

A seven-year record (2006-2013) of nonmethane hydrocarbons (NMHCs) in the subtropical marine boundary layer at the Cape Verde Atmospheric Observatory (CVAO)

S.Punjabi, K.A. Read, L.J. Carpenter, J.R. Hopkins, and
A.C. Lewis - NCAS, University of York

Steve Arnold - Earth and Environment, University of Leeds

M.Heimann – Max-Planck -Institute for Biogeochemistry, Jena,
Germany

E.A Kozlova- College of Life and Environmental Sciences, Exeter

Luis Mendes - INMG, Cape Verde

NOAA ESRL GMAC
Boulder, May 21, 2014

THE UNIVERSITY *of York*

NERC
SCIENCE OF THE
ENVIRONMENT

Measurements and campaigns at site

Ground based long term measurements

- Met data at 4m, 10m and 30m
- Solar radiation
- JO^1D
- O_3 ,
- CO
- NO, NO_2, NO_y
- C_2-C_8 NMHCs and DMS
- Methanol, acetone and acetaldehyde
- Halocarbons
- Mercury

hosted international field projects
RHAMBLE 2007

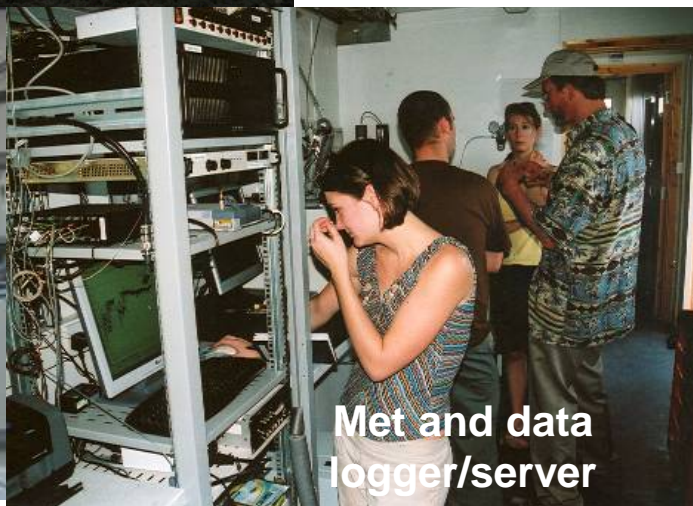


Seasonal Oxidant Study campaign 2009

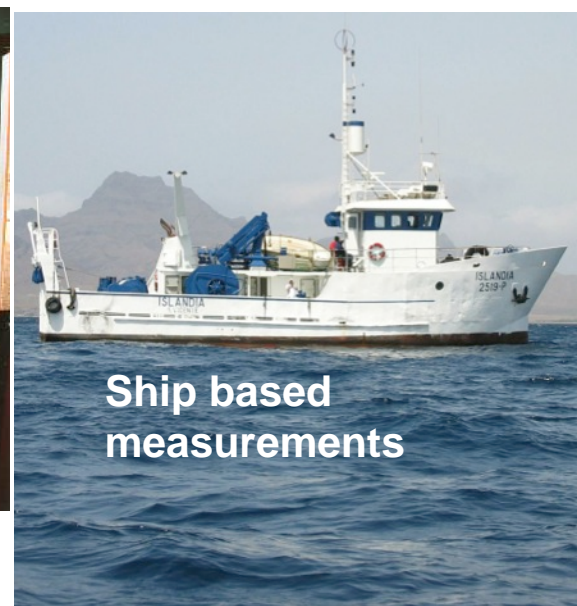


Oceanic Reactive Carbon³ Project June and Sep 2014

staff at site

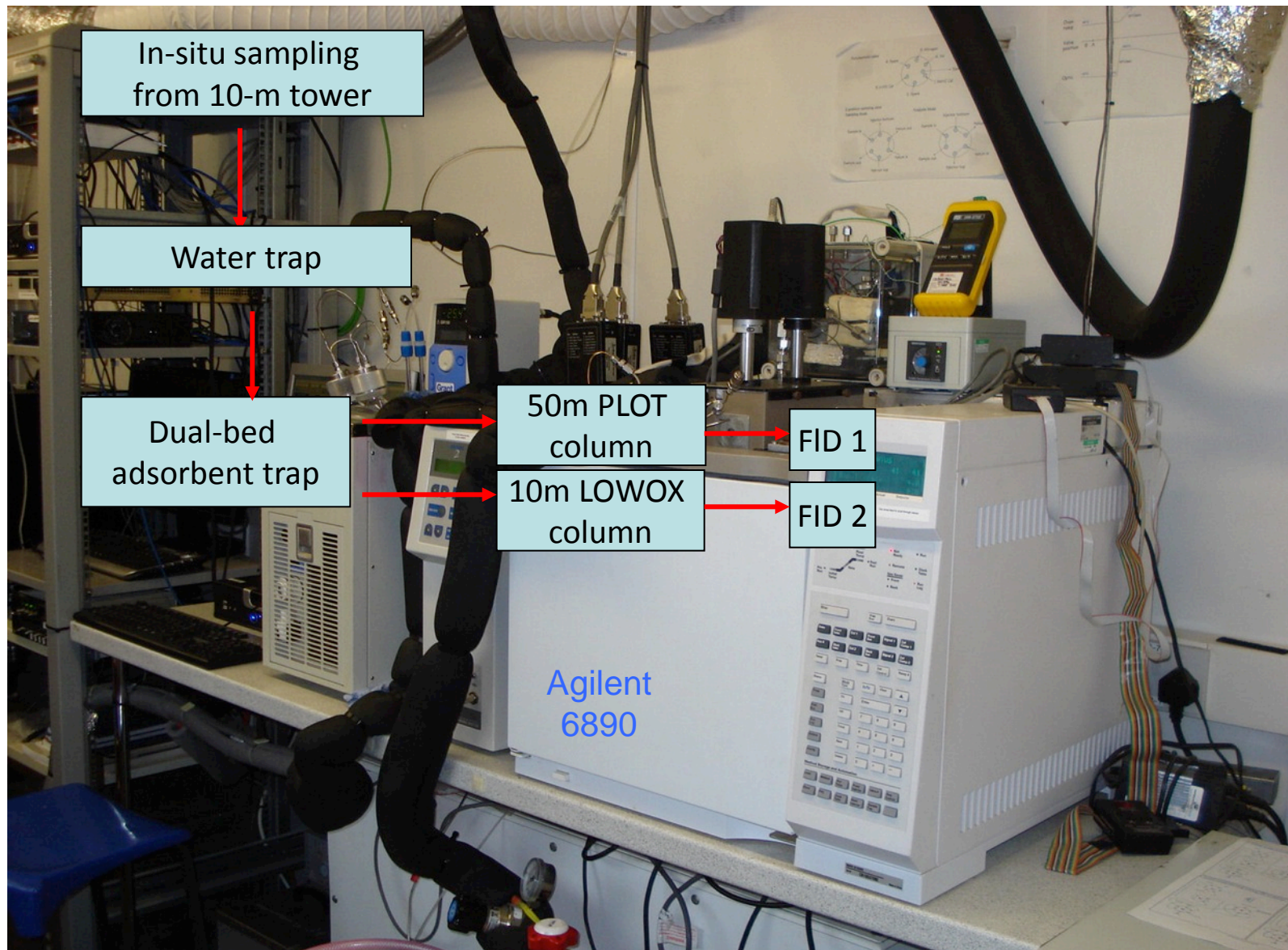


Met and data
logger/server

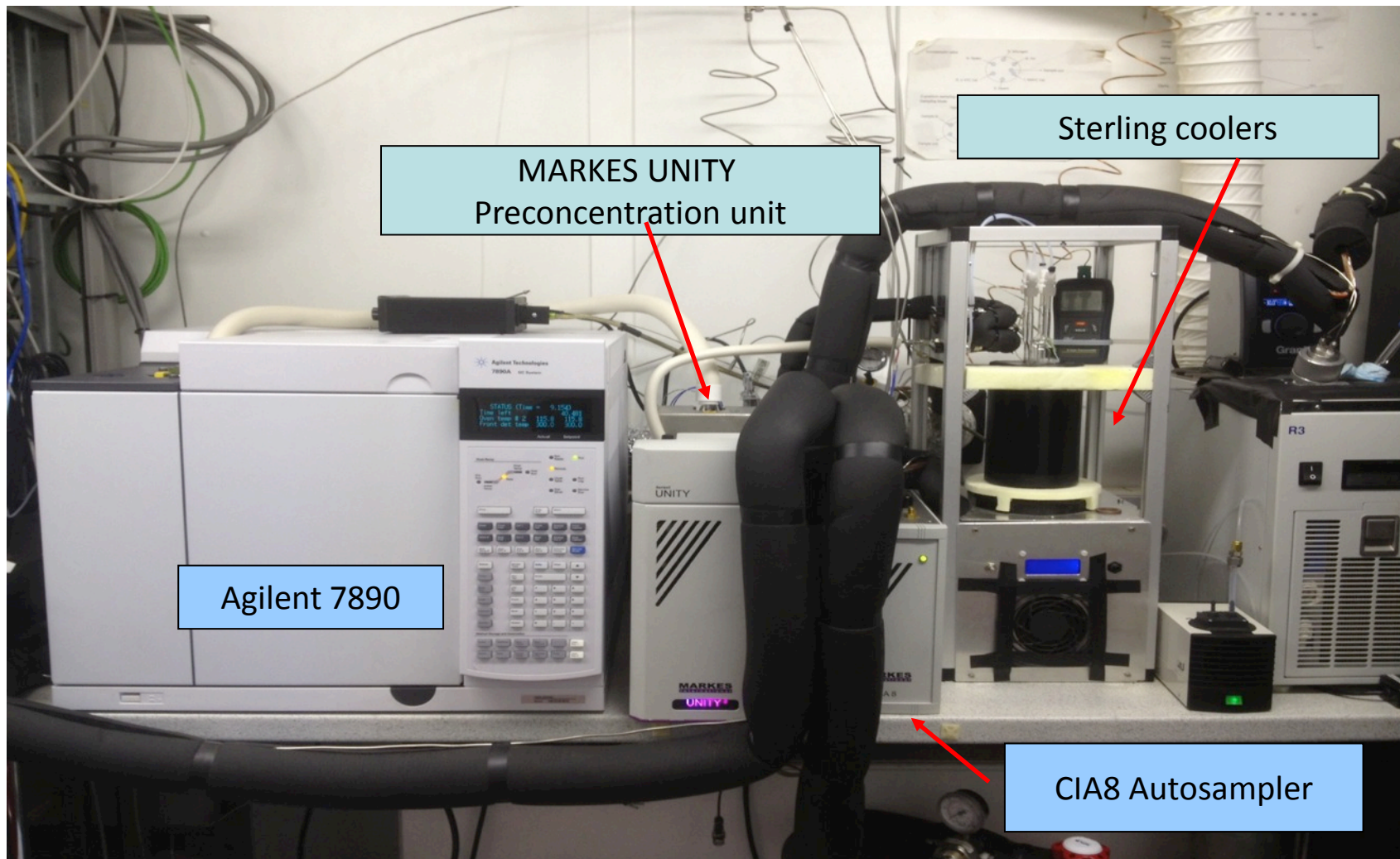


Ship based
measurements

Instrument involved during measurement period (Oct 2006- May 2013)



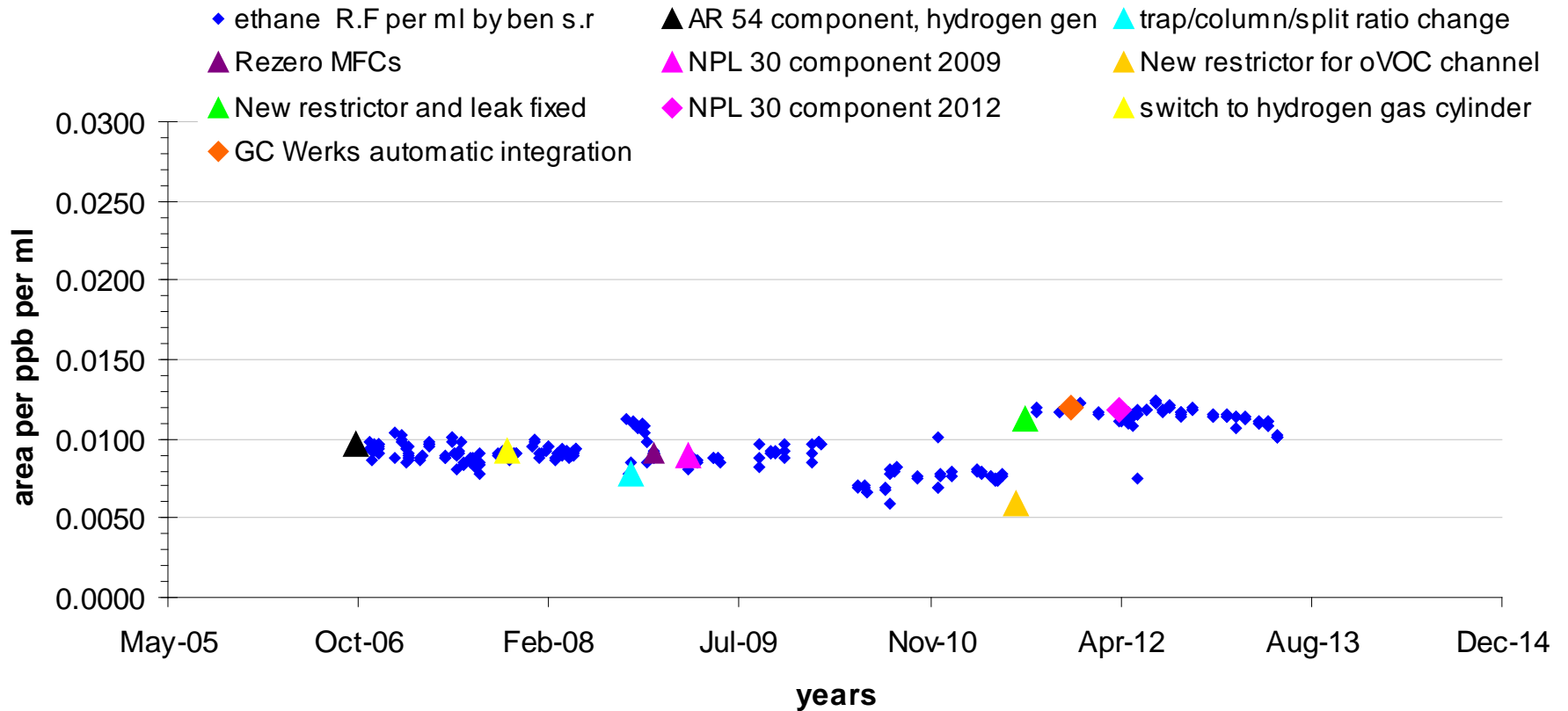
Since June 2013 instrument upgrade



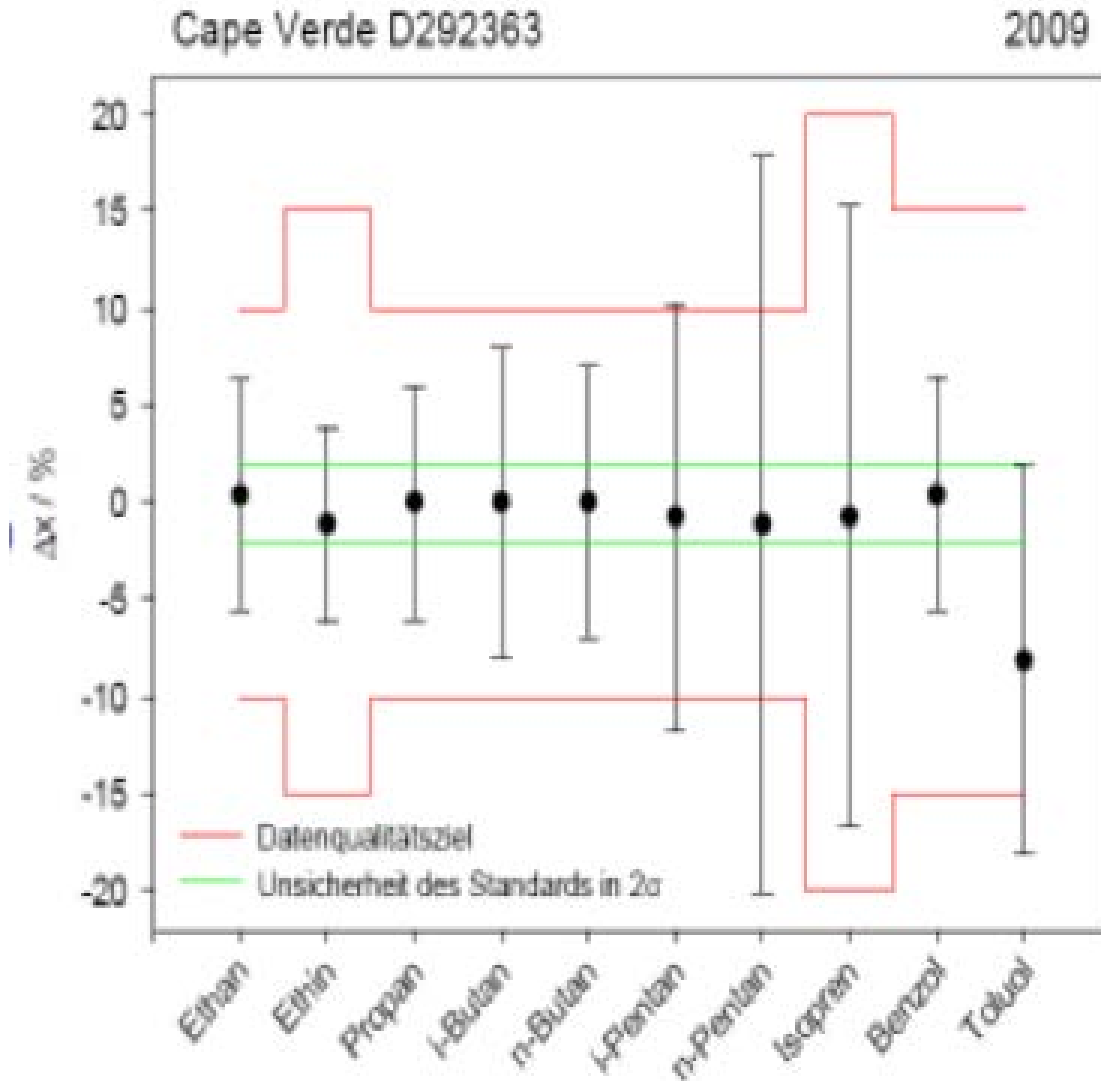
Commercial preconcentration and autosampler system : MARKES Thermal Desorbtion unit (TDU)

Calibration over time

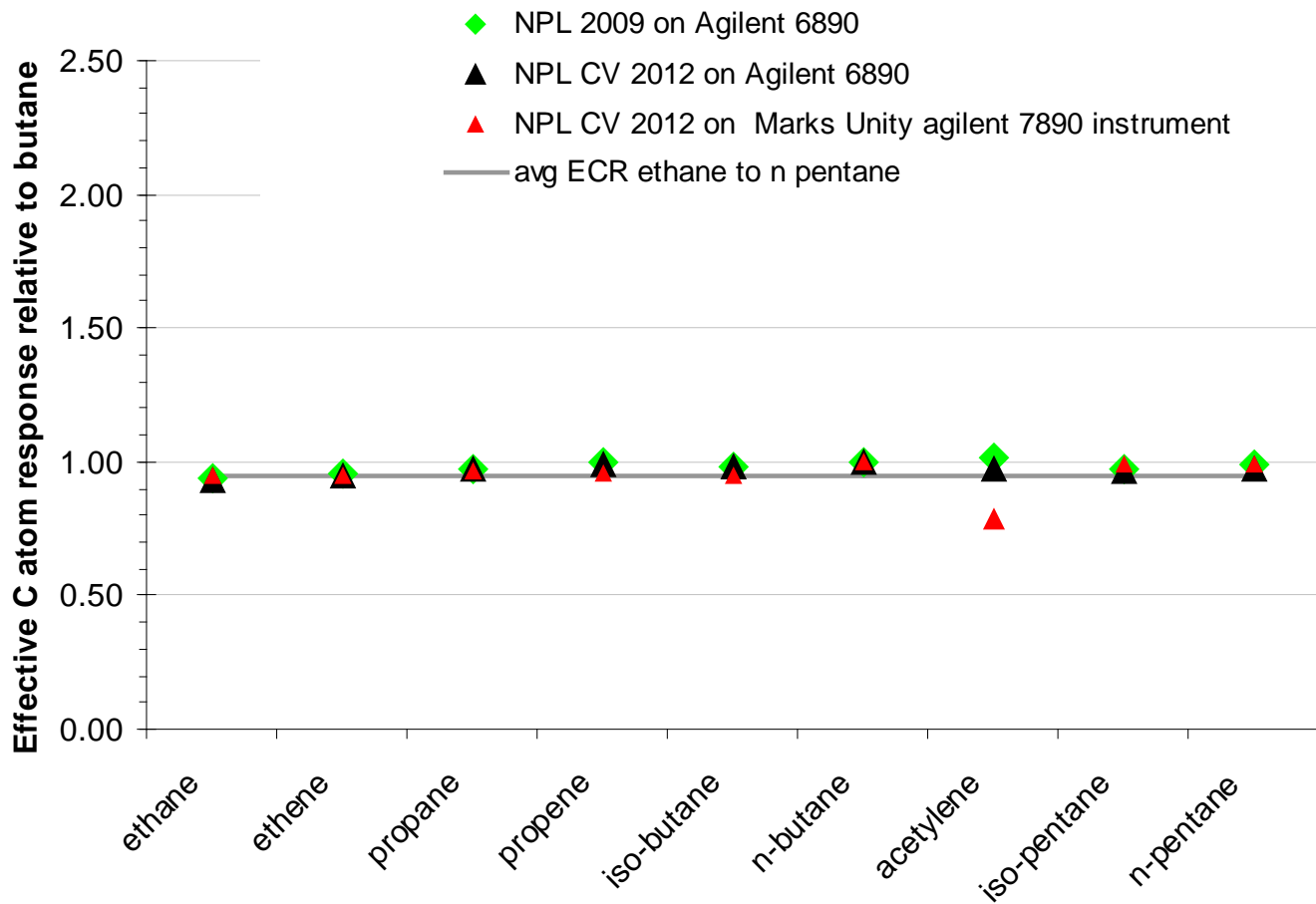
ethane and area per ppb per ml



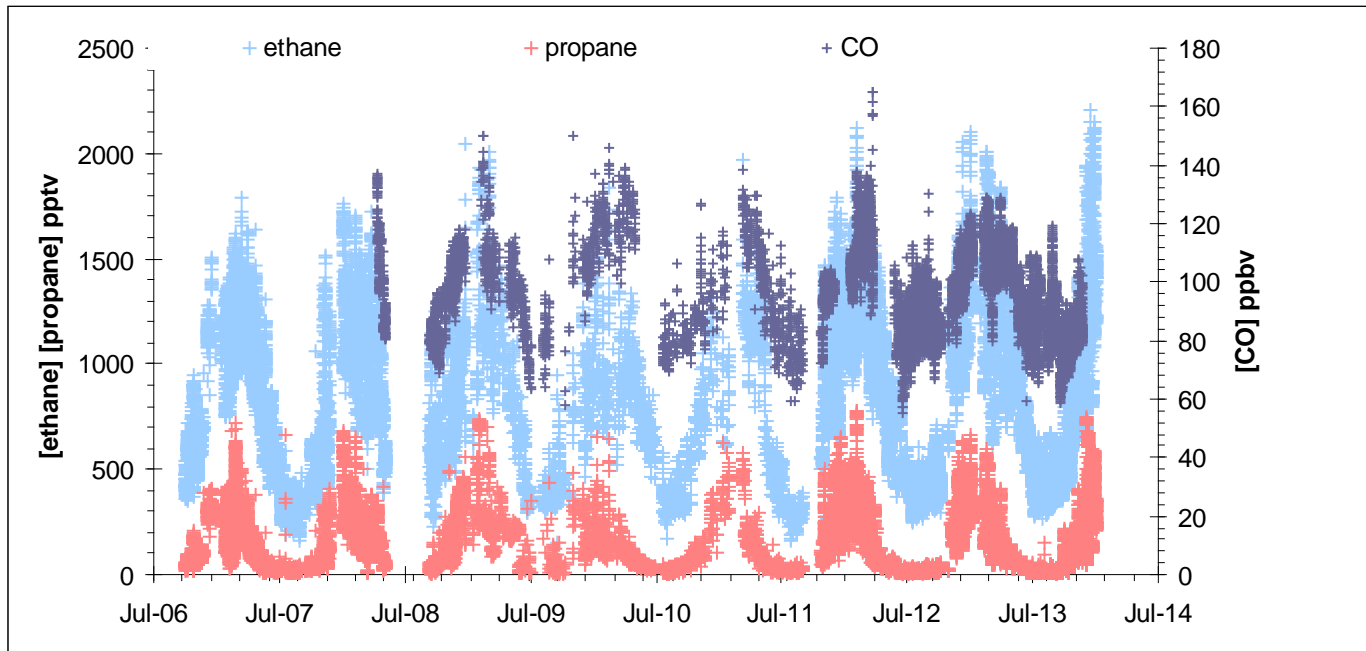
Results of WMO/GAW audit for VOC -2009



Comparison of calibration responses between old and new instrument



Data and time series



Spring maxima and summer minima : in line with the Northern Hemisphere observations

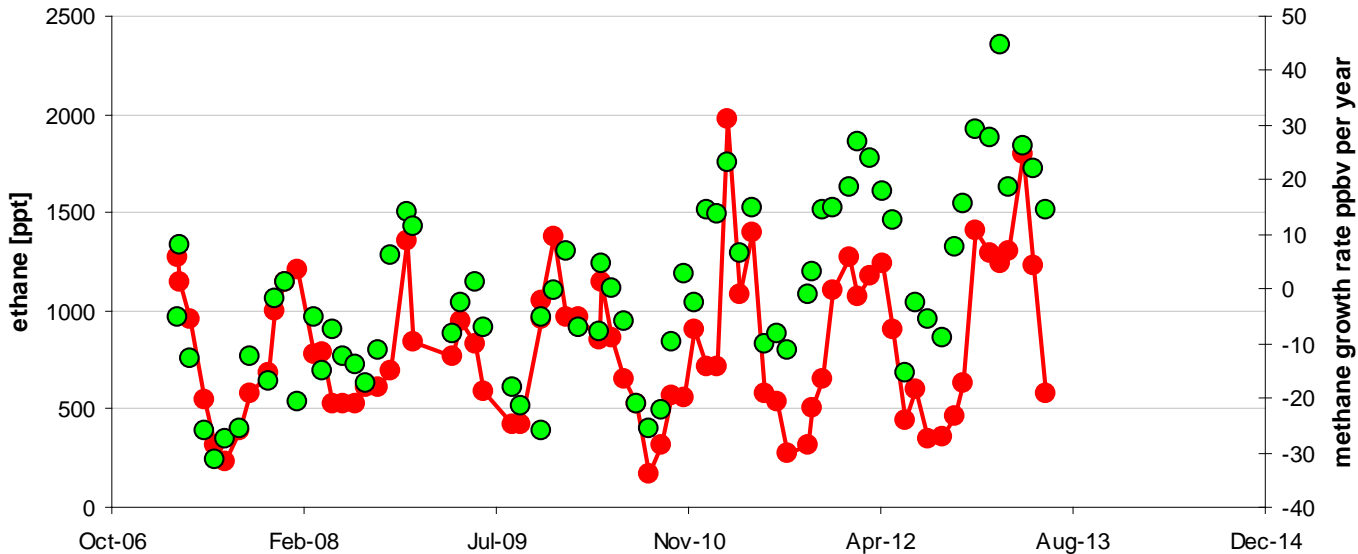
Rise in amplitude suggests a change in source strength or OH?

Ethane and CH₄ growth rate

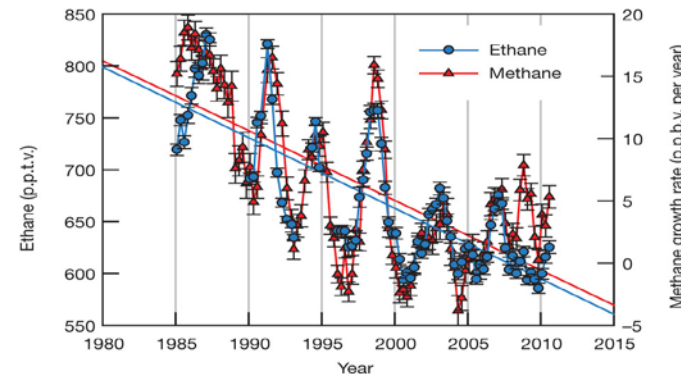
Ethane

ΔCH_4 (Monthly mean - 5 year running mean)

Methane data from
M. Heimann, Jena

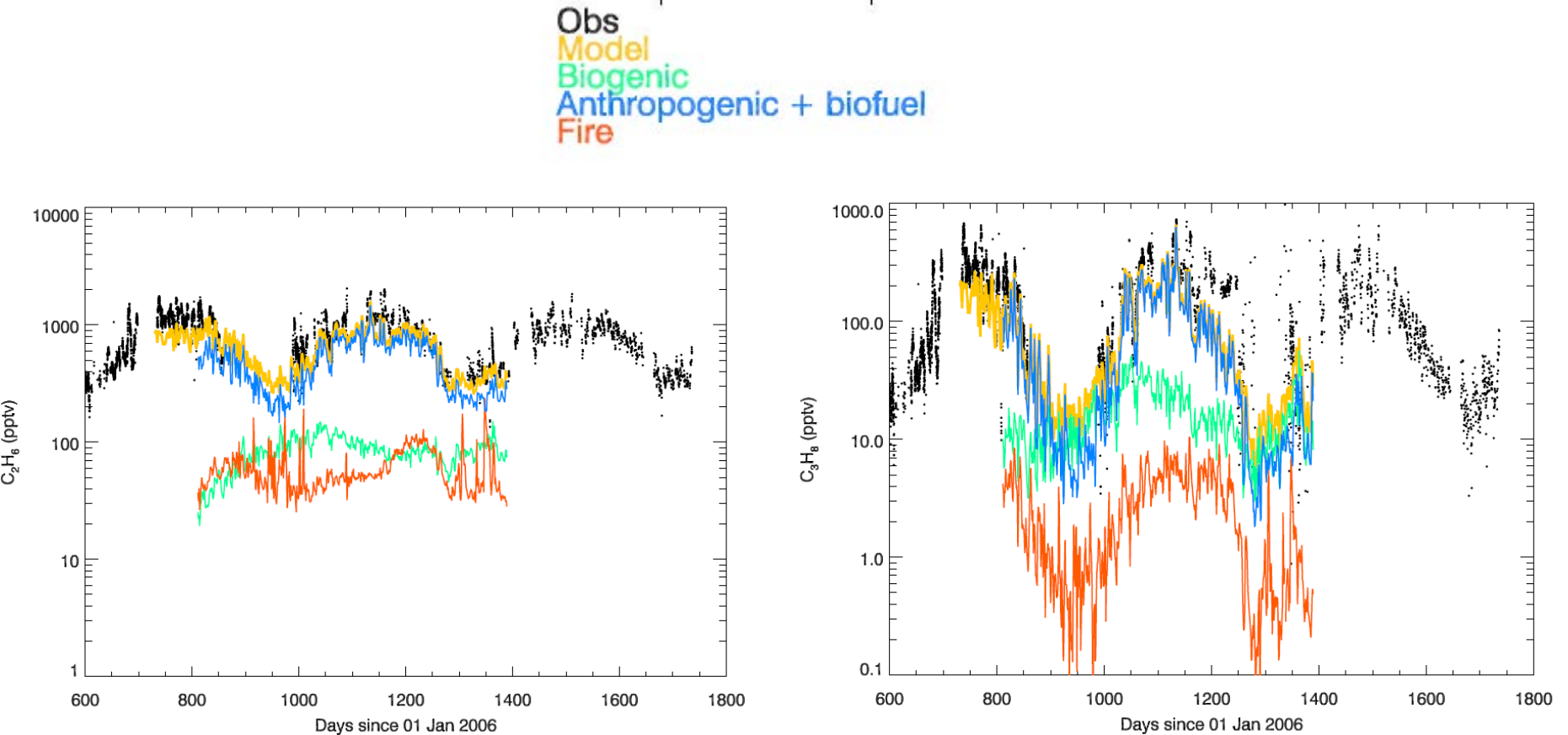


- Methane atmospheric growth rate is a sensitive indicator of fluctuations in methane's emissions.
- 1985-2010 saw global ethane decline of 190 pptv (24%) (Simpson et al., Nature, 2012)
- Declining fugitive fossil fuel emissions



Long-term decline of global atmospheric ethane concentrations and implications for methane, Simpson et al., *Nature* **488**, 490–494 (23 August 2012) doi:10.1038/nature11342

Model (CAM-Chem) and measurement comparison and emission contributions

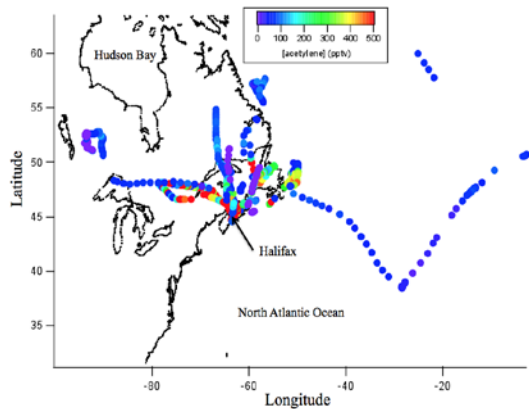


The model suggests that alkanes at Cape Verde are dominated by the anthro + biofuel sector (bioethanol is widely used in USA)

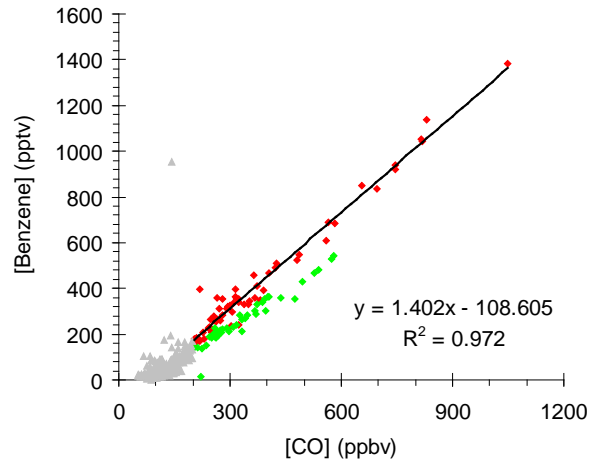
Courtesy: Steve Arnold

Read K.A; Carpenter L.J; Hopkins J.R; Lewis A.C; Lee J.D; **Arnold S.R**; Pickering S.J; Beale R; Nightingale P.D; Mendes L (2012) Multiannual observations of acetone, methanol, and acetaldehyde in remote tropical Atlantic air: Implications for atmospheric OVOC budgets and oxidative capacity, *Environmental Science and Technology*, **46**, pp.11028-11039. [doi: 10.1021/es302082p](https://doi.org/10.1021/es302082p)

Constraining global benzene emissions using Cape Verde

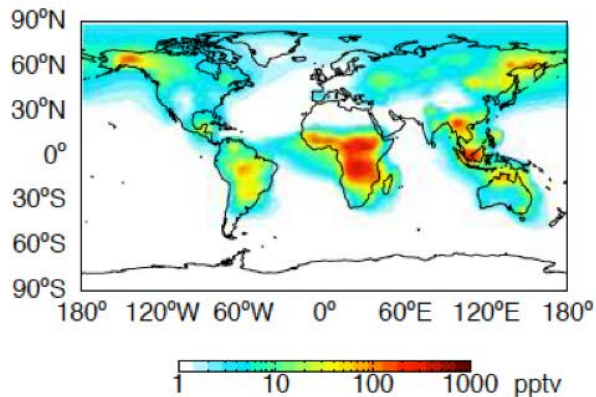


Starting point – boreal plume observations from aircraft

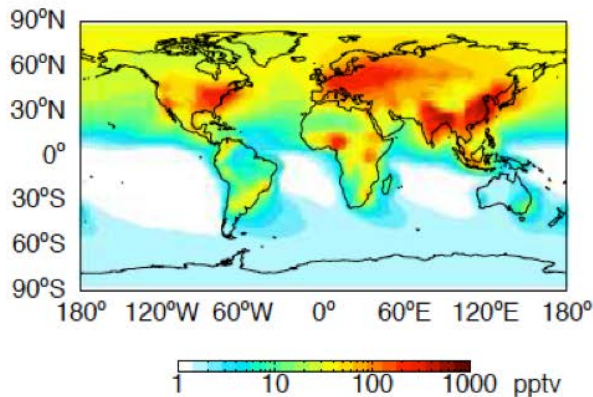


Derive Emission Ratios of benzene to CO (plus use literature values)

Surface mean biomass burning C_6H_6



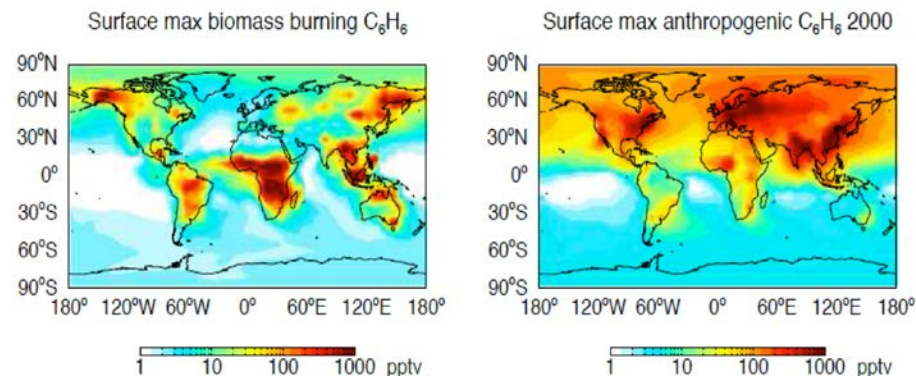
Surface mean anthropogenic C_6H_6 2000



GEOSChem Model – Tagged benzene (scaled to GFED3 CO) + RETRO anthropogenic benzene

Constraining global benzene emissions using Cape Verde

- Cape Verde influenced by both biomass burning and anthropogenic benzene.
- Model / measurement comparison shows overestimation.
- Better fit using RETRO x 0.33 or 0.25
- Reducing RETRO is consistent with major reduction in fuel benzene since 2000.



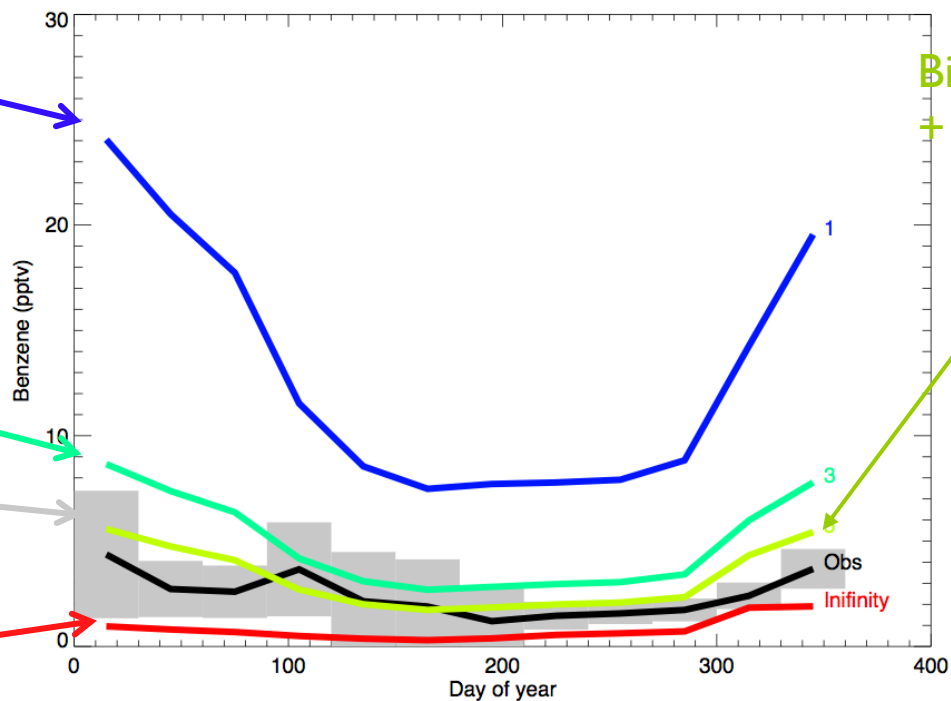
Biomass burning
+ RETRO 2000

Biomass burning
+ 0.33 RETRO 2000

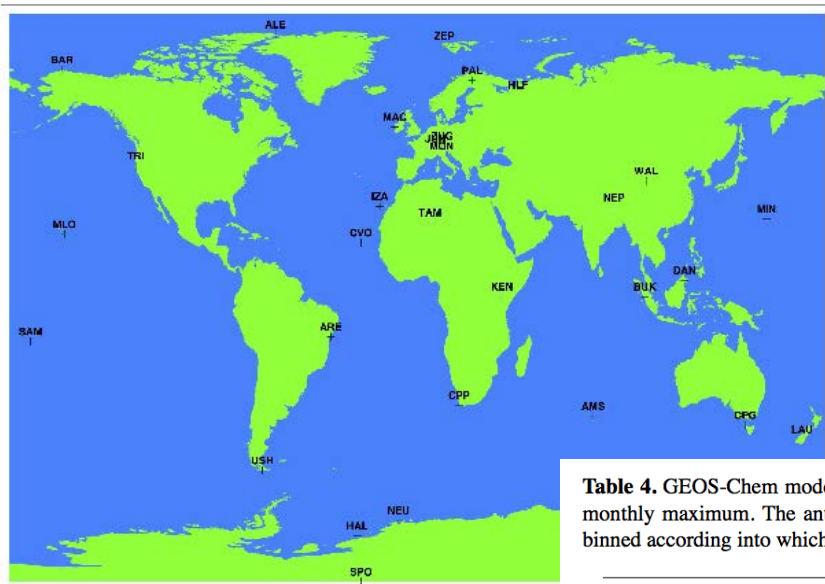
Cape Verde
Observations

Biomass only

Biomass burning
+ 0.25 RETRO 2000



Impact of biomass burning on GAW stations



- Estimated fraction of benzene from biomass burning / anthropogenic arriving at 27 GAW Global stations is calculated.
- Most GAW stations affected significantly in at least one month of the year, biomass influence becomes more pronounced as anthropogenic emissions of benzene decline.

Table 4. GEOS-Chem model estimated fraction of annual benzene associated with biomass burning, given as the annual mean and as the monthly maximum. The anthropogenic emissions used are that of RETRO and $0.33 \times$ RETRO. GAW sites (see Table 3 and Fig. 7) are binned according into which biomass burning fraction range they lie.

Biomass burning/ anthropogenic benzene fraction	Annual Mean	Annual Mean (RETRO · 0.33)	Monthly Maximum	Monthly Maximum (RETRO · 0.33)
0.0–0.2	TAM CVO KEN IZA WAL MIN DAN NEP MLO ARE TRI PAL ZUG MAC MON JUN HLF	IZA WAL NEP PAL ZUG MAC MON JUN HLF	NEP ZUG MON JUN	ZUG MON JUN
0.2–0.4	AMS CPP CPG LAU SAM USH ALE BAR ZEP NEU SPO HAL	TAM CVO KEN MIN DAN MLO ARE ALE TRI ZEP	IZA	NEP
0.4–0.6	BUK	CPP CPG LAU USH BAR	TAM CVO WAL ARE	
0.6–0.8		AMS BUK SAM NEU SPO HAL	KEN CPP MIN DAN SAM TRI PAL MAC NEU SPO HAL HLF	TAM IZA WAL ARE
0.8–1			AMS CPG BUK LAU MLO USH ALE BAR ZEP	CVO AMS KEN CPP CPG BUK MIN DAN LAU MLO SAM USH ALE BAR TRI PAL MAC ZEP NEU SPO HAL HLF

Further plans

- Continuing with long-term measurements programme
- Rigorous checks to ensure data quality