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

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NOAA ESRL GMAC
Boulder, May 21, 2014
Cape Verde Observatory - A GAW Global status station

- Eastern tropical North Atlantic (ETNA) - 16° 52' N, 24° 52' W
- Long range transport and atmospheric - ocean exchange of trace chemicals
- Remote marine boundary location
- Measurement started Oct 2006
- Diverse trade winds arriving at site (North America, Arctic, European and African regions)

https://www.ncas.ac.uk/index.php/en/cvao-home
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

Seasonal Oxidant Study Campaign 2009

Oceanic Reactive Carbon$^3$ Project
June and Sep 2014

Measurements and campaigns at site

Staff at site

Met and data logger/server

Ship based measurements

hosted international field projects
RHaMBLE 2007
Instrument involved during measurement period (Oct 2006 - May 2013)

- In-situ sampling from 10-m tower
- Water trap
- Dual-bed adsorbent trap
- 50m PLOT column
- 10m LOWOX column
- FID 1
- FID 2
- Agilent 6890
Since June 2013 instrument upgrade

Commercial preconcentration and autosampler system: MARKES Thermal Desorption unit (TDU)
Calibration over time

ethane and area per ppb per ml

- ethane R.F per ml by ben s.r
- Rezero MFCs
- New restrictor and leak fixed
- NPL 30 component 2009
- NPL 30 component 2012
- GC Werks automatic integration
- AR 54 component, hydrogen gen
- Trap/column/split ratio change
- New restrictor for oVOC channel
- Switch to hydrogen gas cylinder
Results of WMO/GAW audit for VOC -2009

Cape Verde D292363

2009

\[ \Delta x \% \]

-20
-15
-10
-5
0
5
10
15
20

Ethan
Ethin
Propan
\( i \)-Butan
\( n \)-Butan
\( i \)-Pentan
\( n \)-Pentan
Isopren
Benzol
Toluol

Datenqualitätsziel

Unsicherheit des Standards in 2\( \sigma \)
Comparison of calibration responses between old and new instrument

- NPL 2009 on Agilent 6890
- NPL CV 2012 on Agilent 6890
- NPL CV 2012 on Marks Unity agilent 7890 instrument
- avg ECR ethane to n pentane

Effective C atom response relative to butane

- ethane
- ethene
- propane
- propene
- iso-butane
- n-butane
- acetylene
- iso-pentane
- n-pentane
Spring maxima and summer minima: in line with the Northern Hemisphere observations

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

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

**Constraining global benzene emissions using Cape Verde**

Starting point – boreal plume observations from aircraft

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

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

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

The influence of biomass burning on the global distribution of selected non-methane organic compounds, Lewis, A.C et al

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Further plans

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