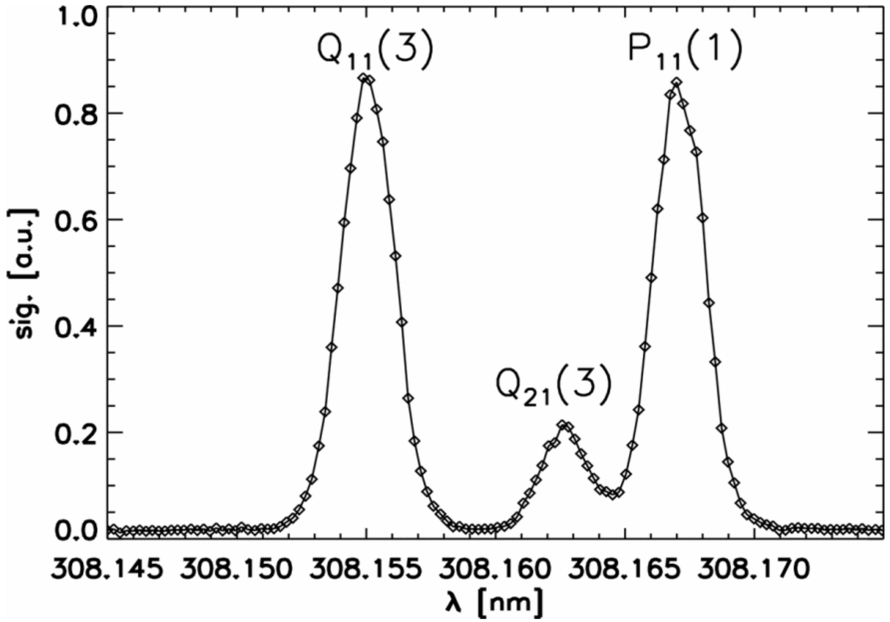
One way to address these questions:

- Experimental determination of radical budgets (OH, HO_2, RO_2, ROx)
- Quantification of unmeasured OH reactants (OH reactivity combined with speciated OH reactants using GC / mass spectrometer instrumentation)

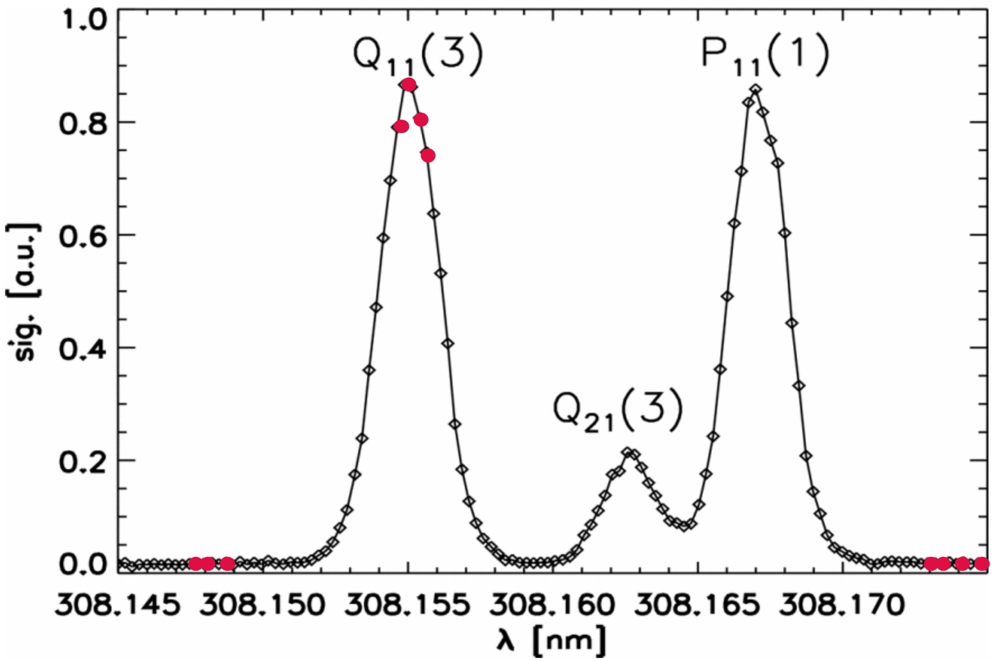
LASER-INDUCED FLUORESCENCE OH DETECTION

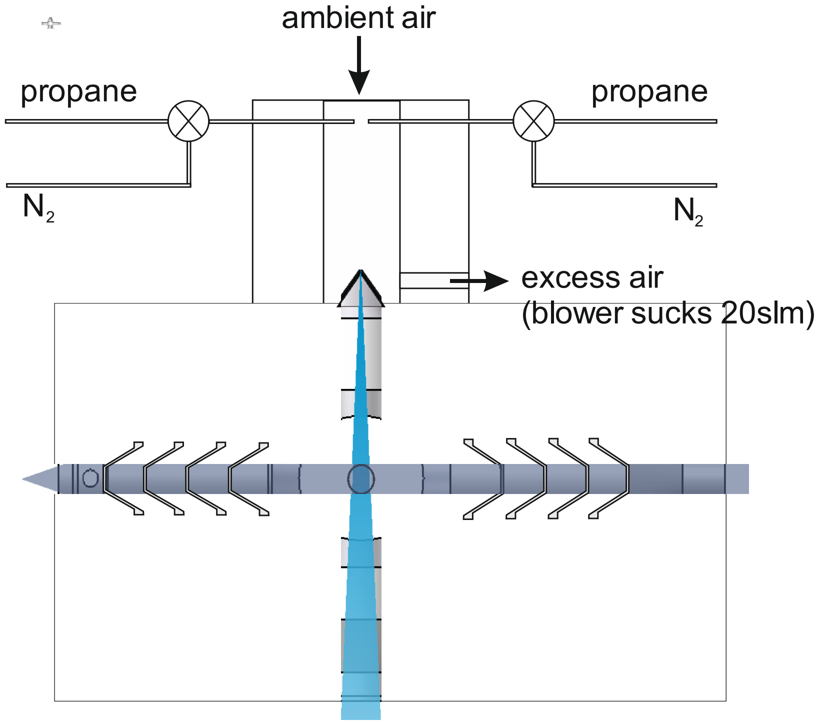
- Gas expansion into low pressure cell
- Excitation of OH at 308nm
- Fluorescence detection at 308nm





OH DETECTION BY LASER-INDUCED FLUORESCENCE





Signal on the detector: $S(\lambda) = S_{Bkg} + S_{Flu}(\lambda)$

→Wavelength scan

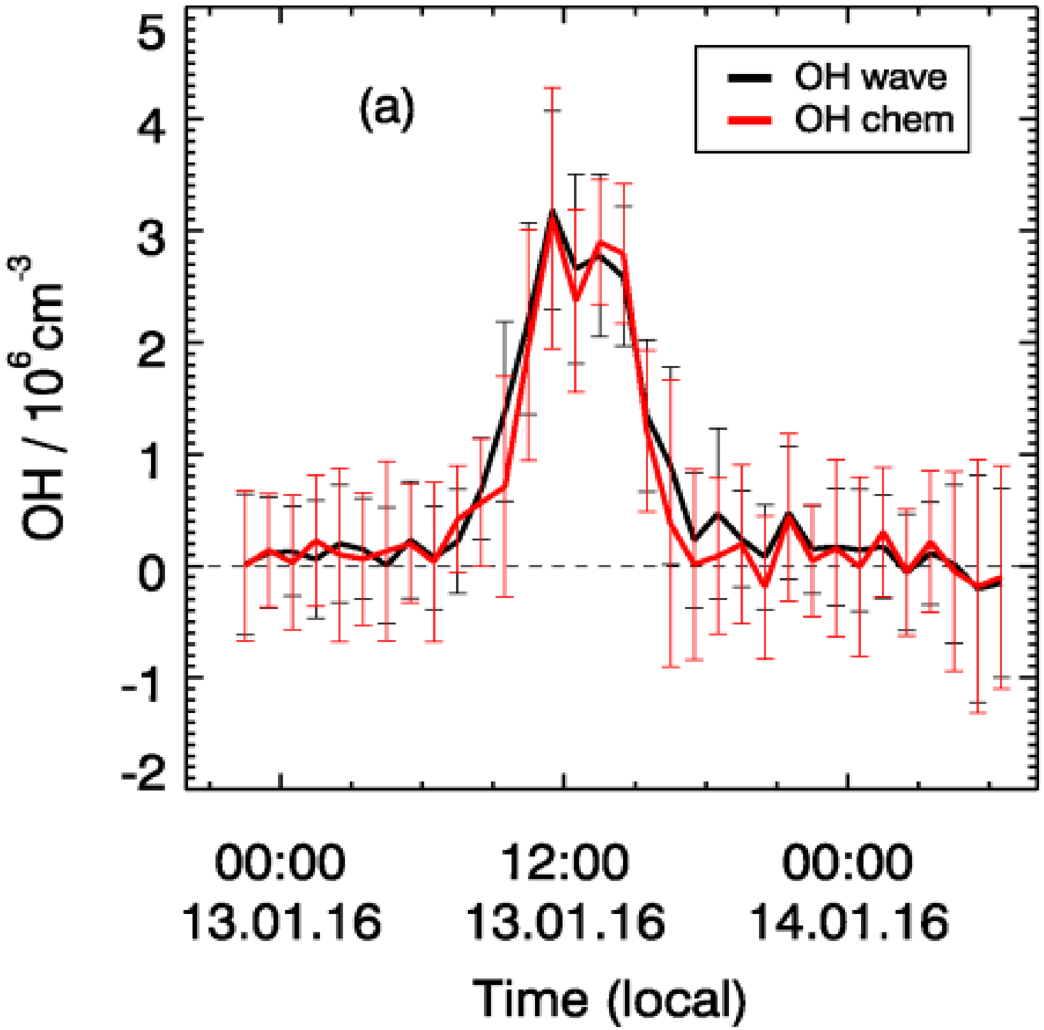
→Internally produced OH is detected as ambient OH

Chemical modulation scheme (Mao et al., 2012)

→Ambient OH scavenged by propane

→Residual signal is internally produced OH

CHEMICAL TITRATION APPLIED IN FIELD CAMPAIGNS



North China Plain winter 2016

- Daylong comparison with improved automated system

→ No significant interference detected

Tan et al., ACPD 2018

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