NO_X AND NO_Y IN THE TROPICAL MARINE BOUNDARY LAYER AT CAPE VERDE

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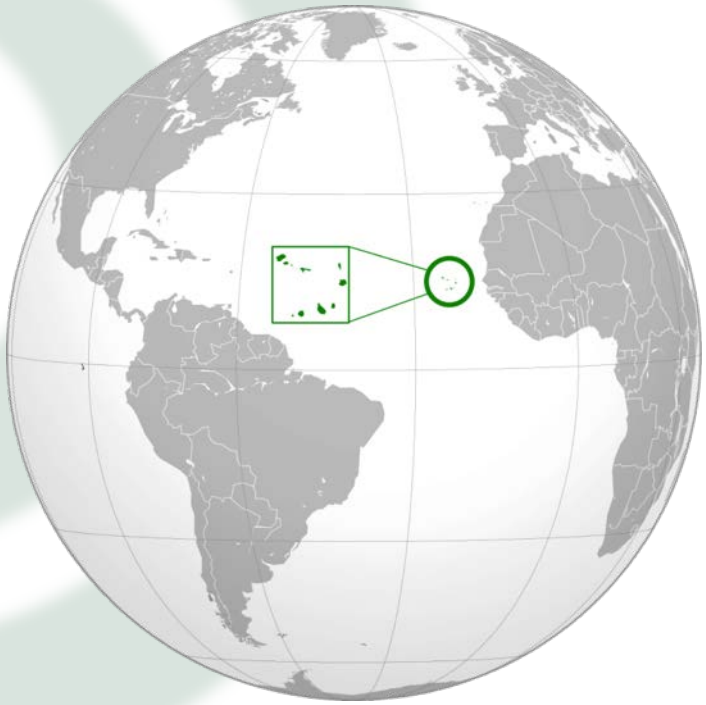
The Cape Verde Atmospheric Observatory (CVO)

Observatory established in 2006 as global GAW station.

Only GAW global station continuously measuring NO & NO_2 in the tropics & at a background site.

Other measurements: O_3, CO, CH_4, CO_2, N_2O, NMHCs, DMS, O-VOCs, Halocarbons, Mercury, Meteorology, Aerosol, Spec-Rad.



NO_x measurements at Cape Verde

Custom dual channel NO chemiluminescence instrument.

Channel 1: NO and NO_x by selective photolytic dissociation of NO_2 @ 395nm or 385nm (since March 2015)

Channel 2: NO_y 4 channel thermal dissociation NO_y (ΣPANs, ΣANs, HNO_3, Σreactive nitrogen.)

LODs; NO ~0.3 ppt, NO_2 ~ 0.35 ppt, NOy ~ 5 ppt / hour.

Calibrated: Sensitivity,
NO_2 converter efficiency,
artifact NO/NO_2 signals on both channels.
Pre-reactor zero signal every 5 minutes

NO_x measuring near continuously since October 2006.

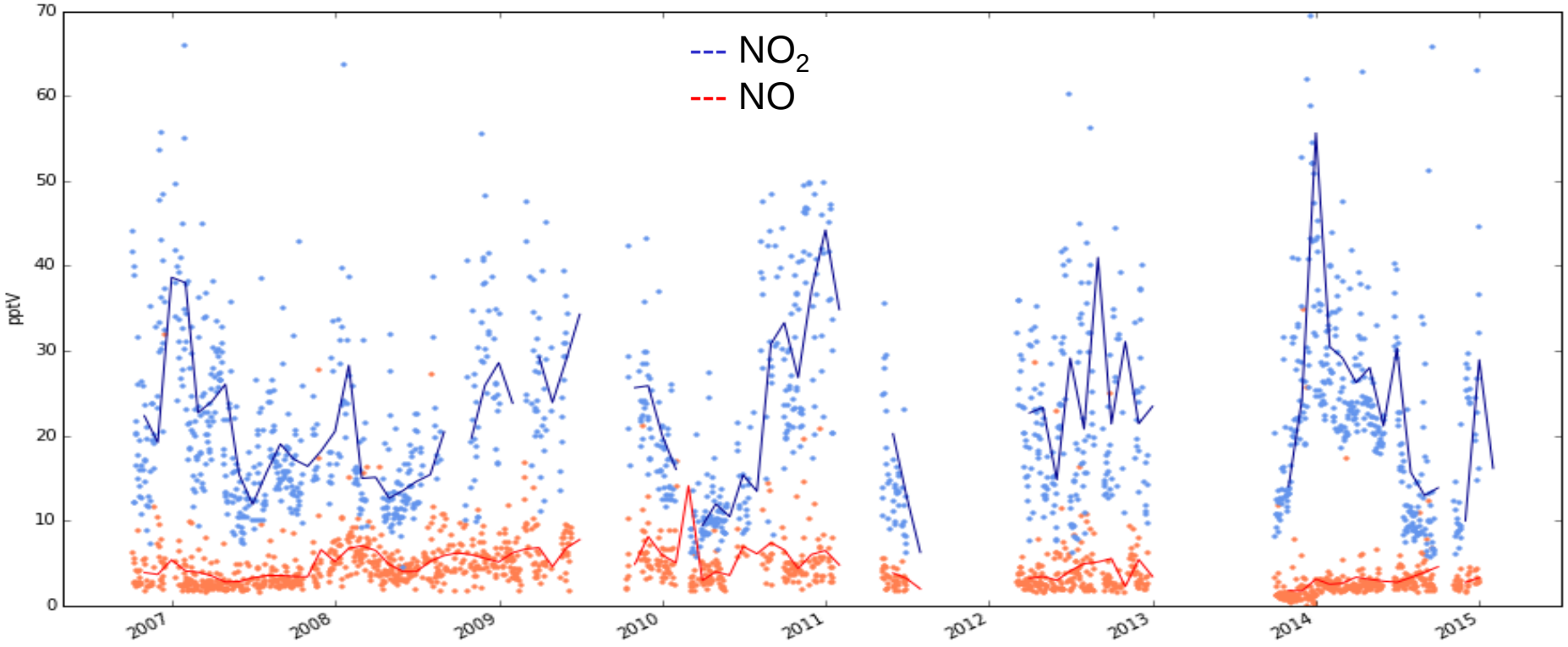
NO_y until 2009,

Speciated NO_y since 2015 – only one anywhere!

Original single channel instrument from 2006 – 2009, upgraded to dual channel 2009 – present. Air Quality Design, inc. Golden, Colorado, USA

NO_x time series

- Typically very low mixing ratios of NO_x; 10 – 50 pptv leading to net ozone destruction

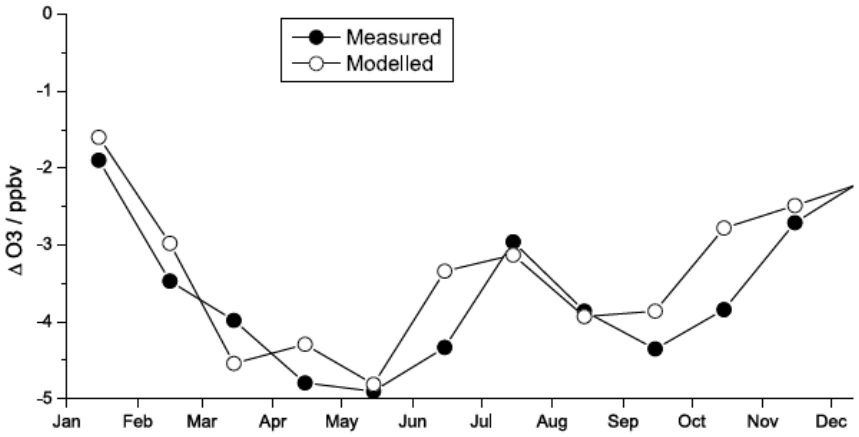


Typically a winter/spring time maximum in NO_x dominated by NO_2.

NO_2 consistently higher than photo-stationary steady state would predict.

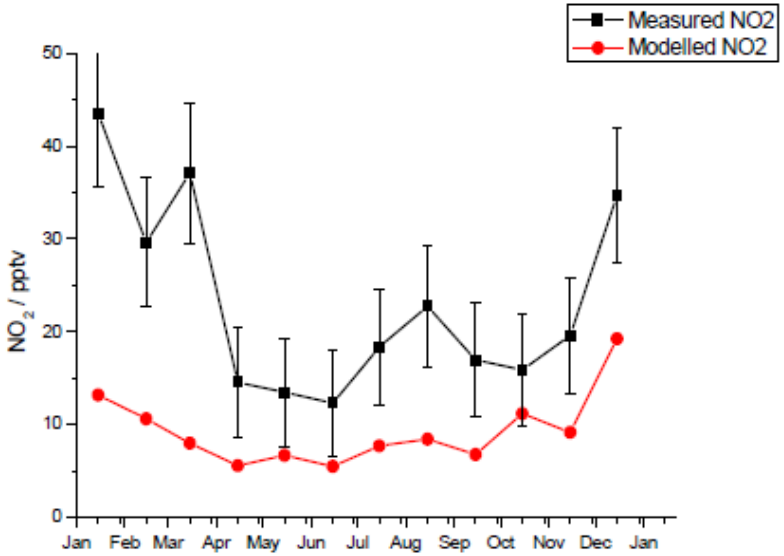
NO and NO_2 consistency with theory

Daily ozone destruction predicted in a box model constrained to observed NO.



Model prediction of O_3 loss at the different NO concentration observed is consistent with the observed O_3 losses

Supports the NO observations

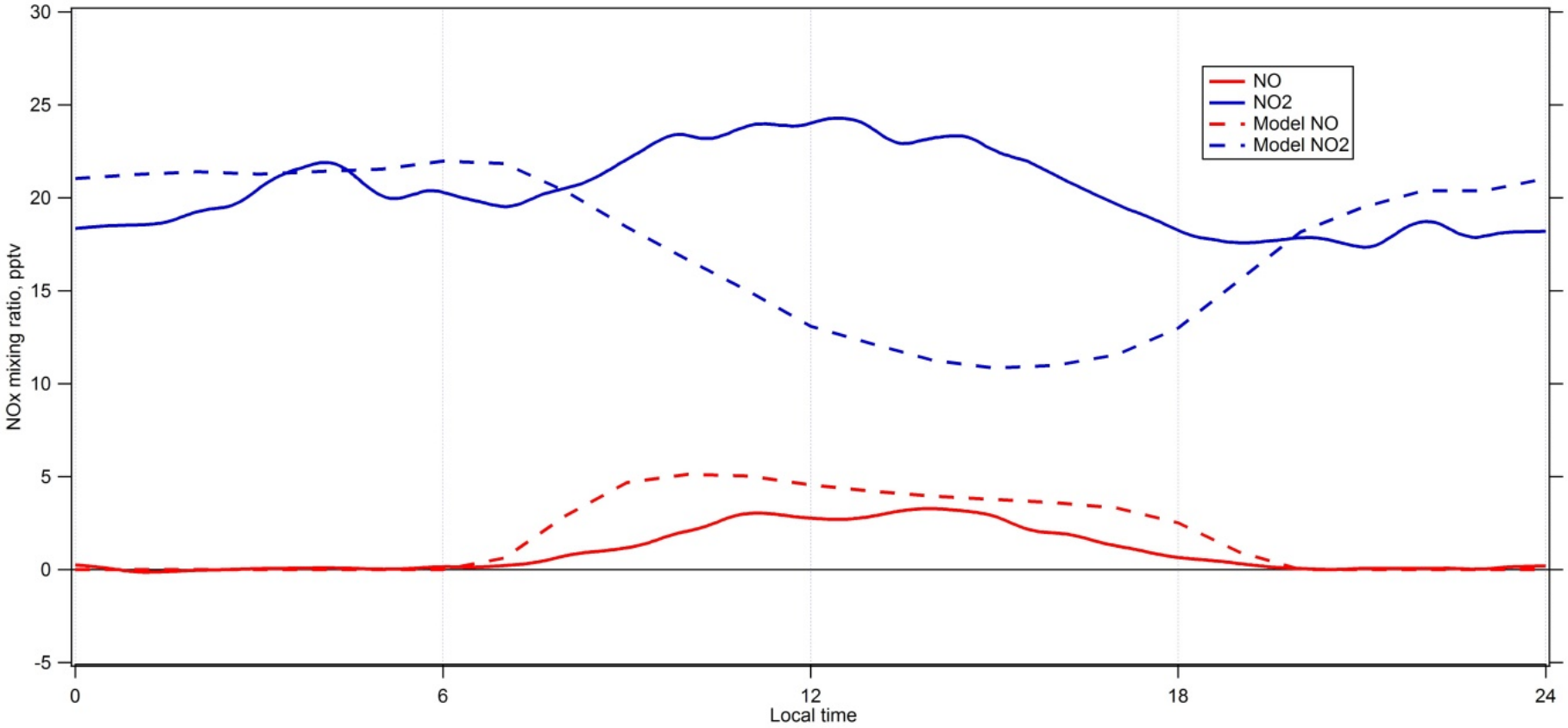


Model prediction for NO_2 concentrations are significantly lower than those observed.

NO:NO_2 observed 1 : 4 - 8
NO:NO_2 simulated 1 : 2

NO_2 diurnal behaviour

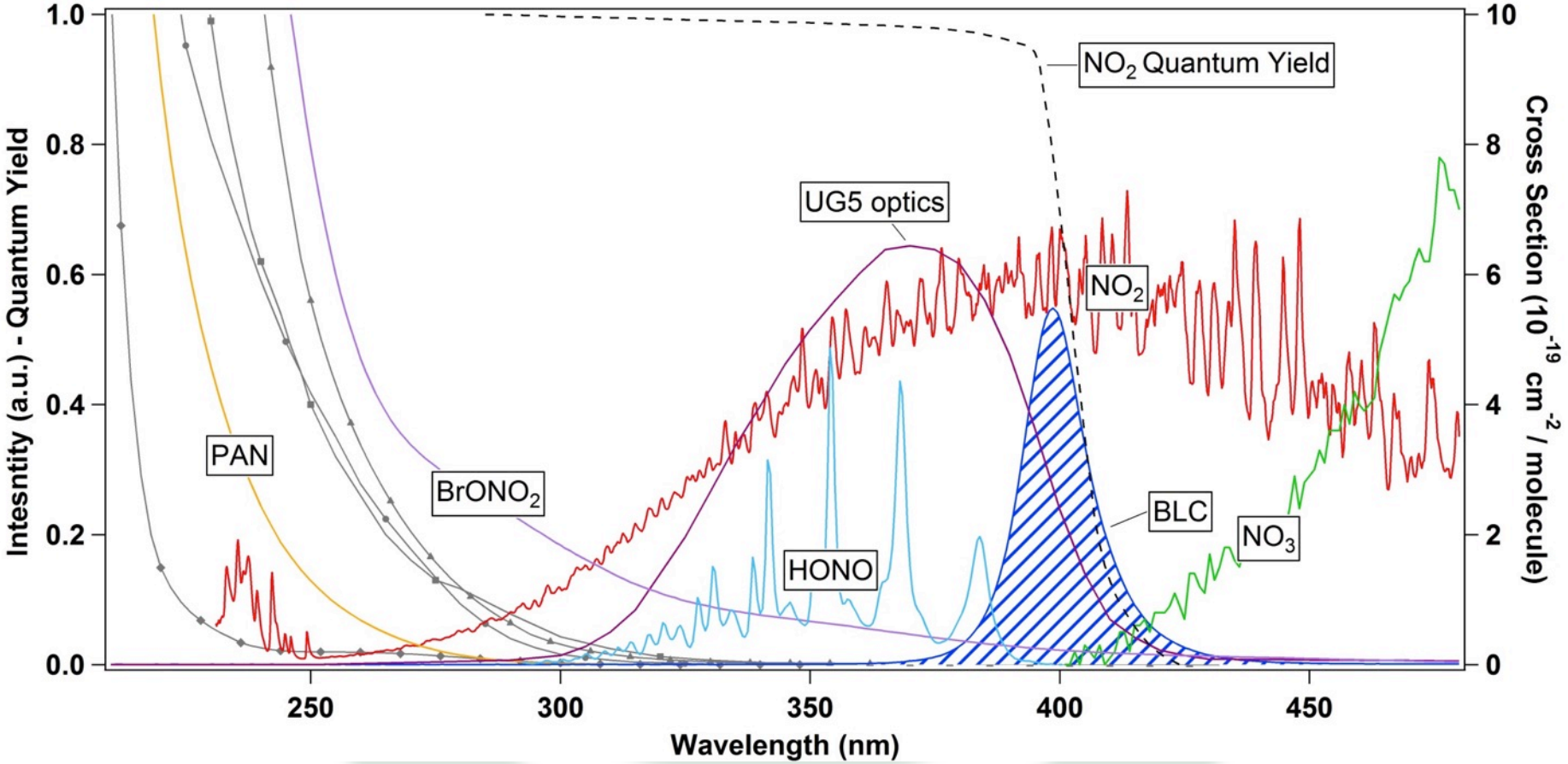
Similar discrepancy seen between GEOS-Chem model and measurements



Night time concentrations are simulated well but diurnal signal in model and measurements are significantly different.

[1] GEOS-Chem model output courtesy of Tomas Sherwen

Possible NO_2 measurement error



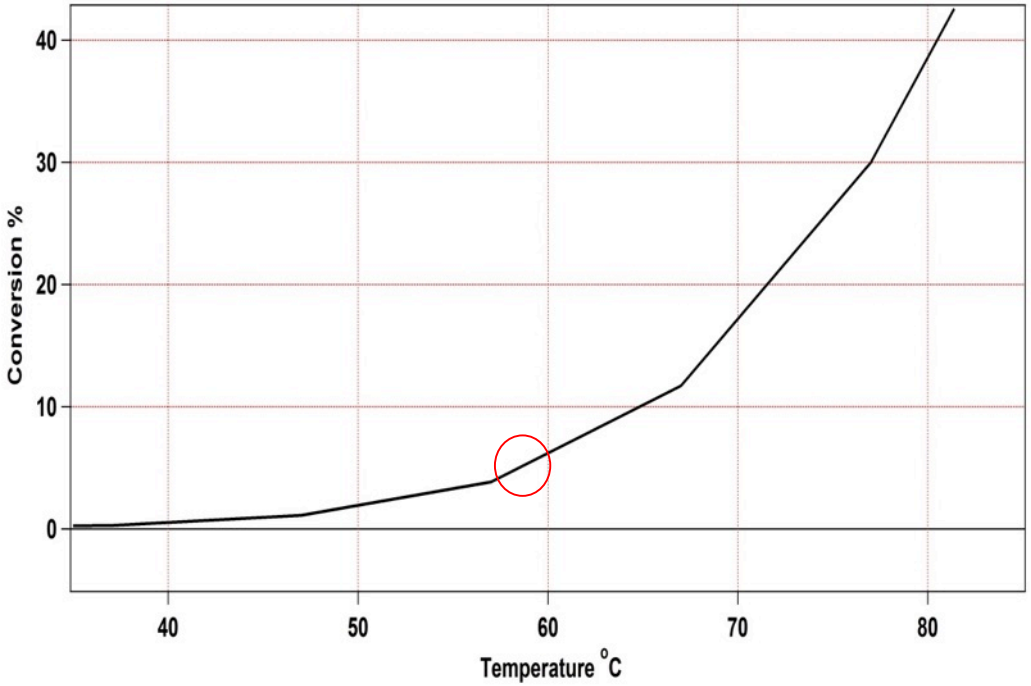
Photolytic converter:

Minor overlap with HONO, nitrate and $BrONO_2$ absorbance bands.

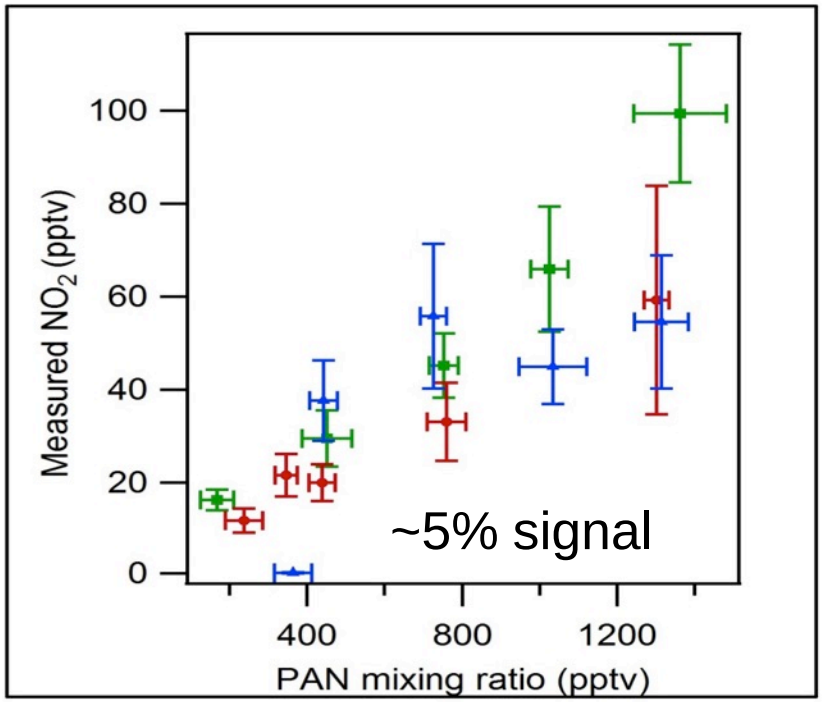
Not expected to be major contributors at Cape Verde.

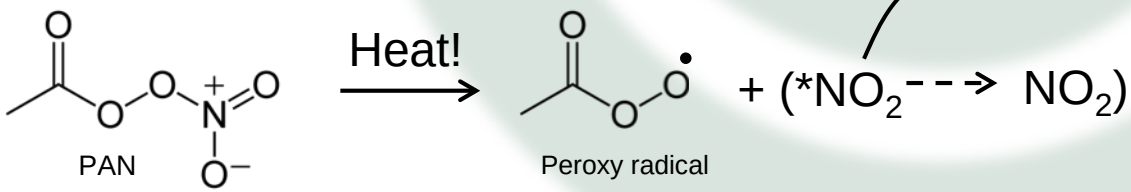
Possible NO_2 measurement error

Modelled PAN thermal decomposition



Measured NO_2 signal from PAN





NO_2* more easily photolysed.

Proportionately greater contribution to NO_2 signal.

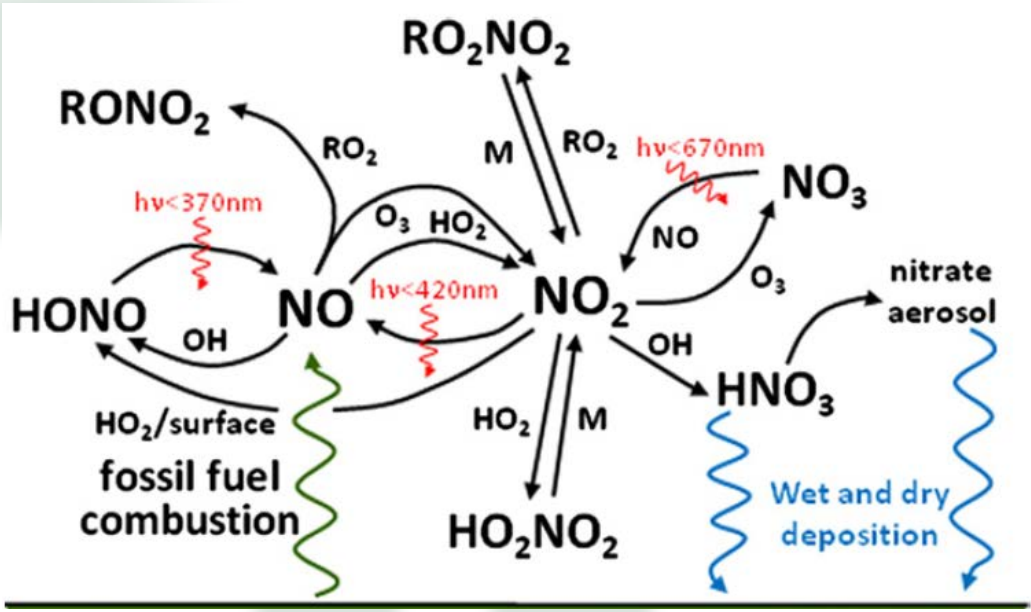
Higher conversion efficiency and lower temperature to reduce the error.

NOy speciation measurements

NO_y species a reservoir for NO_x

Likely source of NO_2 at Cape Verde

Partitioning between gas and particulate phase necessitates speciation measurement.



NO_y inlet mounted on 10m tower

3 heated quartz furnaces

1 molybdenum catalyst

Switchable cyclone

[1] http://www.leos.le.ac.uk/group/mpb/images/trop5.png

NOy speciation measurements

NO_x from thermal decomposition of NO_y species detected quantitatively.

NO_y = NO + NO_2 +

+ PANs+ $XONO_2$ + NO_3+ N_2O_5+ HONO + HO_2NO_2 + RO_2NO_2

∑PANs

+ CH_3ONO_2+ $C_2H_5ONO_2$ + …+ RONO2

∑ANs

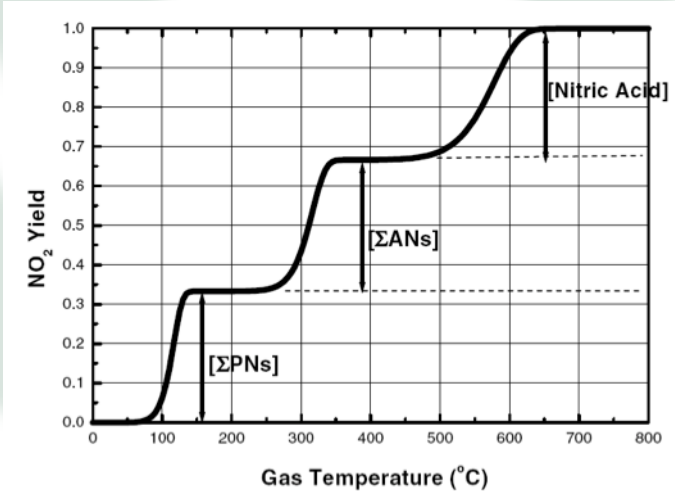
+ HNO_3 + p-NO_3^- + …

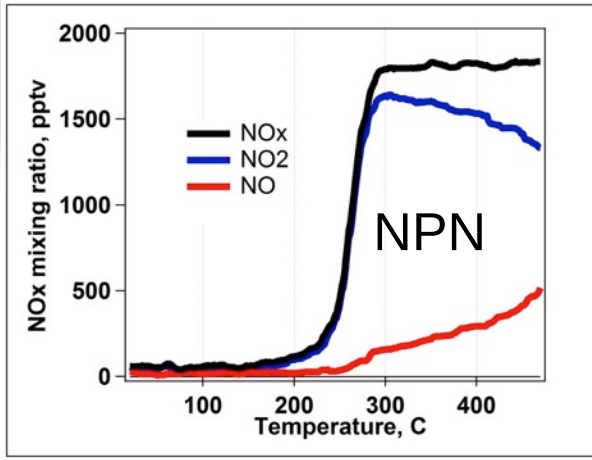
HNO_3

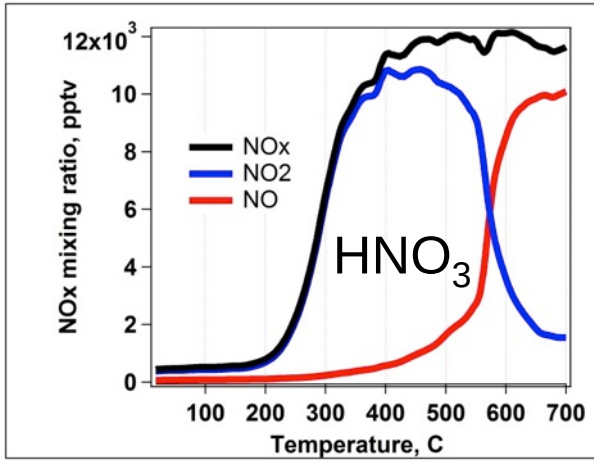
NO and NO_2 observed

Inter-conversion conserves NO_x

Need to measure both

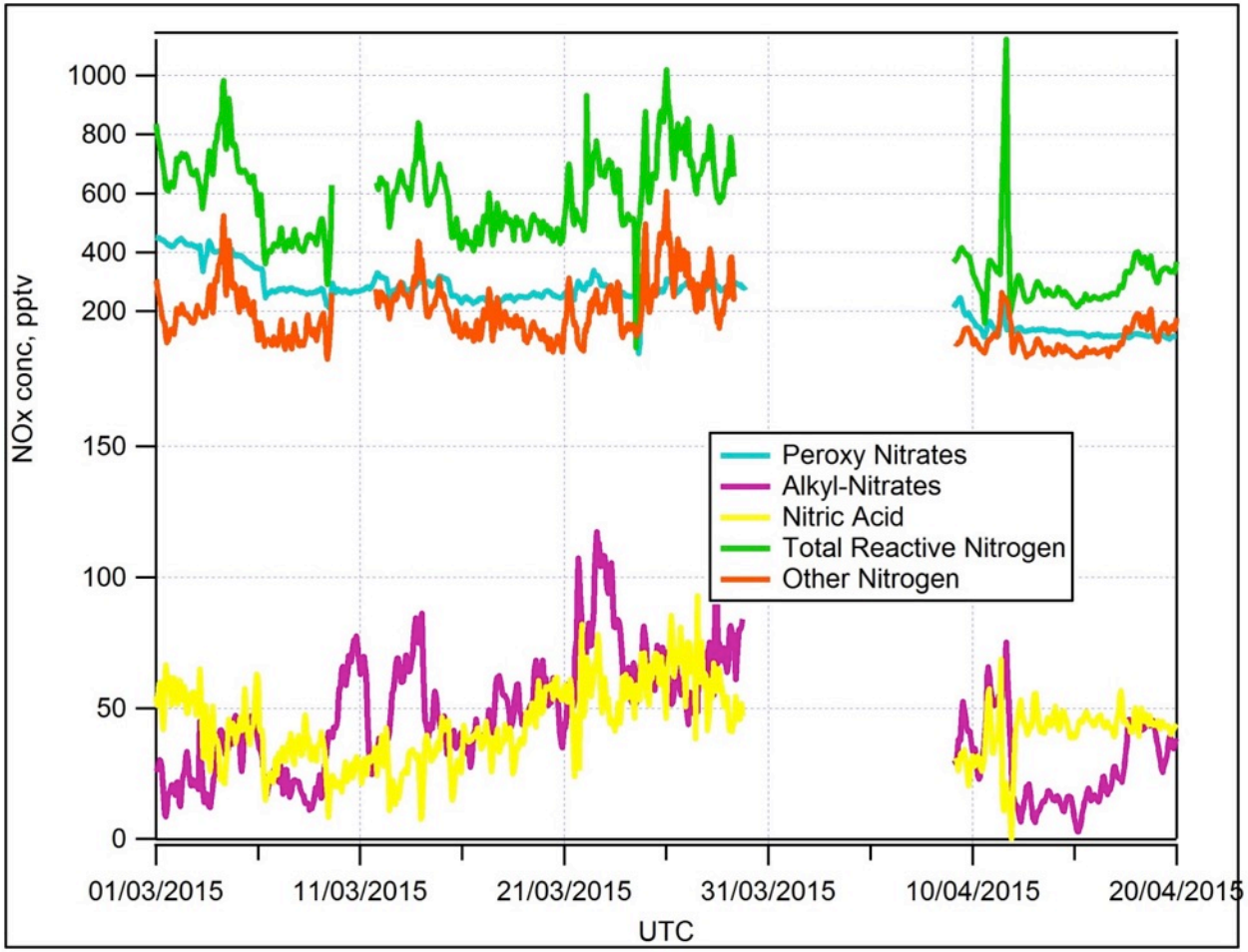






NOy speciation measurements

Time series shows a seasonal decrease from winter to spring in total NOy – especially in ‘PANs’.



‘PANs’ range 150 – 450 ppt. 30 – 50% of NO_y unaccounted for.

Conclusions and Outlook

Conclusions:

- Surprisingly large contribution of 'PANs' or other thermally labile compounds which may also be readily photolysed producing NO_2 during the day.
- Possible interference from thermally labile compounds causing overall offset in NO_2.
- NO_2 diurnal necessitates daytime production of NO_2 in-situ.

Outlook:

- Inclusion of particulate nitrate measurement will better inform what makes up the difference between the nitric acid measurement and total reactive nitrogen.
- NO_2 measurement can still be improved in terms of potential interference.
- Inclusion of NO_y data in model to try and reproduce observed diurnal.

Acknowledgements

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NERC SCIENCE OF THE ENVIRONMENT

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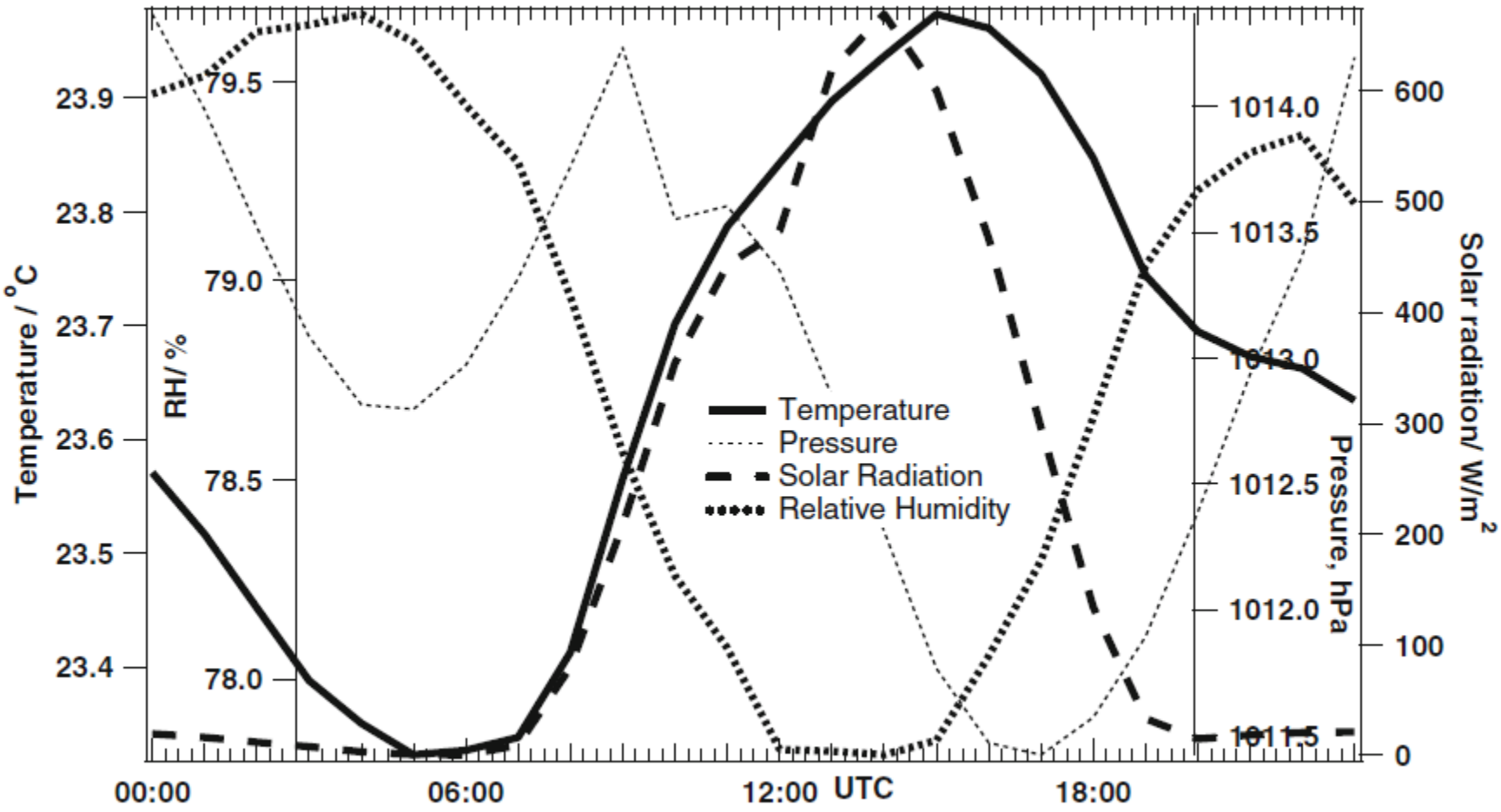
WACL
Wolfson Atmospheric Chemistry Laboratories

AQD
air quality design, inc.
NOxWerx

Extra slides



[1] Atmos Chem (2010) 67:87-140 DOI 10.1007/s10874-011-9206-1

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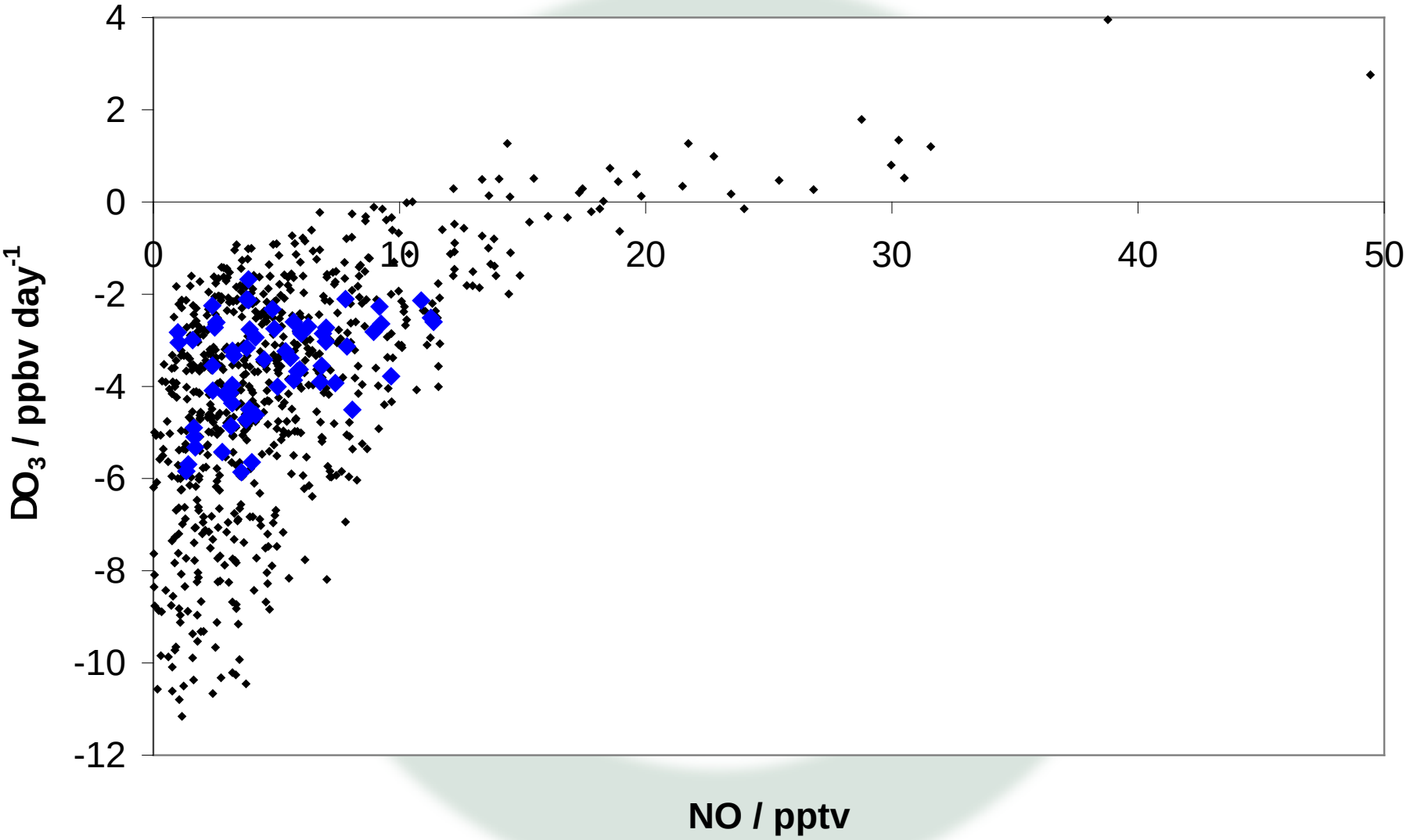

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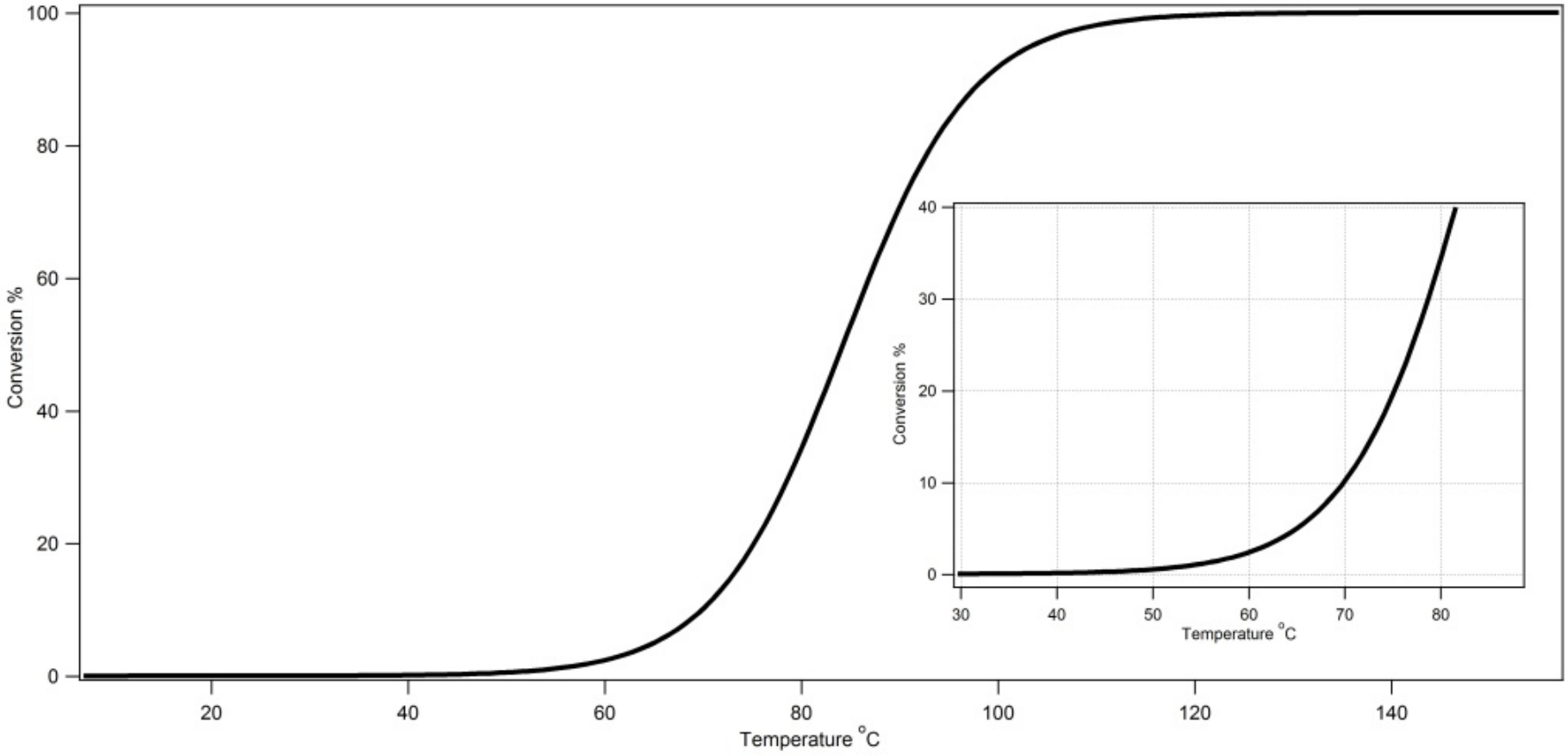

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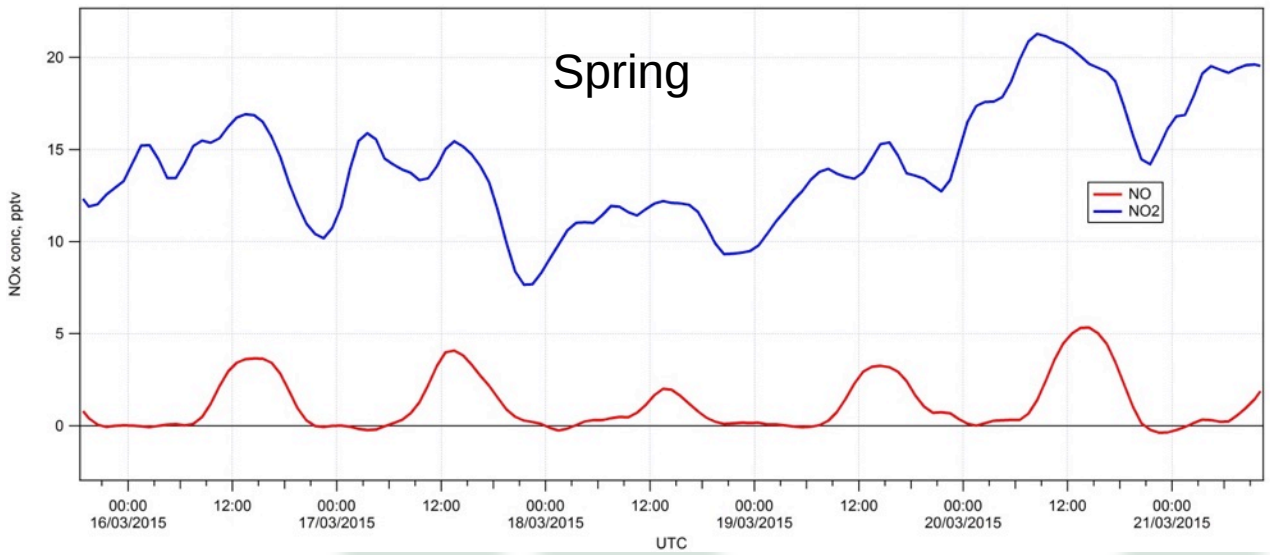

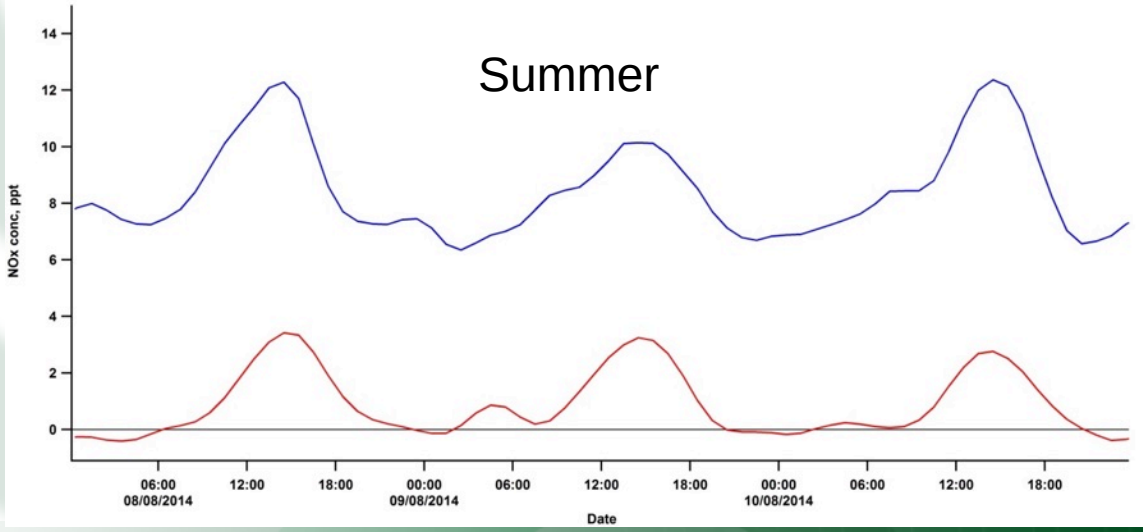

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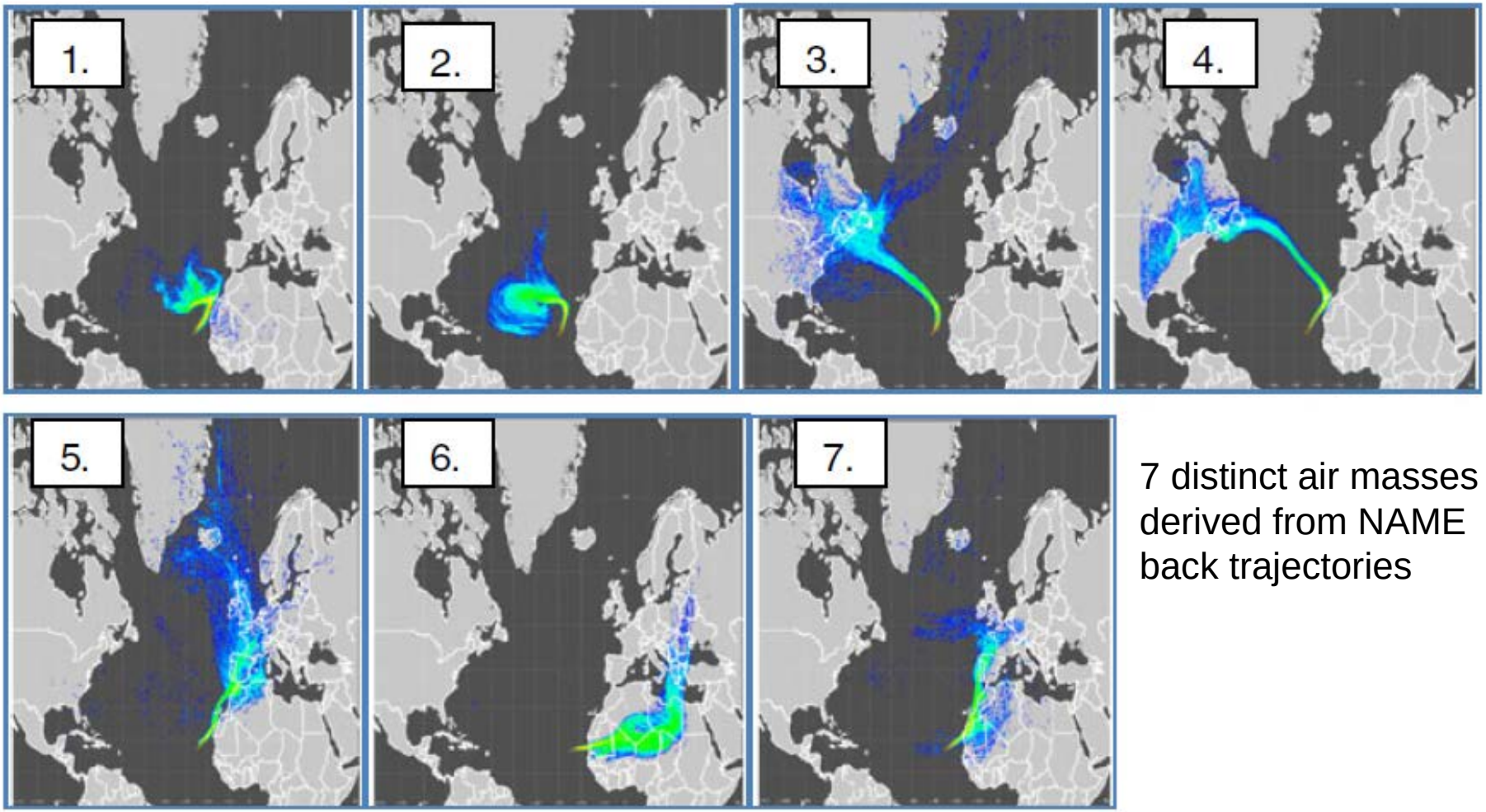
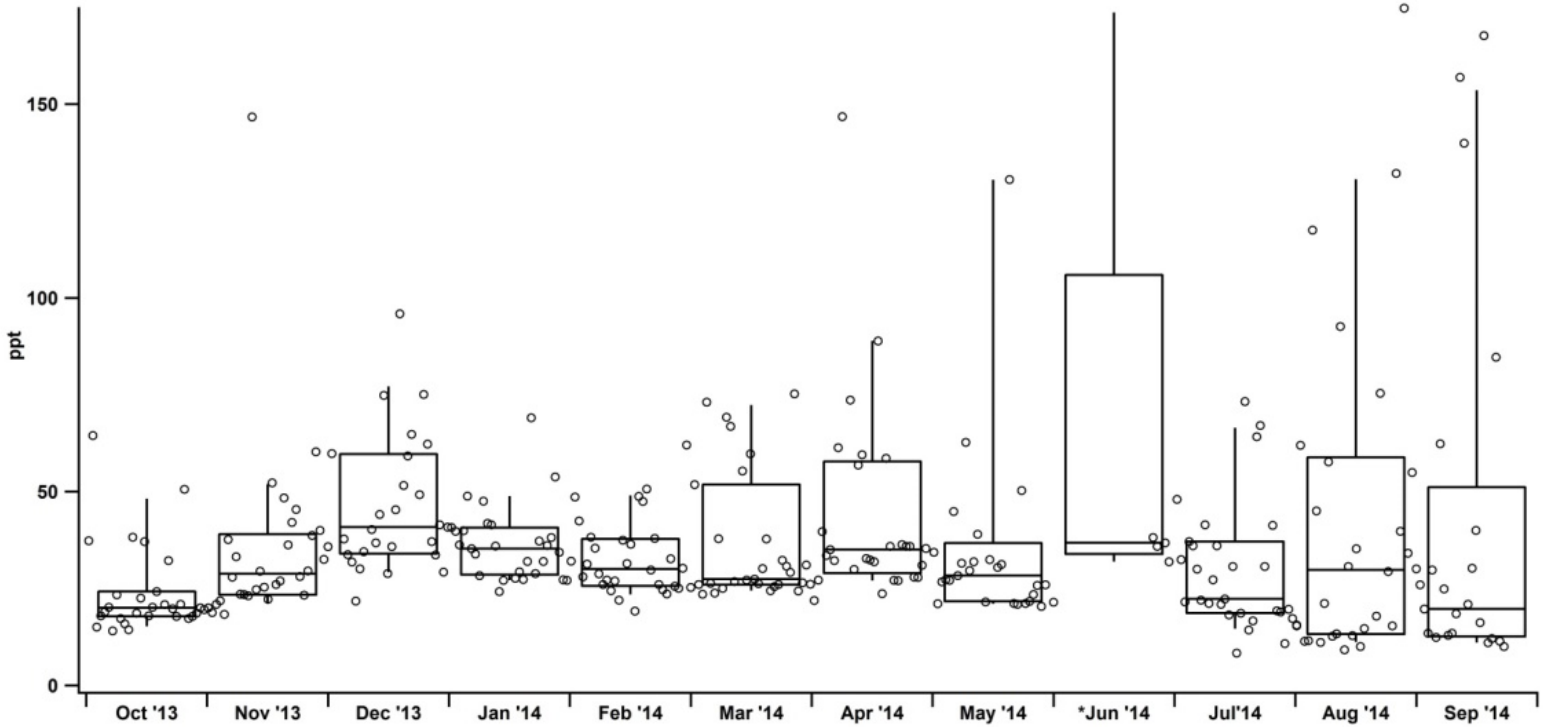
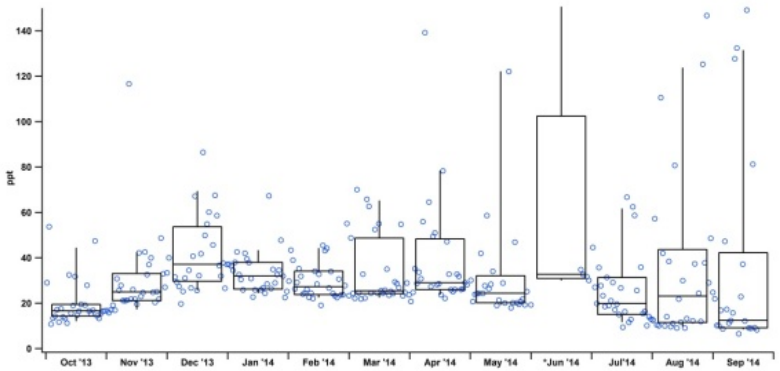
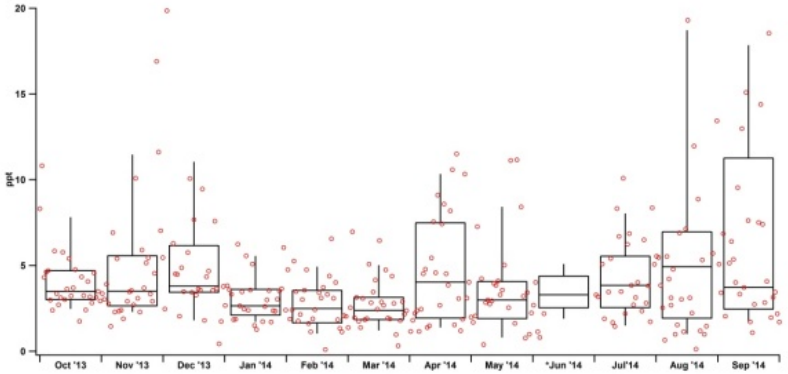


7 distinct air masses derived from NAME back trajectories

Extra slides







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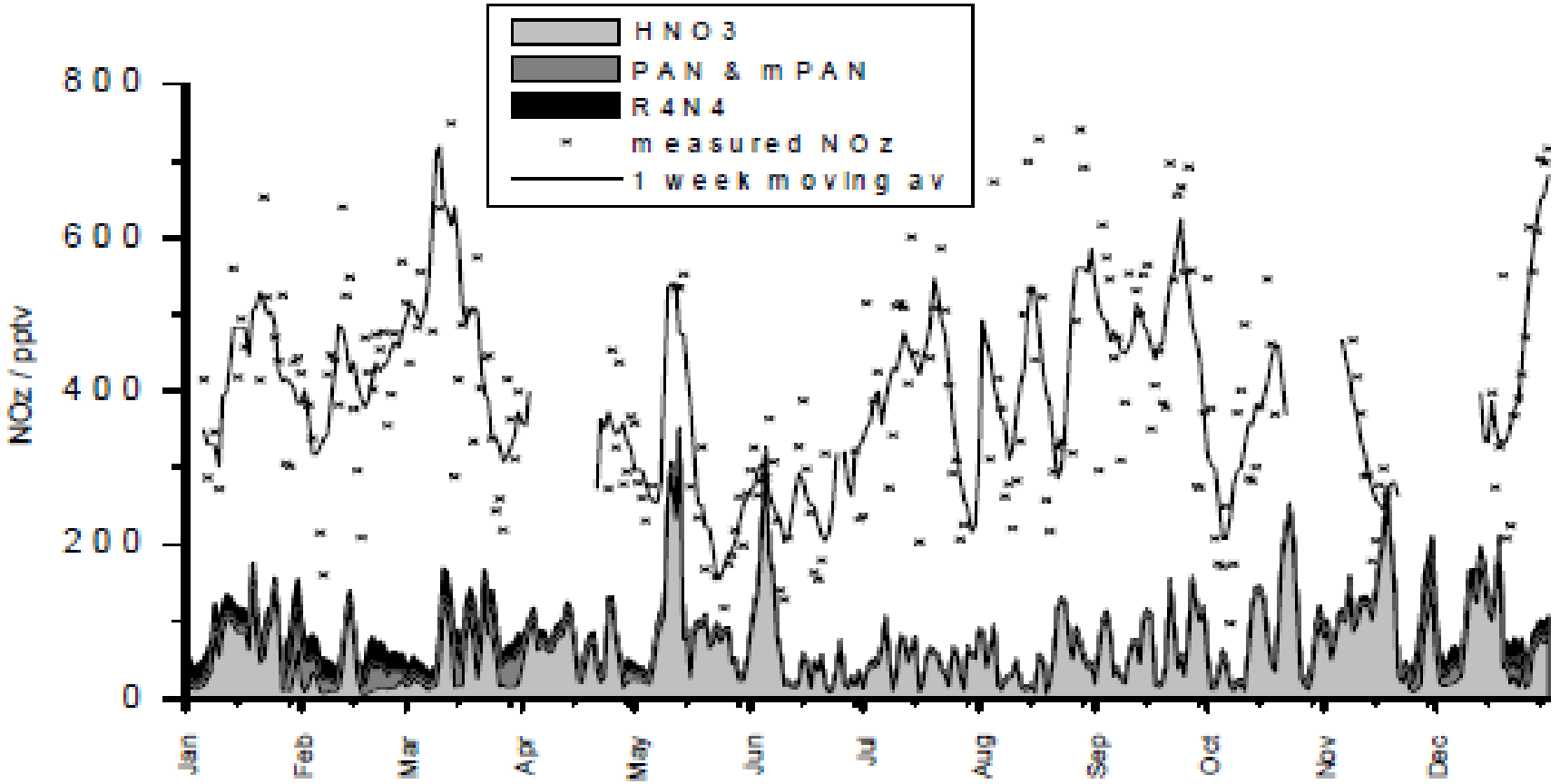

Extra slides

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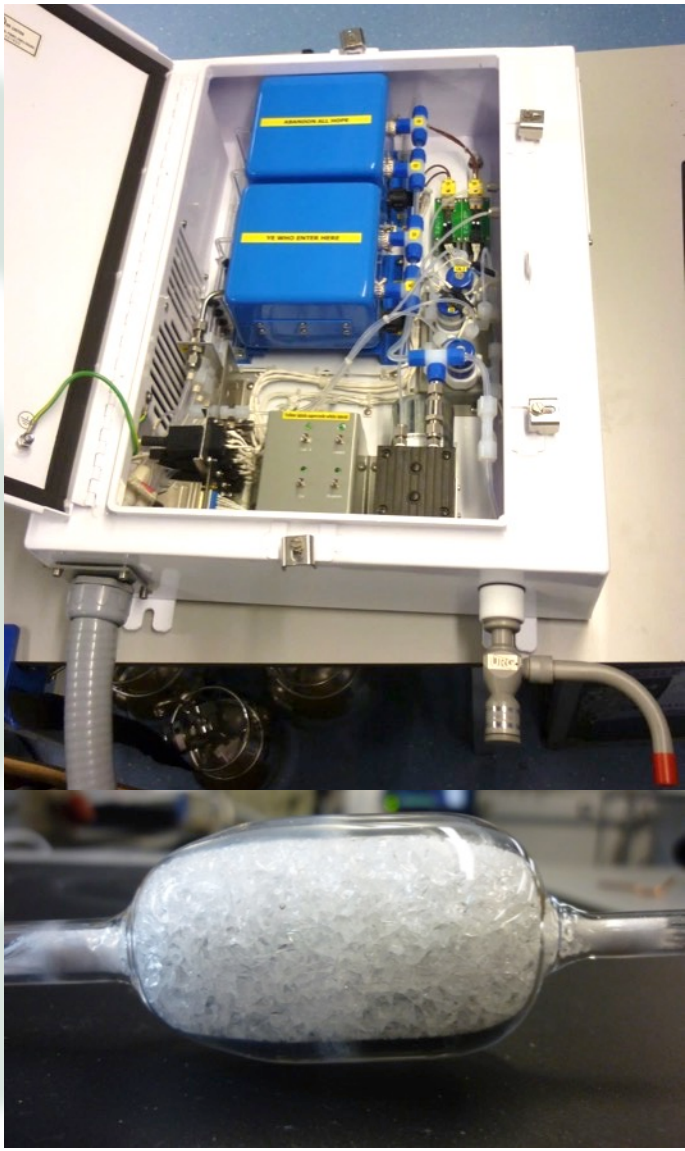
Pros – HNO_3, Tot-Nitrogen, P-Nitrogen, NO

Cons – Slow time resolution

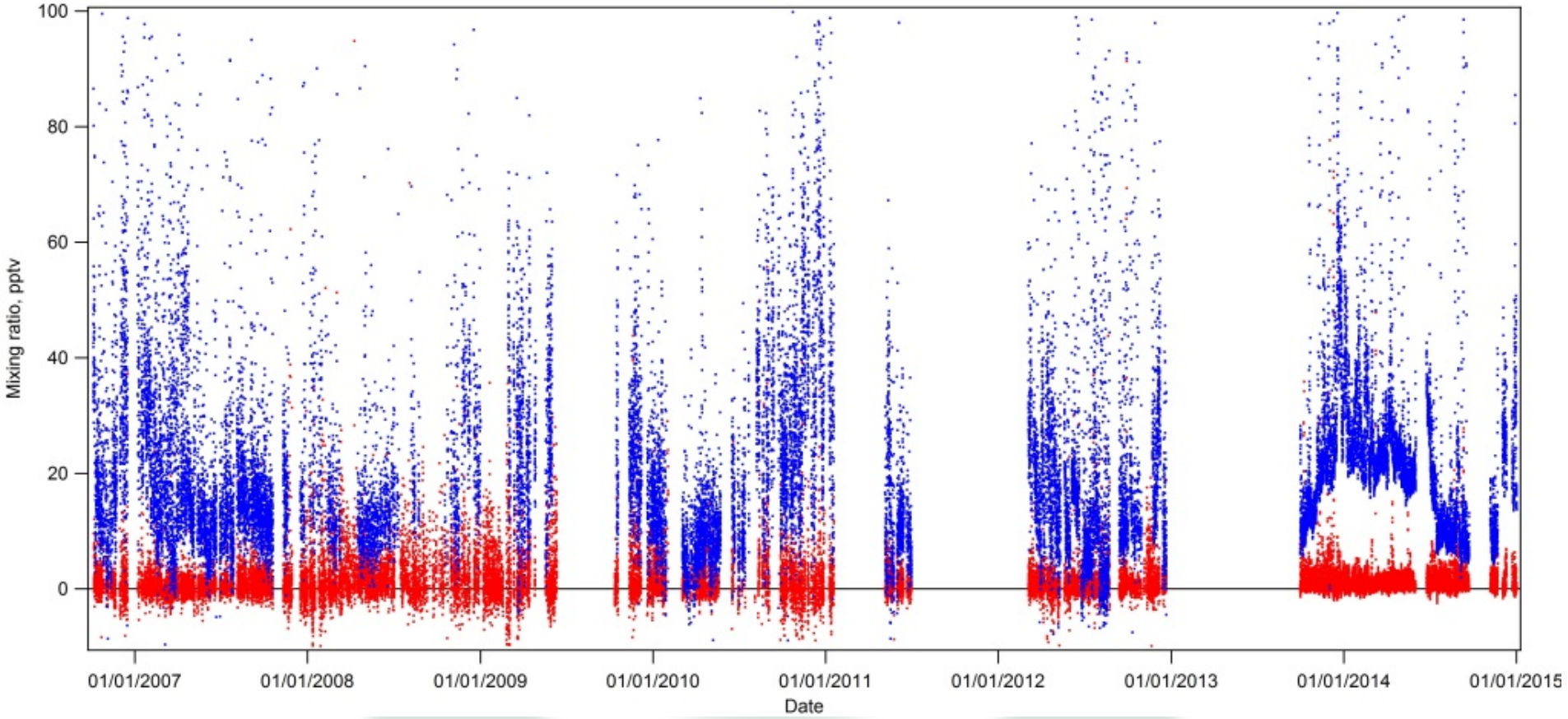
Completely PFA/Teflon inlet and cyclone →



Switching box and ← NO_2 converter.

High surface area completely quartz ovens with cooling region →

Extra slides



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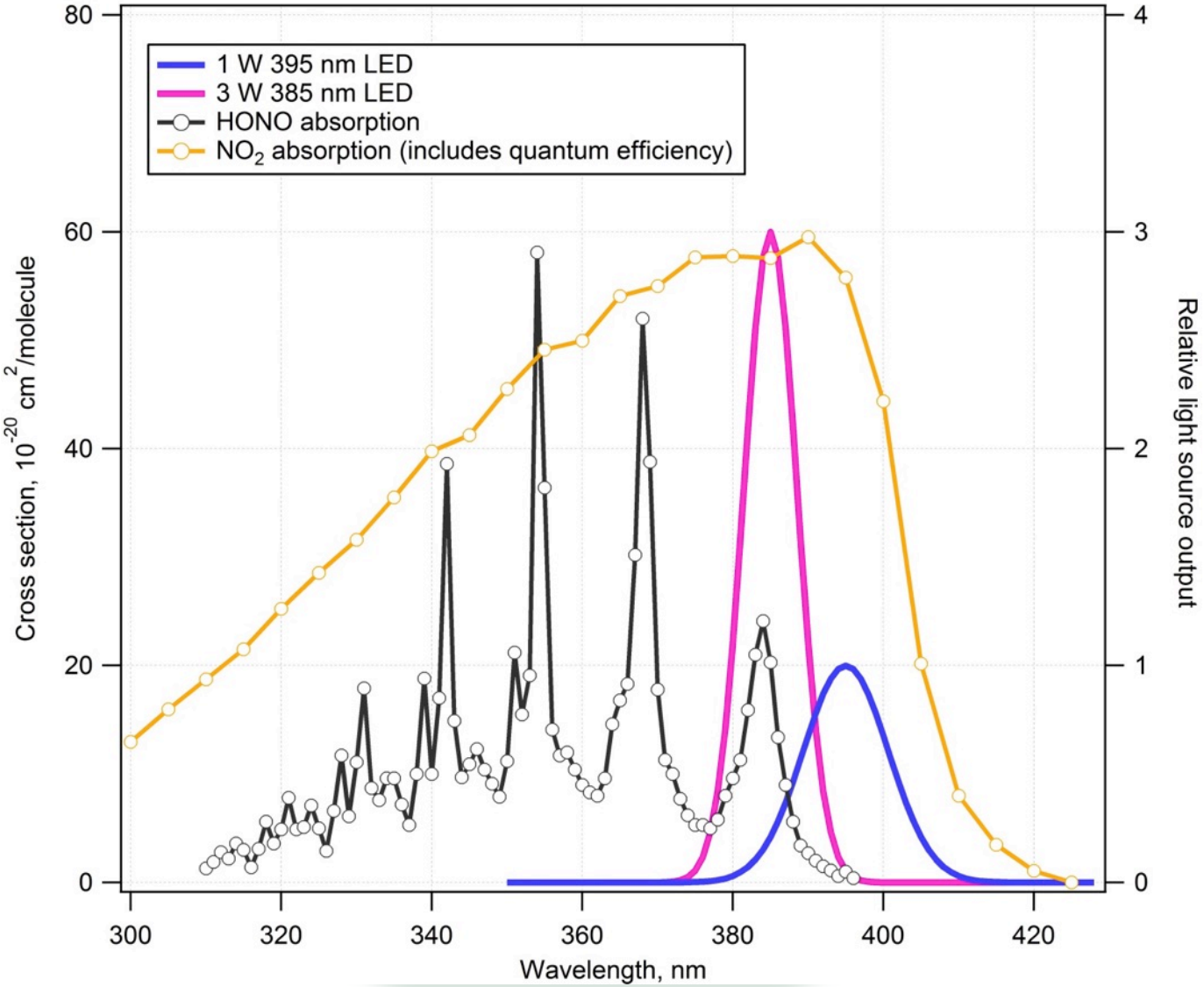

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