Improving understanding of secondary pollutant formation in London and Beijing through radical observations and model comparisons

Lisa Whalley

Poor air quality making headlines

Global pollution kills 9m a year and threatens 'survival of human societies'

Landmark study finds toxic air, water, soils and workplaces kill at least 9m people and cost trillions of dollars every year

A Bangladeshi rickshaw puller rides past smoke created by burning waste materials on a street in Dhaka. Photograph: Anadolu Agency/Getty Images

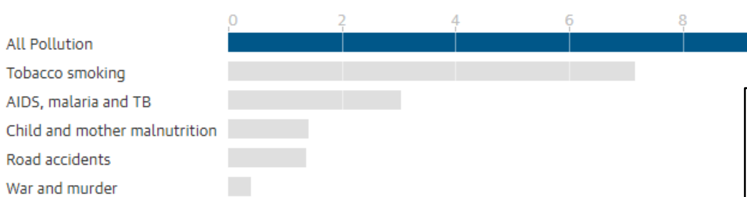
Beijing smog: pollution red alert declared in China capital and 21 other cities

Authorities issue five-day warning and order schools to close, residents to stay indoors and heavy industry to slow or halt production

A photo taken from the China Zun, a skyscraper under construction in Beijing, shows the city being shrouded in heavy smog on Friday. Photograph: VCG via Getty Images

Deaths from pollution dwarf many other major causes

Global deaths by cause in 2015, millions



Guardian graphic | Source: Landrigan et al, The Lancet

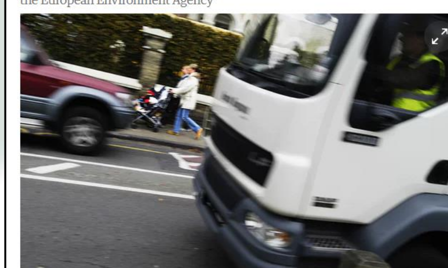
38,000 people a year die early because of diesel emissions testing failures

Global inventory of nitrogen oxide emissions shows highly polluting diesel cars are 'urgent public health issue'

...ph: Prakash

UK has second-highest number of deaths from NO2 pollution in Europe

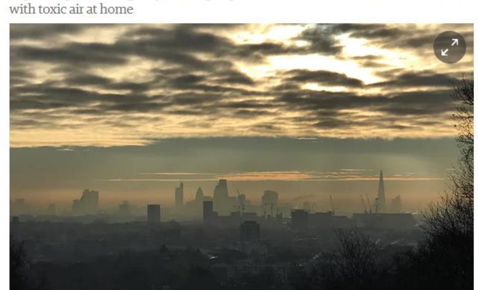
Only Italy has more annual deaths from nitrogen dioxide, according to a report by the European Environment Agency



Nitrogen dioxide is a toxic gas mostly caused by diesel vehicles and is linked to lung problems. Photograph: Rex/Shutterstock

Sadiq Khan triggers alert for high air pollution in London

Capital is given emergency warning as polluted air from the continent combines with toxic air at home



London's pollution alert has been issued seven times in the last 13 months. Photograph: Harriet Tyce/GuardianWitness

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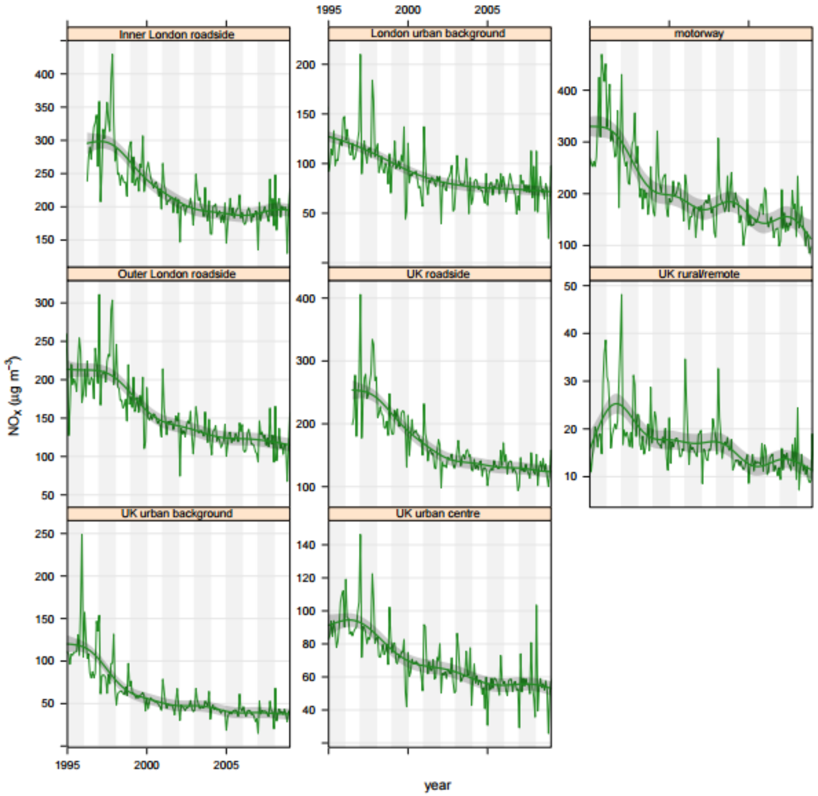
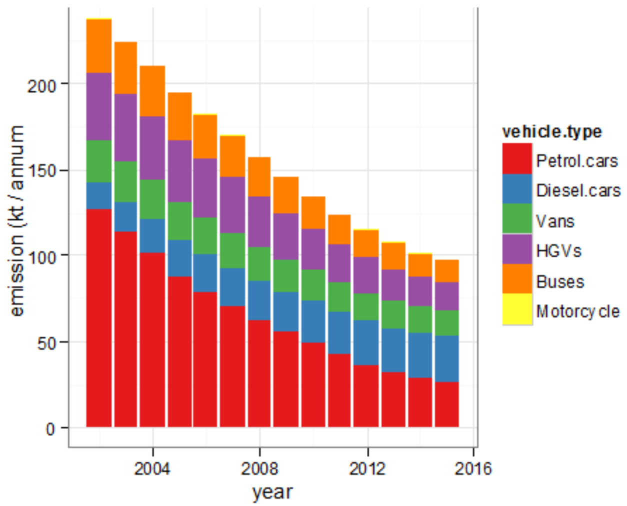
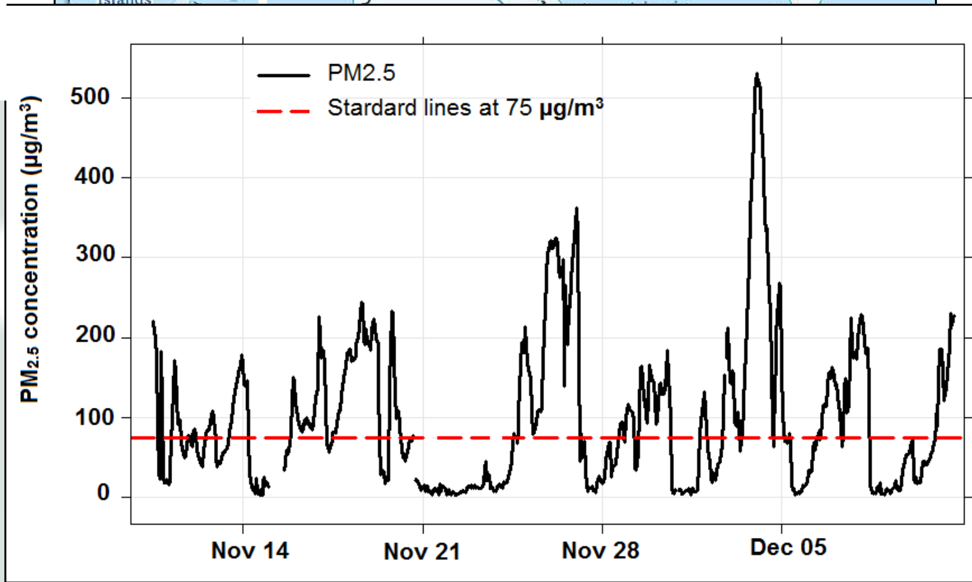
Air quality in London and Beijing



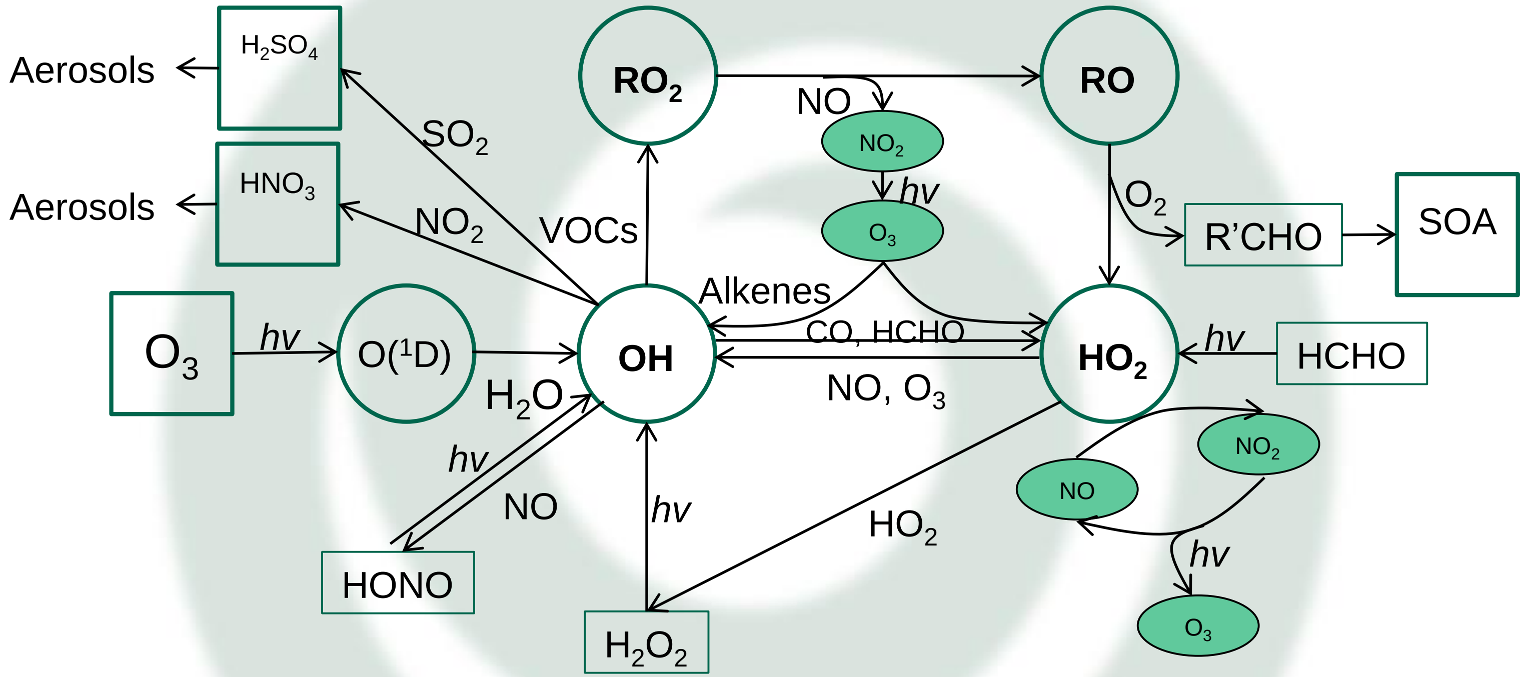
- Industry and power generation located to south of Beijing





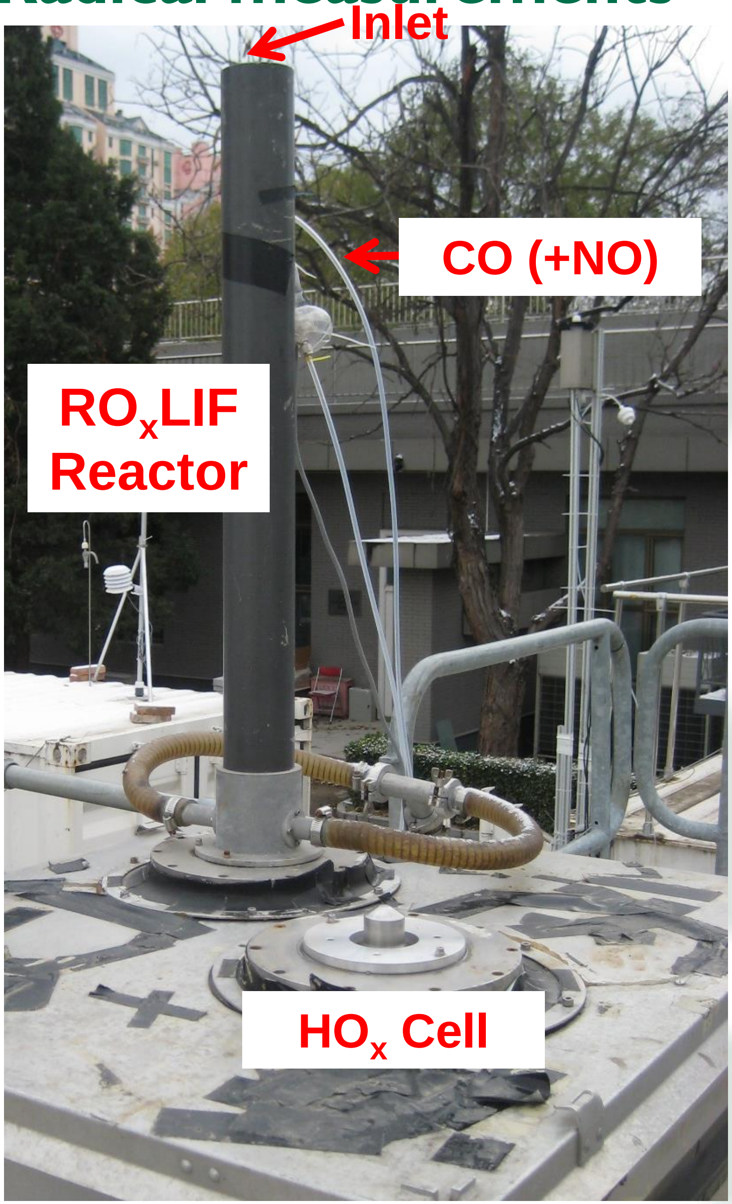
Formation of secondary pollutants

- OH mediates virtually all of the oxidative chemistry in the atmosphere

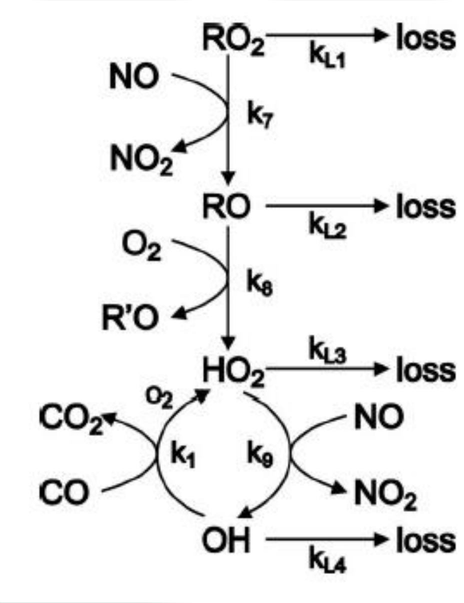


- OH initiates the removal of primary emitted trace species which are directly harmful to humans
- OH initiated oxidation of VOC, HCHO and CO generates peroxy radicals which by reaction with NO form NO_2 resulting in the pollutant O_3

Radical measurements



FAGE Cell 1:
OH
HO_2
RO$_x$LIF Cell 2:
HO_2+RO_2 (NO on in reactor)
HO_2^* (NO off in reactor)

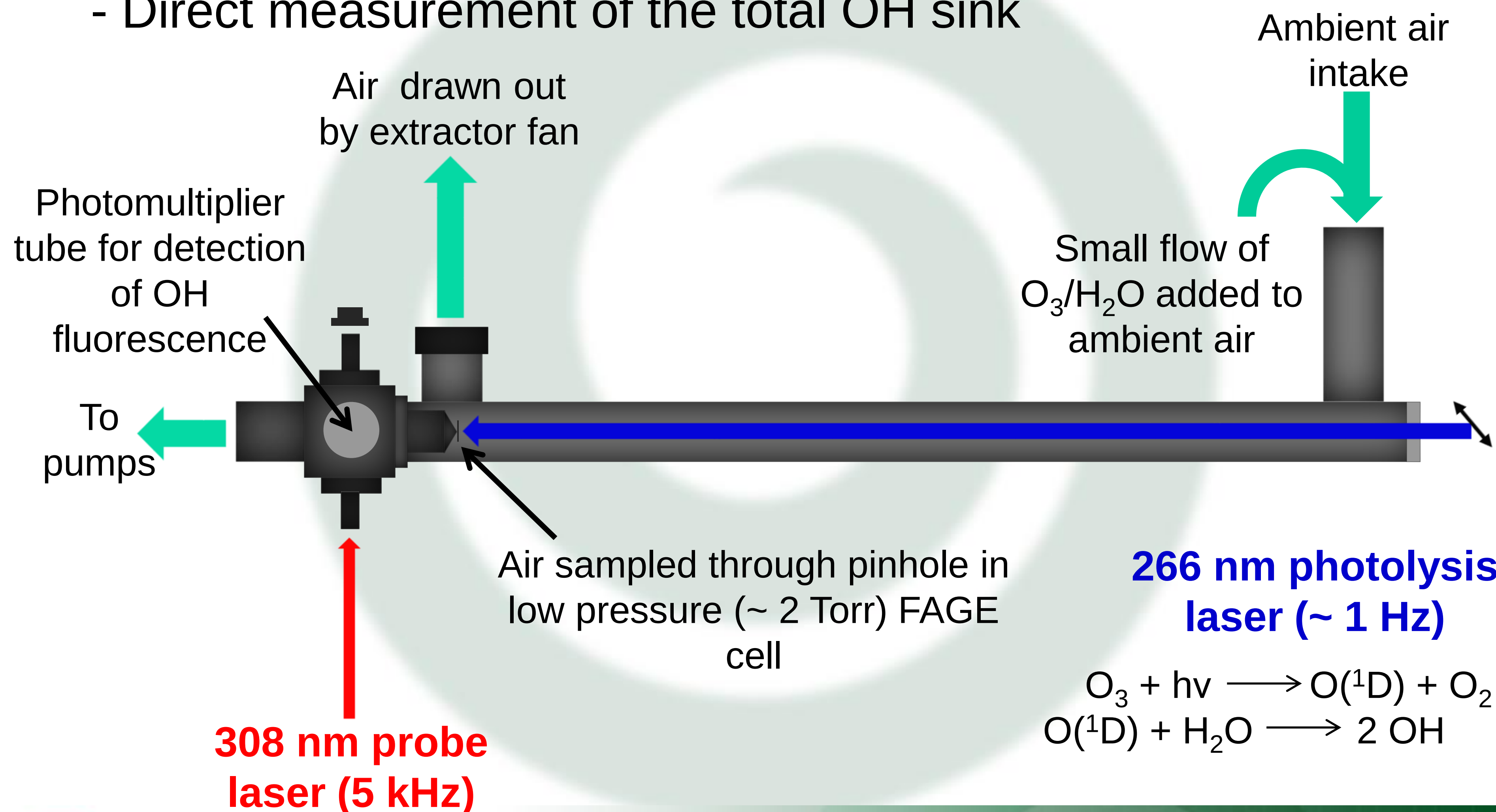


Whalley et al., AMT, 2015

OH reactivity instrument

OH reactivity (k'_{OH}) is the rate of OH loss in ambient air

- Direct measurement of the total OH sink



$$O_3 + h\nu \longrightarrow O(^1D) + O_2$$

$$O(^1D) + H_2O \longrightarrow 2\,OH$$

Stone et al., AMT, 2016

Master Chemical Mechanism

- The Master Chemical Mechanism is a near-explicit tropospheric chemical mechanism describing the complete gas-phase degradation of **135** primary emitted VOCs and the resultant generation of ozone and other secondary pollutants

22 alkanes (C_1-C_{12})
16 alkenes (C_2-C_6)
2 dialkenes (C_4-C_5)
2 monoterpenes (C_{10})
1 alkyne (C_2)
18 aromatics (C_6-C_{11})
6 aldehydes (C_1-C_5)
10 ketones (C_3-C_6)
18 alcohols and glycols (C_1-C_6)
10 ethers and glycol ethers (C_2-C_7)
8 esters (C_2-C_6)
3 carboxylic acids (C_1-C_3)
2 other oxygenates (C_3)
15 chlorocarbons (C_1-C_3)
2 bromocarbons (C_1-C_2)

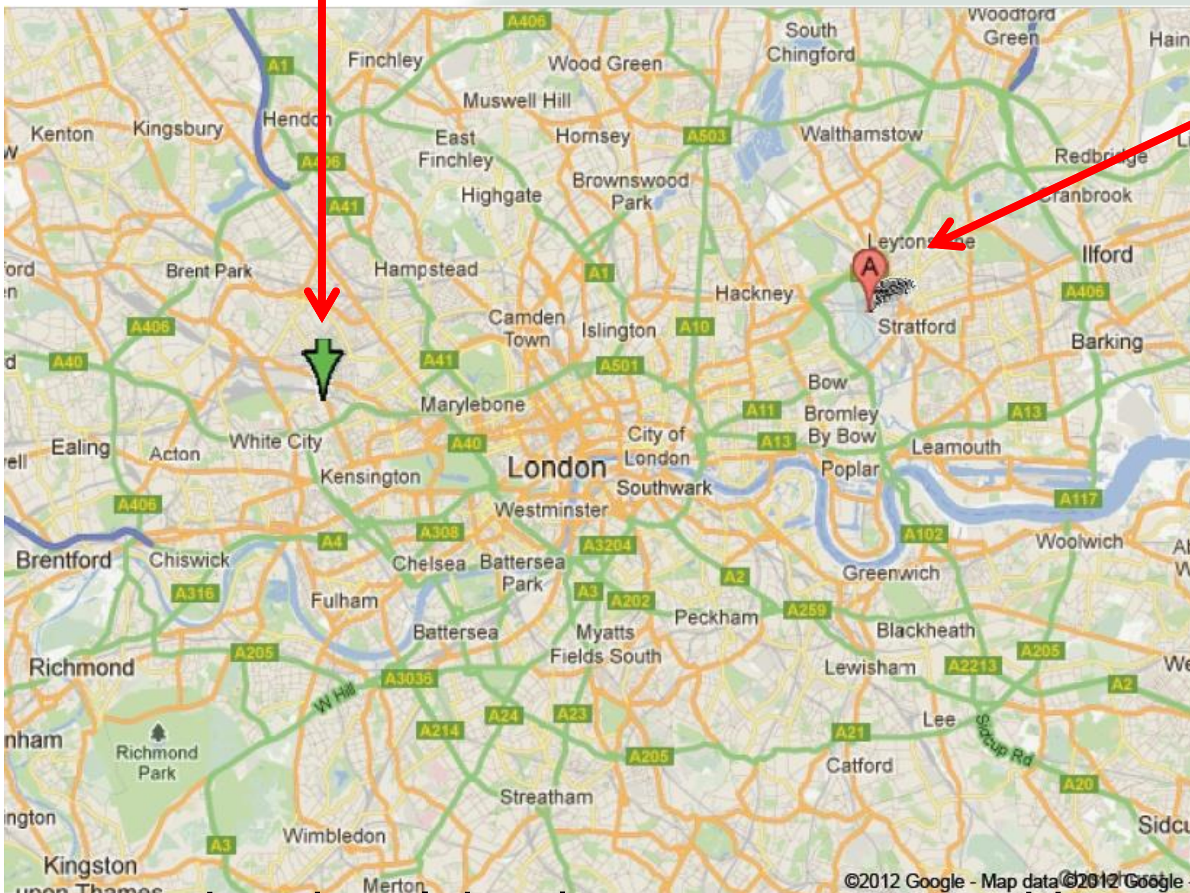
c.a. 6700 species; 16700 reactions

Model parameters
T, P, H_2O, NO, NO_2, O_3, CO
HONO, surface area, mixing height
Alcohols, C1 – C4 (4)
Alkanes, C1 – C12 (15)
Alkenes, C2 – C5 (8)
Alkynes, C2 (1)
Carbonyls, C1 – C6 (12)
Aromatics, C6 – C9 (16)
Dialkenes, C4 – C5 (2)
Monoterpenes, α-pinene, limonene
Hydrochlorocarbons, (2)
Esters, (2)

- Rate constants and product branching ratios are taken from the latest experimental/theoretical data or are estimated from structure activity relationships (SARs).


ClearfLo
University of Reading
The University of York
University of Leicester
University of Leeds
UEA
University of East Anglia
King's College London
Manchester 1824
University of Cambridge
Centre for Ecology & Hydrology
Natural Environment Research Council
Met Office
Per Ardua Ad Alta
TSS 213

Clearflo (Clear Air for London)
North Kensington, London, 2012



Summer (Jul/Aug) and Winter (Jan/Feb) campaigns

Large project involving long term composition and met. measurements at several sites (upwind, downwind, BT Tower, rooftops), plus IOPs

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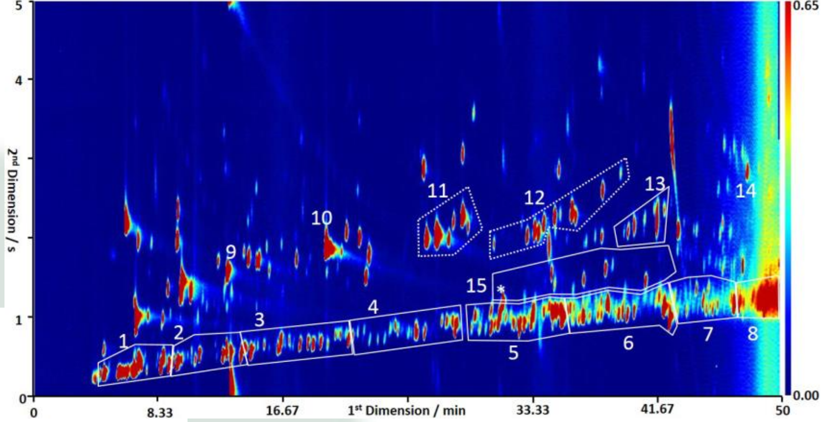
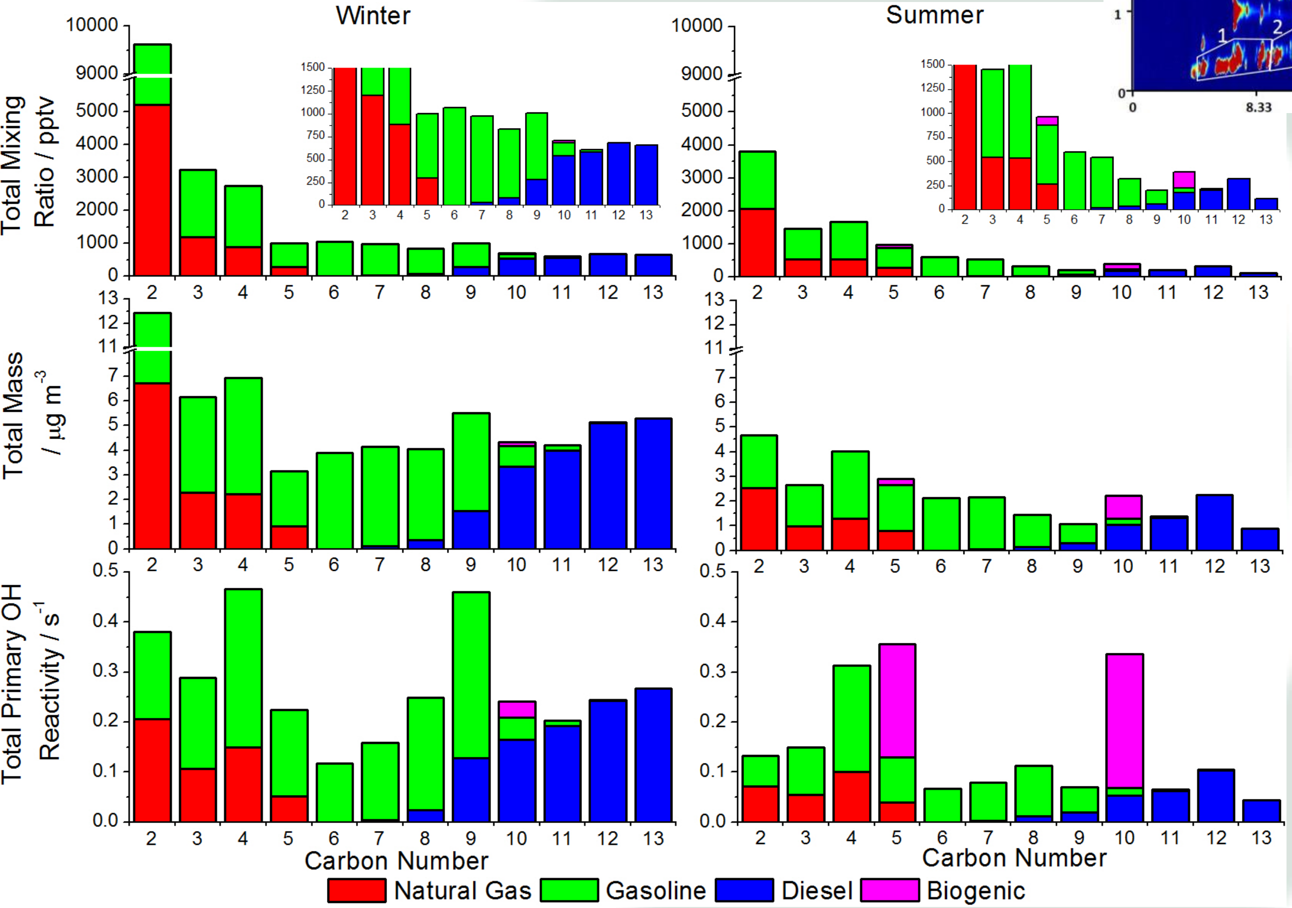
ClearfLo – some findings so far..

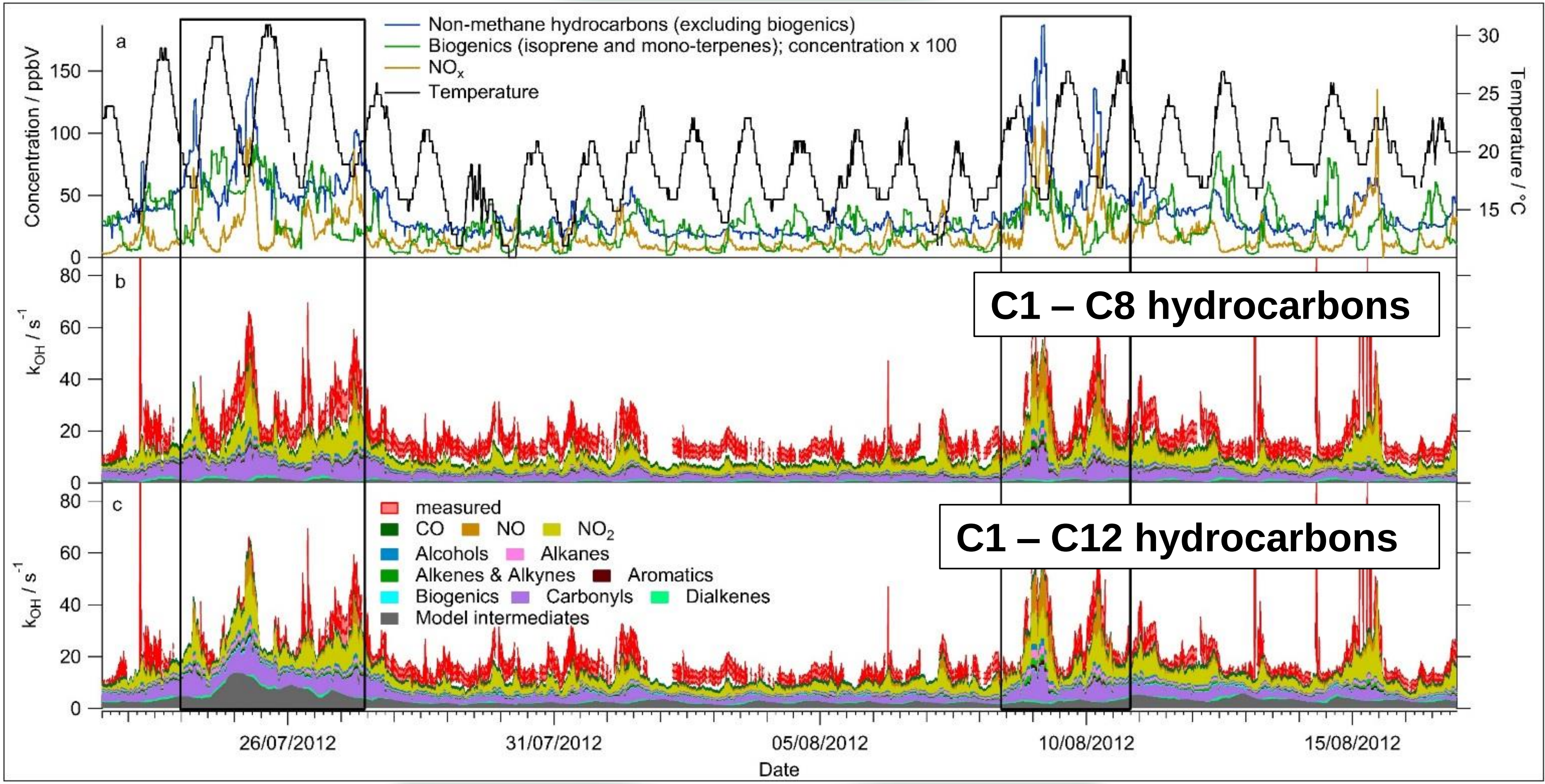




Diesel-related hydrocarbons can dominate gas phase reactive carbon in London

Dunmore et al. Atmos. Chem. Phys., 15, 9983, 2015

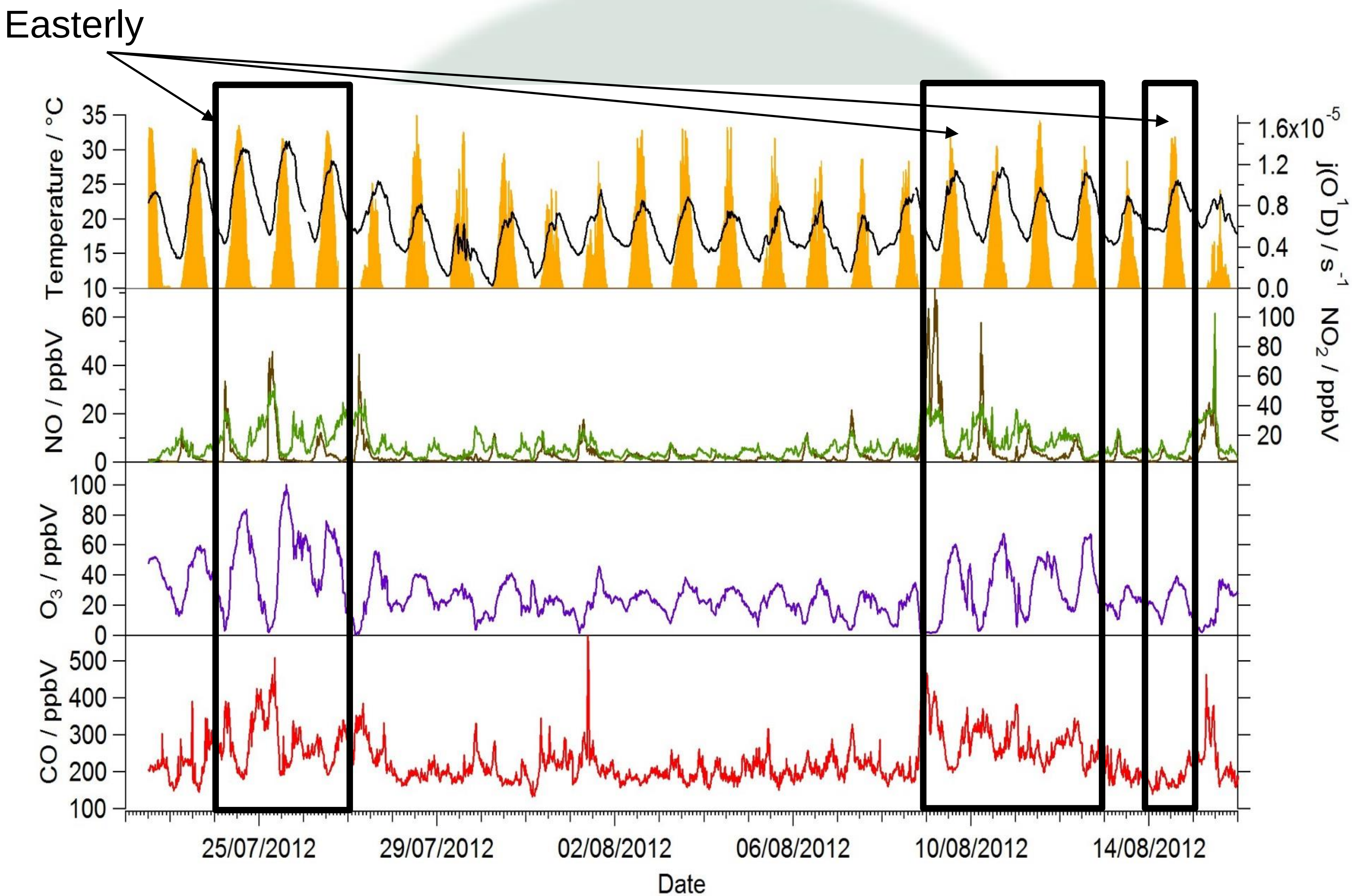
ClearfLo – some findings so far..



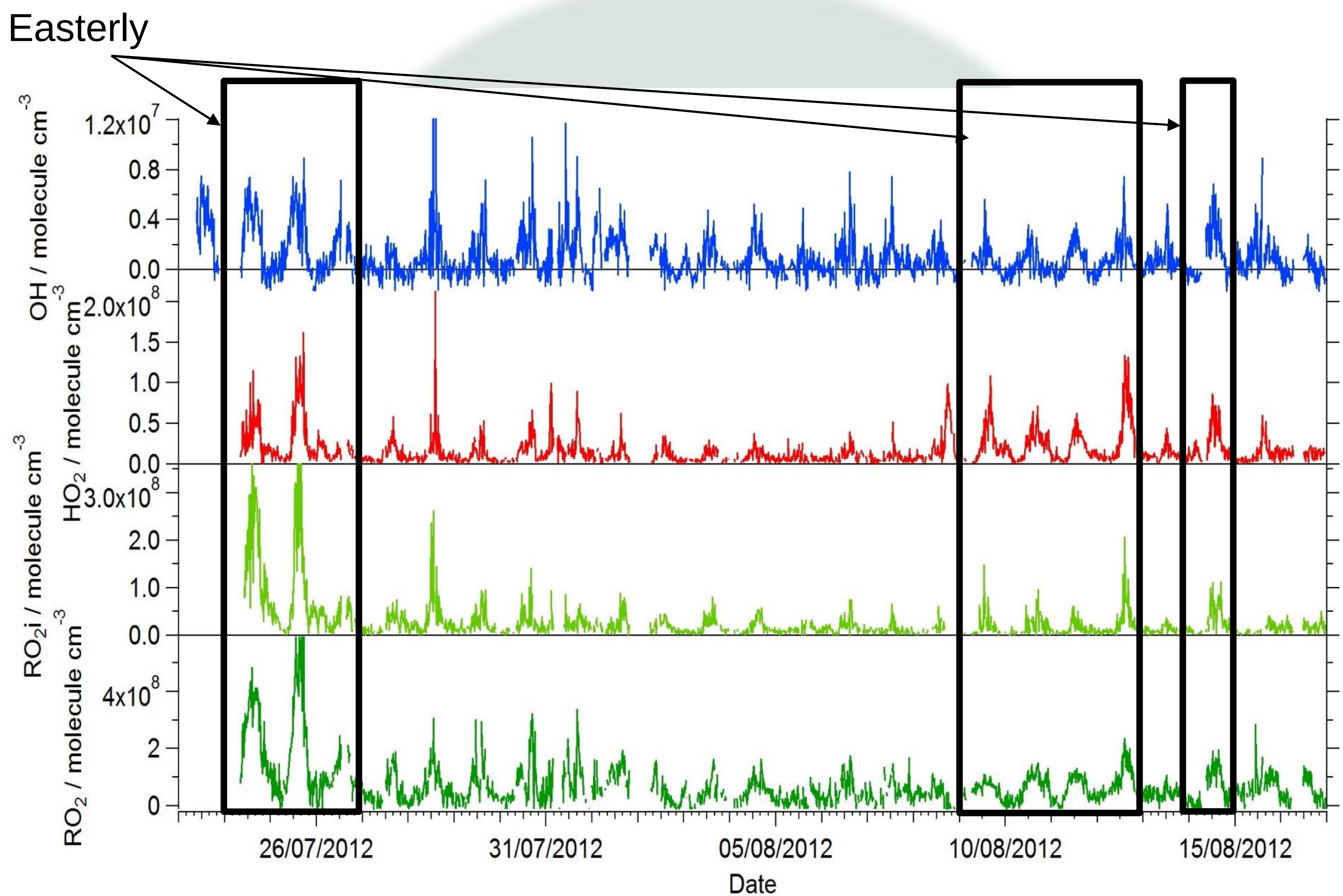
Oxidised products of biogenic VOC important for OH reactivity budget

Whalley et al. Atmos. Chem. Phys., 16, 2109, 2016

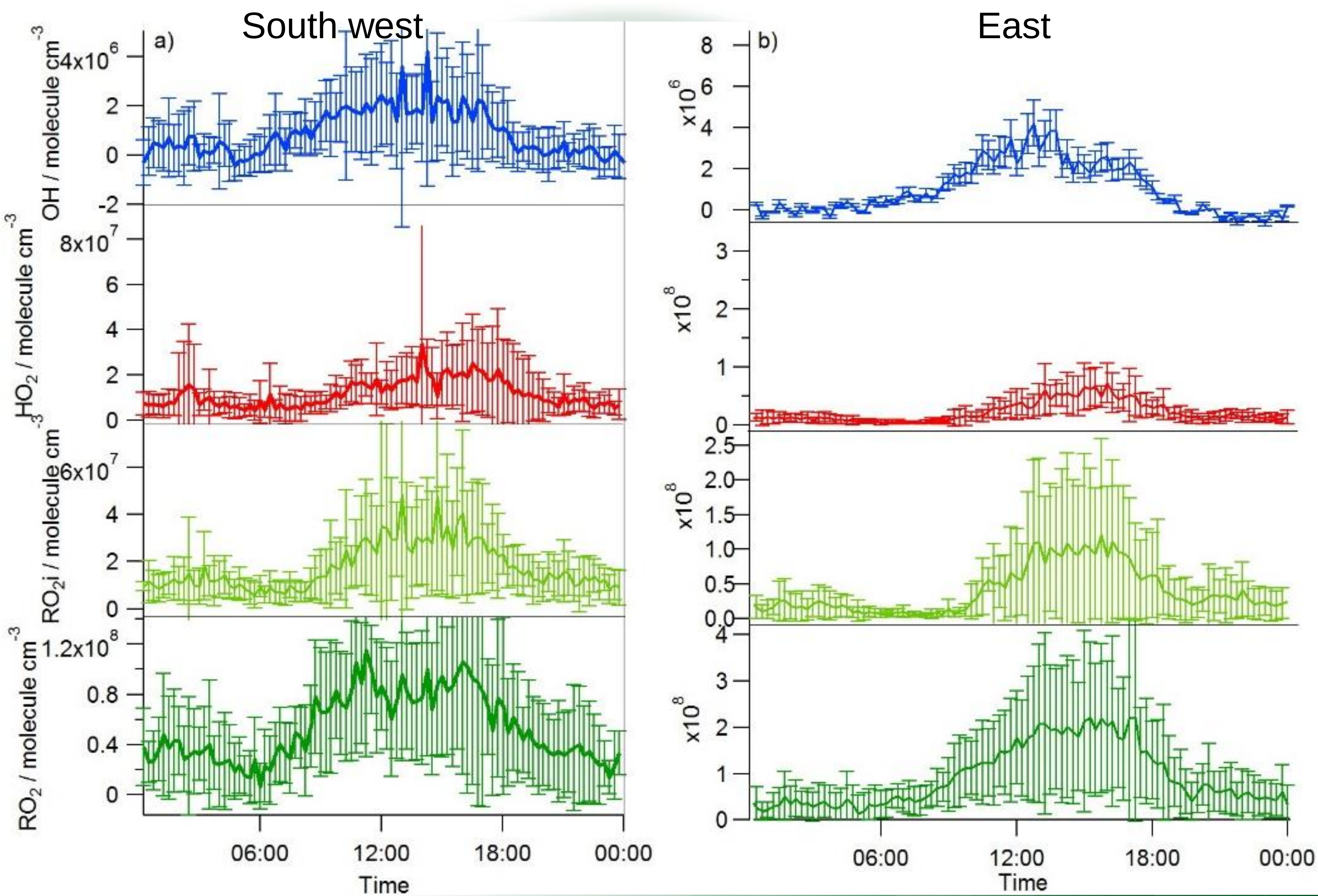
Summer ClearfLo measurements and conditions



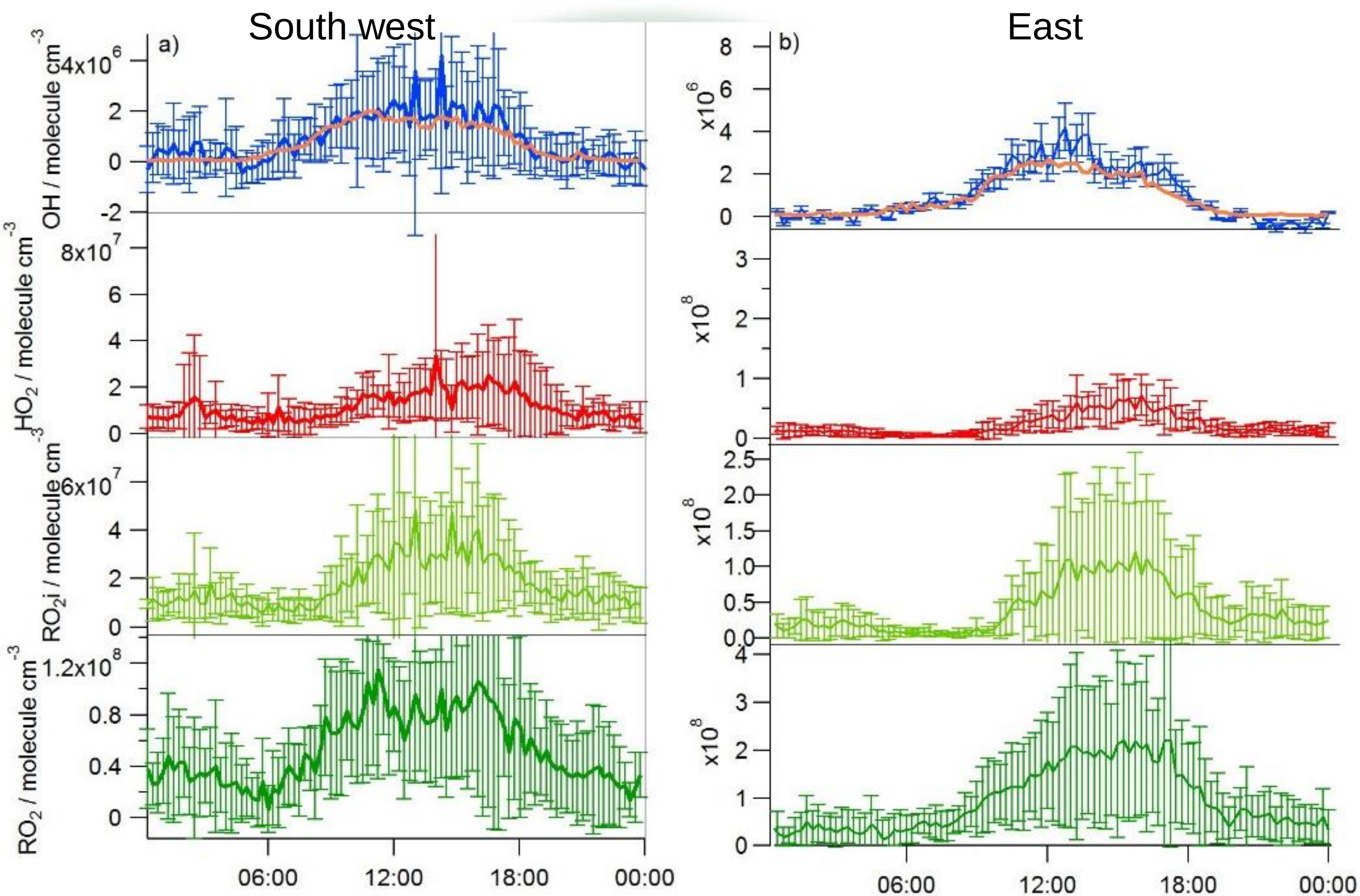
Radical Observations



Radical measurement diurnals

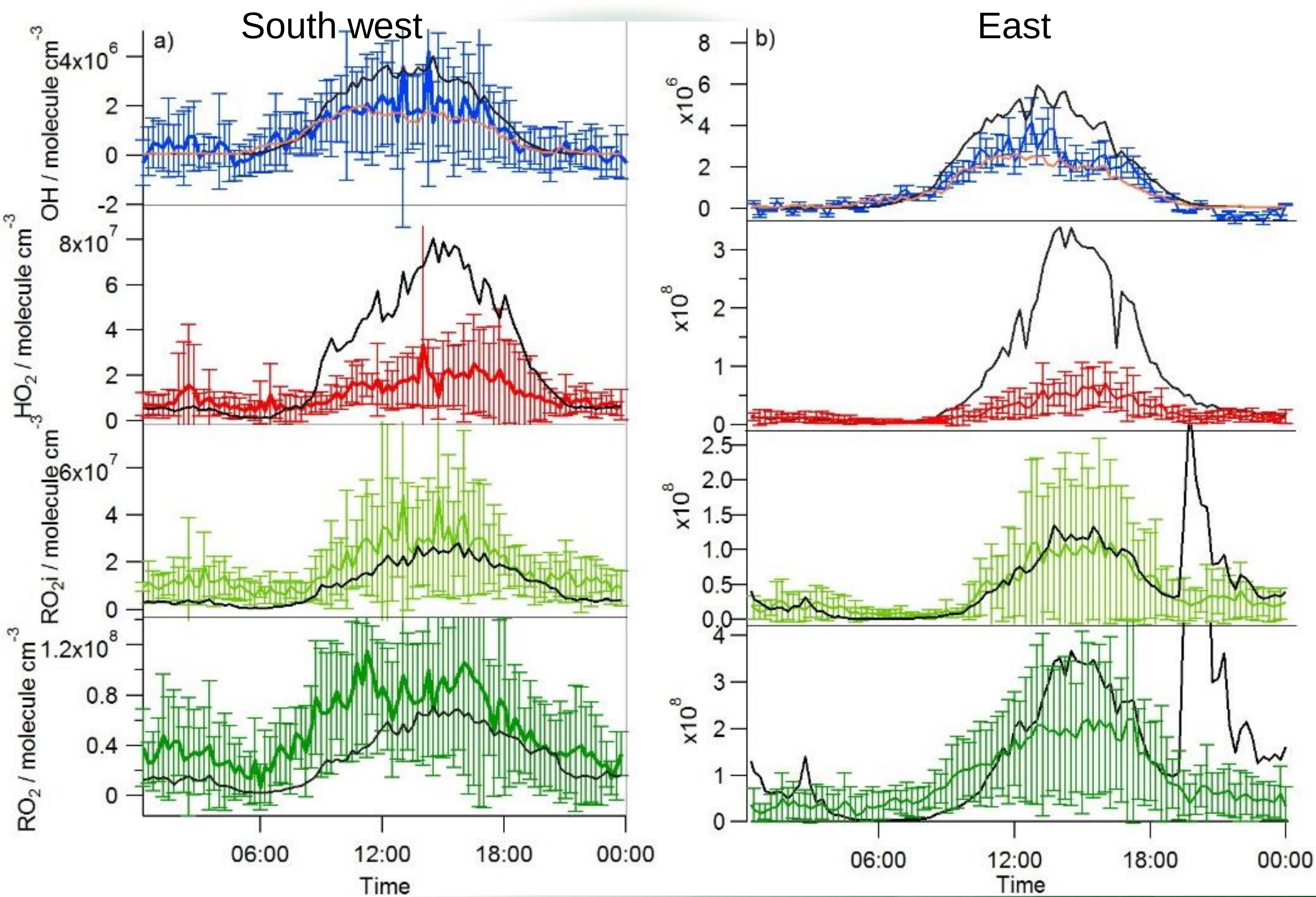


PSS calculation, measurement comparison

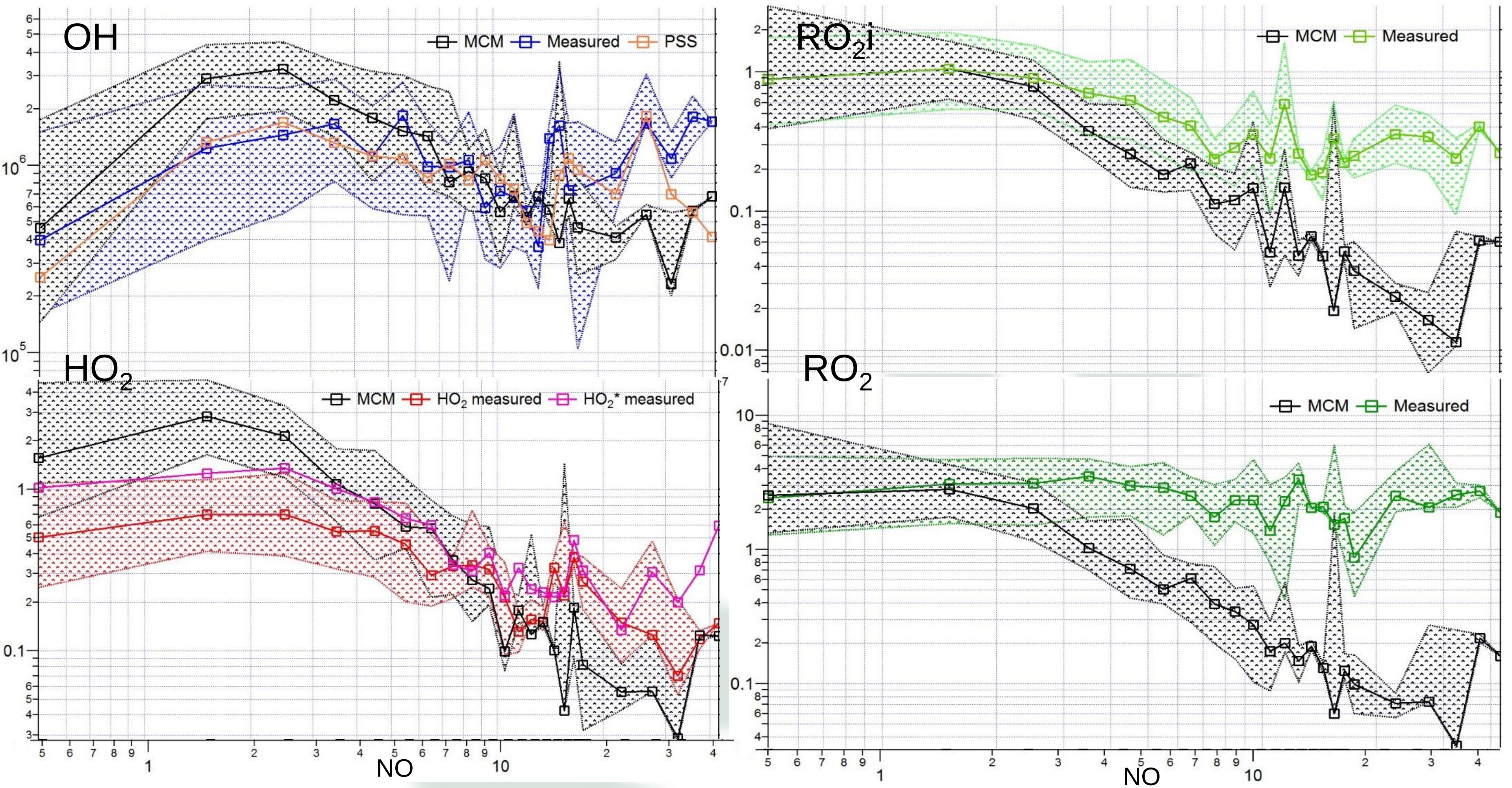


$$[OH]_{PSS} = \frac{p(OH) + j(HONO)[HONO] + k[O_3][alkene] + k[HO_2][NO]}{k_{OH}}$$

Model measurement radical comparison

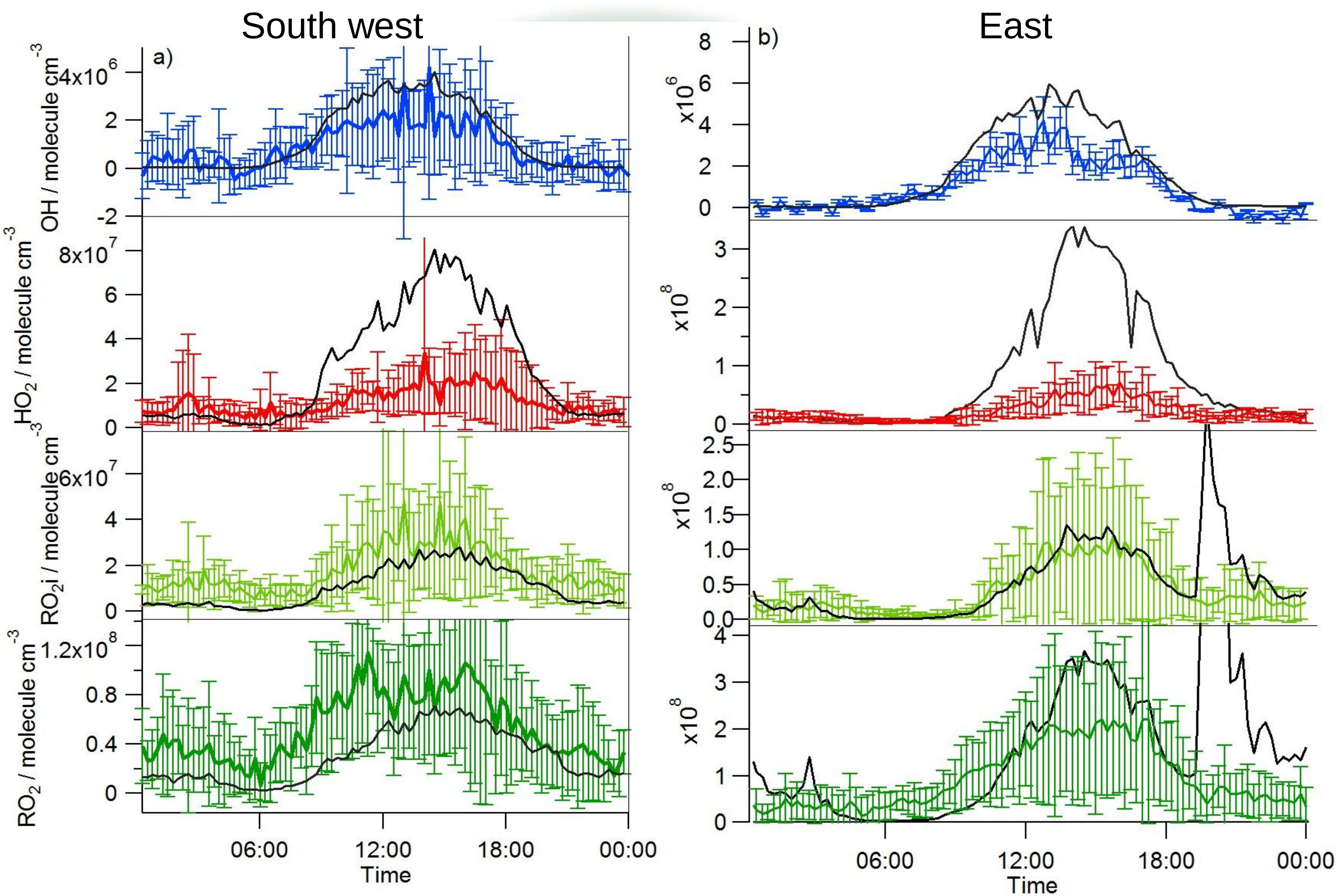


Model measurement agreement as a function of NO

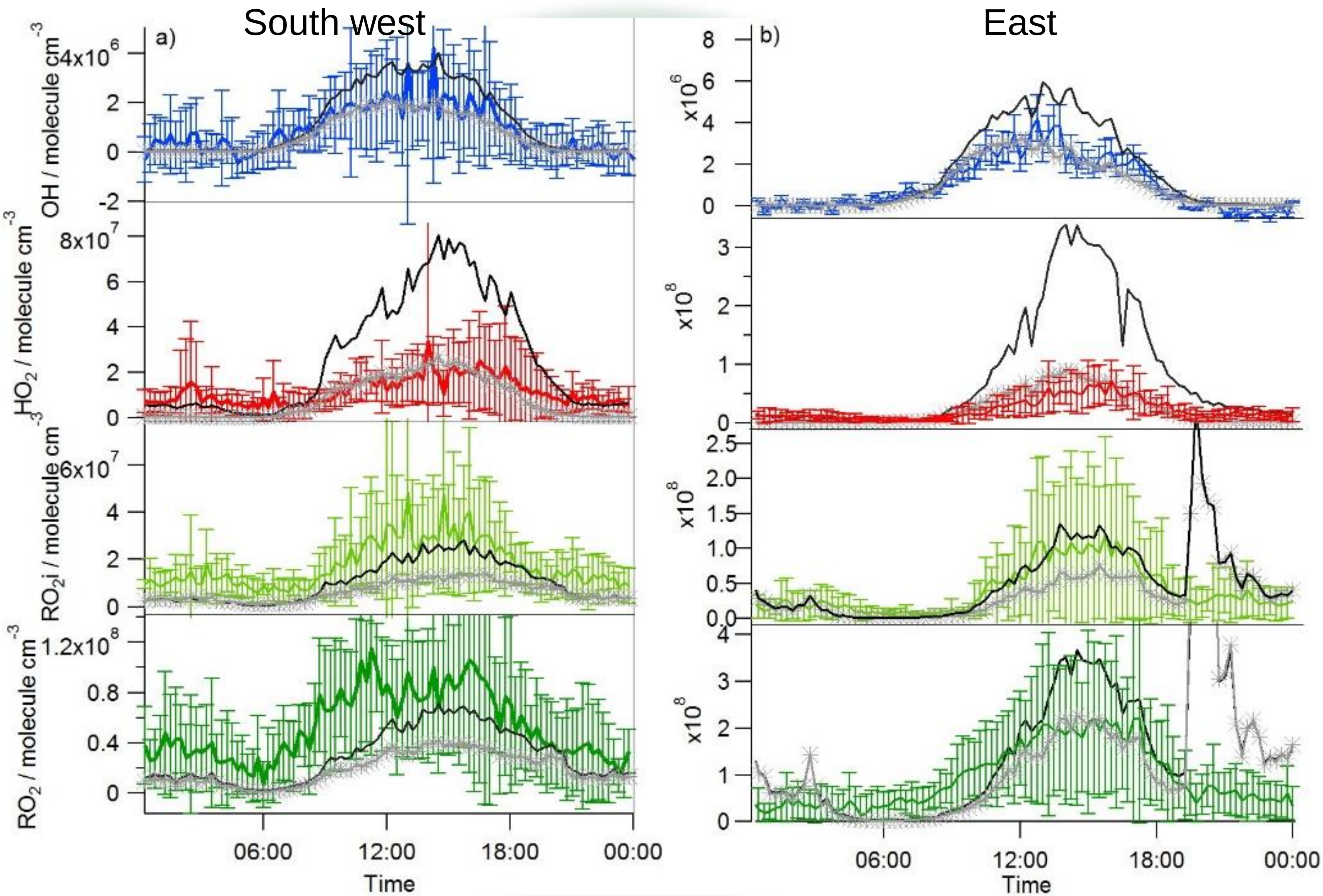


- Missing HO_2 radical sinks under low NO_x
- Reasonable agreement between HO_2 model and observations at higher NO_x levels, but increasing under-prediction of RO_2 (also in Beijing during the winter)

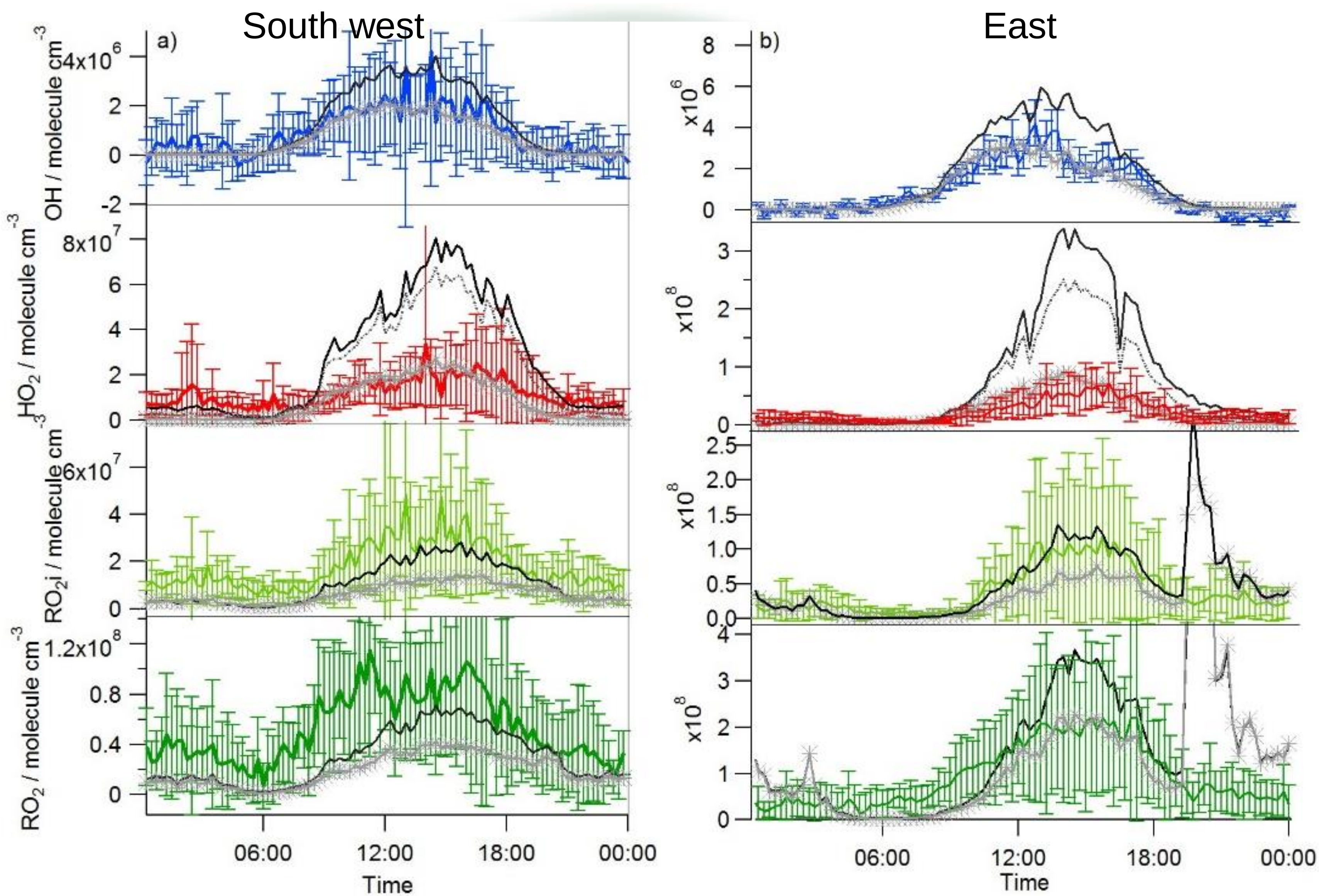
Model measurement radical comparison



First order loss of HO_2 = 0.3 s^{-1}

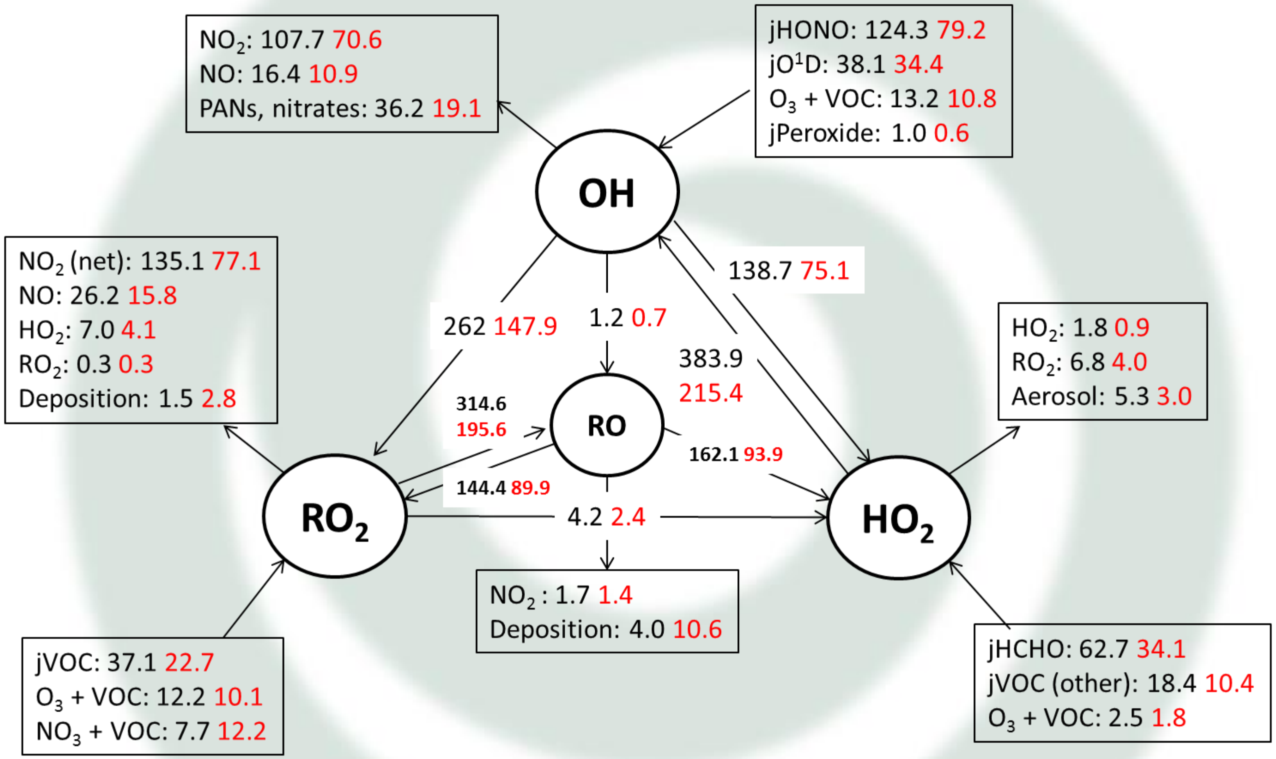


First order loss of HO_2 = 0.3 s^{-1}, γ_{HO2} = 1



Modelled radical flux

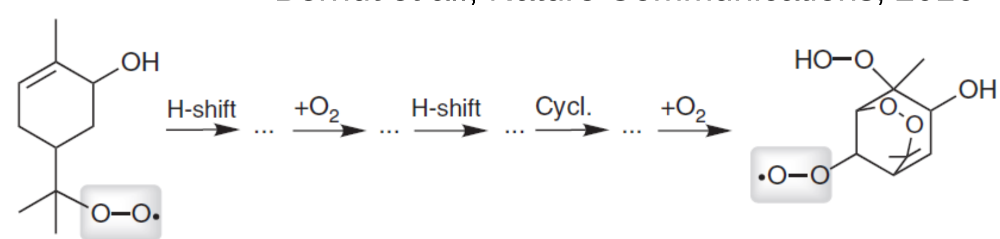
mean daytime (11am – 3pm, black and 6am – 9pm, red) rates of reaction for formation, propagation and termination of radicals in units of 10^5 molecule cm^{-3} s^{-1}.



- Missing HO_2 termination?
- Uncertainties in RO_2 to HO_2 propagation?
- Is autoxidation relevant for the complex RO_2 deriving from diesel and mono-terpene VOCs?

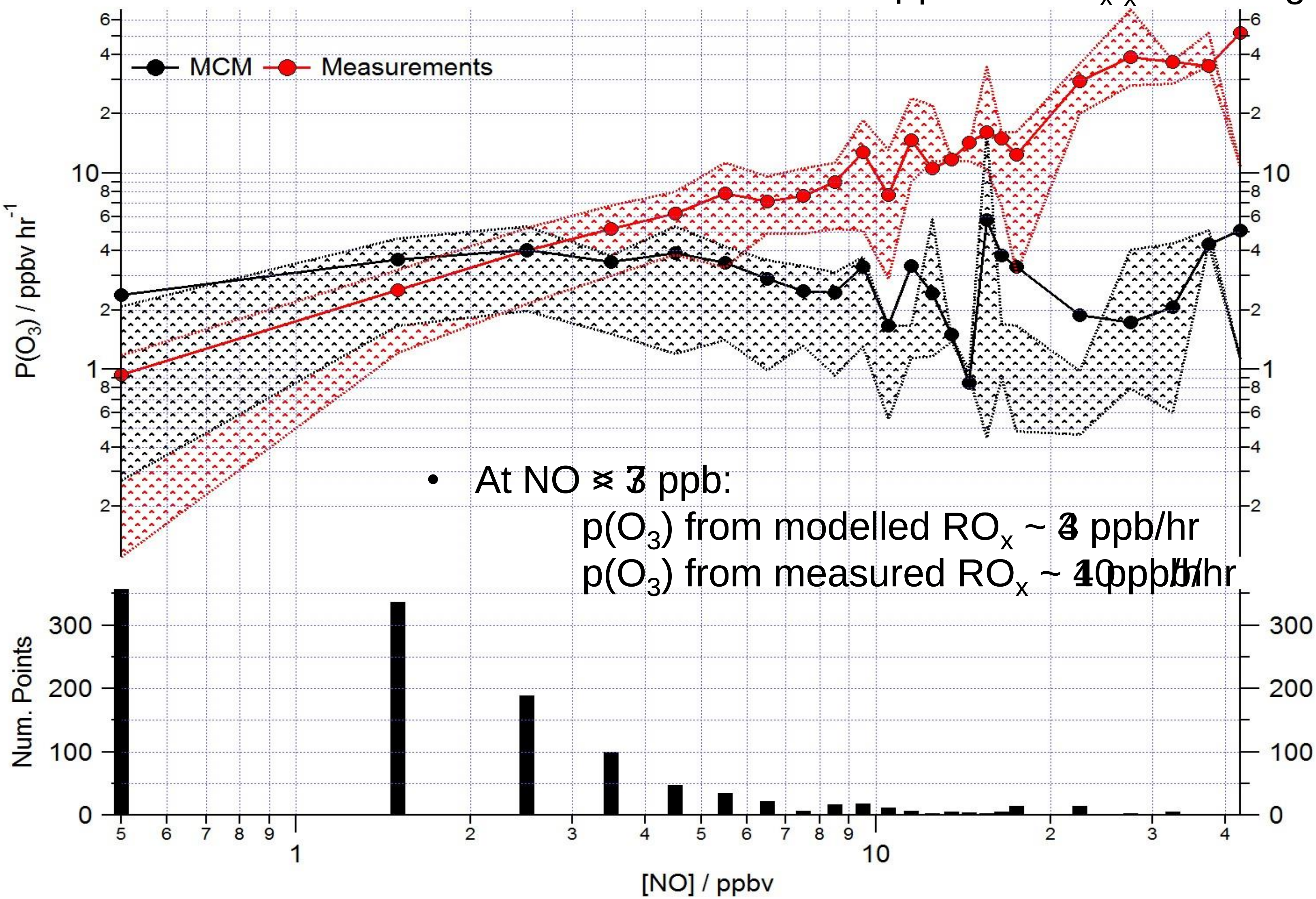
b

Berndt et al., Nature Communications, 2016



Impact of model uncertainties on in-situ ozone production

- Model over-predicts RO_x under low NO_x
- Model under-predicts RO_x under high NO_x



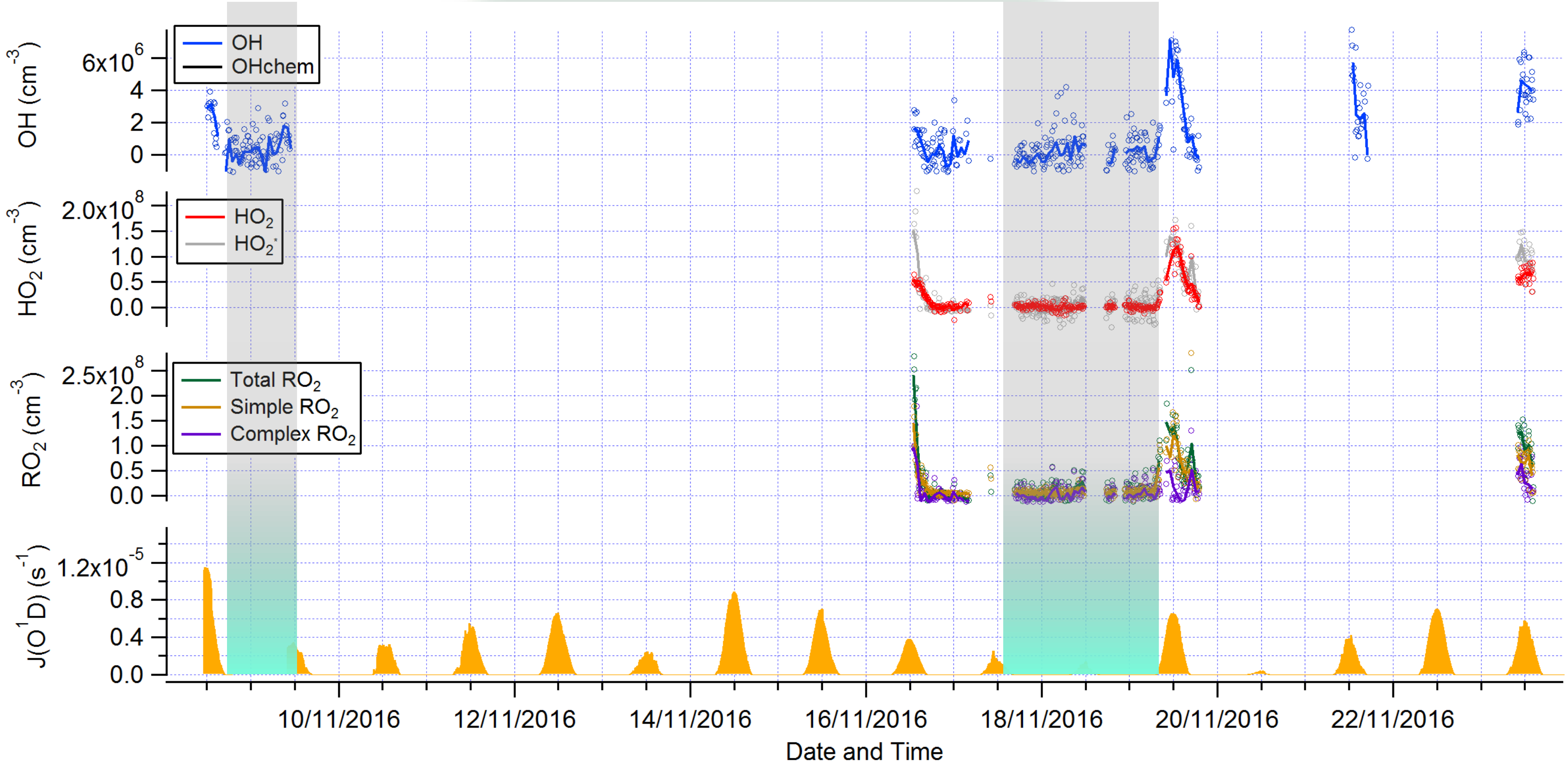
- At NO < 3 ppb:
  - $p(O_3)$ from modelled RO_x ~ 3 ppb/hr
  - $p(O_3)$ from measured RO_x ~ 4 ppb/hr
- At NO > 7 ppb:
  - $p(O_3)$ from modelled RO_x ~ 4 ppb/hr
  - $p(O_3)$ from measured RO_x ~ 10 ppb/hr

$$P(O_3) = k_{HO_2+NO}[HO_2][NO] + k_{RO_2+NO}[RO_2][NO] - k_{OH+NO_2+M}[OH][NO_2][M] - k_{HO_2+O_3}[HO_2][O_3] - P(RONO_2)$$

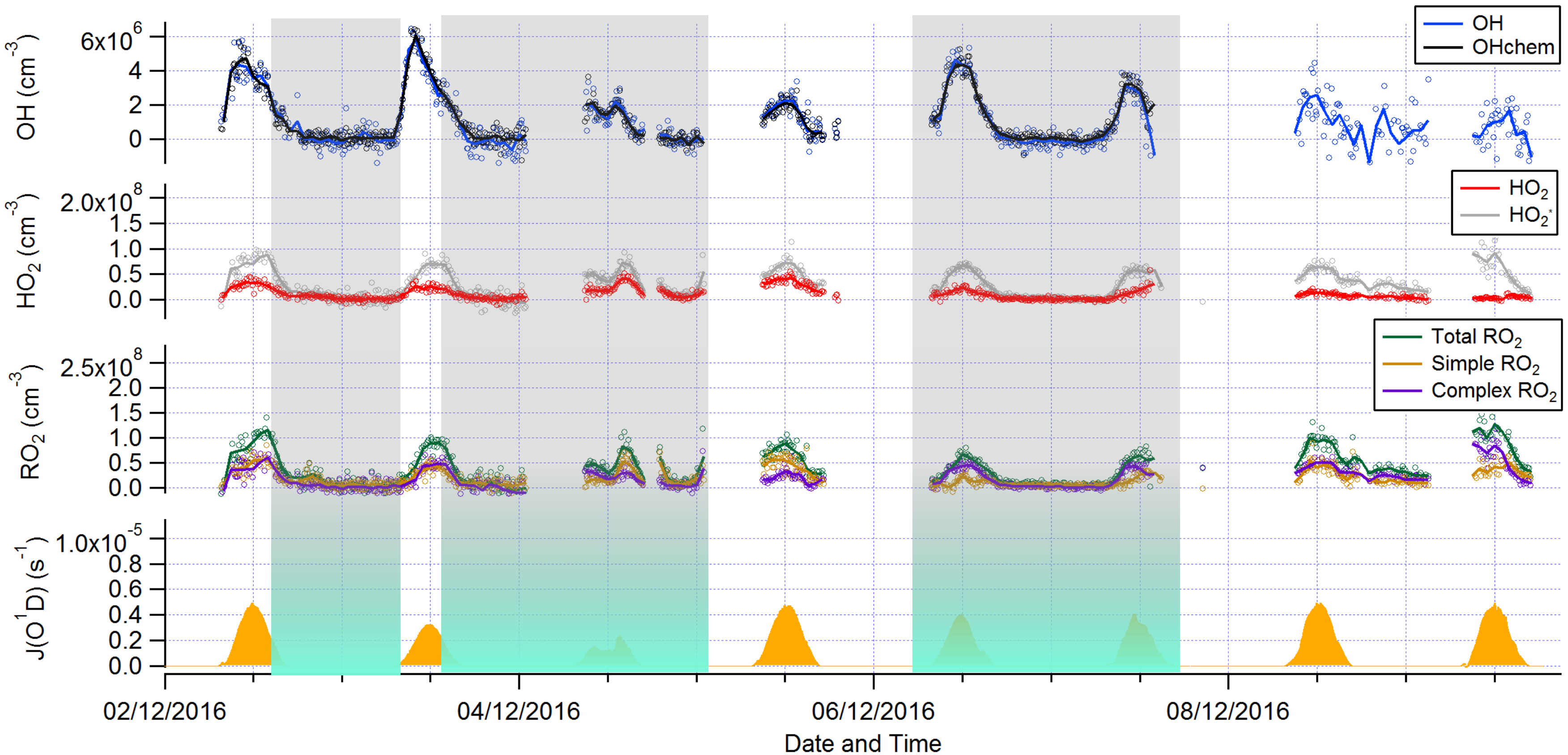
Airpro – An Integrated Study of AIR Pollution PROcesses in Beijing

- Part of the Air Pollution and Human Health in a Chinese Megacity programme (APHH).
- Involved winter (Nov, Dec 2016) and summer (May, June 2017) intensive field observations.
- Aimed to better understand the chemical and physical processes responsible for the frequent haze events (winter) and high ozone episodes (summer).
- Goal to improve numerical model used to predict air quality and to develop effective air pollution control strategies.

Radical time-series - November

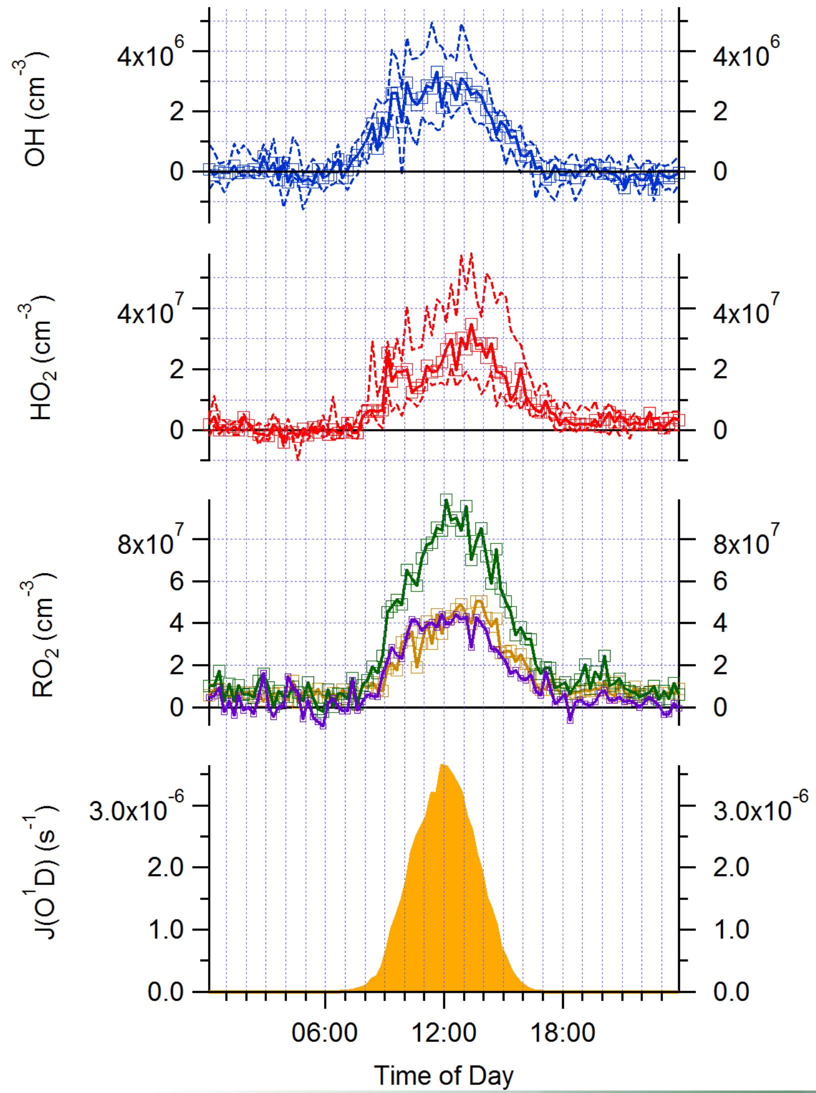


Radical time-series - December



Average diurnals of radicals

Reasonably high levels of OH despite low j(O^1D)



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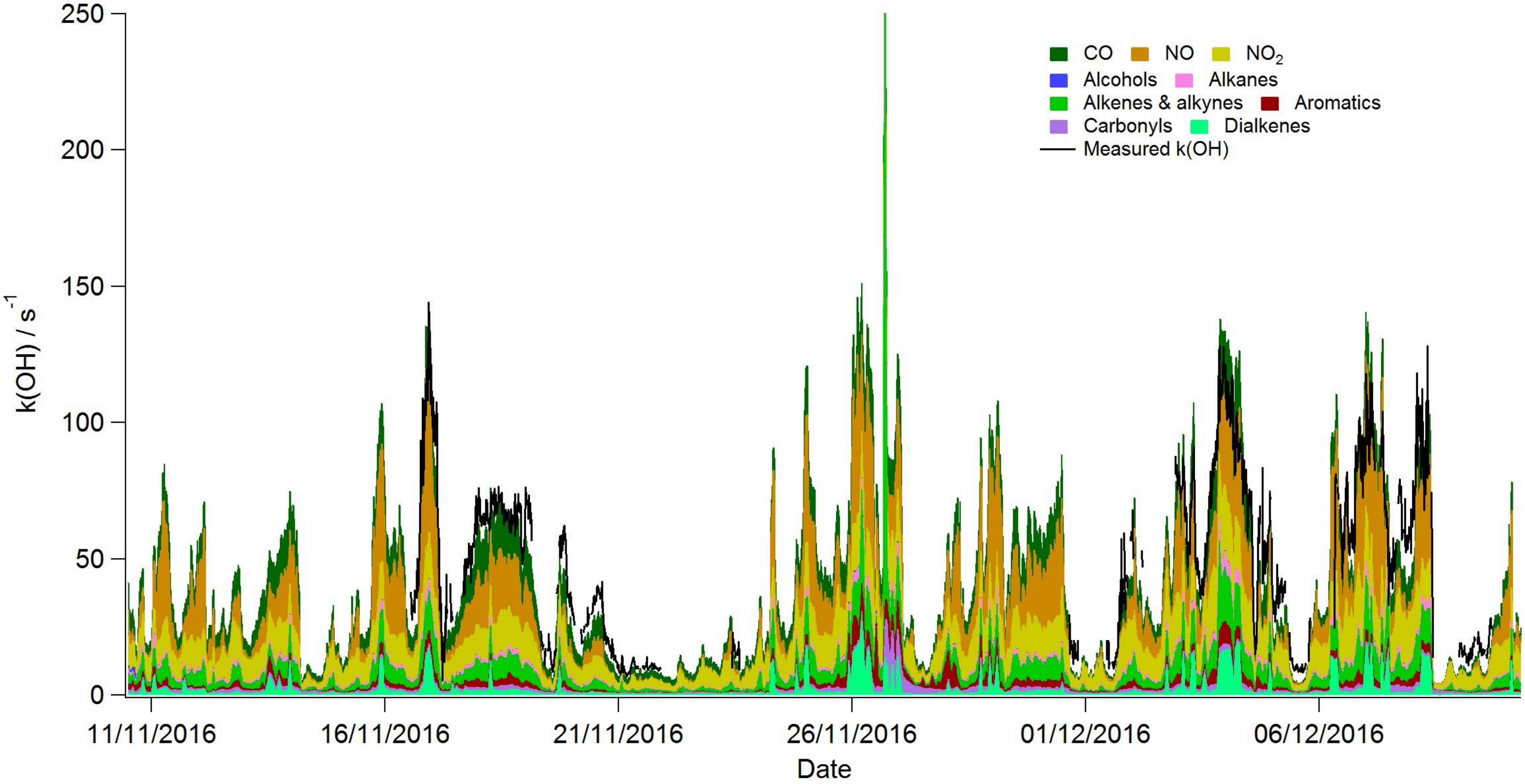
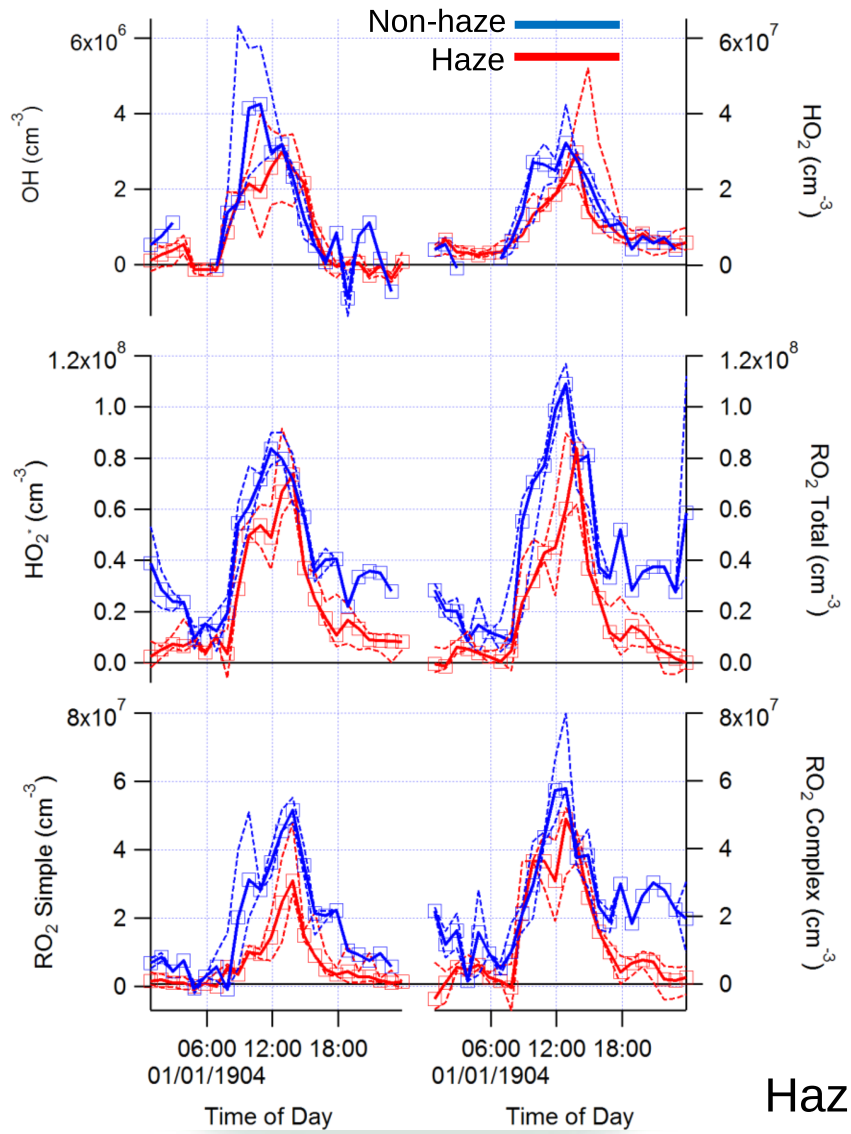
k(OH) measured and calculated from co-located VOCs, NO_x and CO

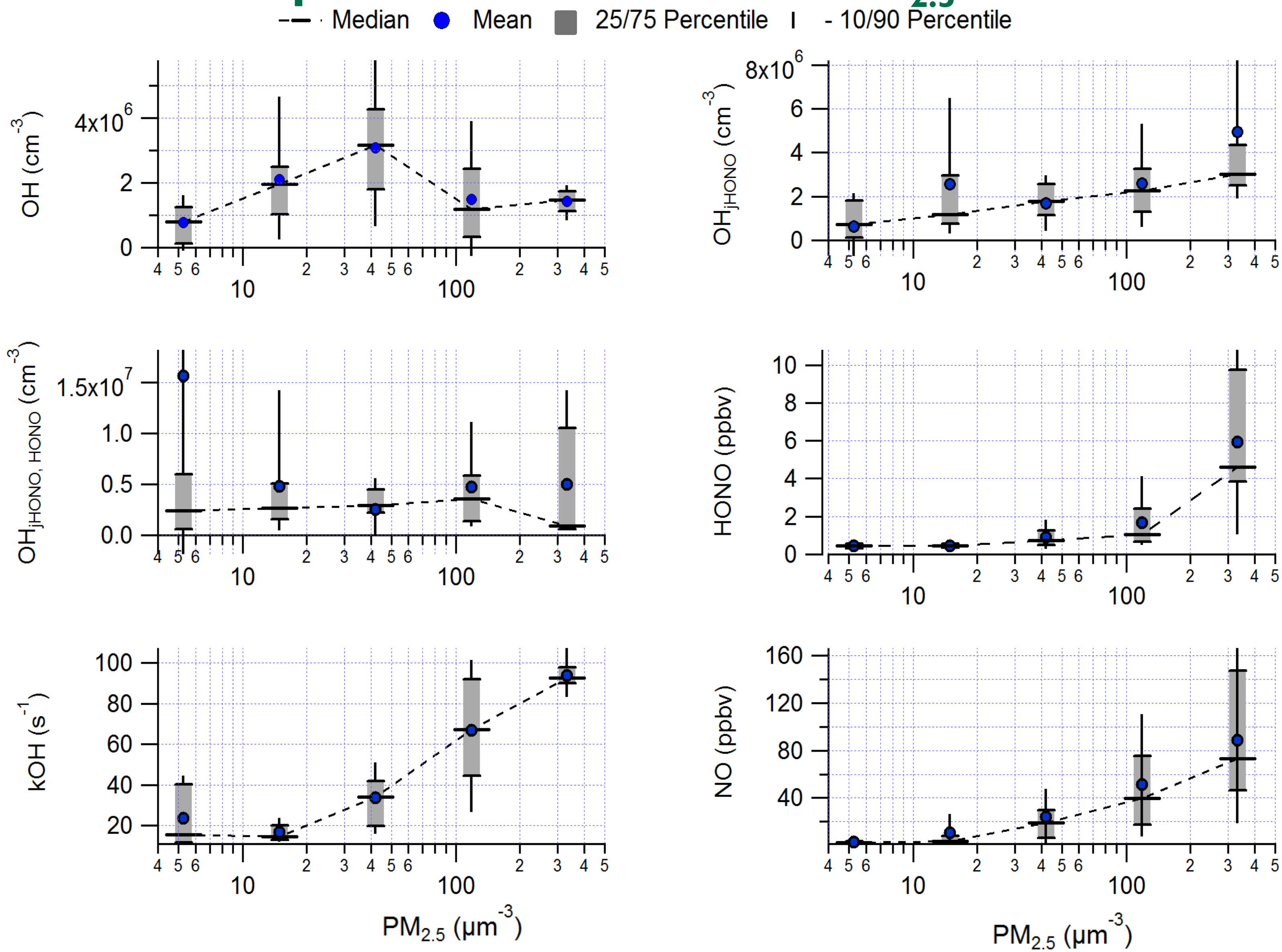


Radical diurnals inside and outside of haze events

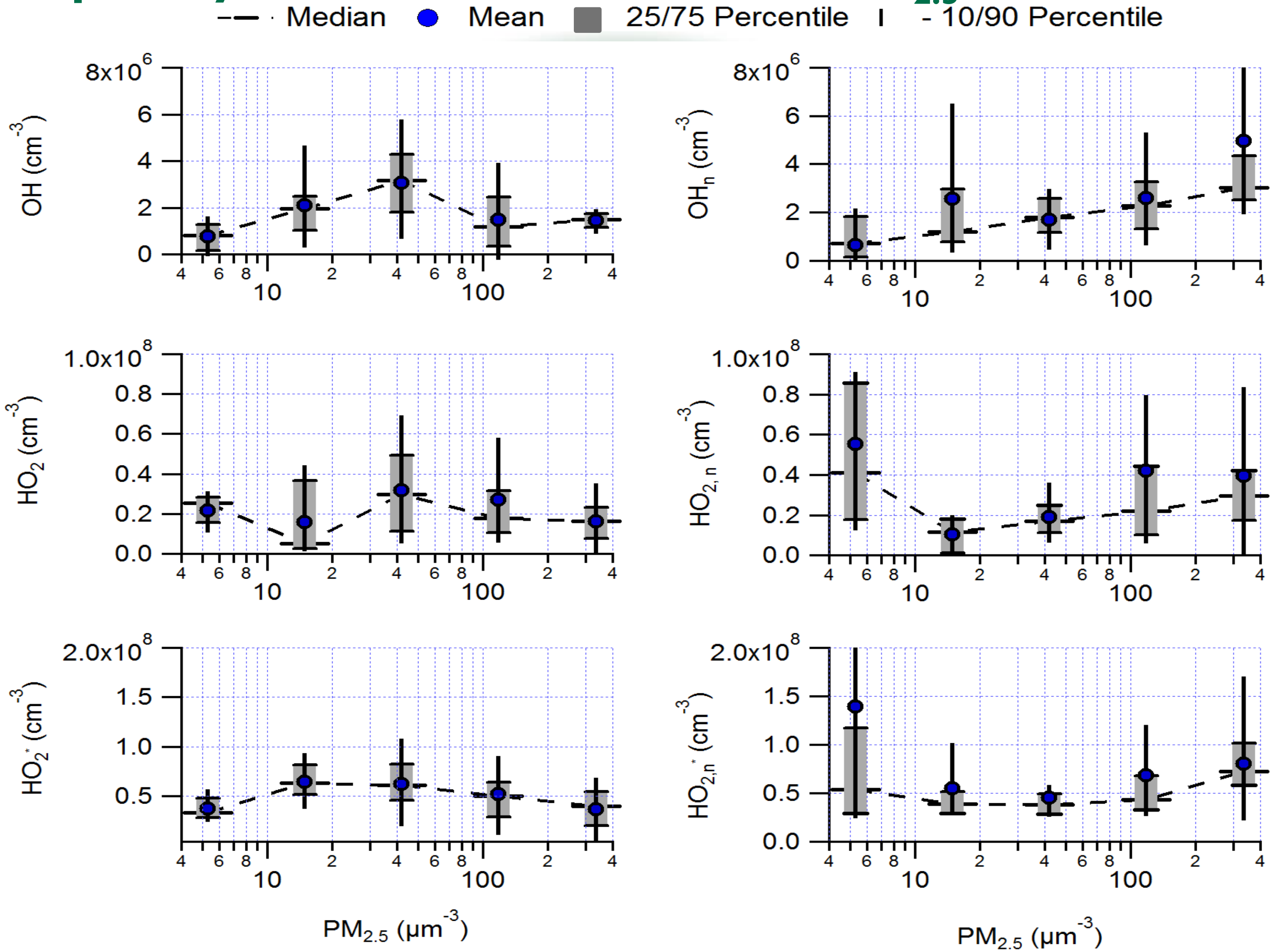


Haze = $PM_{2.5}$>75µgm-3

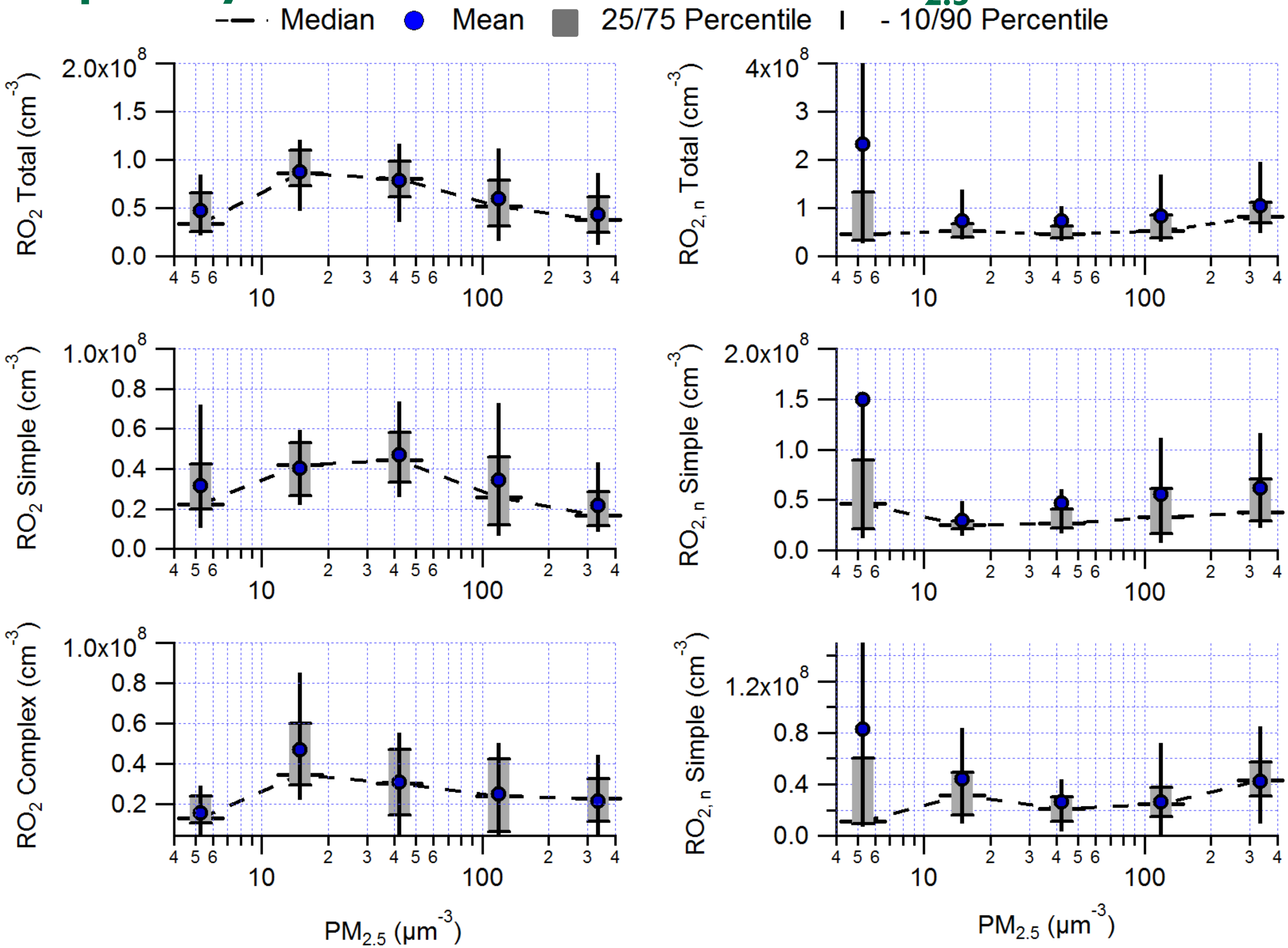
OH and related species as a function of $PM_{2.5}$



OH and peroxy radicals as a function of $PM_{2.5}$

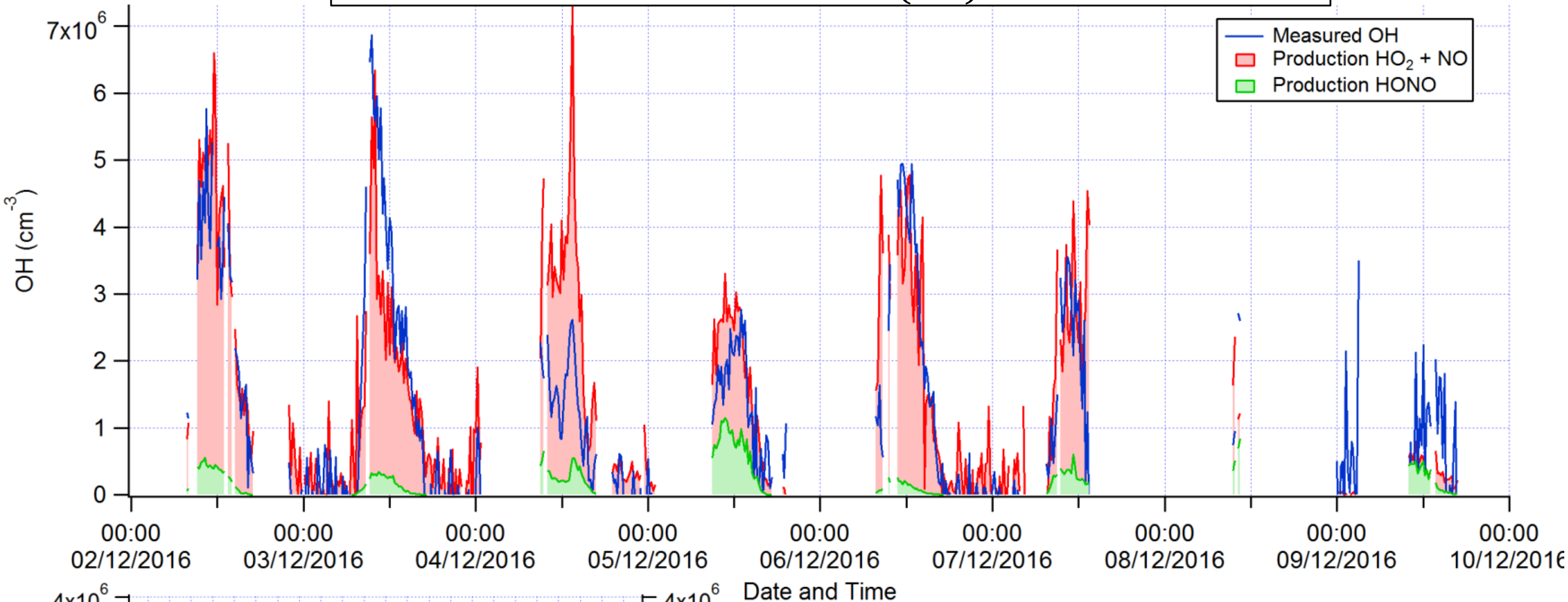


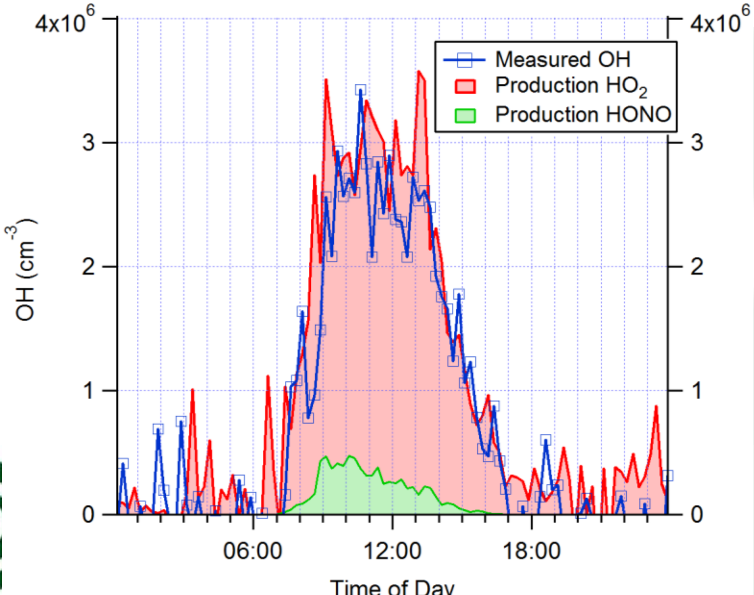
OH and peroxy radicals as a function of $PM_{2.5}$



Photostationary steady state OH calculation

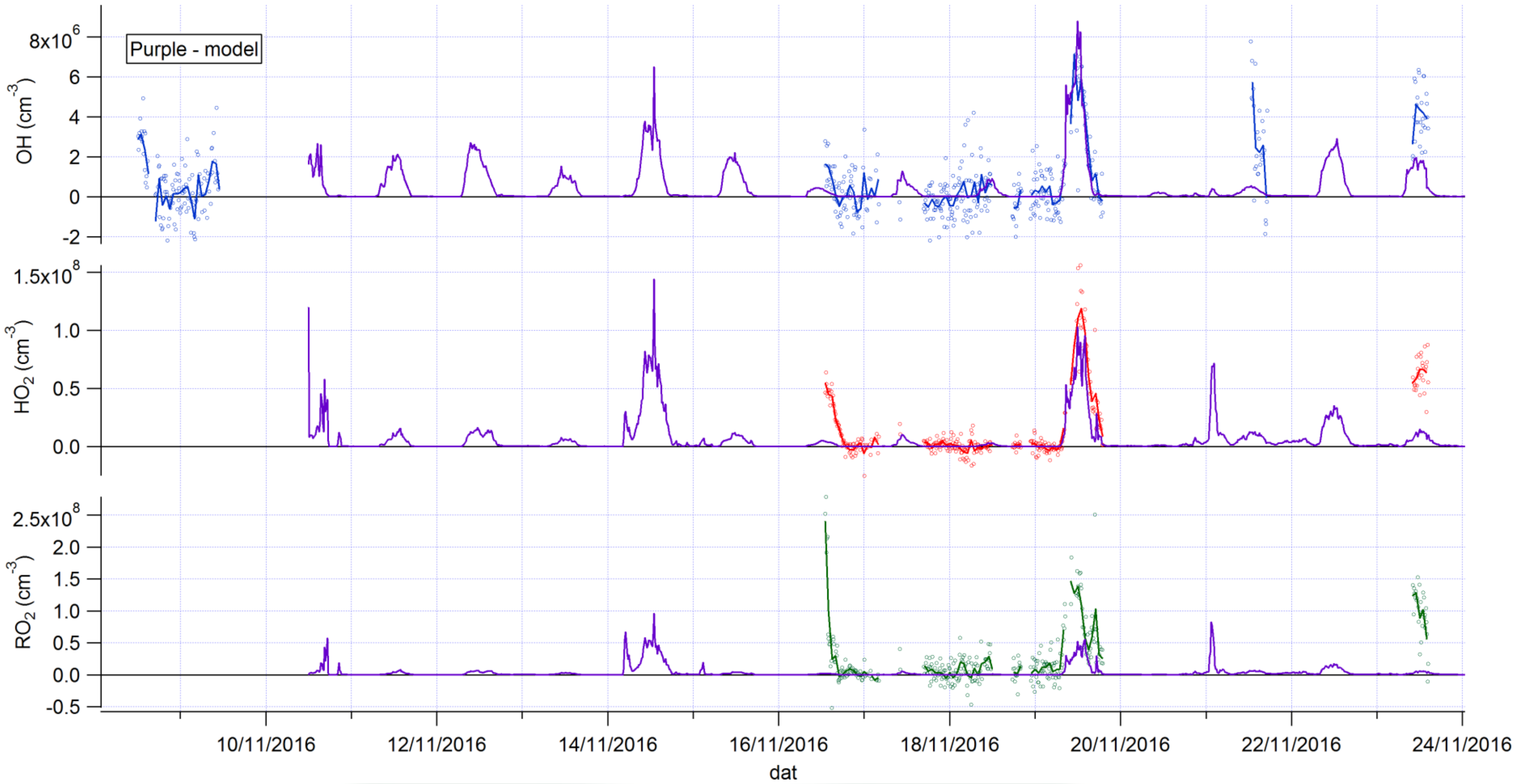
$$OH_{PSS} = \frac{k_{HO_2+NO}[HO_2][NO] + j(HONO)[HONO] + \dots}{k(OH)}$$



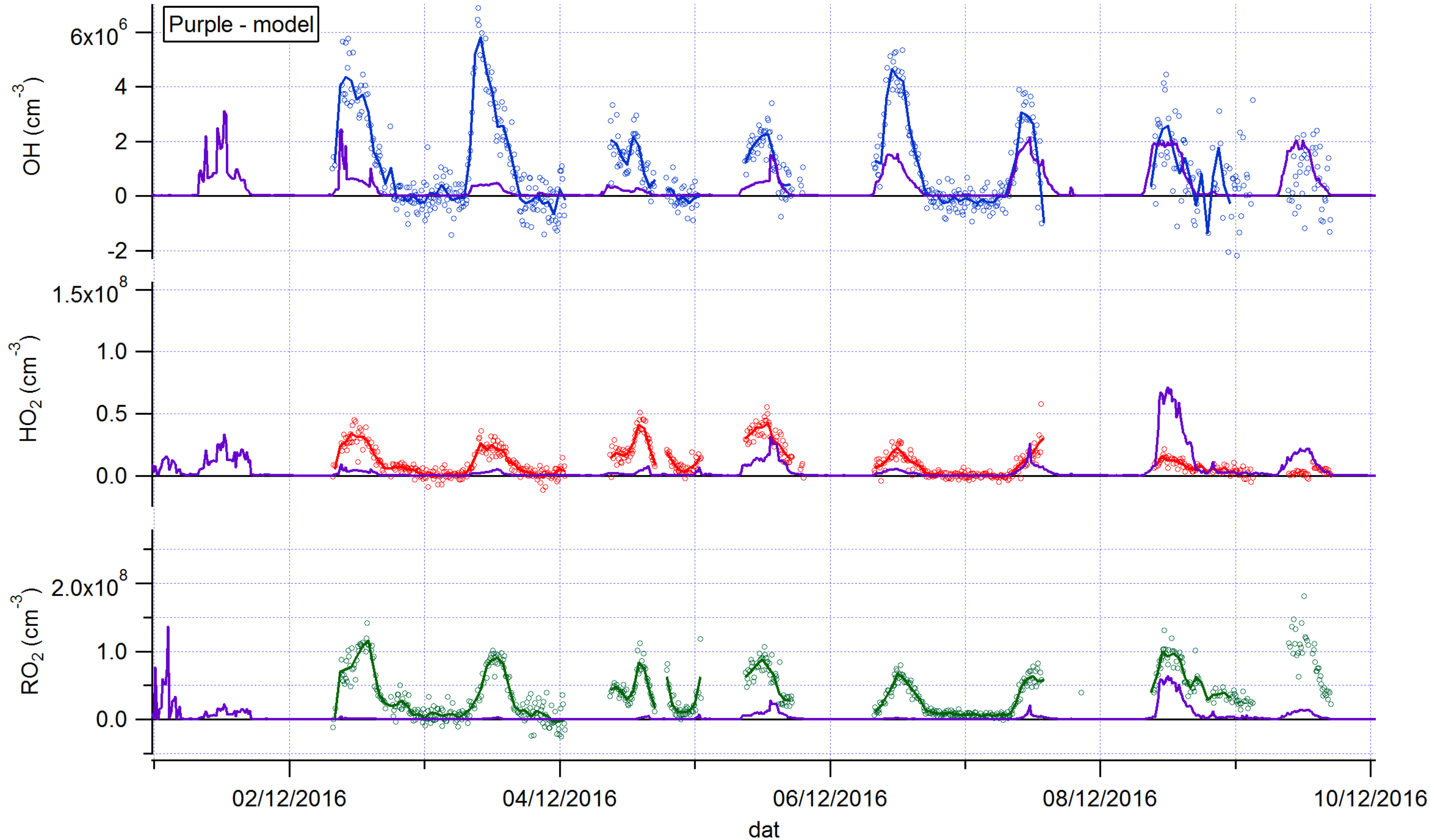


- HO_2+NO is the dominate source of OH
- HONO photolysis accounts for 10 -15 % of the total OH source
- In general, good agreement between OH_{OBS} and OH_{PSS}

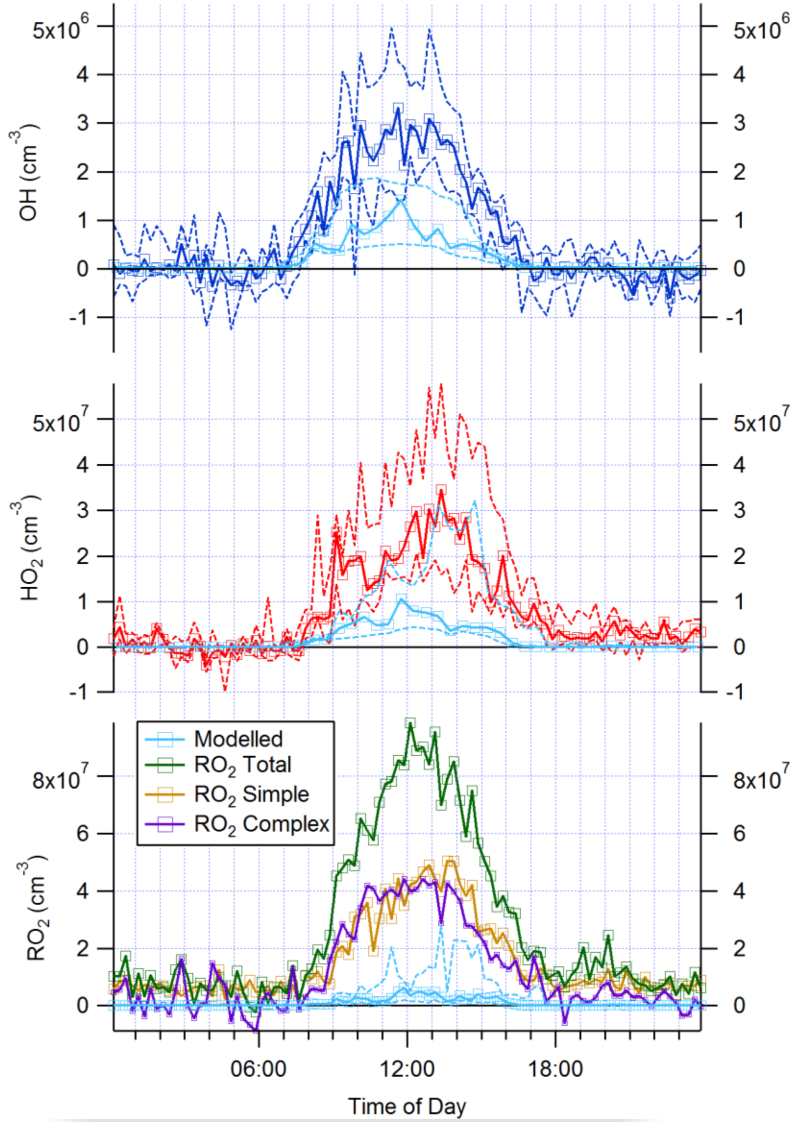
Model - Winter



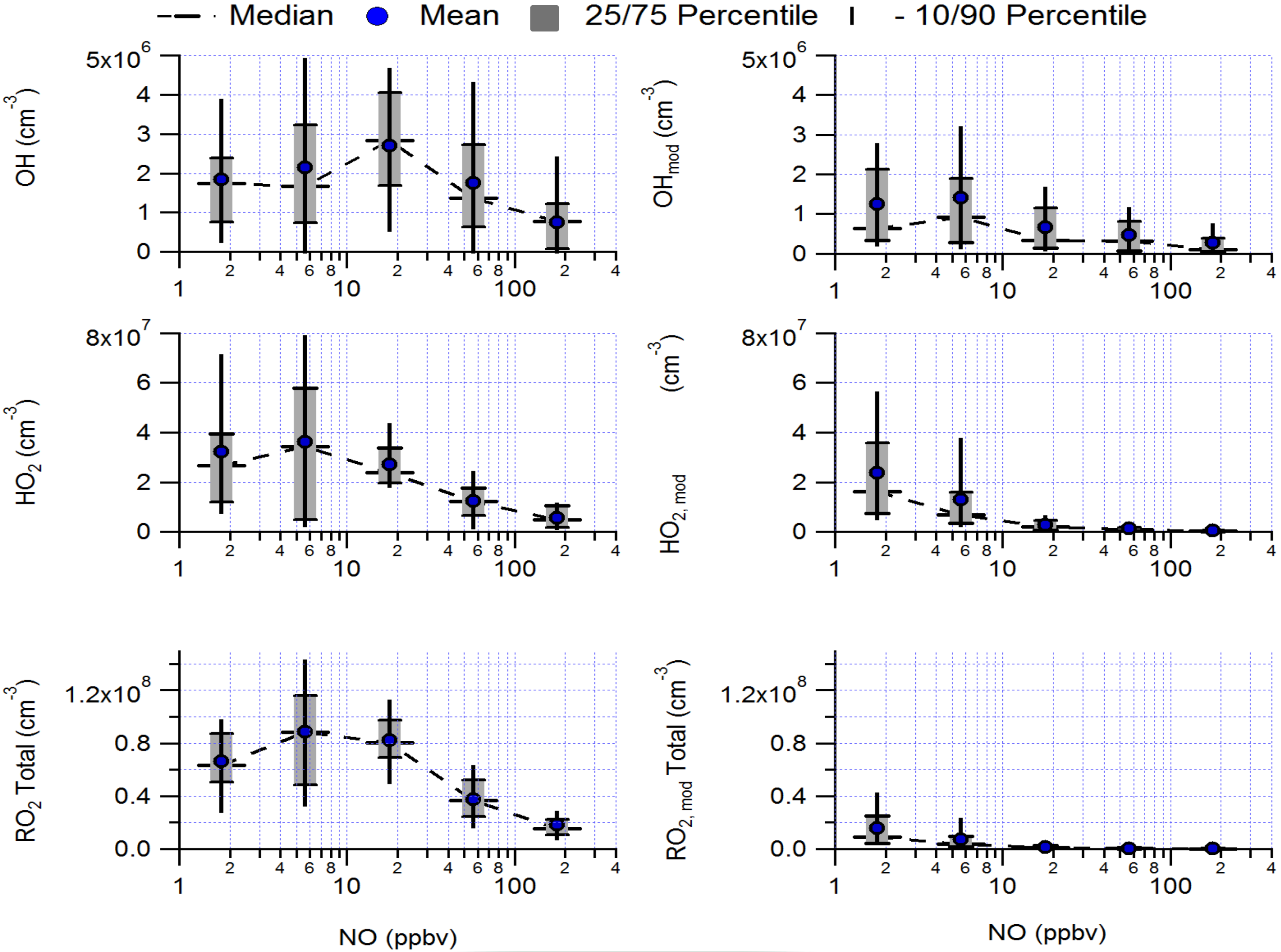
Model - Winter



Radical measurements and MCM model diurnal



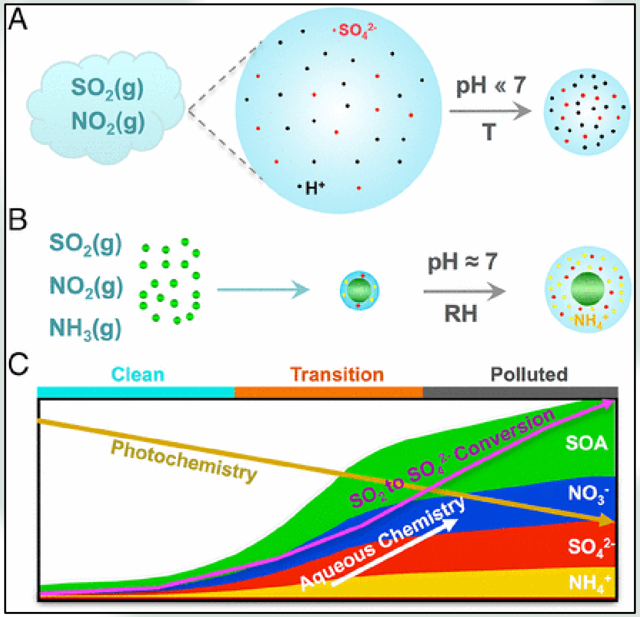
Radical measurements and MCM model vs NO



Missing sulphate formation mechanism in models

Missing sulphate formation mechanism in models, with novel aqueous phase oxidation mechanisms recently postulated.

In addition to this aqueous phase oxidation process involving NO_2, our observations highlight that the OH generated (potentially from the HONO formed via this mechanism) could further enhance sulphate formation during haze events. This gas-phase oxidation process remains active despite the reduction in photolysis rates.



$$2NH_3+SO_2(g)+2NO_2(g)+2H_2O(aq)\longrightarrow 2NH_4{+}(aq)+SO_4^{2-}(aq)+2HONO\ (g)$$

Wang et al., PNAS, 2016

Conclusions

- Poor representation of chemistry of complex VOCs deriving from biogenic sources and diesel
- Significantly more ozone production predicted using modelled peroxy radical concentrations vs those measured at a time when ozone destruction (by NO titration) is slow
- Under high NO_x, model predicts lower ozone production than calculated from peroxy radical observations
- Model under-predicts OH, even when constrained to the observed HONO, due to the large under-prediction of peroxy radicals, highlighting a poor understanding of the gas phase oxidation chemistry under high NO_x conditions and within haze

Acknowledgements

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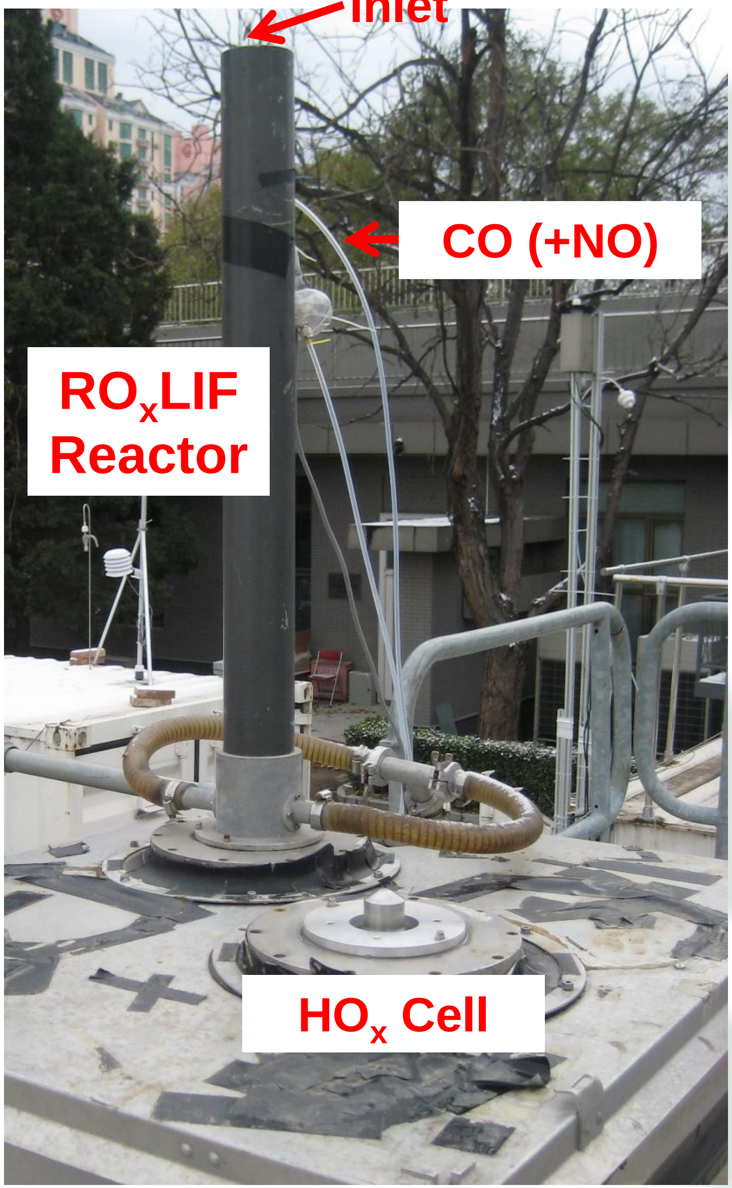
Airpro participants: Eloise Slater, Chunxiang Ye, Robert Woodward-Massey, Leigh Crilley, Louisa Kramer, William Bloss, Tuan Vu, James Hopkins, Rachel Dunmore, Jacqueline Hamilton, James Lee, Freya Squires, Alistair Lewis, and Dwayne Heard

Radical measurements

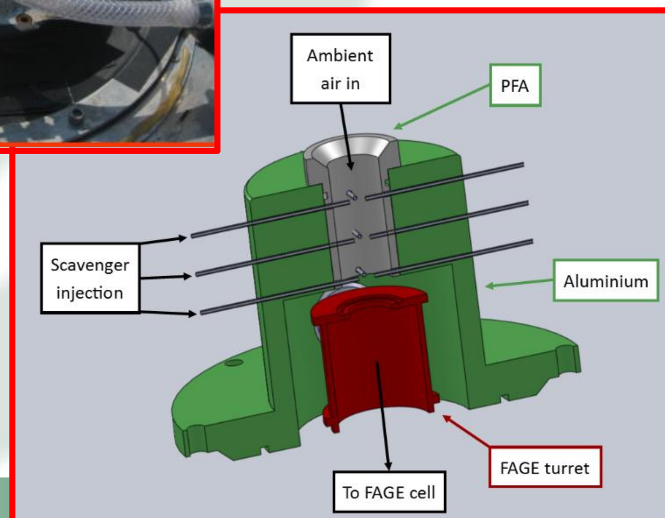


Whalley et al., AMT, 2015

FAGE Cell 1:
OH
HO_2
RO_xLIF Cell 2:
HO_2+RO_2 (NO on in reactor)
HO_2^* (NO off in reactor)

FAGE Cell 1 with Inlet pre-injector (IPI):

OH_{CHEM} and OH_{WAVE}



Woodward-Massey et al., in prep.

OHchem and OHwave

OH_{WAVE} vs OH_{CHEM}