Unaccountably high OH vs Unaccountably short OH lifetime-An Attempt for a Reconciliation

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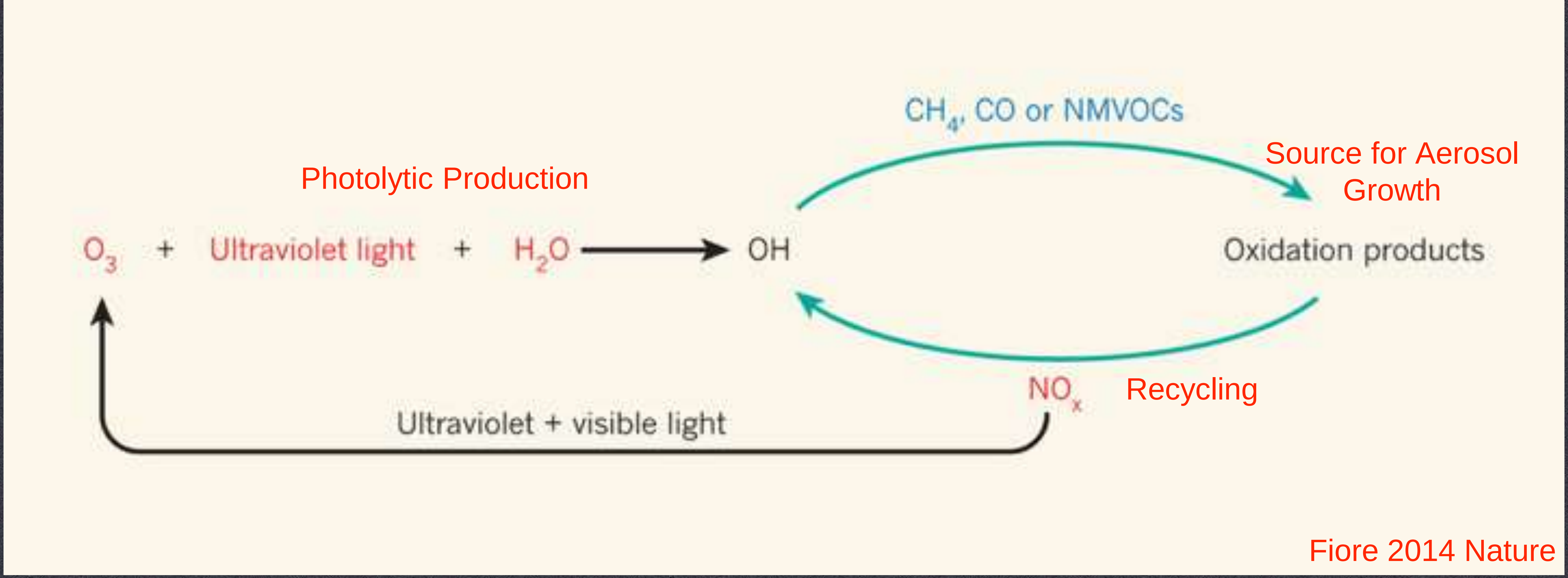
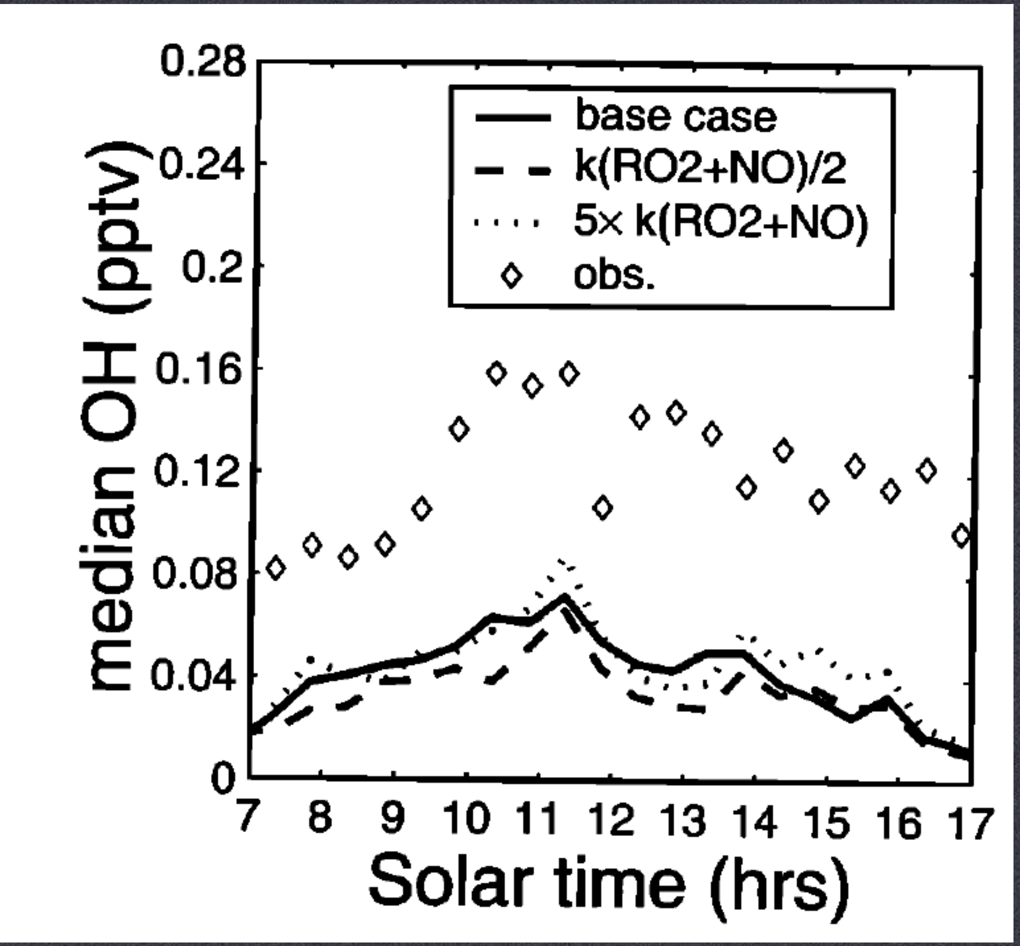
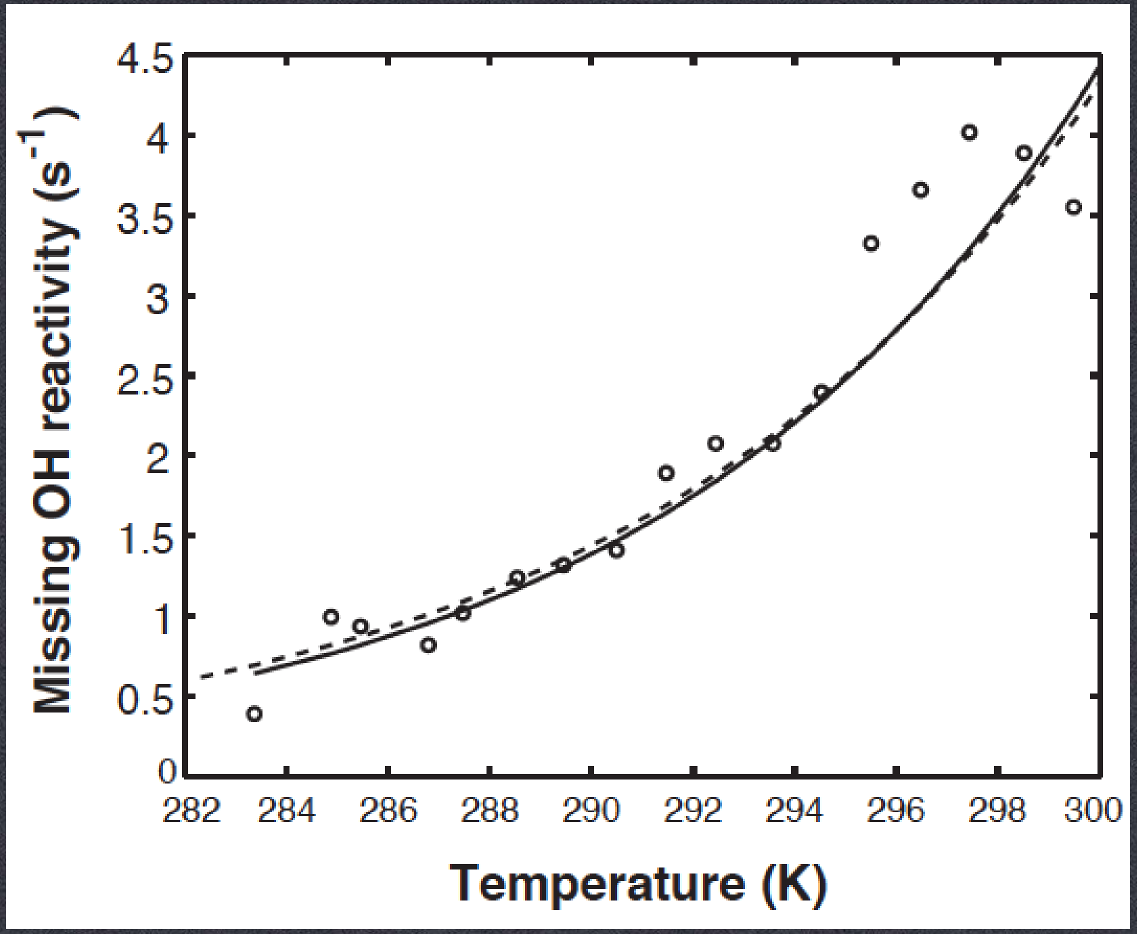
Grant # R835400



THE UNDERSTANDING - AT LEAST IT HAD BEEN



Tan et al. 2001 JGR



Di Carlo et al. 2004 Science

Unobserved reactive monoterpenes ($C_{10}H_{16}$) and sesquiterpenes species ($C_{15}H_{24}$) $\xrightarrow{\text{ozonolysis}}$ products + OH

A SERIES OF RESEARCH RESULTS FROM THE PROPHET TOWER

UNKNOWN EMISSIONS?


Vol 452 | 10 April 2008 | doi:10.1038/nature06870 nature

LETTERS

Atmospheric oxidation capacity sustained by a tropical forest

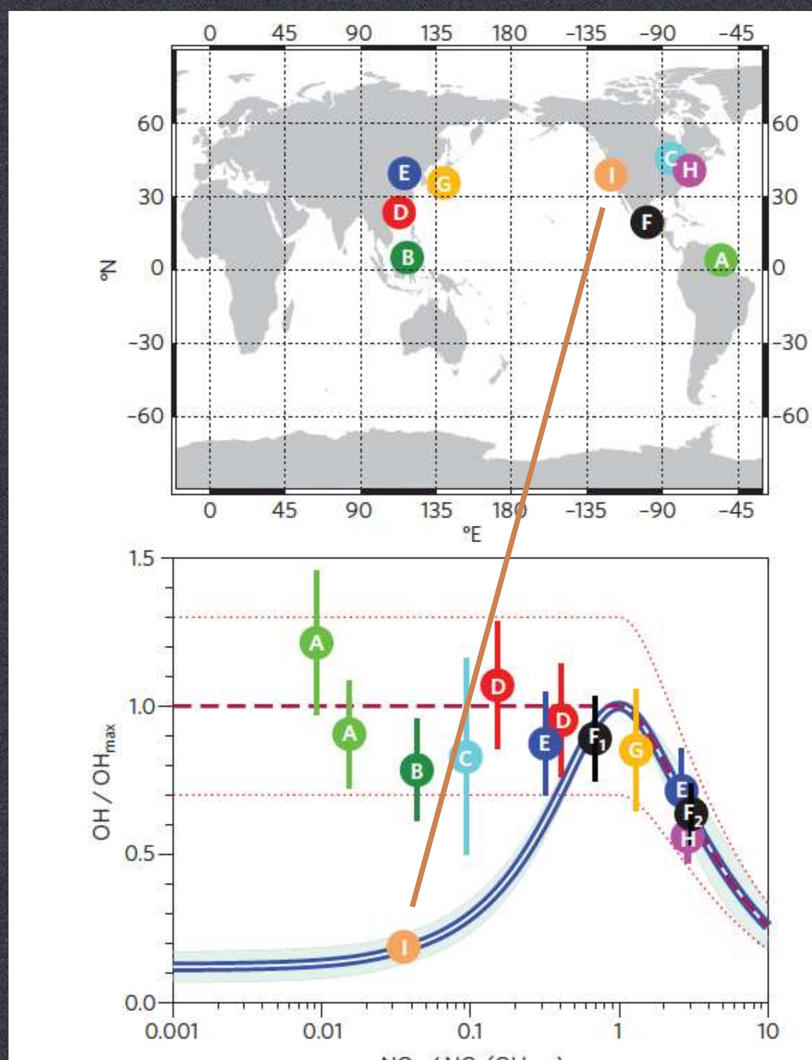
J. Lelieveld[1], T. M. Butler[1], J. N. Crowley[1], T. J. Dillon[1], H. Fischer[1], L. Ganzeveld[1], H. Harder[1], M. G. Lawrence[1], M. Martinez[1], D. Taraborrelli[1] & J. Williams[1]

Similarities

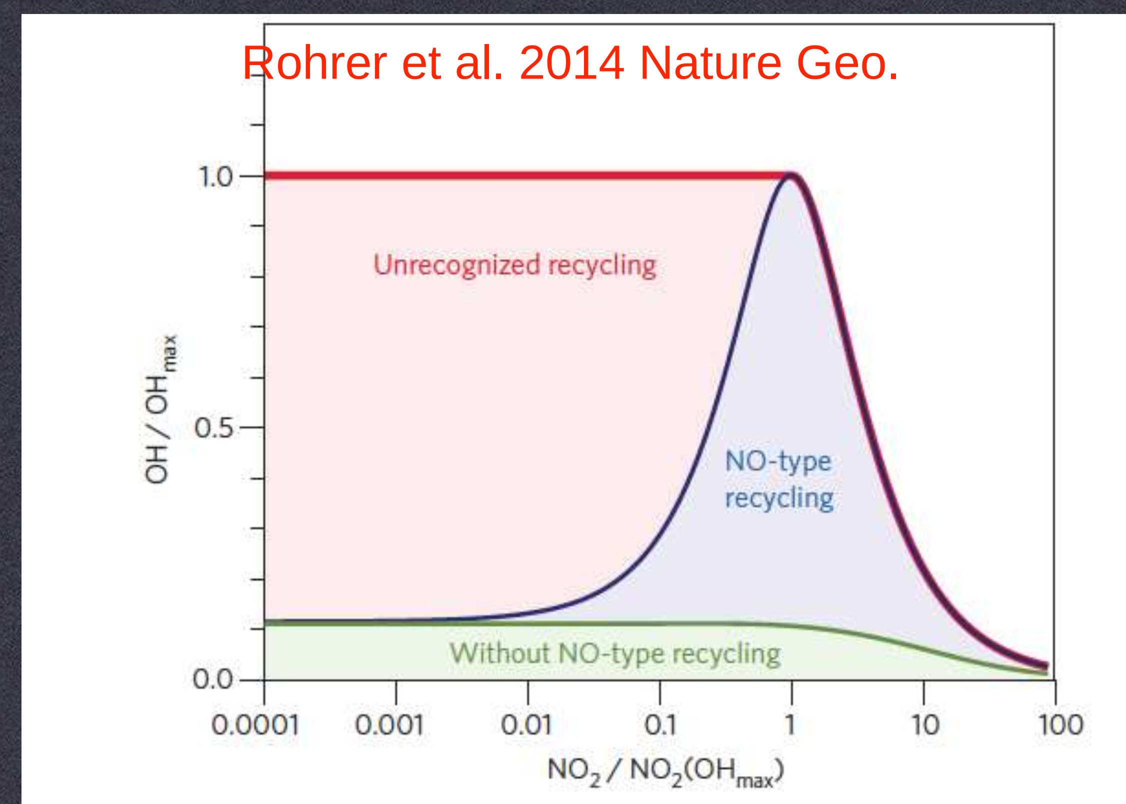
- High BVOC (isoprene) and low NO conditions
- LIF Techniques

One exception

- BEARPEX 09 (point I): LIF with a different bkg characterization method (Mao et al., 2012 ACP)



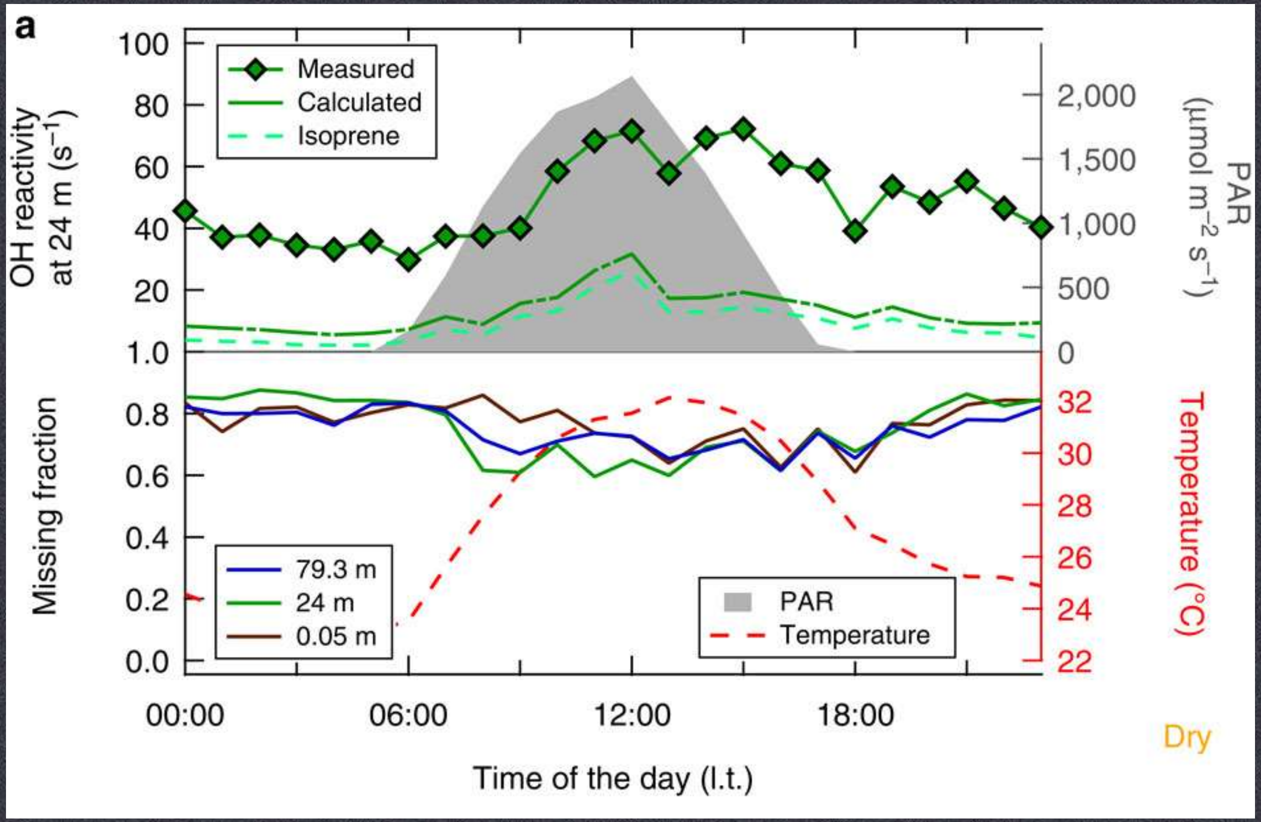
Rohrer et al. 2014 Nature Geo.

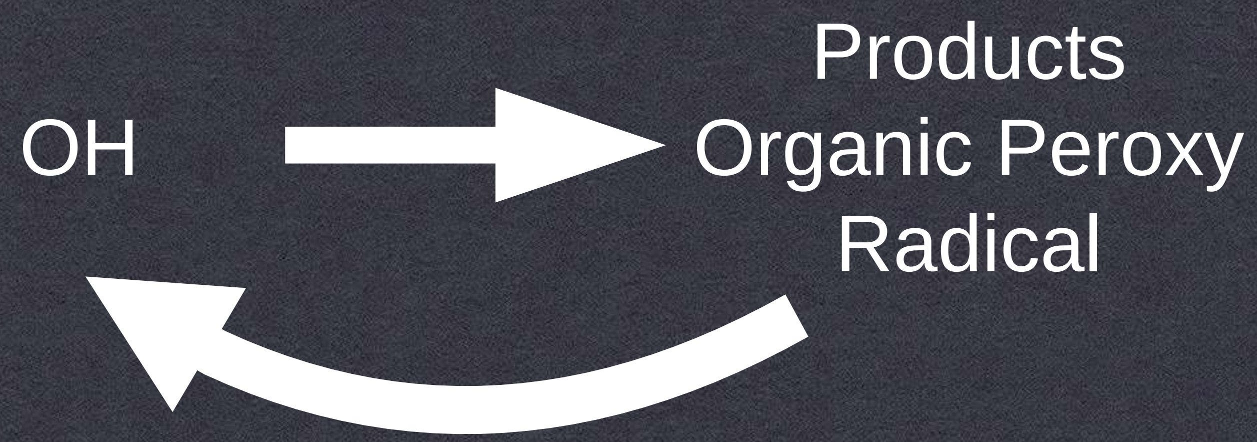


Rohrer et al. 2014 Nature Geo.

ROLES OF ISOPRENE IN LOW NOX

LELIEVELD ET AL. 2008 AND FOLLOW UP STUDIES

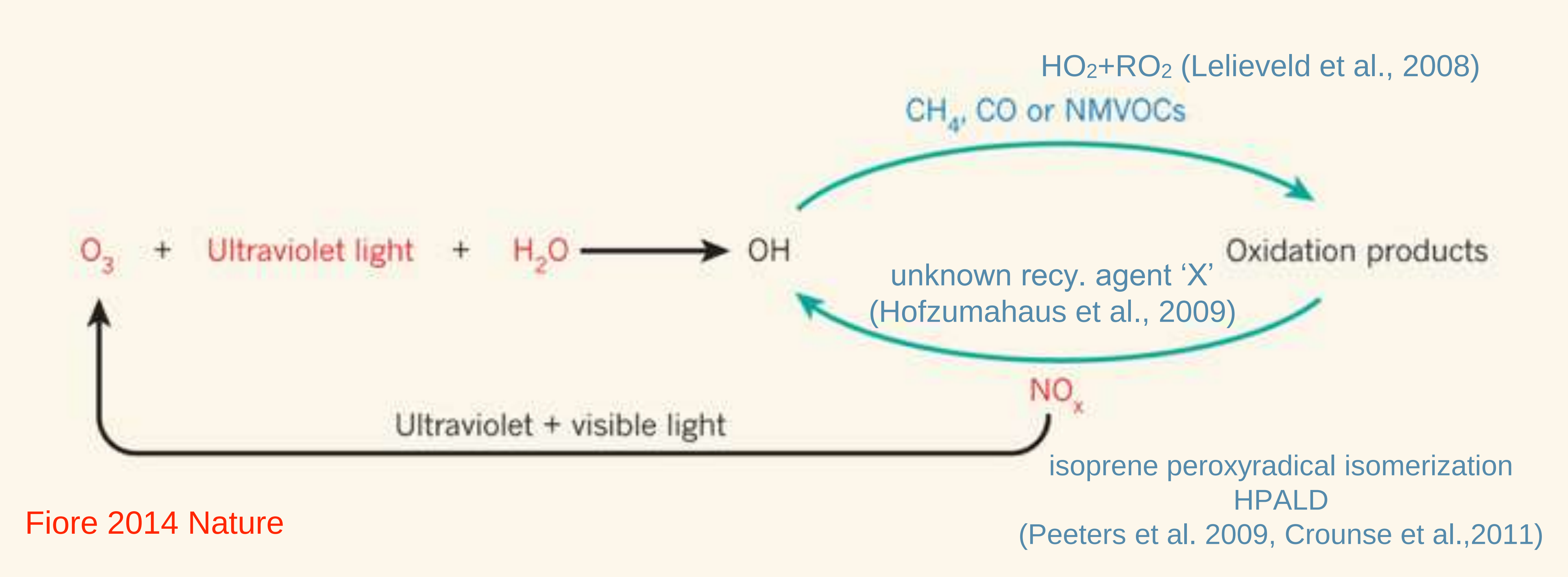


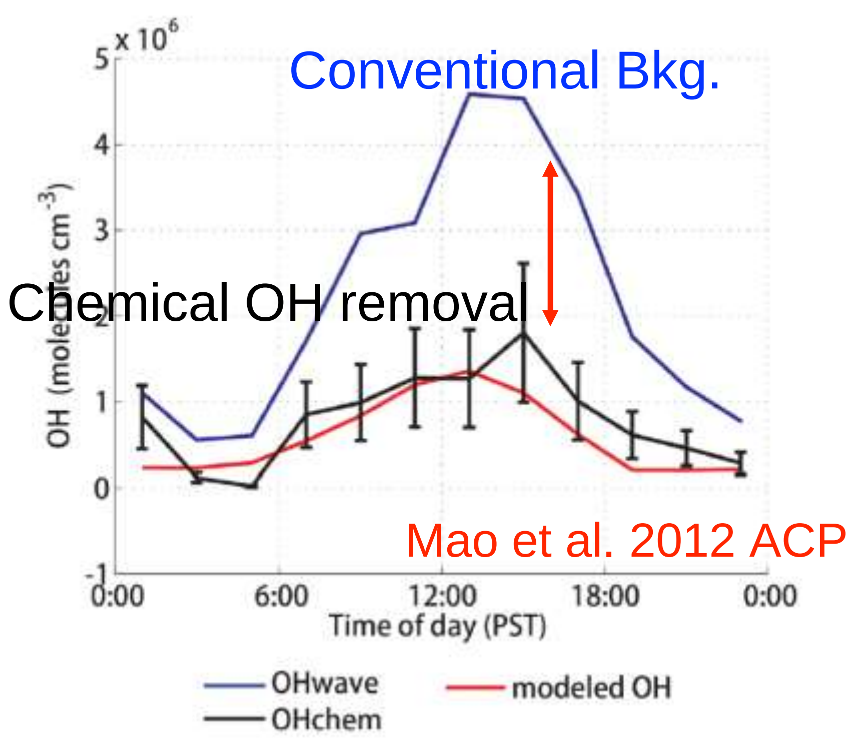


Additional recycling processes other than NO

HIGHER THAN EXPECTED OH REACTIVITY - SHORTER OH LIFETIME THAN EXPECTED

NOLSCHER ET AL. (2016) NAT. COMM.





- The uncertainty in chemical mechanisms directly affect our ability to constrain OH and OH reactivity

- The uncertainty in observationally constraining OH directly propagates into our ability to constrain OH and OH reactivity

CONFUSIONS IN TWO FRONTS

CHEMICAL MECHANISMS VS ANALYTICAL UNCERTAINTY

3200 A. Guenther et al.: MEGAN estimates of global isoprene

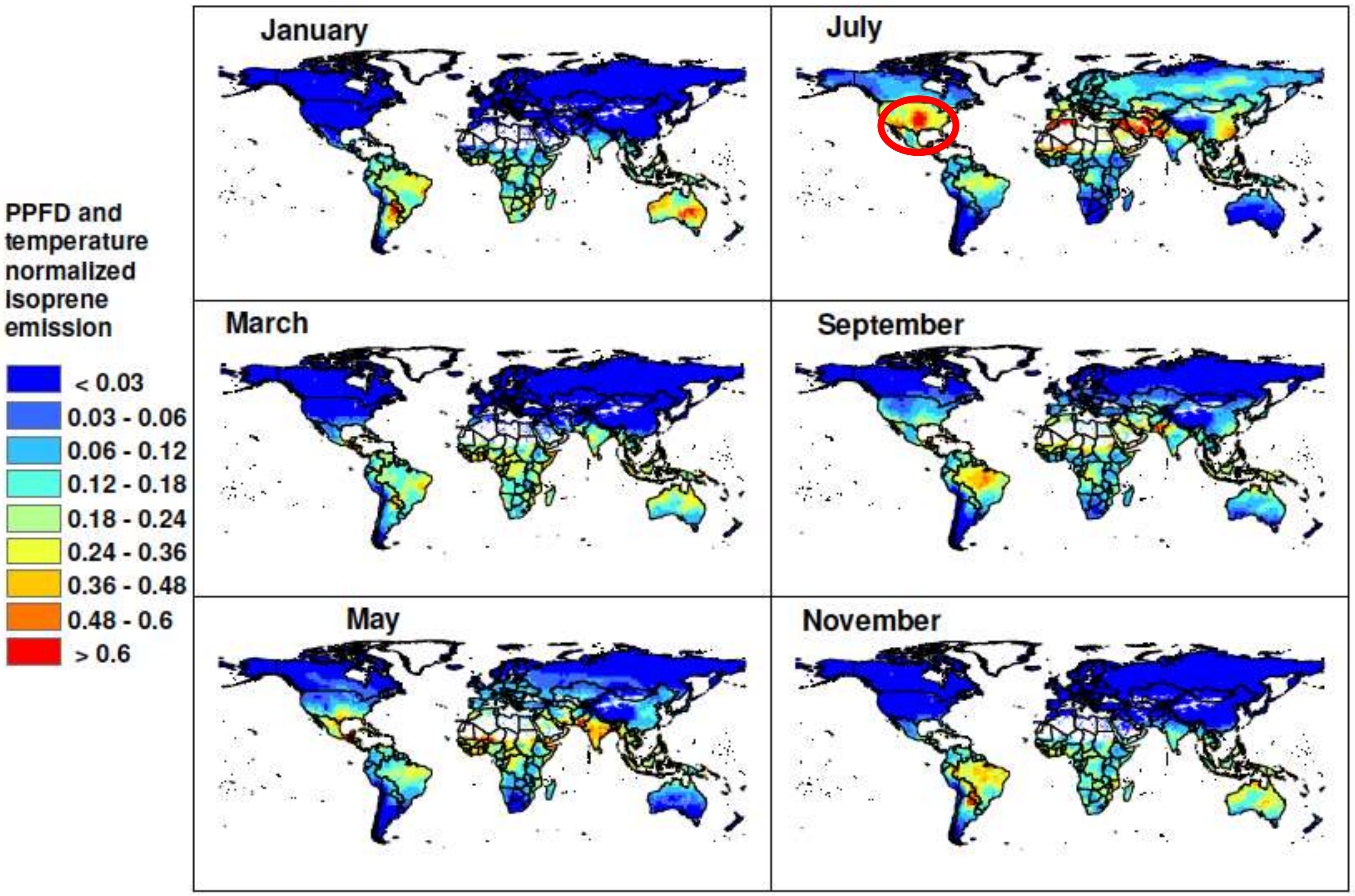
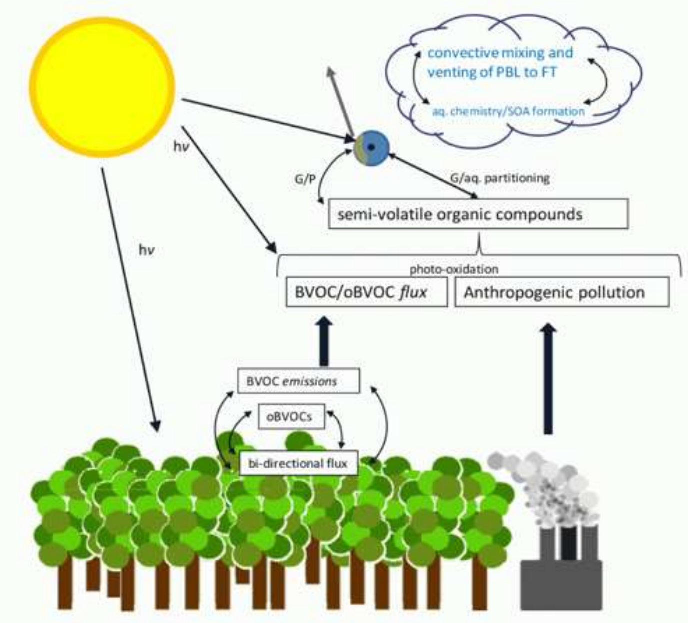


Fig. 9. Monthly normalized isoprene emission rates estimated with MEGAN for 2003. Rates are normalized by the emission estimated for standard temperature (=303 K) and PPFD transmission (60%). These normalized rates illustrate the variations associated with changes only in temperature and PPFD transmission; i.e. all other model drivers are held constant.

SOAS

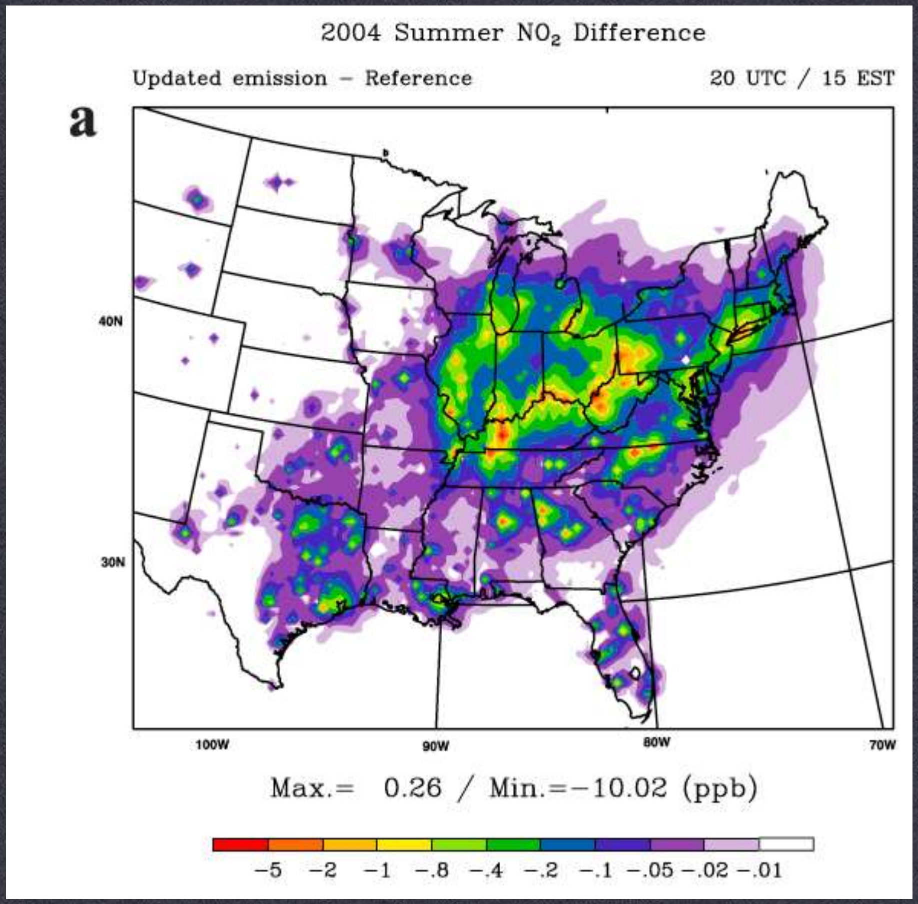
Southern Oxidant & Aerosol Study



Biogenic emissions and anthropogenic pollution interact and affect atmospheric photo- oxidation chemistry and subsequently air quality and climate.

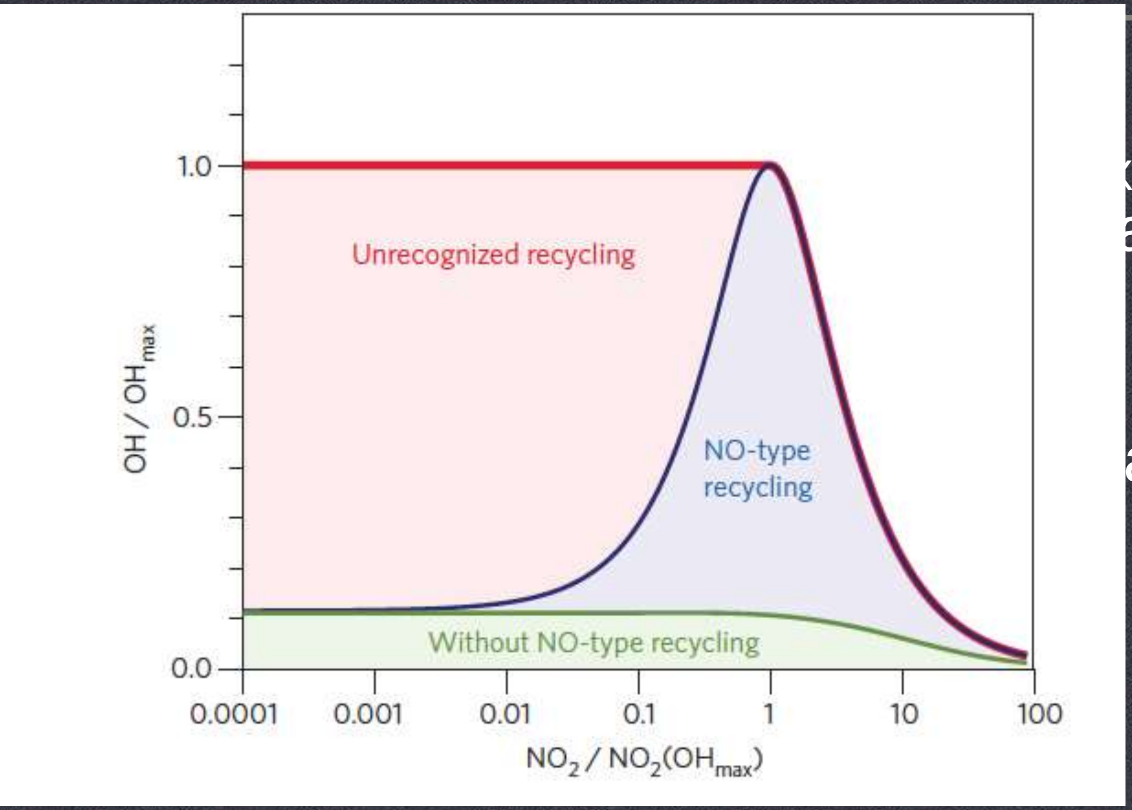
SOAS

ROLES OF ISOPRENE IN NOX TRANSITIONS

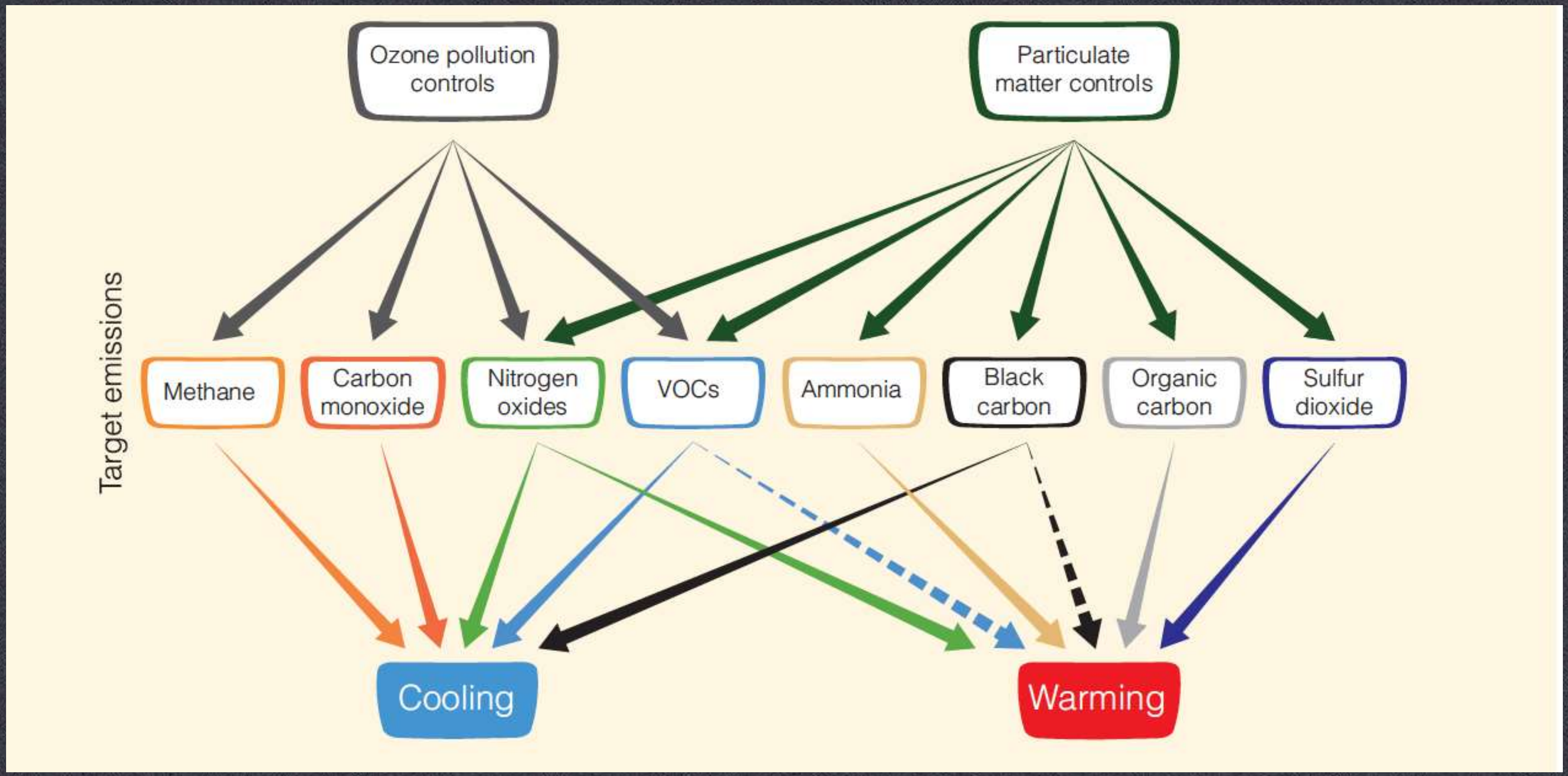


Kim et al. (20
emissions fr
arly
2000)

NO_X emissio
ally
in the U.S. a

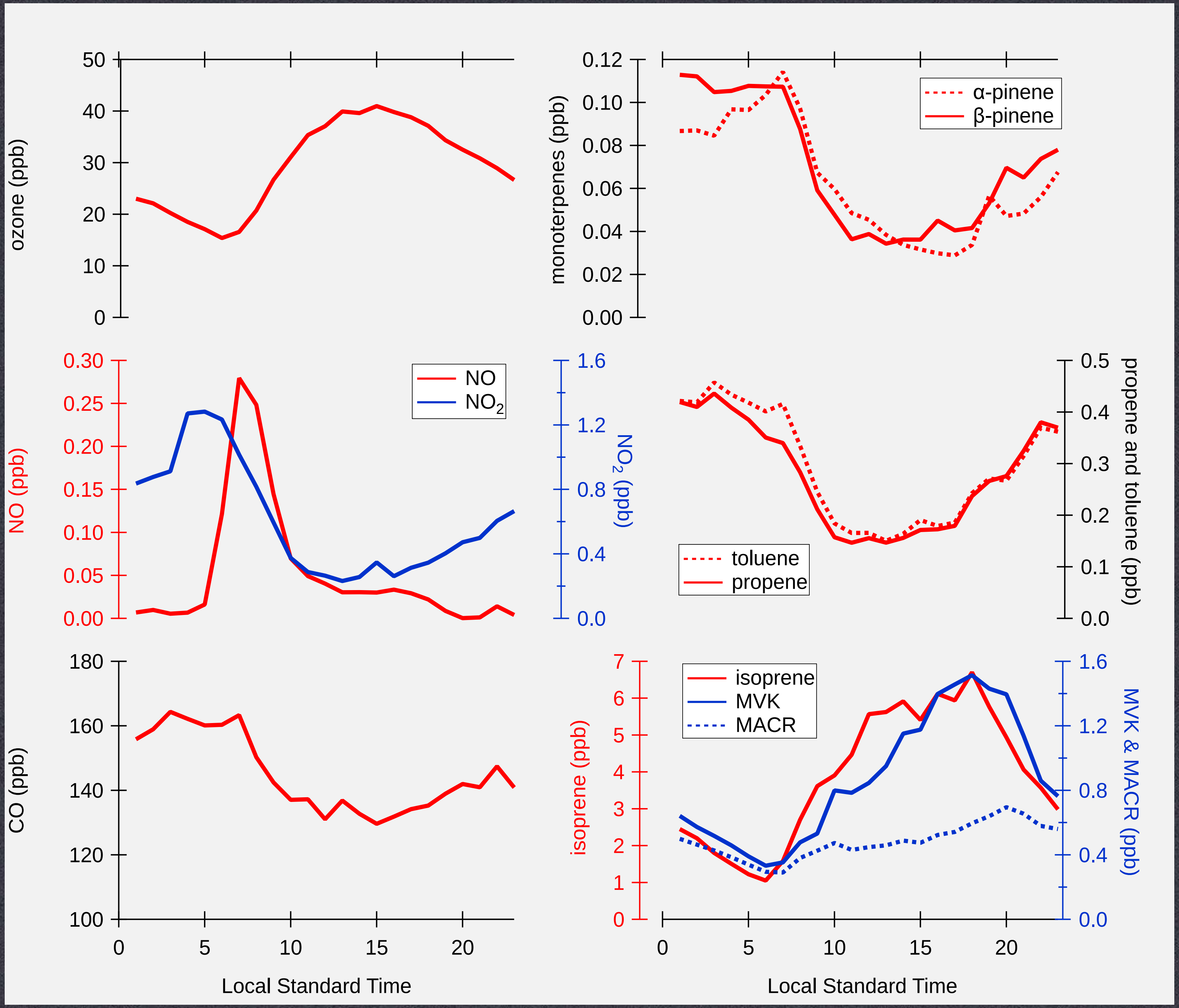


The EPA's direction to manage air quality and climate requires precise understanding in photochemical oxidation processes governed by OH



MANAGING AIR POLLUTION AND CLIMATE

AIR POLLUTION AND CLIMATE CHANGE MANAGEMENT ASPECTS



CO, NO_X, Ozone, and anthropogenic VOCs are very low
(NO is in the range of the low NO regime)

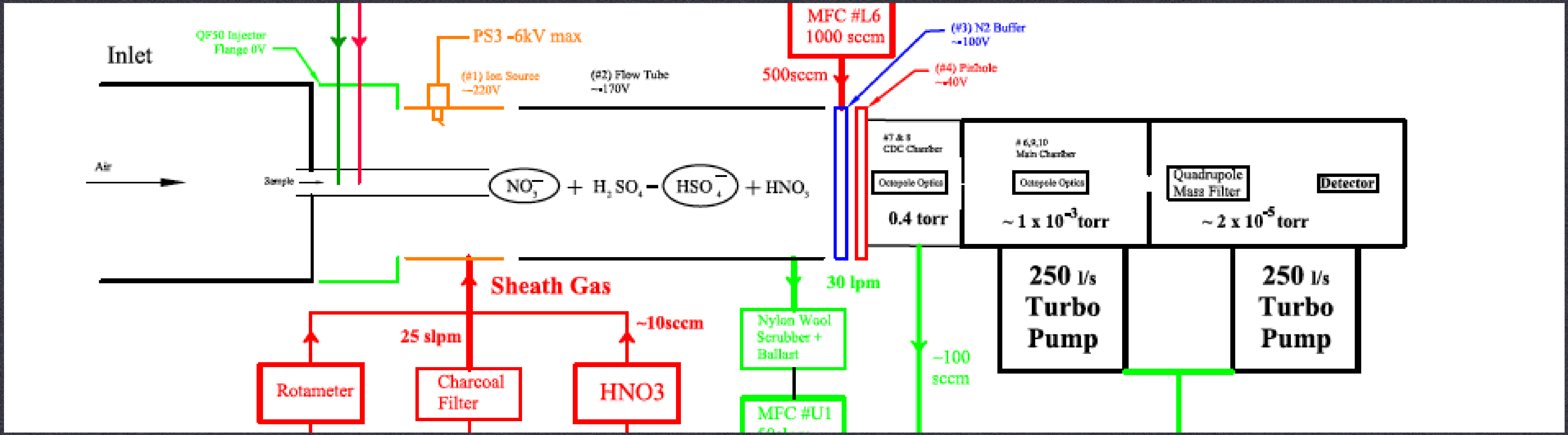
Isoprene (and its oxidation products) and monoterpenes show contrast diurnal variations

Isoprene accounts a substantial fraction of OH loss among the observed trace gas species

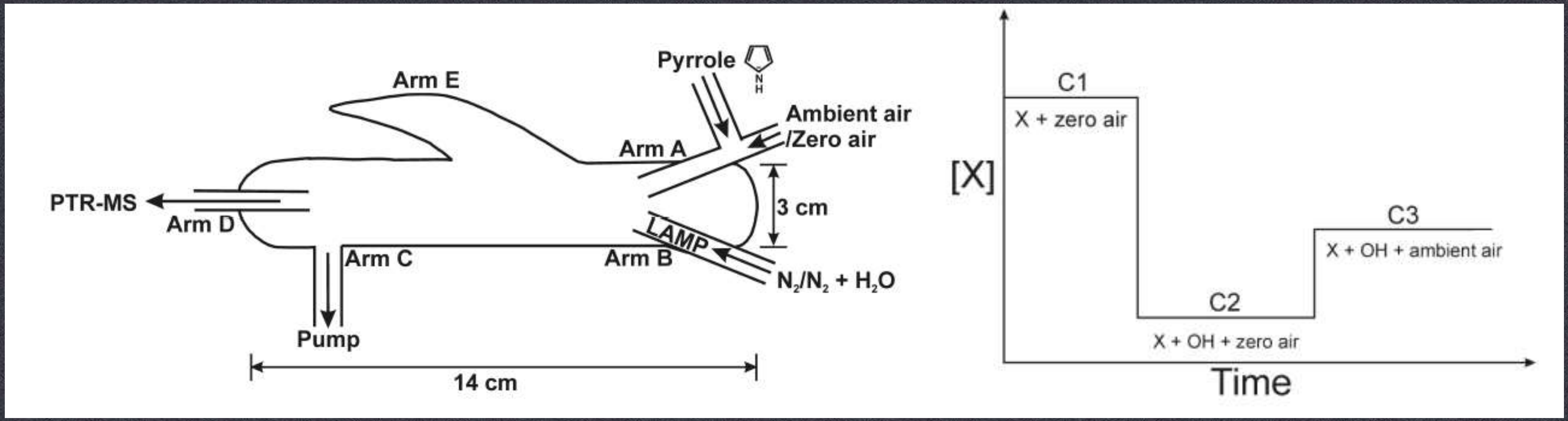
TRACE GAS DISTRIBUTIONS

SOUTH BECOMES A MUCH CLEANER PLACE

CIMS based OH quantification (Tanner et al., 1997)

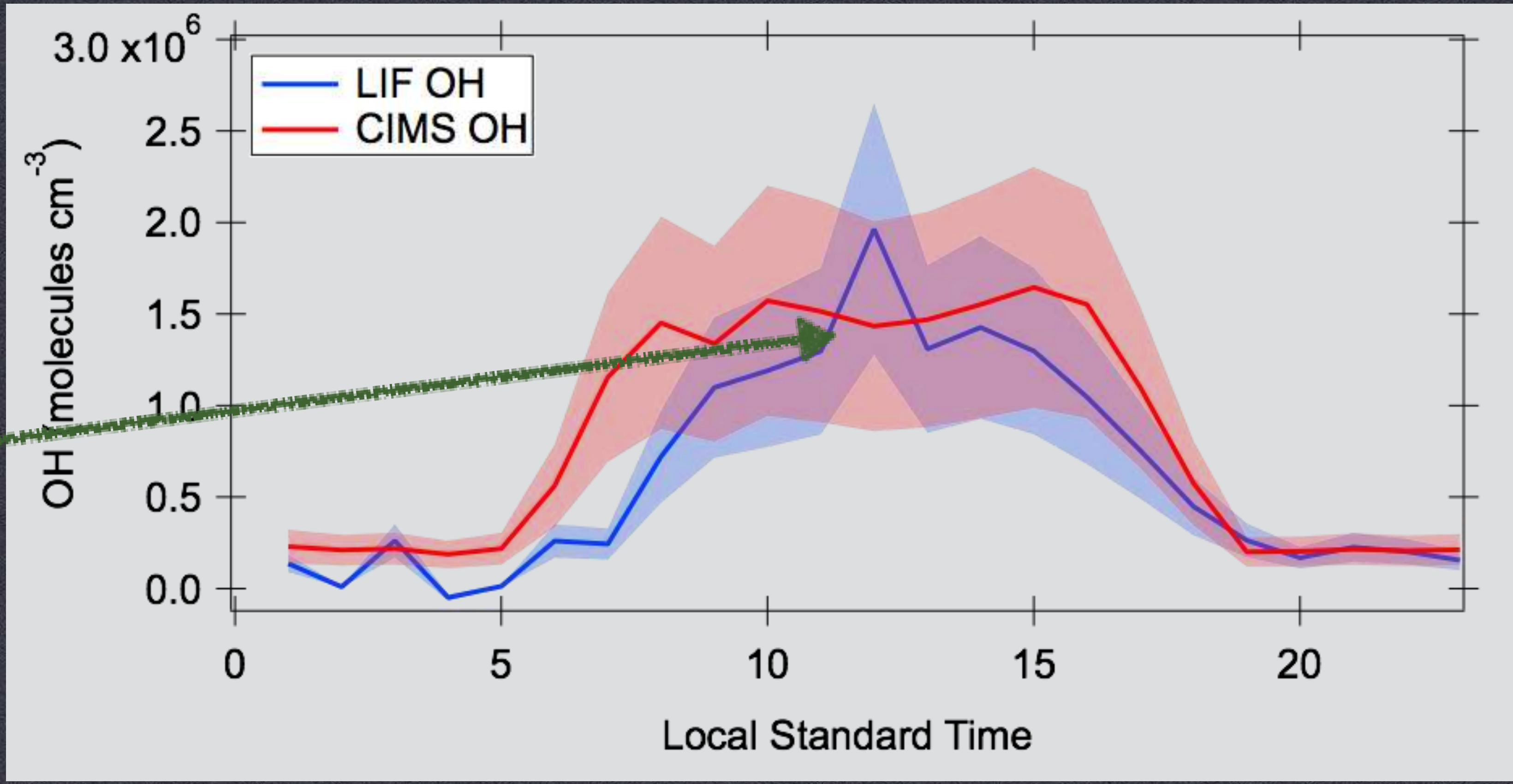


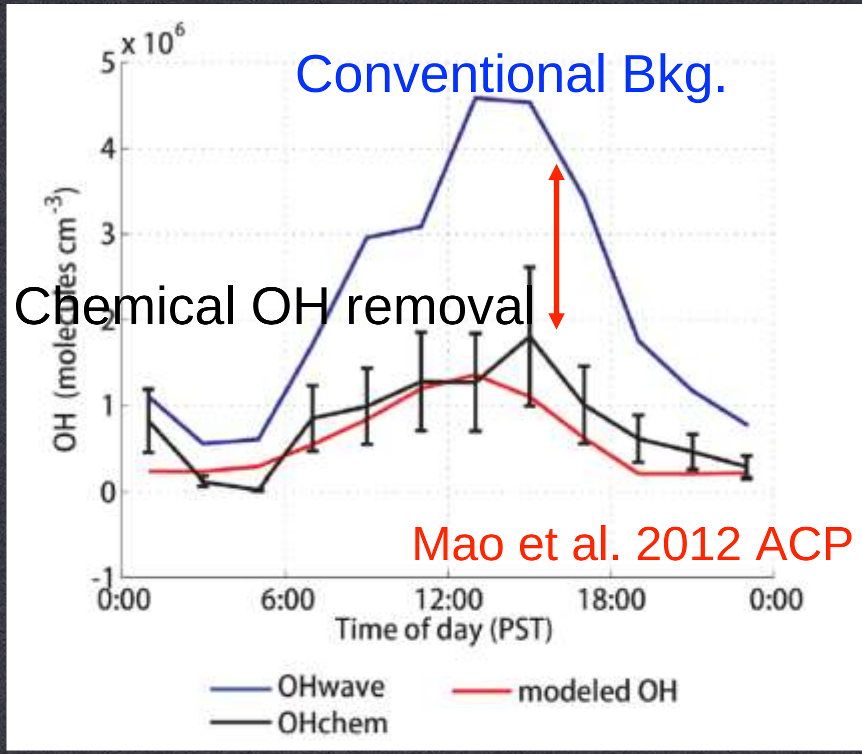
CIMS-CRM OH reactivity quantification (Sinha et al. 2008)



CHEMICAL IONIZATION BASED OH AND OH REACTIVITY OBSERVATIONAL SUITES

- CIMS and LIF (with the chemical removal method, Penn State) intercomparisons: within the analytical uncertainty

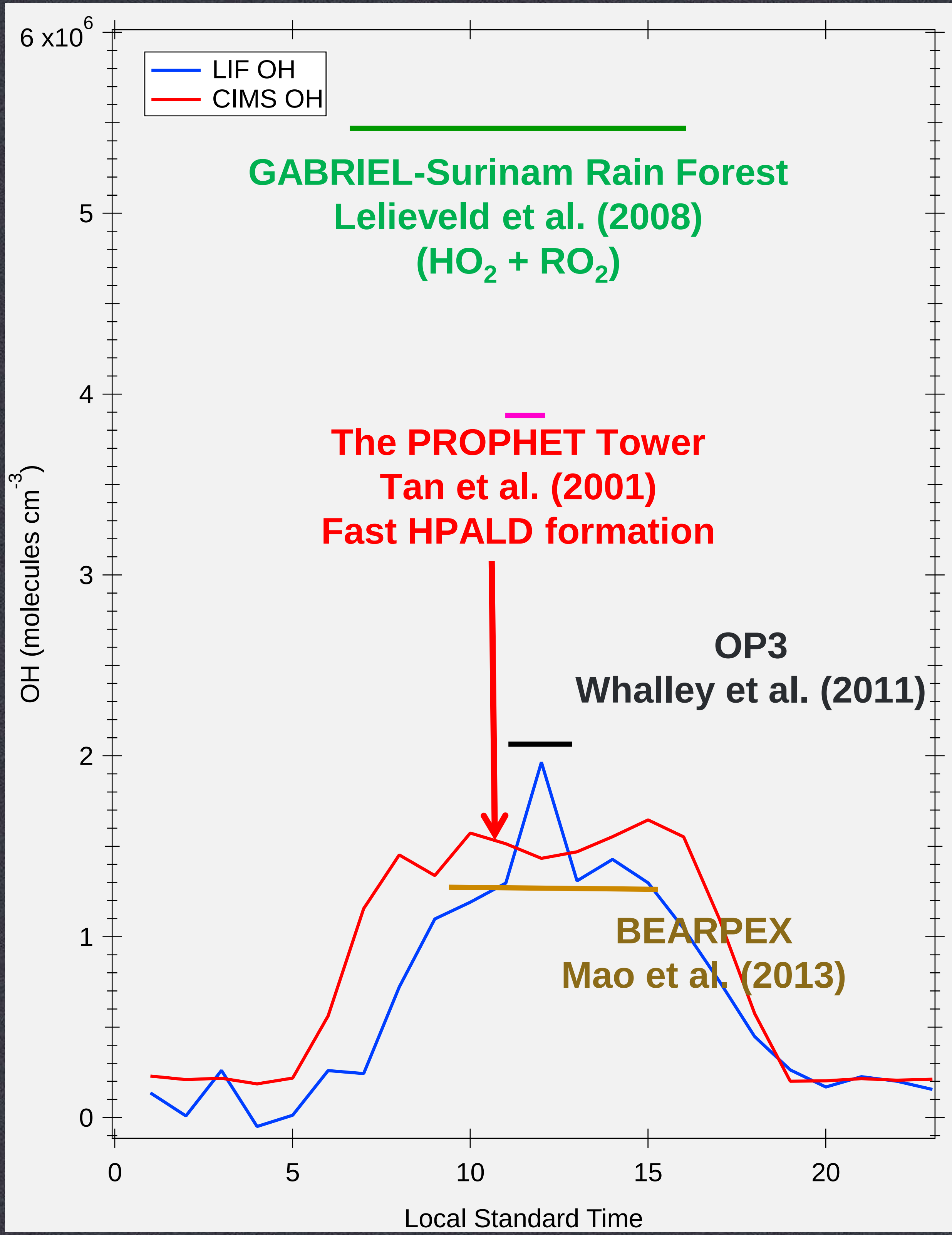




- The CIMS results correspond with classical understanding in OH recycling and observational outcomes from LIF with updated bkg characterization system.

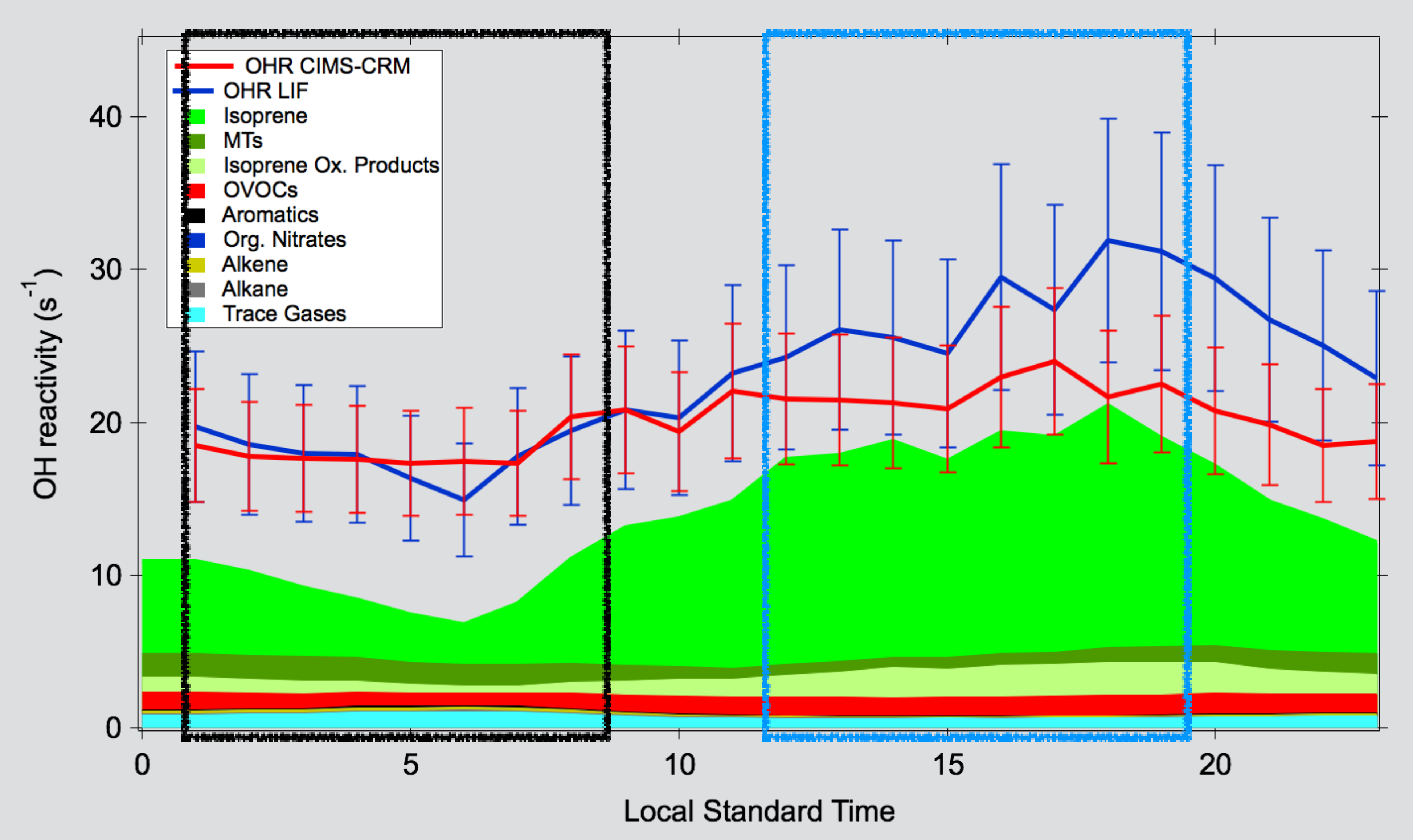
SOAS-CIMS VS LIF OH

- A wide range of OH in high isoprene and low NO conditions summarized by Rohrer and colleagues (2014)
- The reported elevated OH (utilizing LIF) cannot be accounted by any single updated isoprene oxidation mechanisms.



- Observational outcomes using CIMS and LIF with an updated bkg. technique are consistent.

PUT THE NUMBER IN CONTEXT – IN A QUALITATIVE SENSE



LIF 25.9 s^{-1}
CIMS 21.7 s^{-1}
Calc. OHR 17.7 s^{-1}
Missing Portion
:31 % - 18 %

LIF 17.6 s^{-1}
CIMS 17.7 s^{-1}
Calc. OHR 8.78 s^{-1}

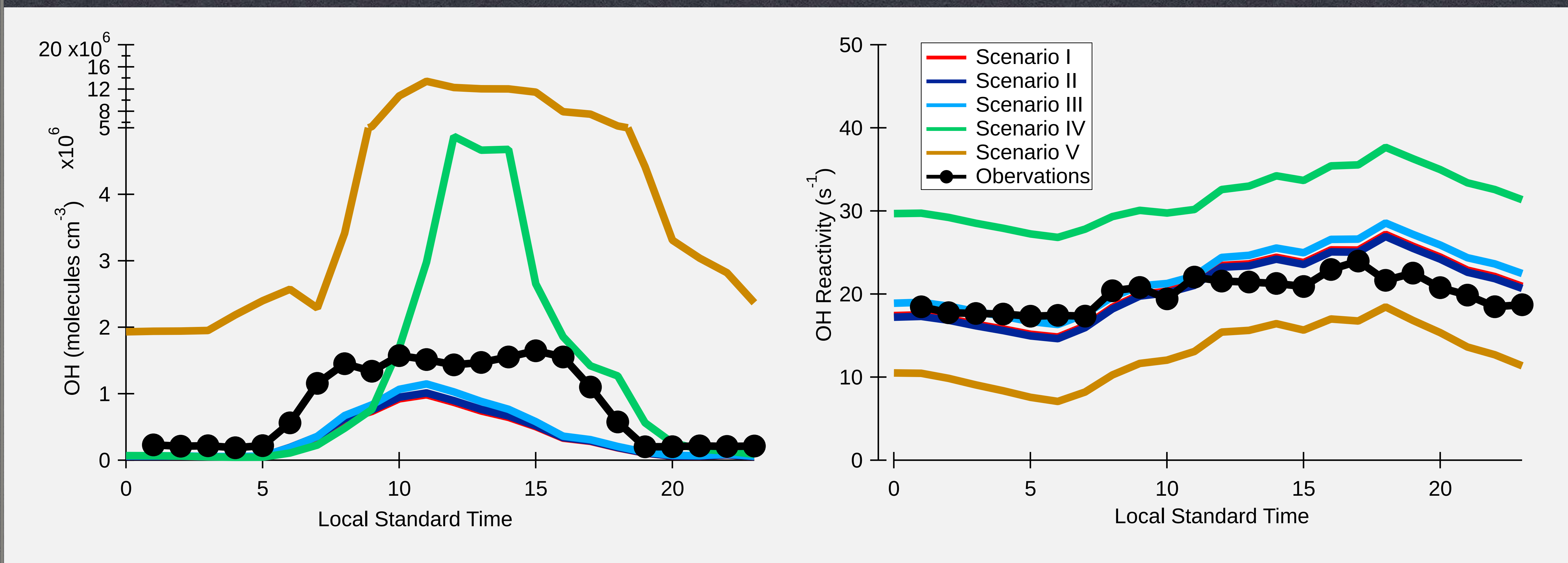
Missing Portion
: 50 %

- Calculated OHR is dominated by isoprene, MTs, and isoprene oxidation products
- Two different techniques show an agreement within the analytical uncertainty
- The LIF technique observed higher OHR towards in the late afternoon (The differences in sampling methods could be the cause)

SOAS-CIMS VS LIF OH REACTIVITY

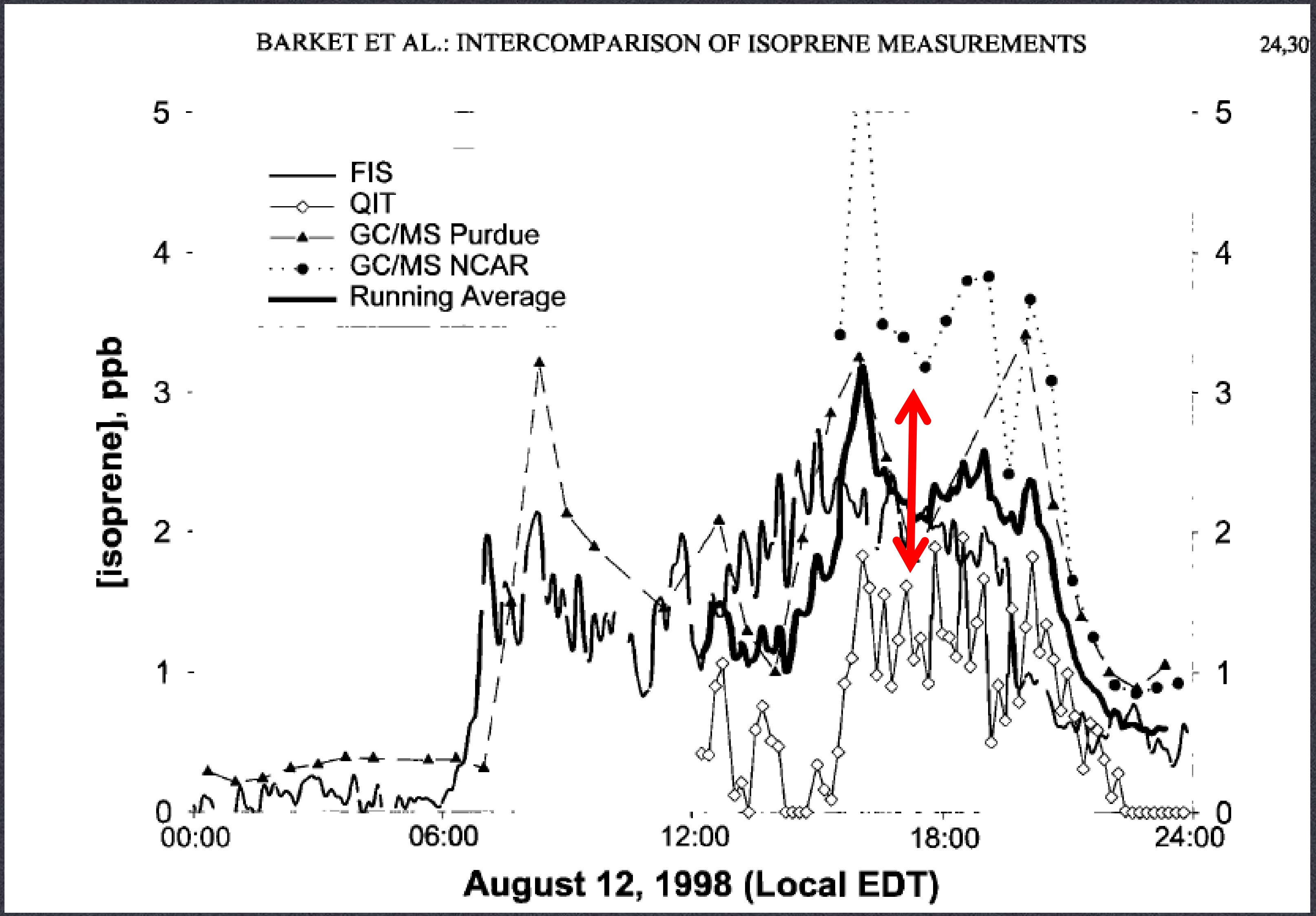
Scenario I	MCM 3.2
Scenario II	MCM 3.2 + Crounse HPALD
Scenario III	MCM 3.3.1
Scenario IV	HO_2+RO_2 recycle (Rohrer and colleagues)
Scenario V	X (Rohrer and colleagues)

- NO Driven OH recycling
- Additional Recycling



UNCERTAINTY FROM CHEMICAL MECHANISMS

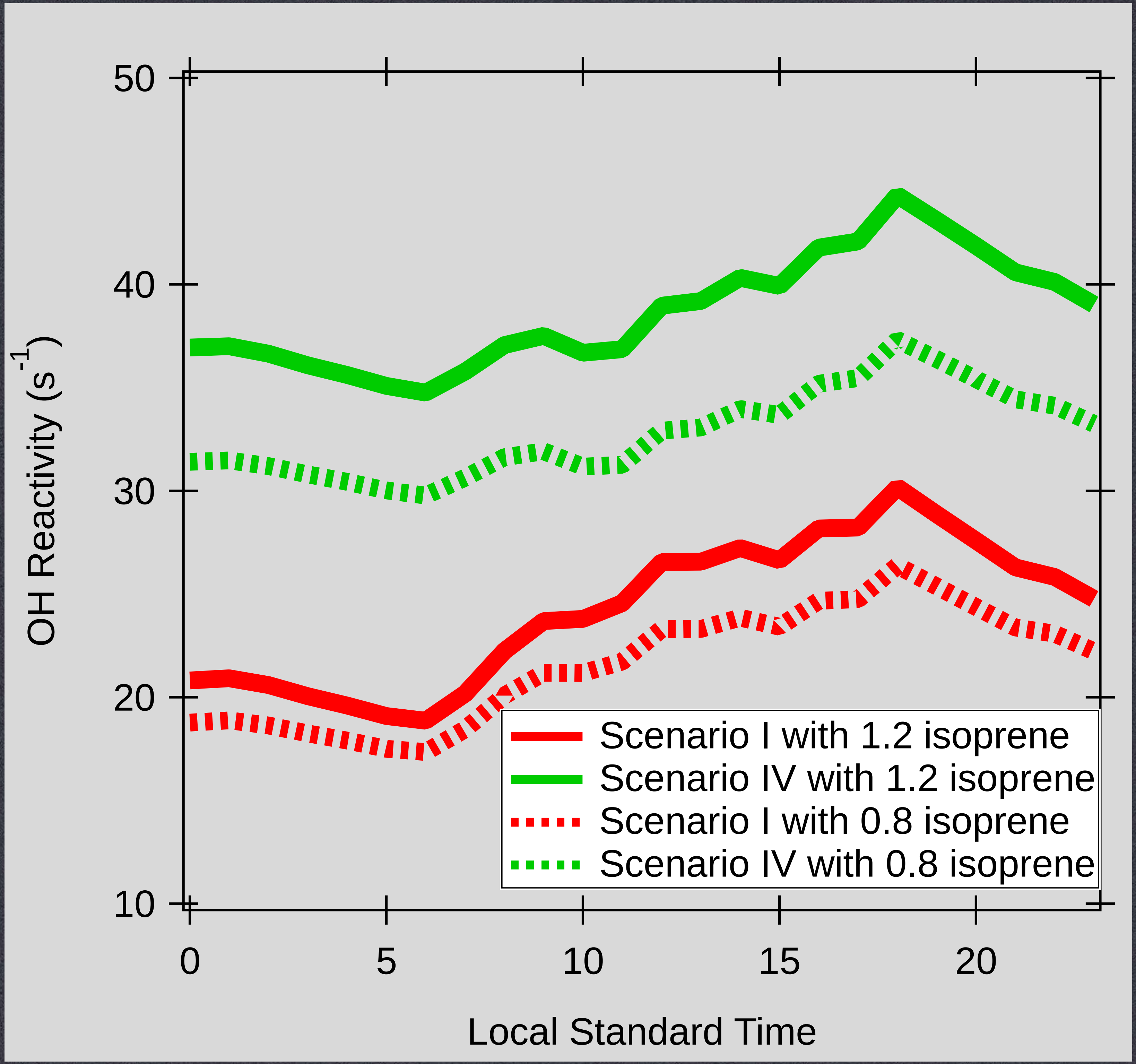
UWCM MODEL WITH MCM 3.2 (WOLFE AND THORNTON 2011 ACP)



- Multiple instruments were deployed for the SOAS campaigns for independent observations
- Careful efforts were exercised among the instrumentations such as cross calibration
- Barket et al. (2001) reported differences in the range of 21 % - 88 % among the analytica techniques for isoprene quantification from a find inter comparison exercise

CONSEQUENCES IN UNCERTAINTY IN COMMONLY MEASURED REACTIVE GASES

A CASE STUDY

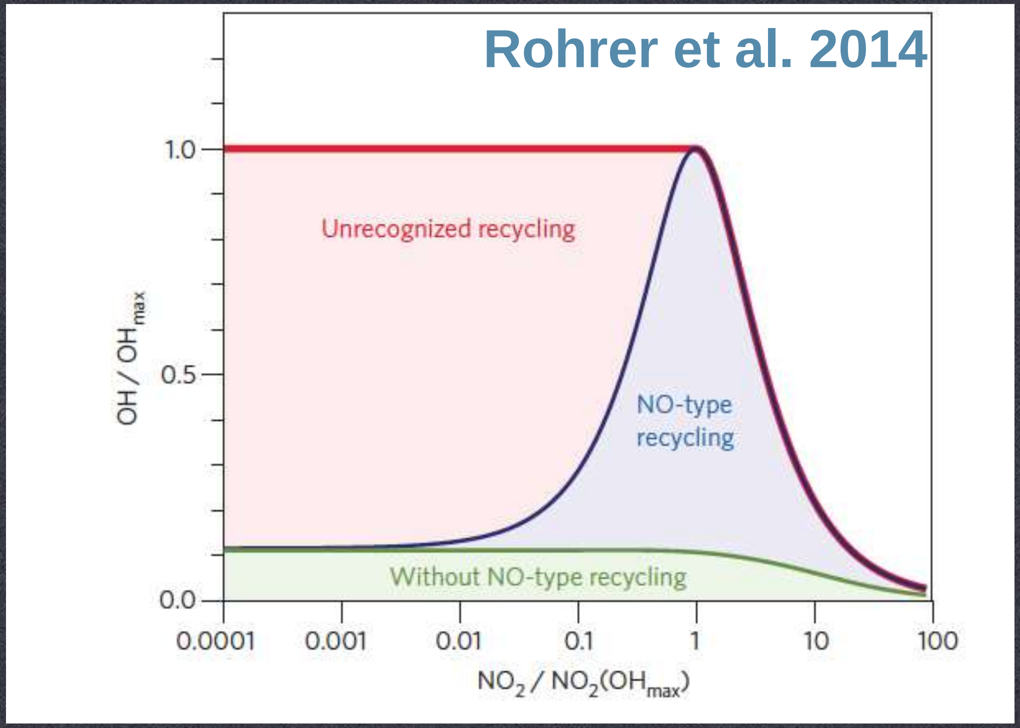


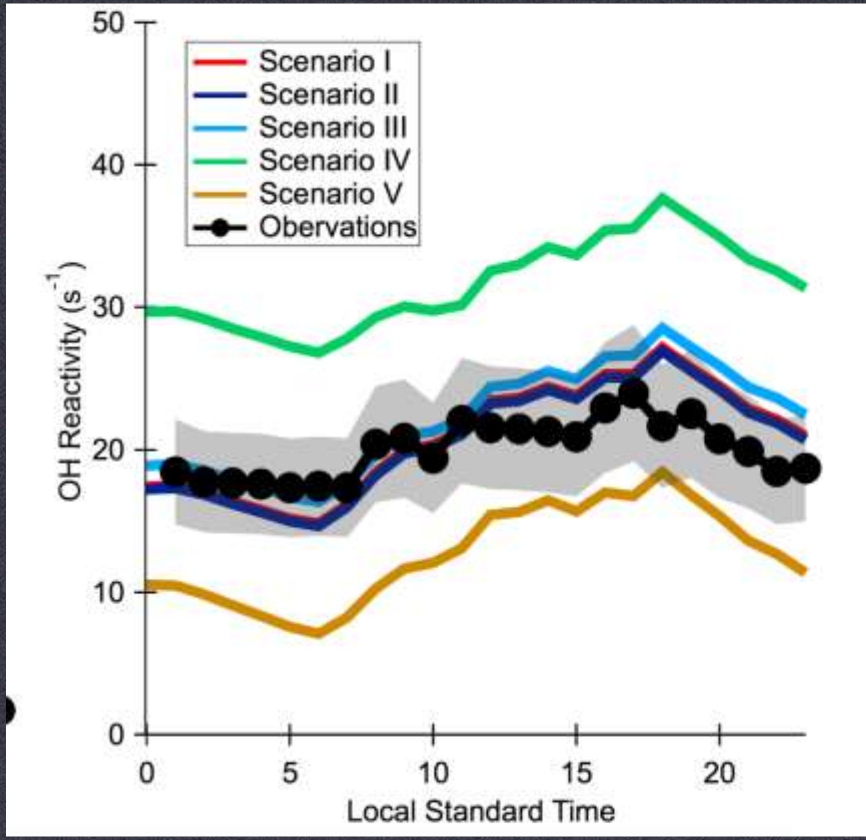
±20 % of isoprene differences can cause significant differences in OH reactivity estimations (40- 50 %)

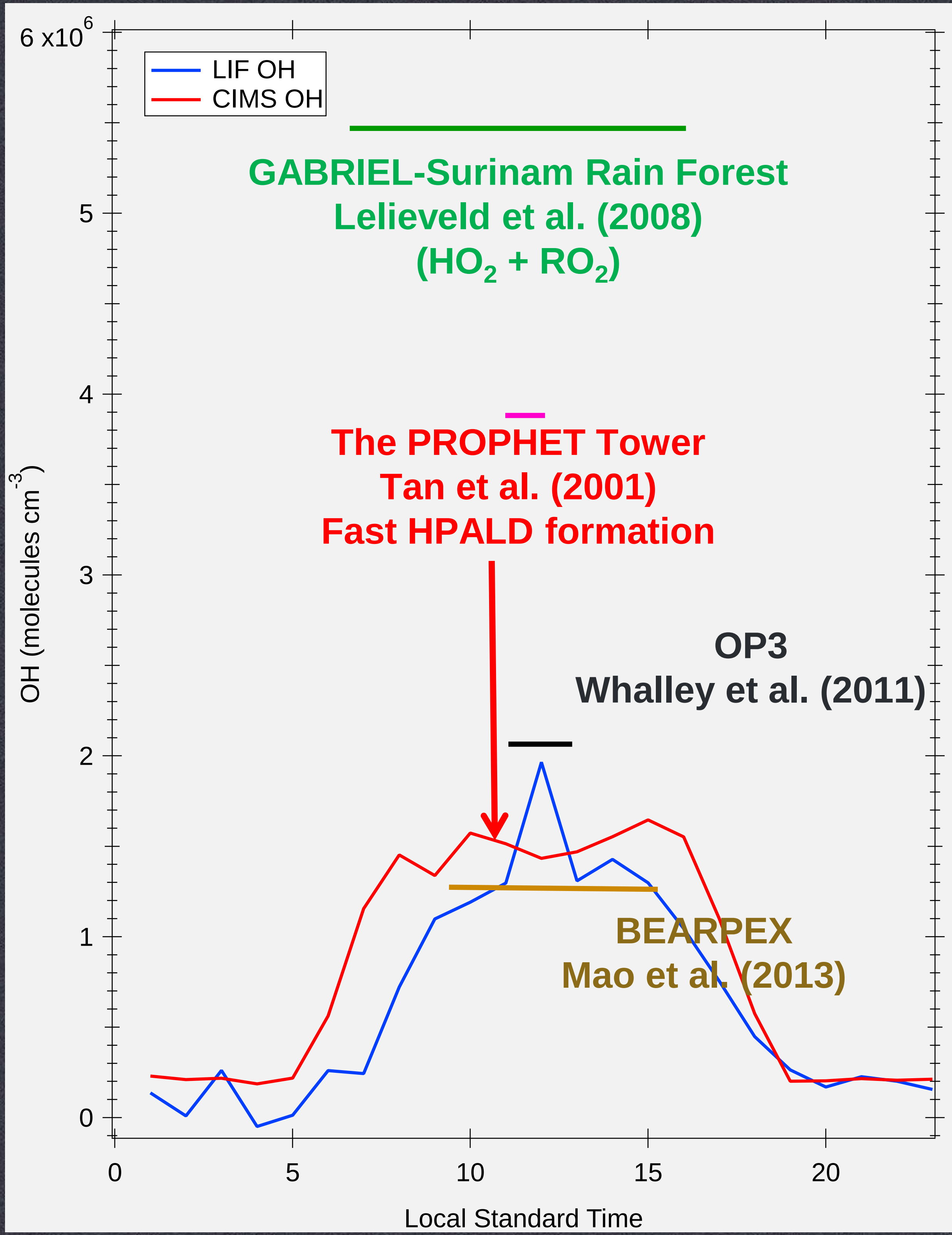
The discrepancy gets augmented by applying different isoprene oxidation mechanisms – up to 100 %

MODELED OHR UNCERTAINTY USING DIFFERENT ANALYTICAL TECHNIQUES

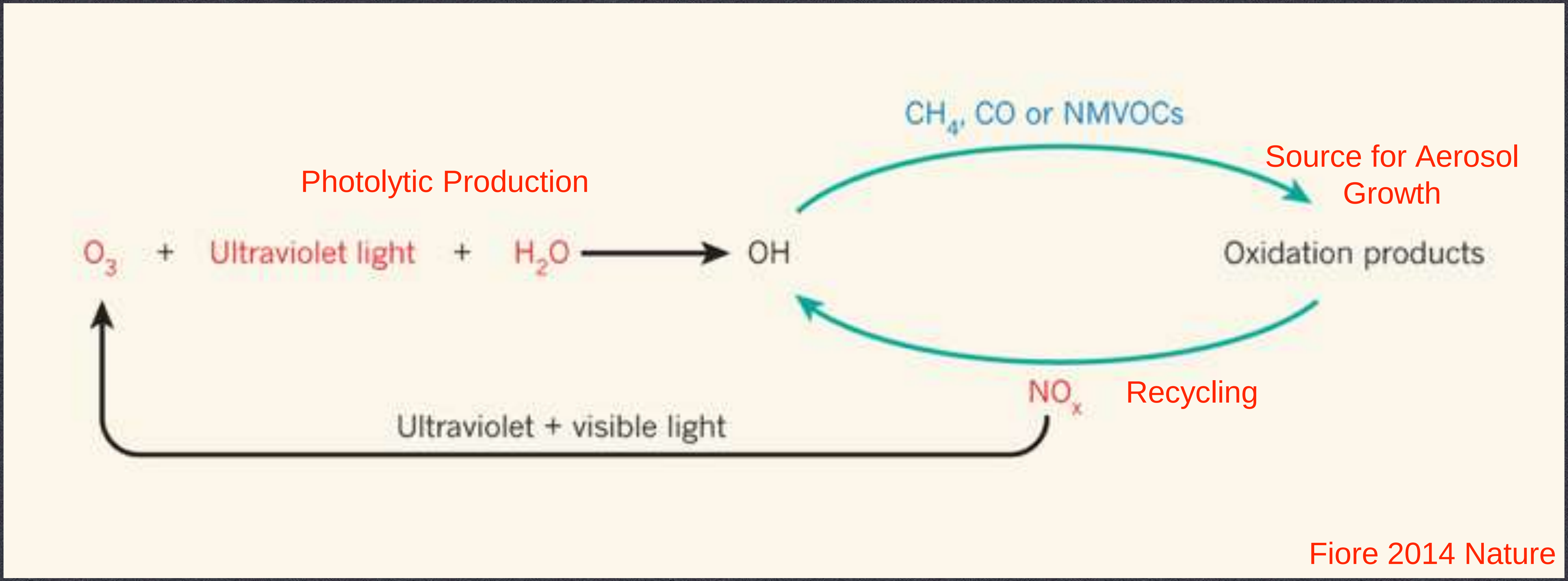
UWCM MODEL WITH MCM 3.2 (WOLFE AND THORNTON 2011 ACP)


Rohrer et al. 2014
1.0
0.5
0.0
OH / OHmax
Unrecognized recycling
NO-type recycling
Without NO-type recycling
0.0001
0.001
0.01
0.1
1
10
100
NO2 / NO2(OHmax)

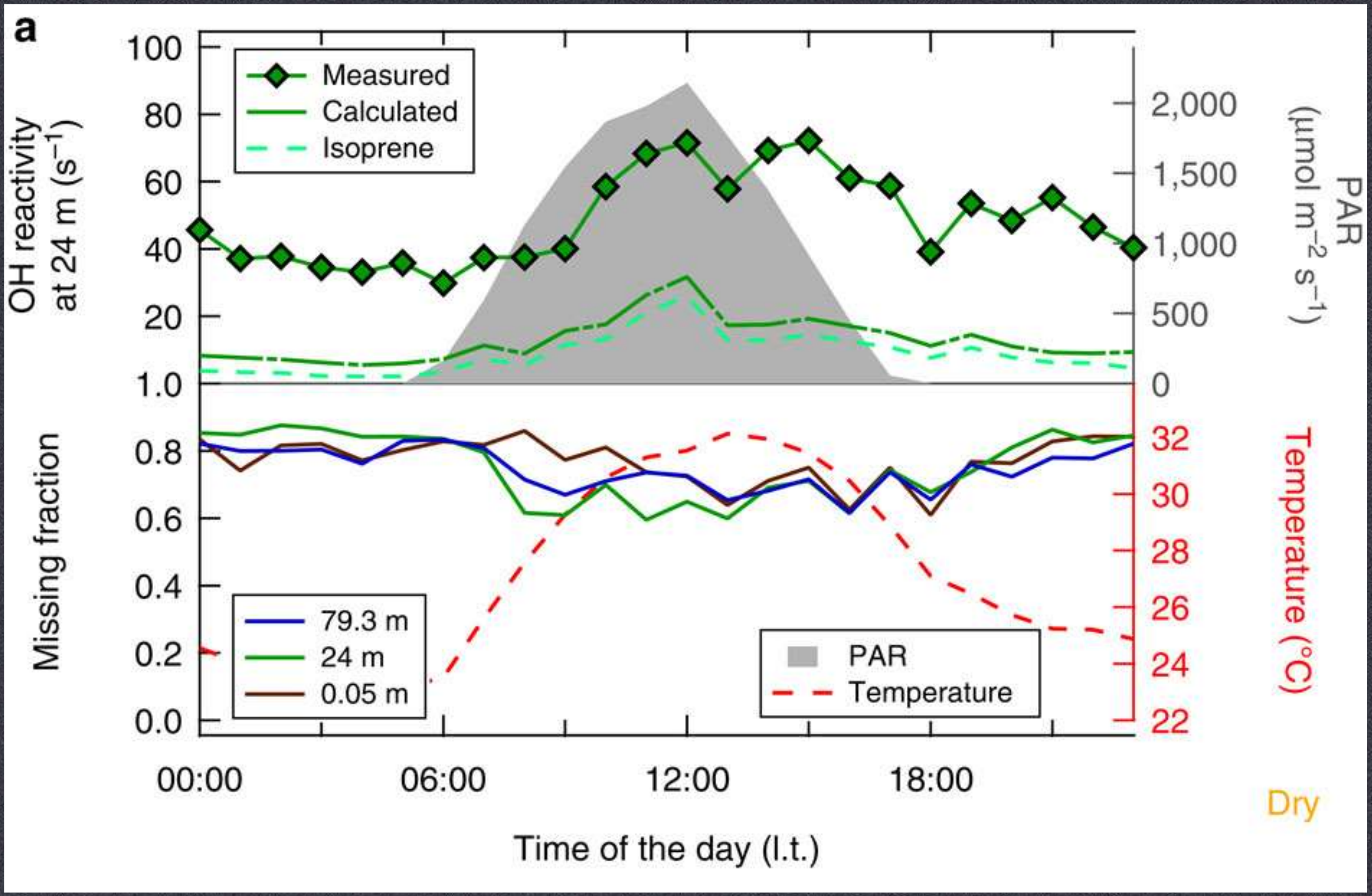

Scenario I
Scenario II
Scenario III
Scenario IV
Scenario V
Obervations
OH Reactivity (s-1)
50
40
30
20
10
0
5
15
Local Standard Time


6 x10^6
LIF OH
CIMS OH
GABRIEL-Surinam Rain Forest
Lelieveld et al. (2008)
(HO2 + RO2)
The PROPHET Tower
Tan et al. (2001)
Fast HPALD formation
OP3
Whalley et al. (2011)
BEARPEX
Mao et al. (2013)
OH (molecules cm-3)
Local Standard Time
0
5
10
15
20

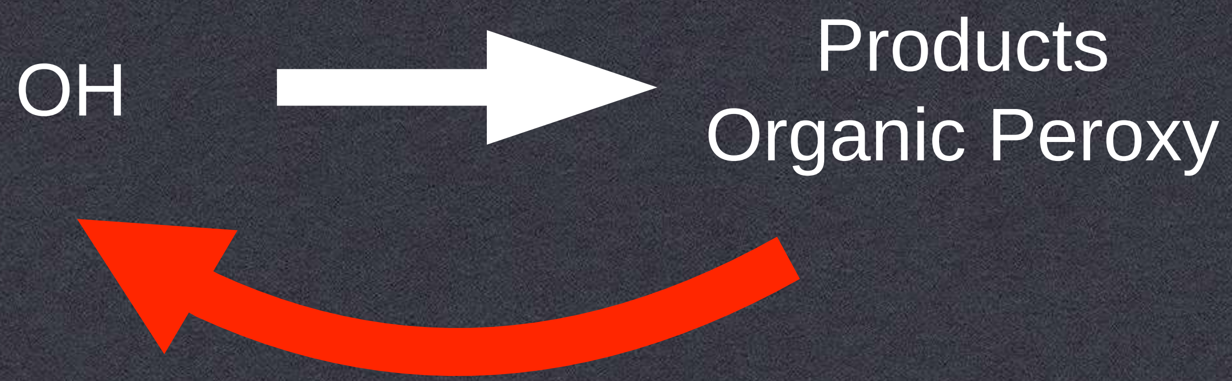
SUMMARY



THE UNDERSTANDING – MAY BE STILL HOLD IN THE SE US



OH neutral degradation?



AN ELEPHANT IN THE ROOM

NOLSCHER ET AL. (2016) NAT. COMM.