Science highlights from the Cape Verde Observatory (CVAO)

Lee, J.D.[a], **Read, K.A.[b]** , Carpenter, L.J.[a], Lewis, A.C.[a], Moller, S.J.[a], Mendes, L.M.[c], Fleming Z.[d], Evans, M. J.[e]

[a] National Centre for Atmospheric Science (NCAS), University of York, UK

[b]Facility for Ground based Atmospheric Measurements (FGAM), NCAS, University of York, UK

[c]Instituto de Naçional de Meteorologia e Geofísica (INMG), Mindelo, Cape Verde

[d] NCAS, University of Leicester, UK

[e] University of Leeds, UK

Cape Verde Observatory

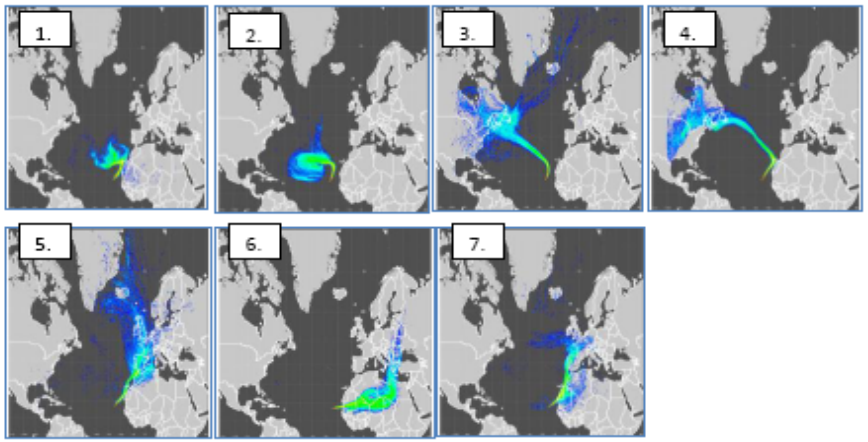
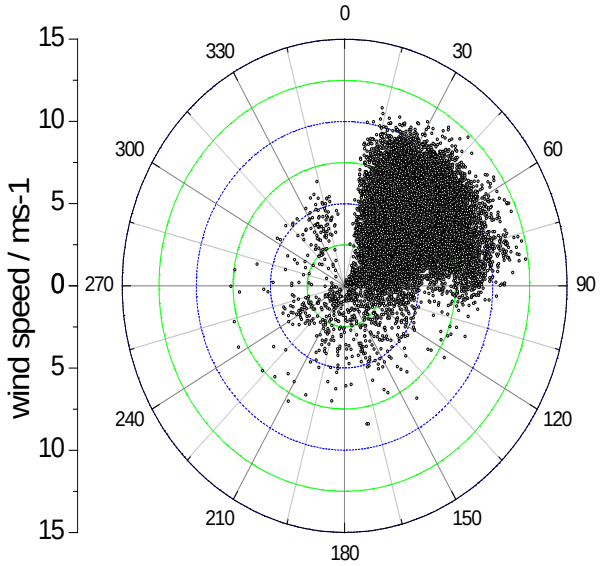


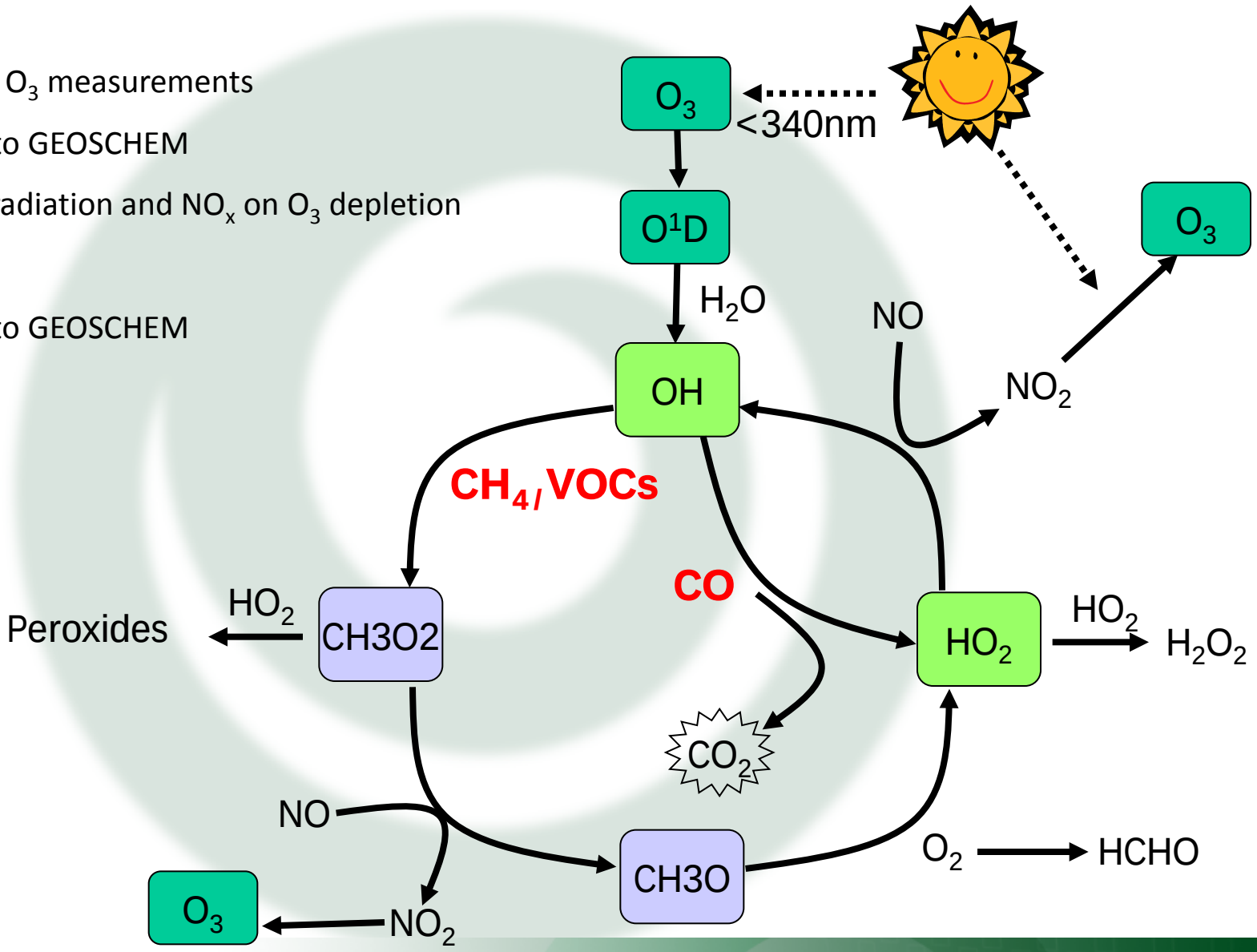
Figure 5. Typical 10-day back trajectory types used to classify air masses arriving at Cape Verde. 1) Atlantic and African coastal - AAC, 2) Atlantic marine - AM, 3) North American and Atlantic only - NAA, 4) North American and coastal African - NCA, 5) European (with minimal African influence) - EUR, 6) African (with minimal European influence) - AFR, 7) European and African – EUR/AFR.



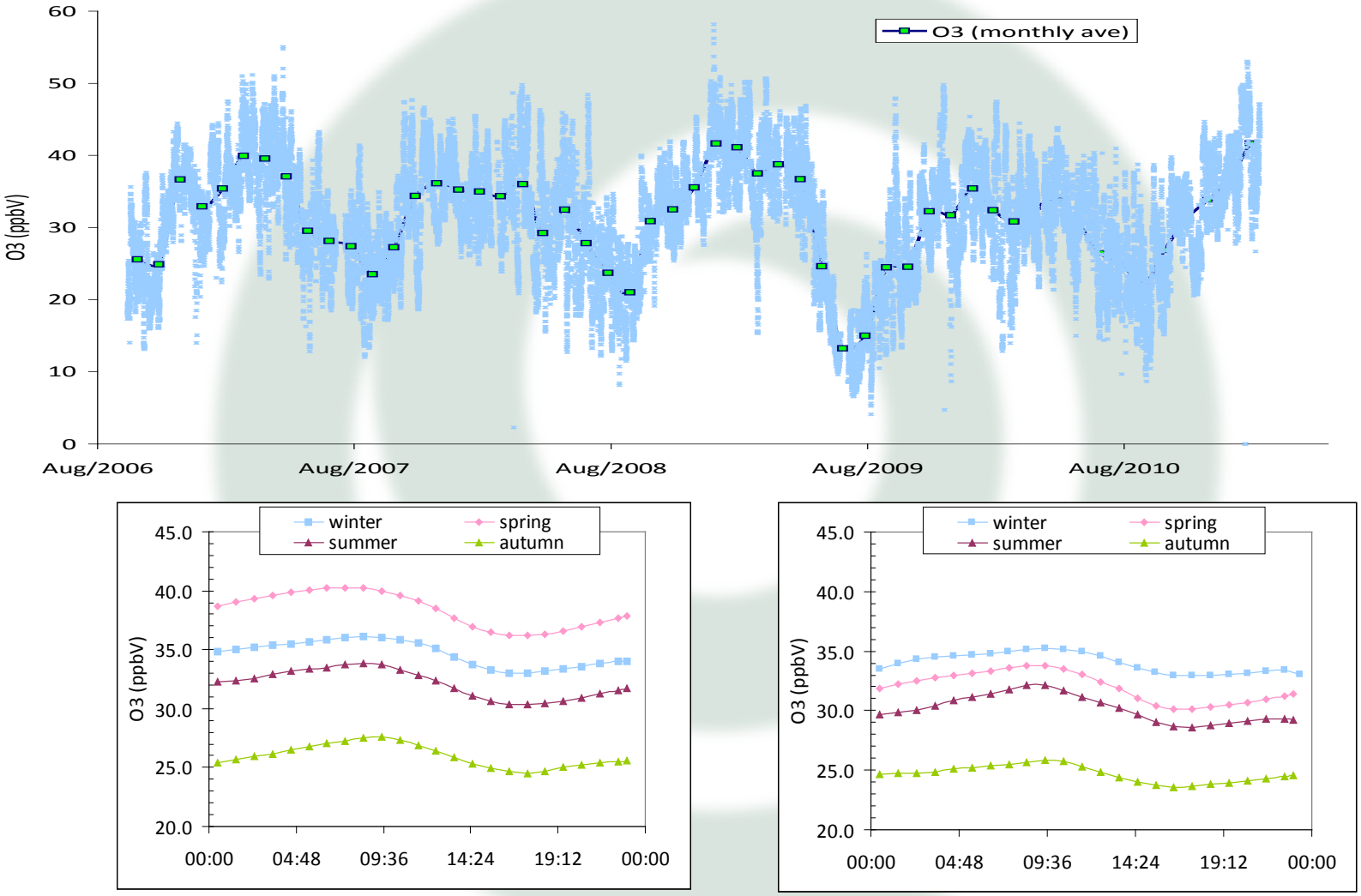
Using Met office NAME model, Carpenter et al., 2011

Overview of Talk

- Discussion of O_3 measurements
- Comparison to GEOSCHEM
- Influence of radiation and NO_x on O_3 depletion
- CO record
- Comparison to GEOSCHEM



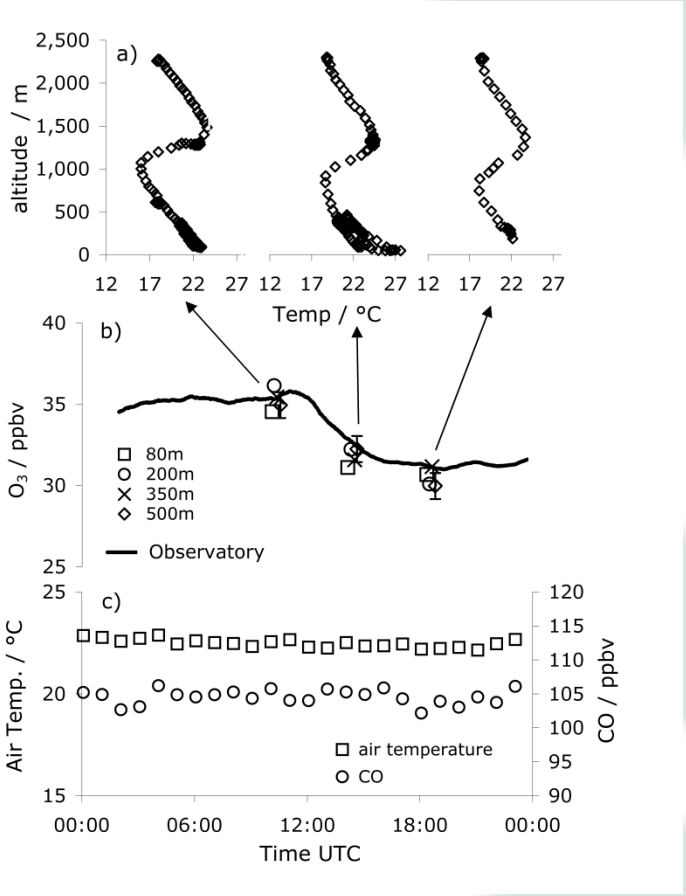
Tropospheric ozone record

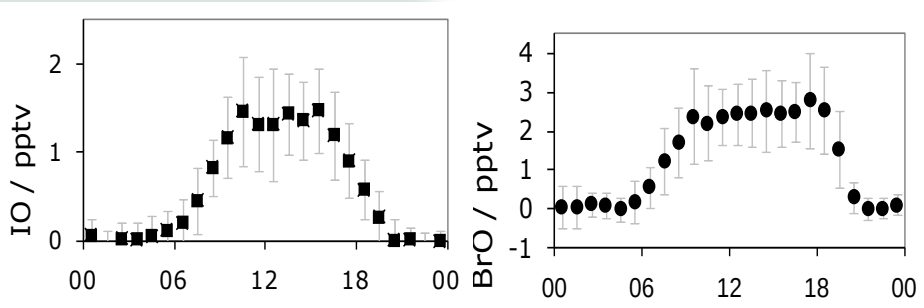


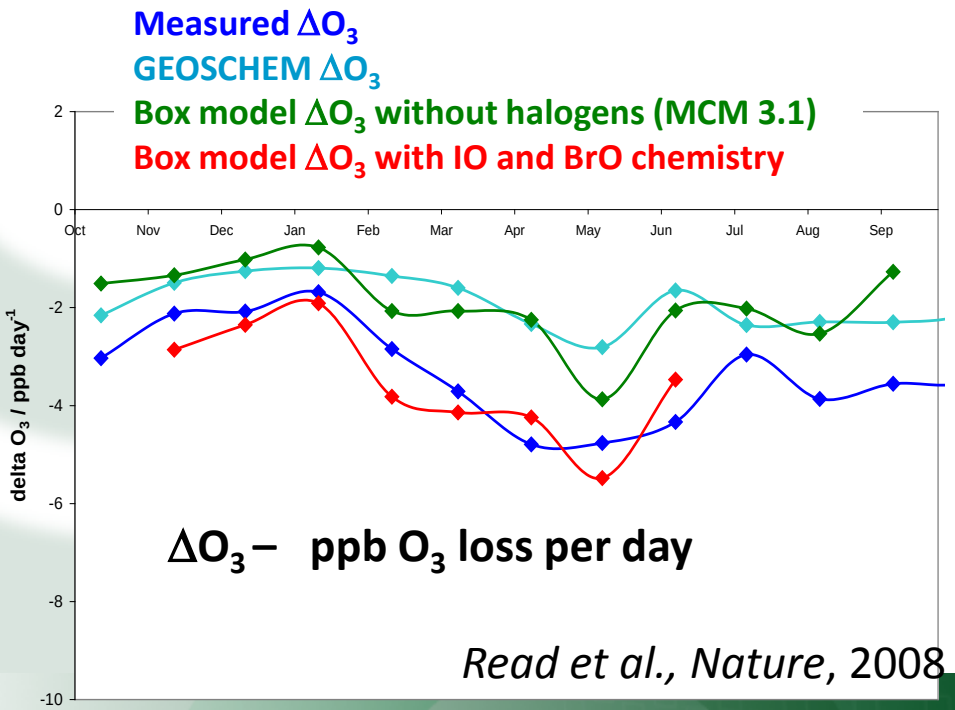
Diurnal cycle of O_3 by season for 2007 (left) and 2010 (right).

Ozone diurnals and halogen influence

In 2008 we published a paper where we modelled the depletion and found that we had to invoke halogen chemistry to reproduce the measurements.







Read et al., Nature, 2008

Tropospheric O_3 budget

• Photolysis plays a significant role although balanced to some extent by the entrainment term.

• Competition between photochemical loss and production of O_3 through: -

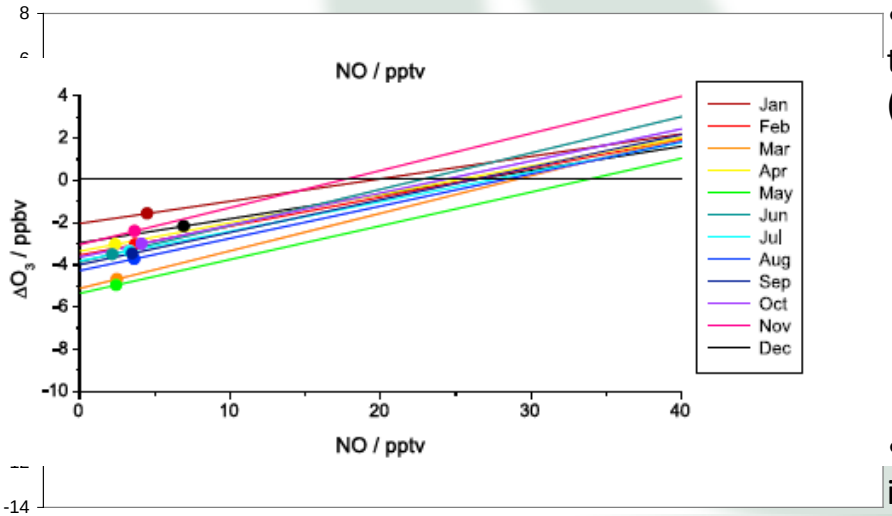
$NO_2 + hv\ (+O_2) \rightarrow NO + O_3$

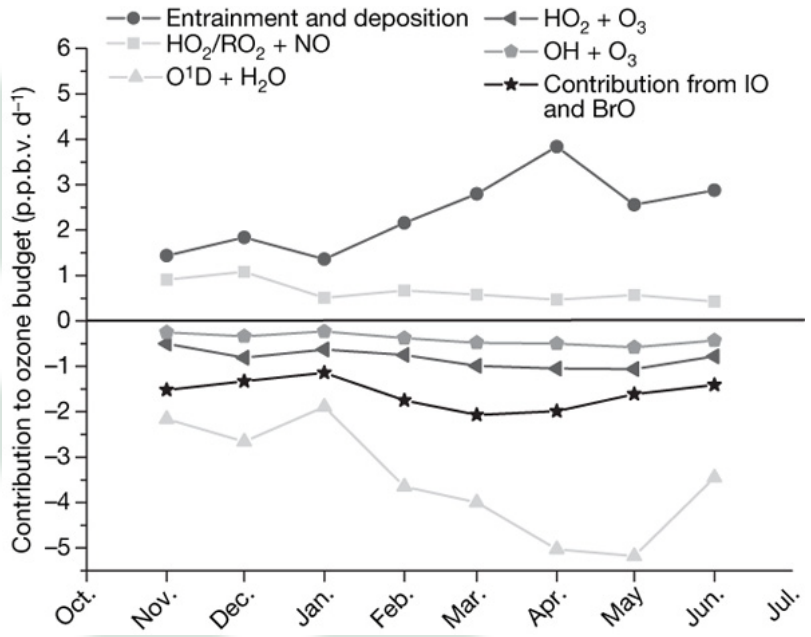
$NO + HO_2 \rightarrow OH + NO_2$

$OH + RO\ (+O_2) \rightarrow HO_2 + RO_2$

….leads to a nonlinear dependency of O_3 on NO_x.

• Lee et al. looked at this relationship and found that in this region there is a level of NO_x at which there is a switch from net destruction to production of O_3, the "O_3 compensation point" (Lee et al., J. Geophys. Res., 2009).





• In the MBL bromine and iodine atoms have been shown to be important in the role of O_3 destruction in this region (Read et al., Nature, 2008).

$X + O_3 \rightarrow XO + O_2$

$XO + XO \rightarrow 2X + O2$

$XO + IO \rightarrow X + OIO$

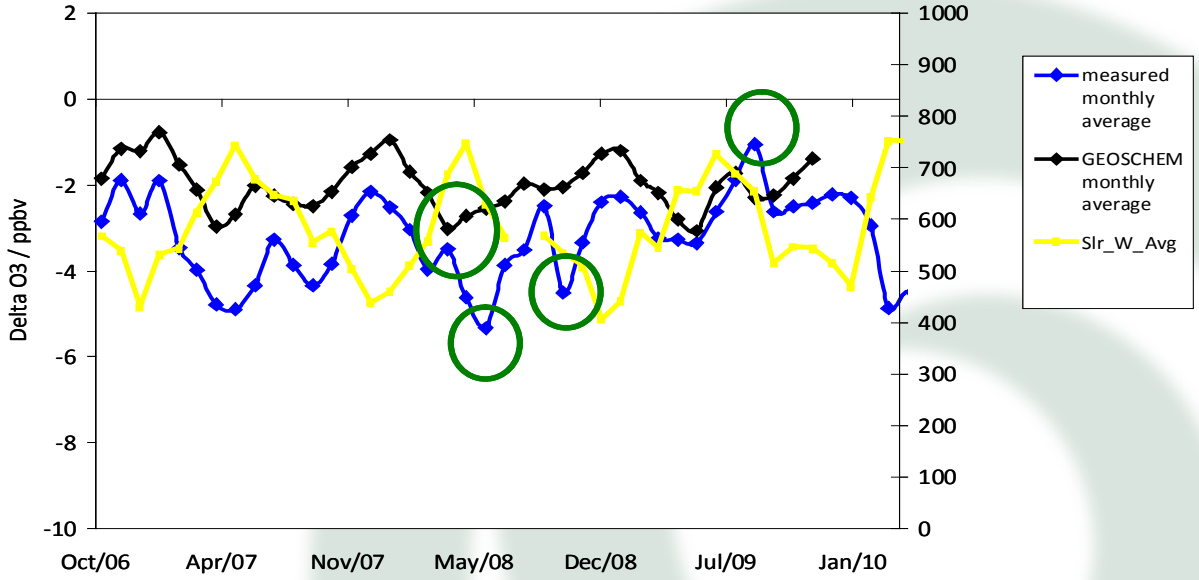
$XO + HO_2 \rightarrow HOX + O_2$

$HOX + hu \rightarrow OH + X$

$XO + NO \rightarrow NO_2 + X$

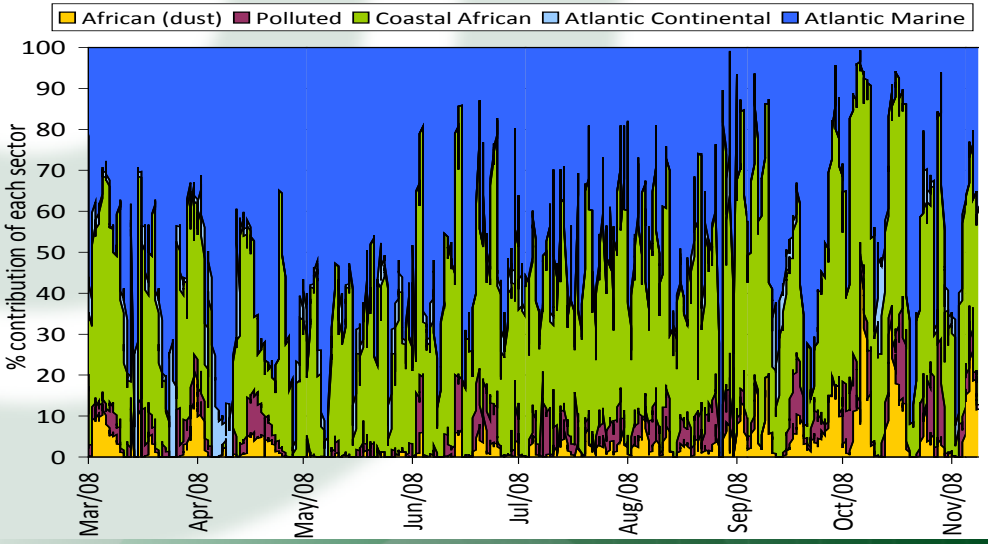
• XO causes a decrease in the NO/NO_2 ratio but O_3 is not increased because the X formed will likely destroy O_3.

Delta O_3 , the role of photolysis and air mass history

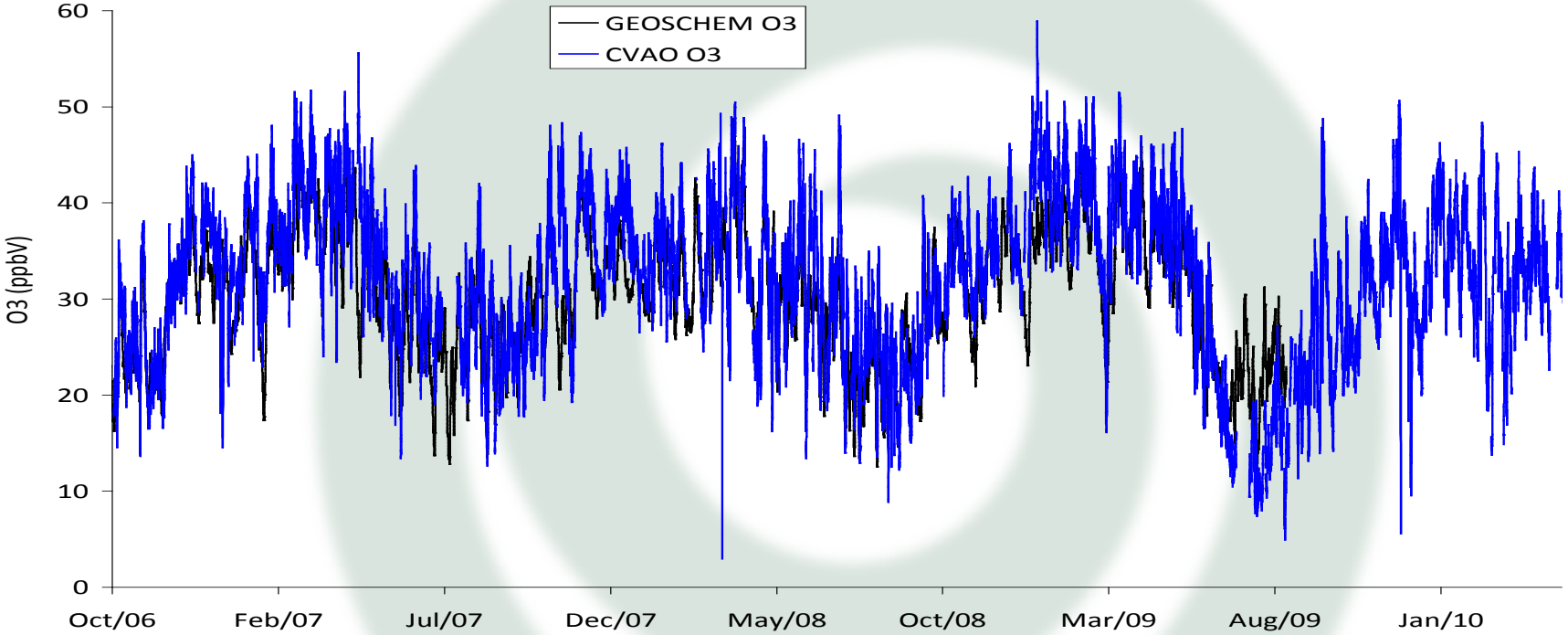


- The modelled and measured follow the same trend most of the time in-line with the dominance of the O_3 photolysis term.

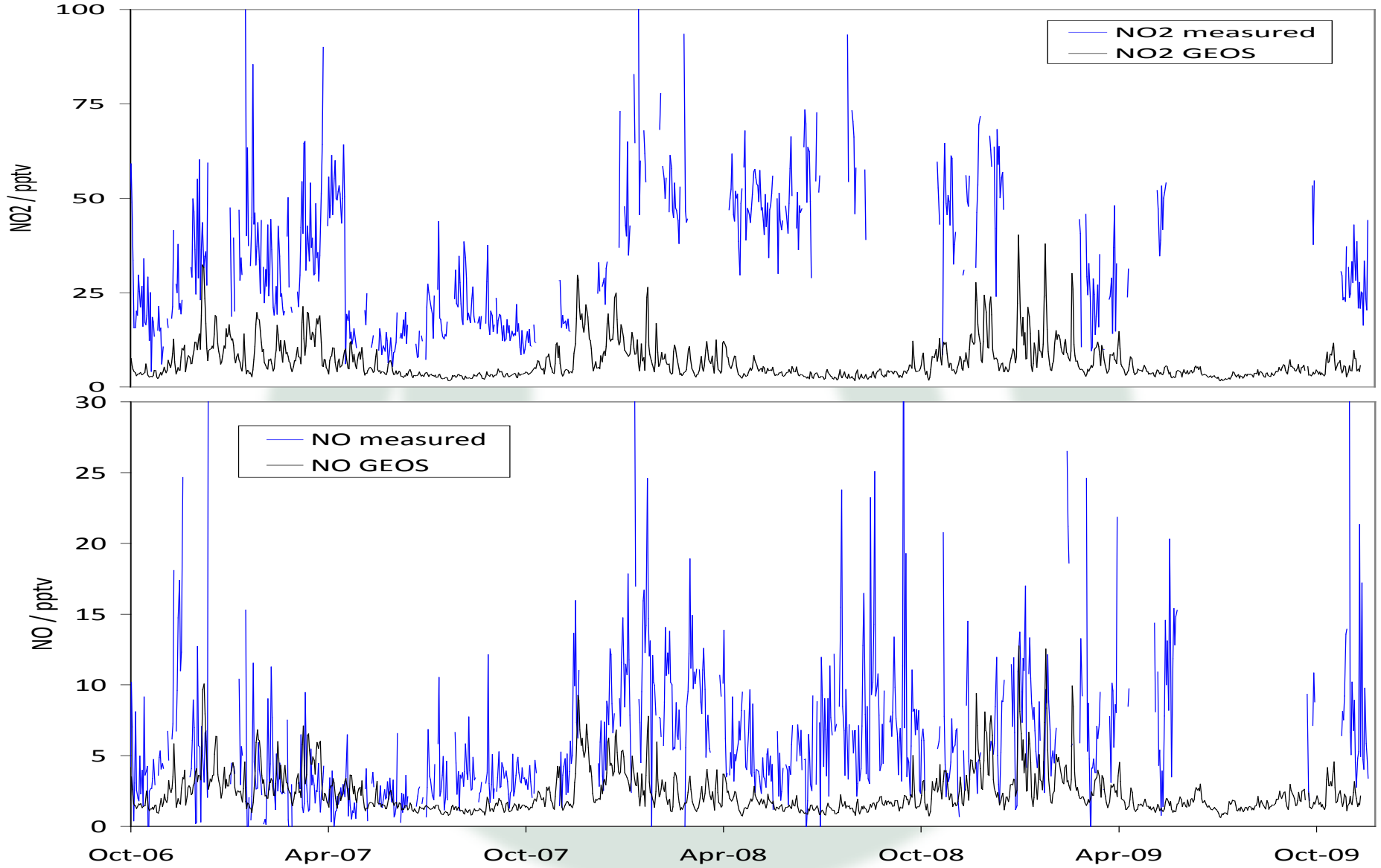
- Better agreement when sampling Atlantic conditions than coastal African conditions.



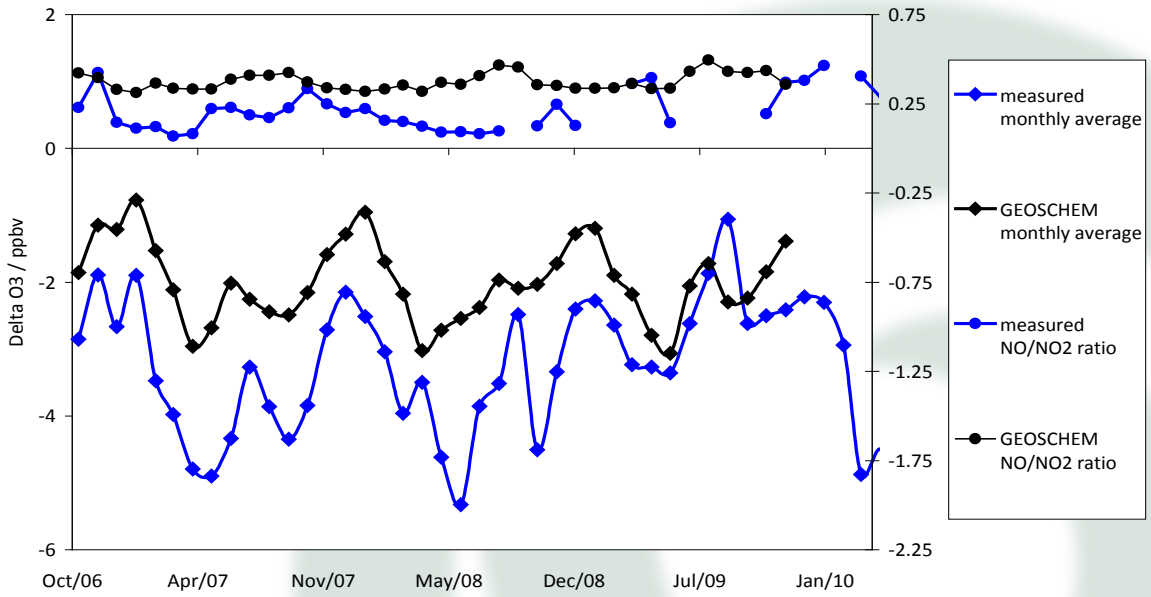
GEOS CHEM comparisons O_3



NOx

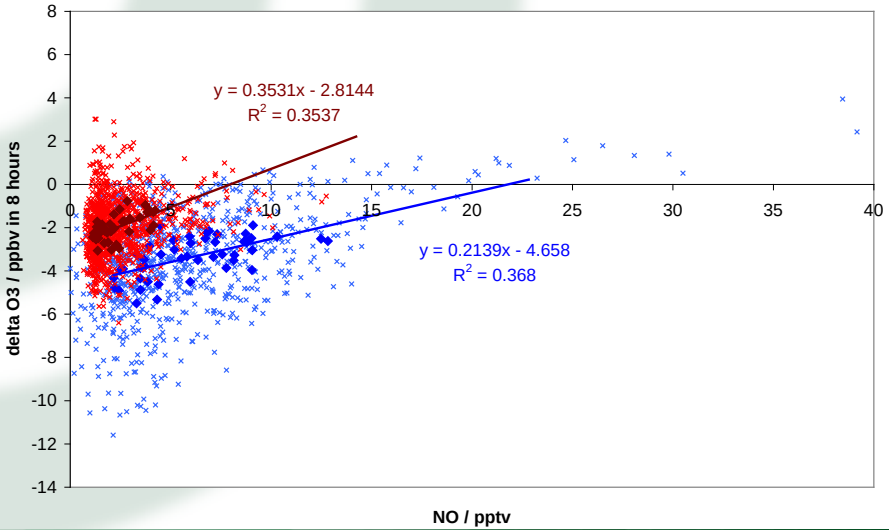

NO2 measured
NO2 GEOS
NO2 / pptv
100
75
50
25
0
NO measured
NO GEOS
NO / pptv
30
25
20
15
10
5
0
Oct-06
Apr-07
Oct-07
Apr-08
Oct-08
Apr-09
Oct-09

Delta O_3 and NO/NO_2 ratio

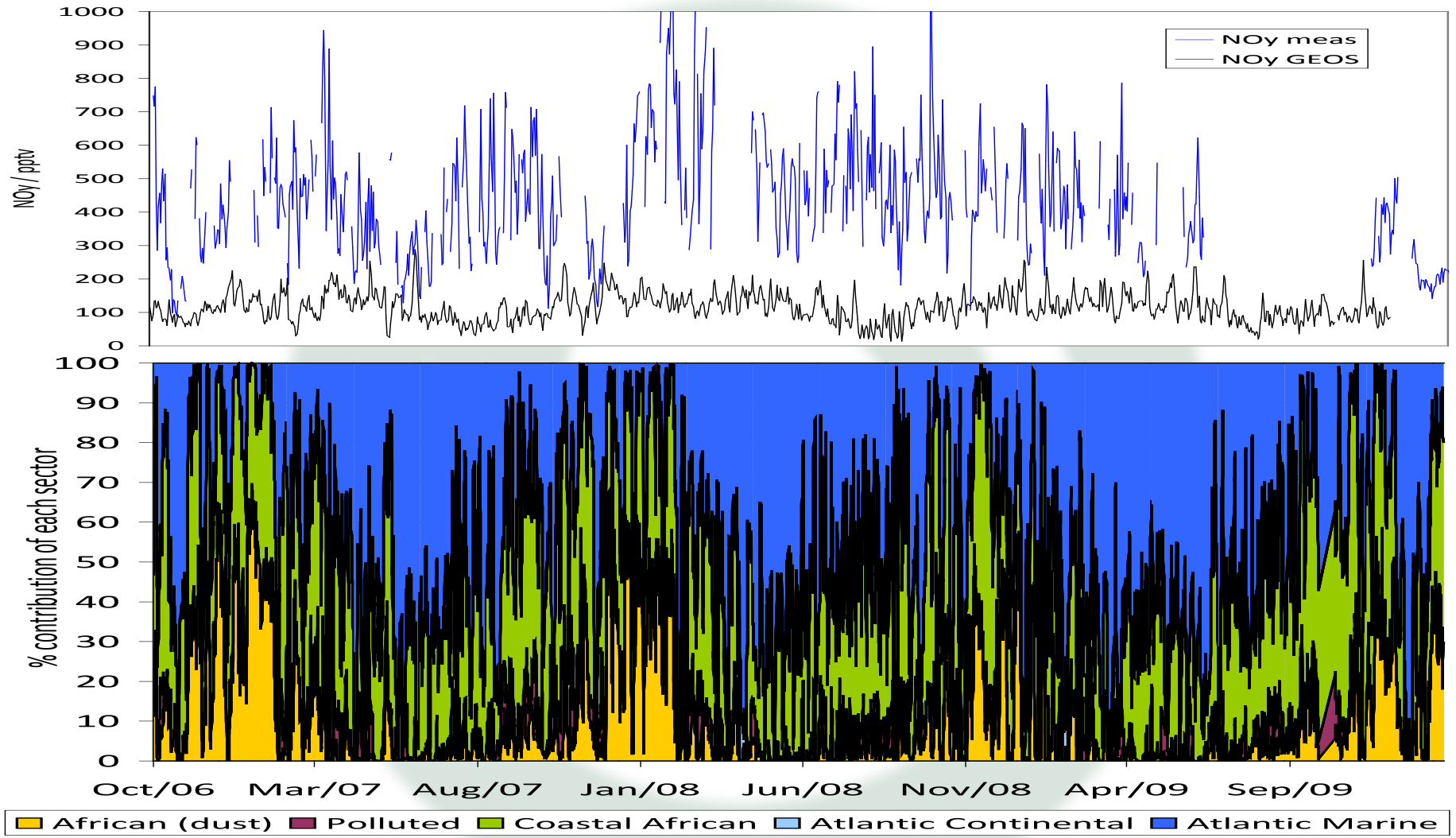


- The modelled NO/NO_2 ratio is generally too high although agrees better in 2009.
- However NO_2 (and often NO- see plot below) are also much higher in the measurements compared to the model (sometimes by 5x).
- NO correlates with delta O_3 in the measurements and model

- Not enough XO to explain the difference in modelled to measured NO / NO_2 ratio
- Other processes going on

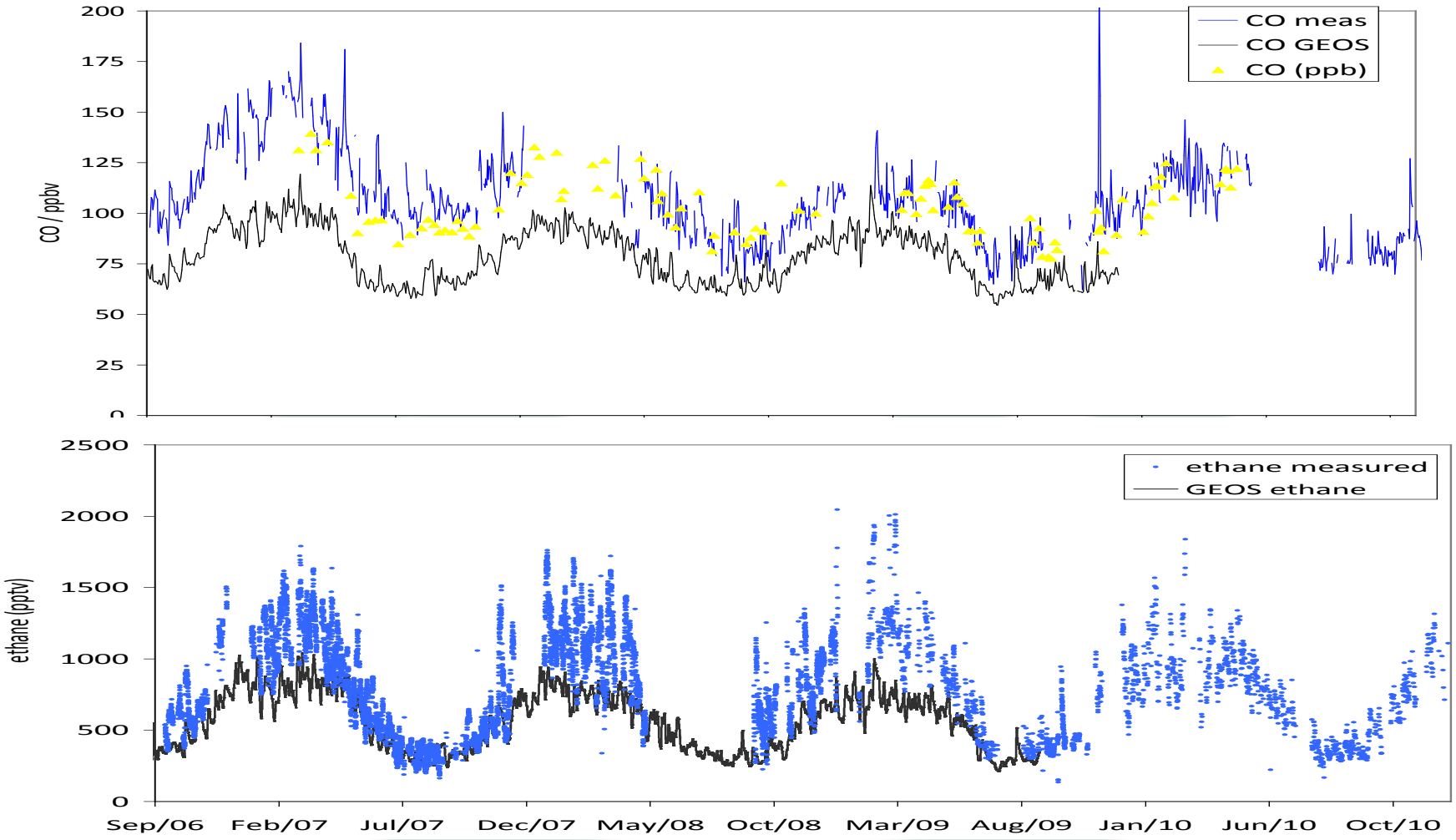


GEOS / meas comparisons NOy



NOy = Sum NOx, NO_3, HNO_3, N_2O_5, PANs, HONO, alkyl nitrates and particulate nitrate.

CO and ethane comparison to GEOS CHEM

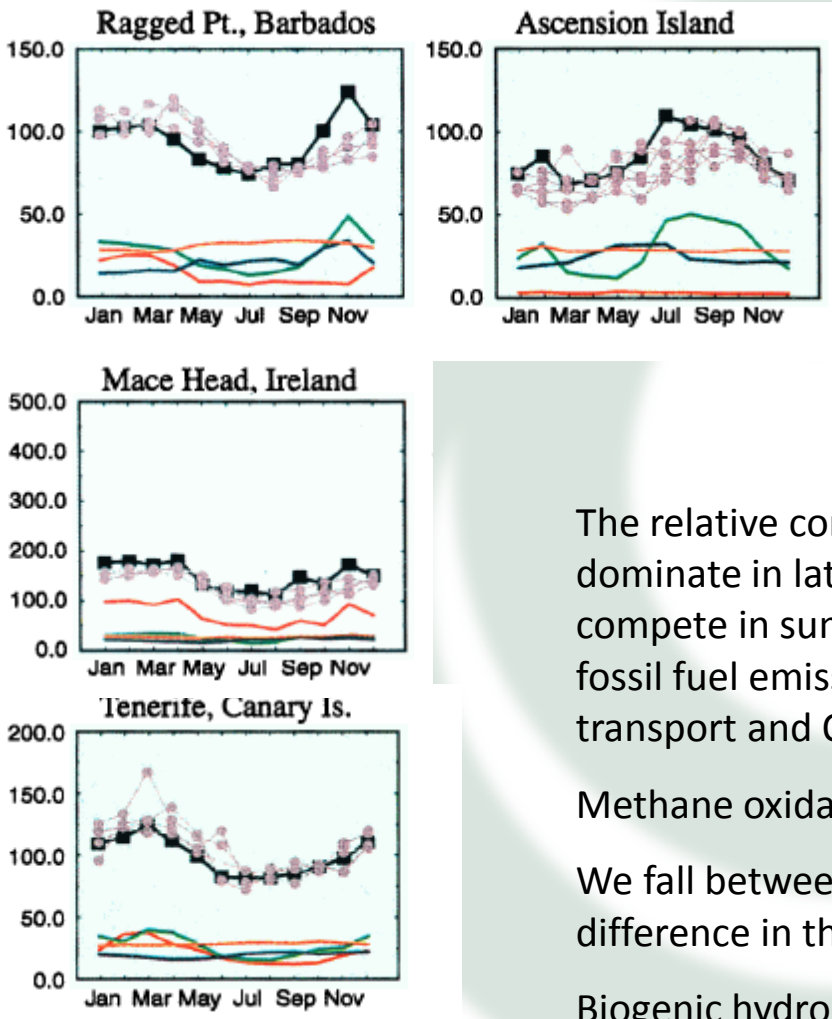


Is the amplitude of the CO correct for the wrong reasons?

Can the emissions be underestimated all year?

If we increase the Spring emissions to similar to those needed for ethane then the amplitude is too large, need additional sources in summer.

Other sites CO with GFDL GCTM model



Holloway et al., 2000

Purple measured

Black-modelled

Red-Fossil fuel

Blue- Biogenic hydrocarbon

Green-Biomass

Orange - Methane oxidation

The relative contributions show that fossil fuel emissions dominate in late winter/early spring but other sources compete in summer. No seasonal distribution assumed in fossil fuel emissions so changes arise from changes in transport and OH conc.

Methane oxidation is similar all year.

We fall between Tenerife and Ascension, you can see the difference in the contributions between the two sites……

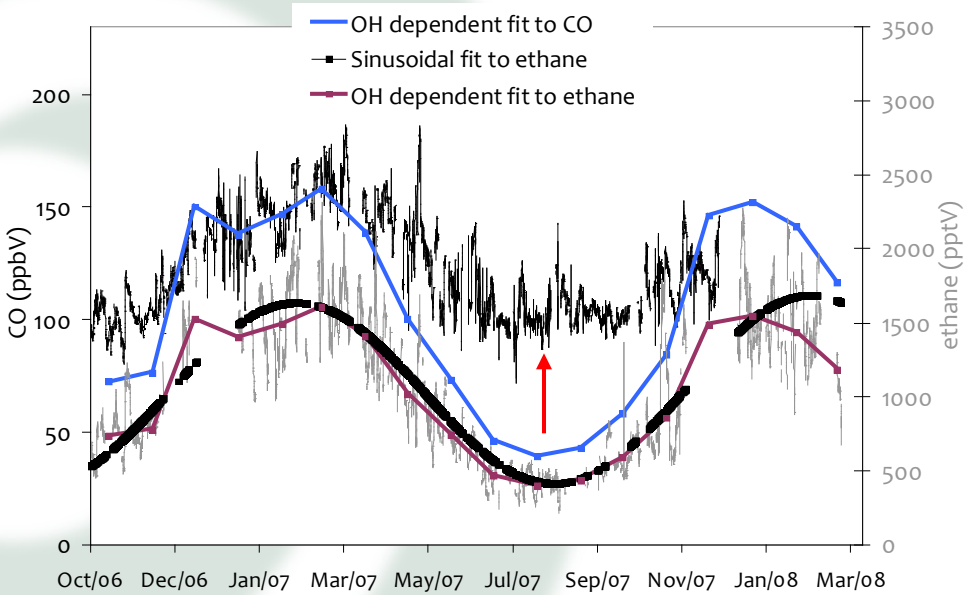
Biogenic hydrocarbon influence in summer….

Using ethane to interpret CO

- CO and ethane share some common sources e.g. fossil fuel emissions, and biomass burning. The ratio of CO : ethane emissions from these sources is not thought to vary seasonally.

- "n[OH]" can be calculated from ethane and applied to calculate a theoretical CO assuming no other sources exist and all loss routes are also shared.

- If the modelled CO amplitude is correct then is there a year-round underestimate of emissions?

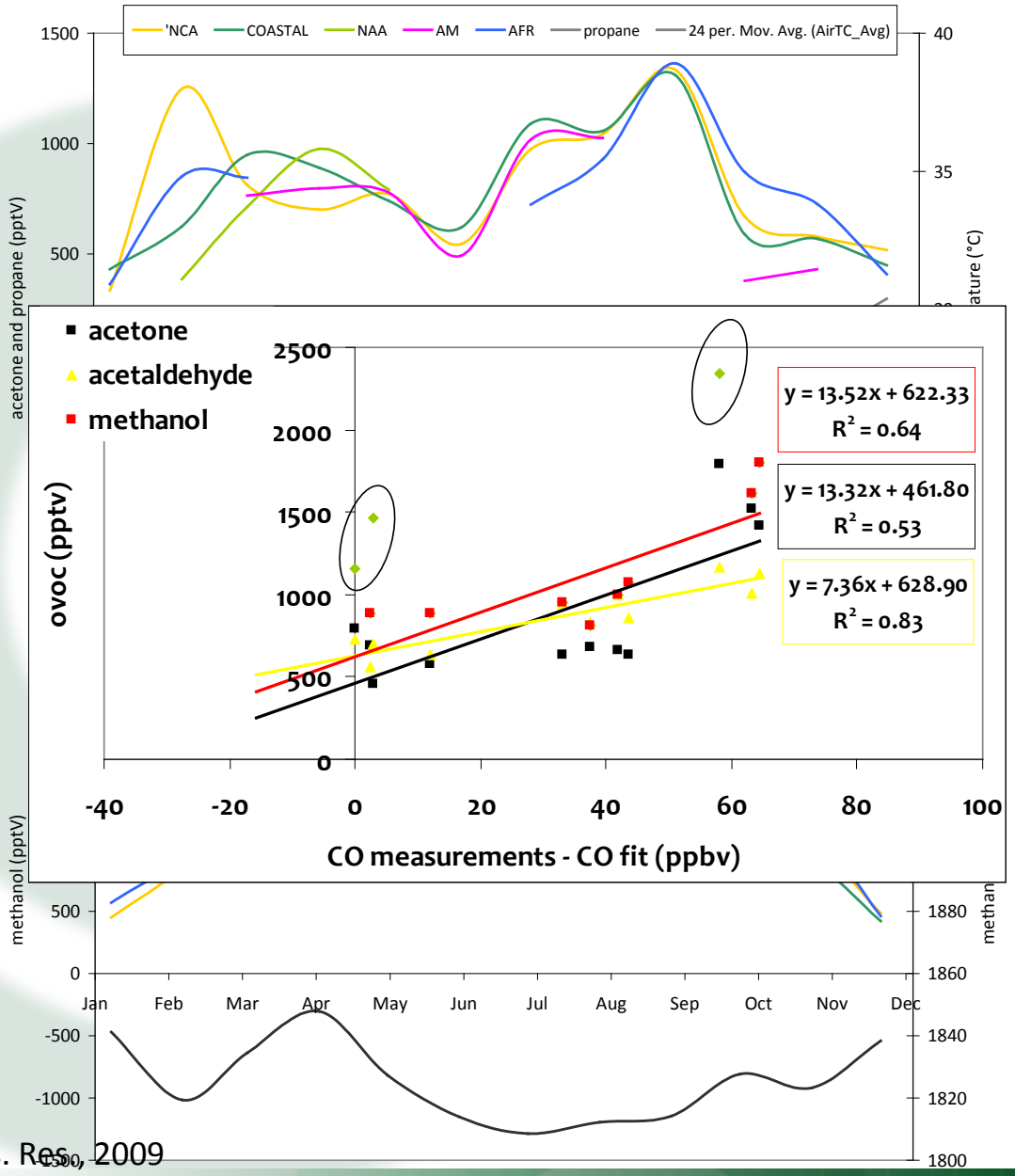


Read et al., J. Geophys. Res., 2009

Seasonal distribution

- Methanol shows variability with air mass trajectory.
- Higher levels during Spring (Mar-Apr) in-line with the precursor NMHC and their shared sources (later for methanol than acetone). OH is also lowest at this time.
- June-radiation decreases.
- (Elevated levels are also observed in Aug-September correlating with maximum in air temperature (increased biogenic sources, photochemical influence on secondary chemistry).
- Source of CO from NMVOC is a cause of high uncertainty (>factor of 3) in models (Holloway et al., 2000)

Potentially up to 60% of the observed summer CO is from summertime increases in the seasonal trend of NMVOC (and methane) oxidation.



Read et al., J. Geophys. Res., 2009

Summary

- The O_3 depletion measurements have inspired much interest in the Observatory.
- Poorer model/measured delta O_3 agreement when NO and ratio of NO/NO_2 is low. Is the difference in measured O_3 depletion between 2007 and 2008 (with changing NO) simply due to measurement variability of budget terms? What is the impact of halogens?
- Better agreement with the global model when the NO is higher, and the ratio of NO/NO_2 is higher but the concentrations of NO and NO_2 are underestimated.
- The distribution of NO_x is well simulated in Atlantic marine conditions but not when considering data from the continents. More NO_x source information is needed to be addressed through NO_y measurements.
- CO shows fairly poor agreement to the global model.
- Additional emissions in spring would lead to overestimation of concentrations in summer.
- oVOC (acetone and methanol) peak in summer and through secondary production could explain CO concentrations at this time.

Acknowledgements

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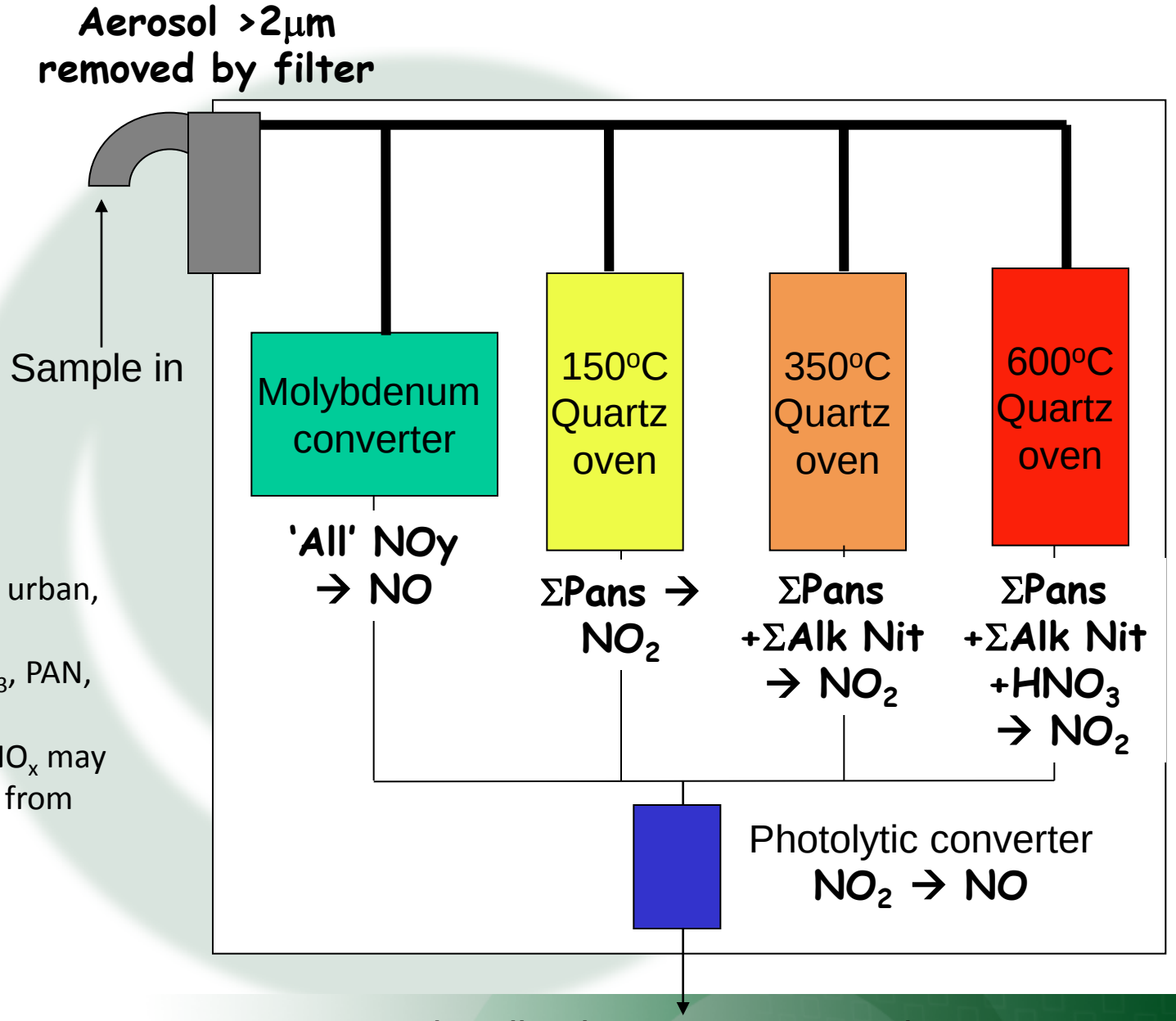
Elena Koslova, Martin Heimann for CO data

Zöe Fleming for NAME analyses

SOLAS, TENATSO and now the National Centre for Atmospheric Science (NCAS) through FGAM for funding

NO_y speciation



- NO_x-main sources urban, industrial areas
- Oxidation to HNO_3, PAN, alkylnitrates <1 day.
- Diurnal cycles in NO_x may indicate production from PAN, HNO_3, HONO