Observations and modelling of oxygenated VOCs in the tropical Atlantic boundary layer

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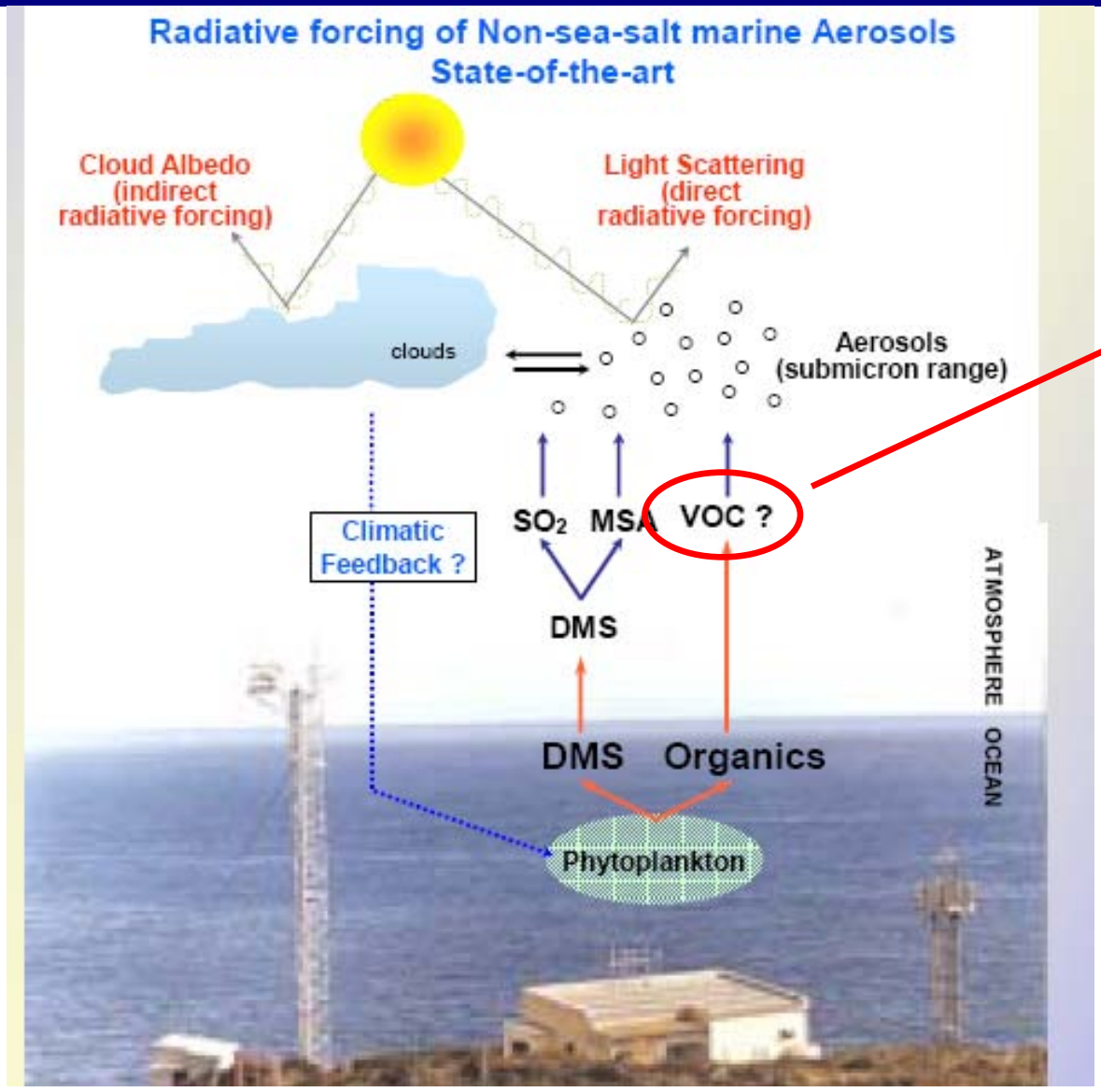
Read, K.A et al., (2012), *Environ. Sci. Technol.*, 46 (20), 11028-11039, doi:10.1021/es302082p.

A role for oceanic organics in climate?



Isoprene?
Monoterpenes?
Glyoxal??
oVOC?

Graphic courtesy Jean Sciare

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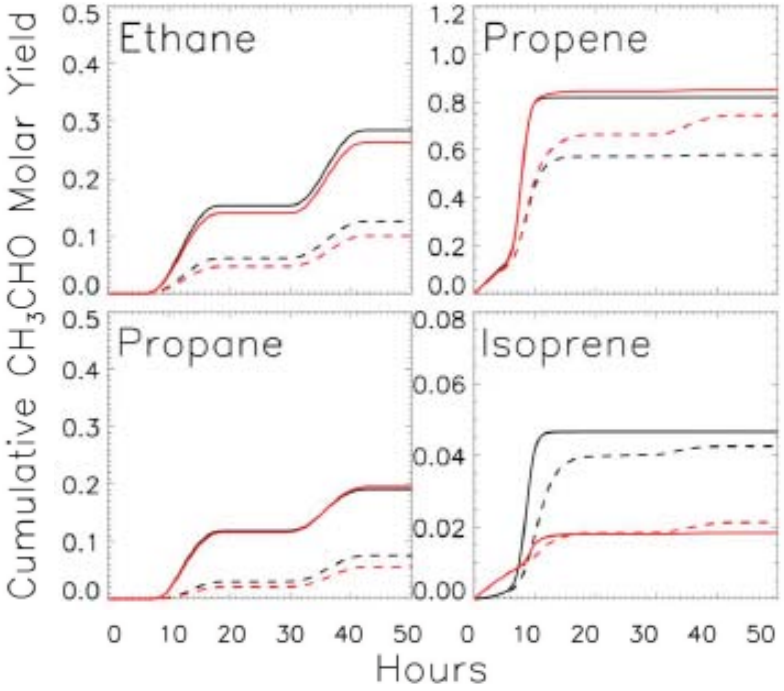
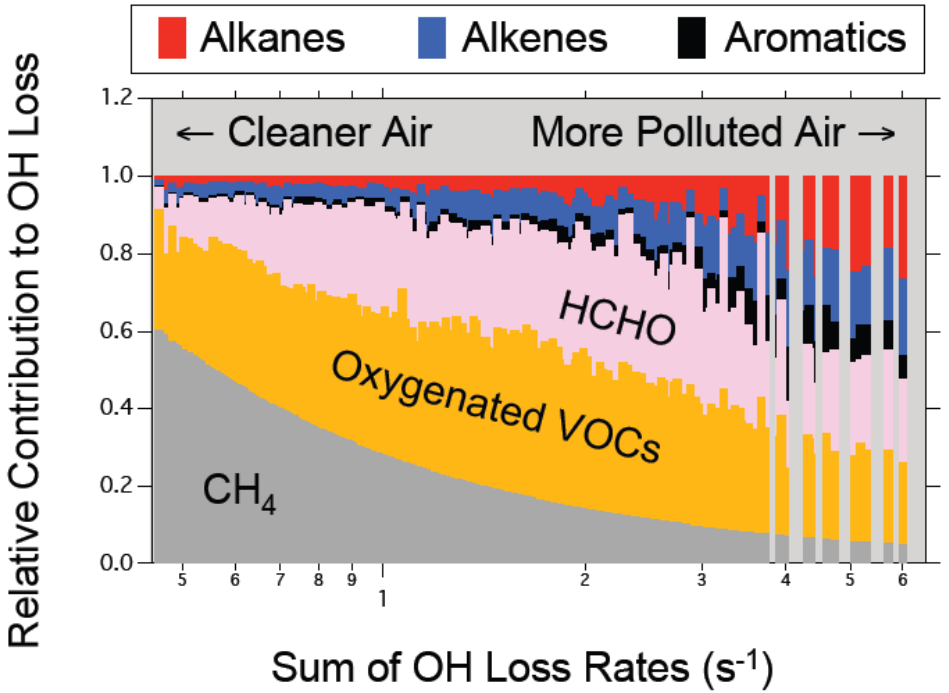
Oxygenated VOCs

- Ubiquitous throughout troposphere
- Directly emitted, but also large source from atmospheric oxidation of primary VOCs.

CH_4 → .. → CH_3OH (methanol)
C_2H_6 → .. → CH_3CHO (acetaldehyde)
C_3H_8 → .. → CH_3COCH_3 (acetone)



Millet et al., (2010)



Goldan et al., (2004)

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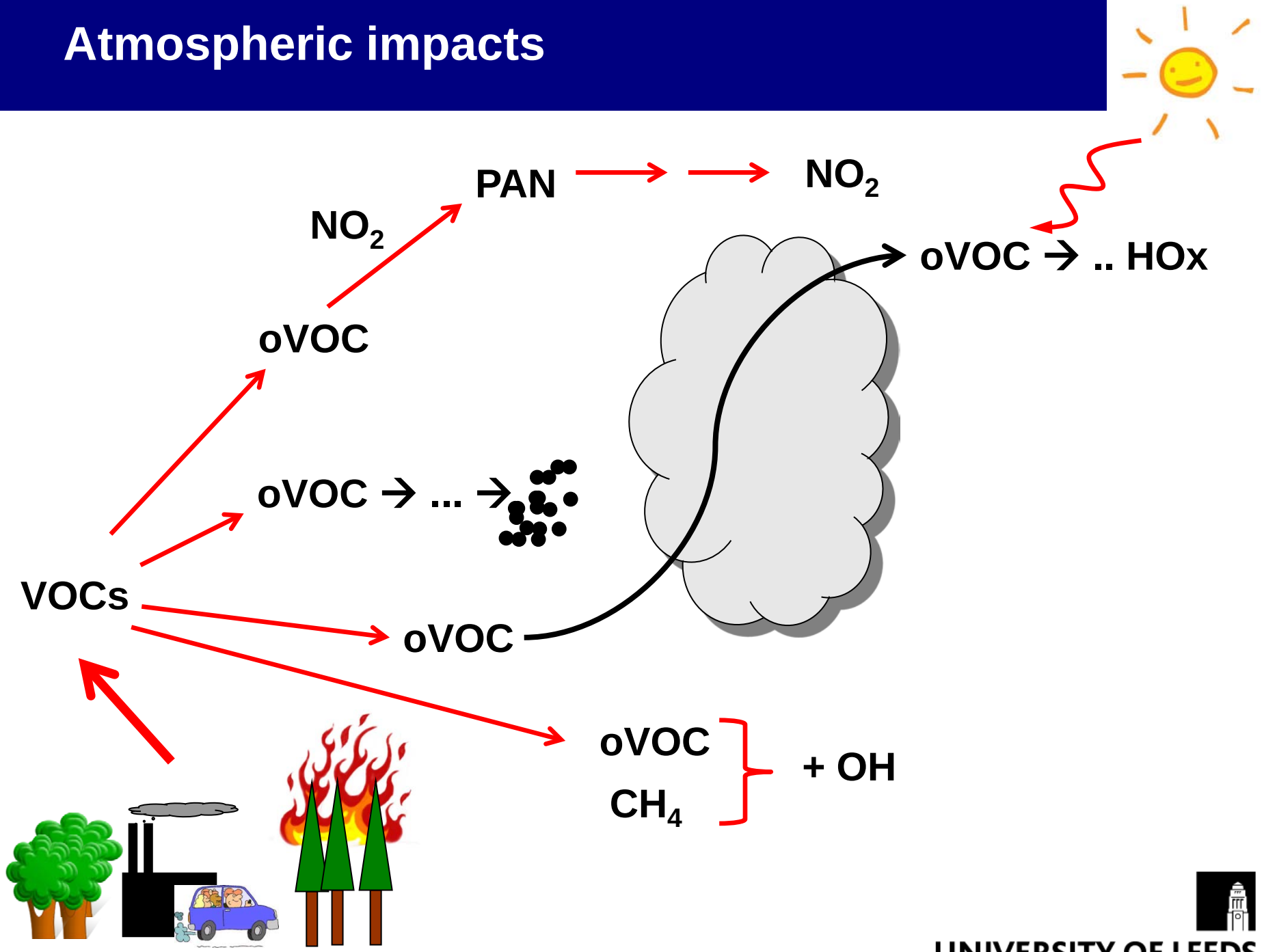
Atmospheric impacts



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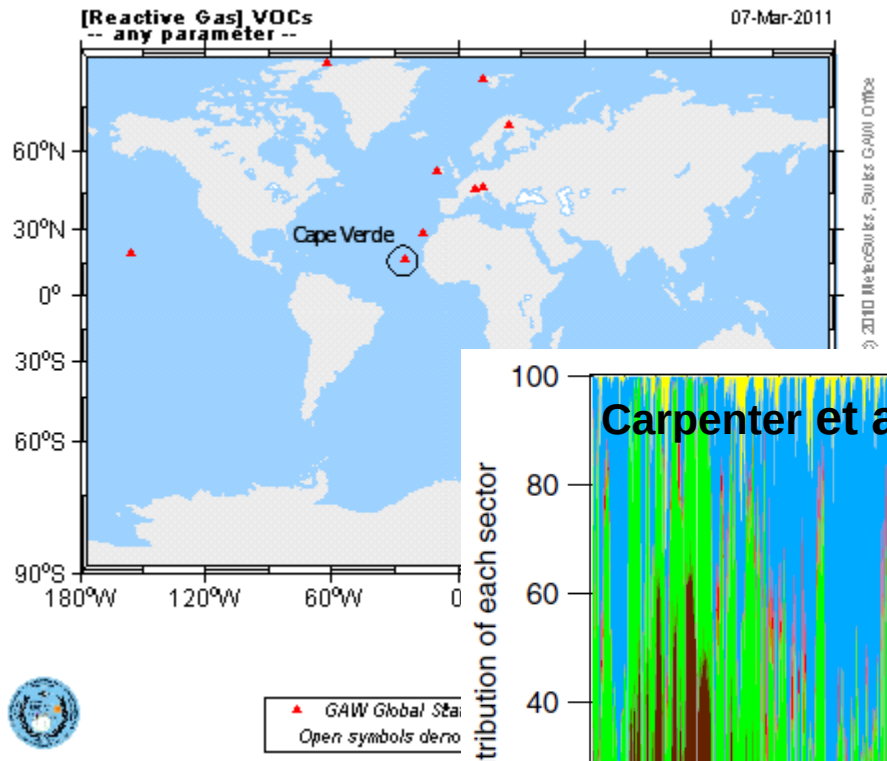
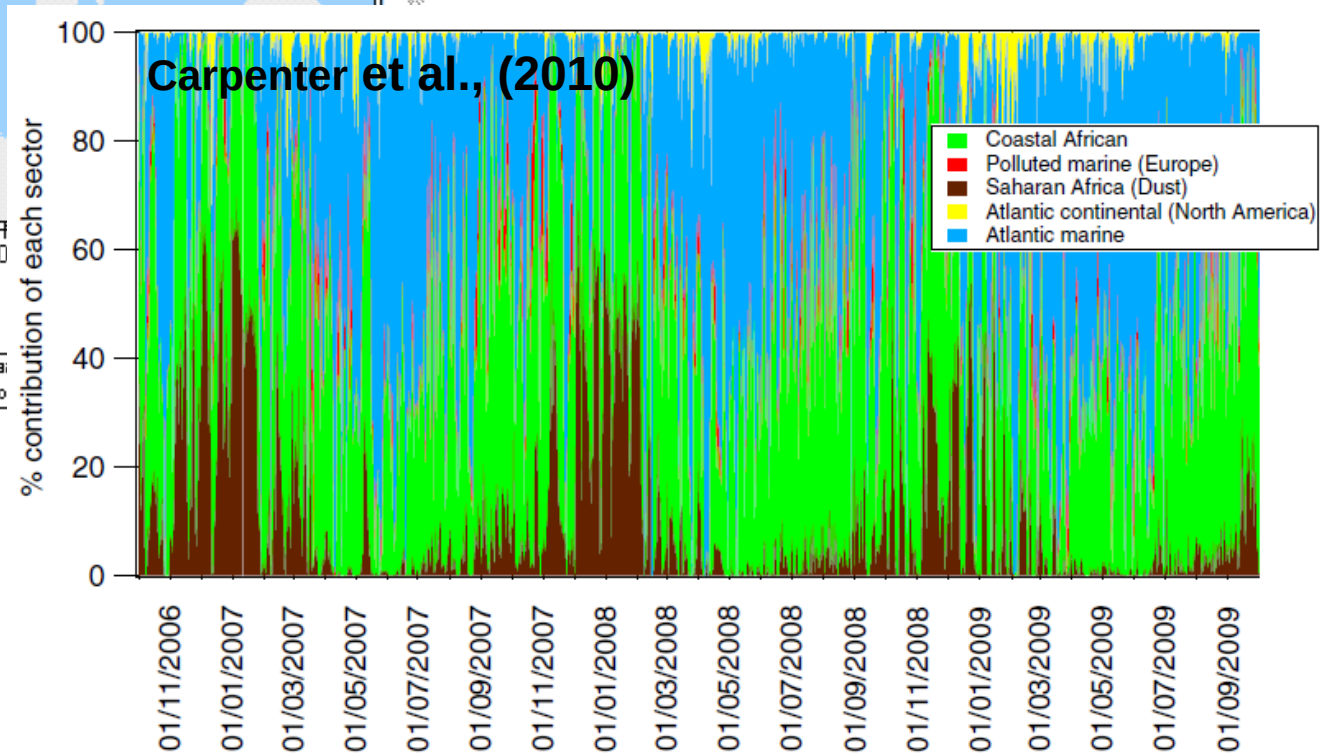
Cape Verde observatory





5 years of oVOC observations (methanol, acetaldehyde, acetone).

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CAM-Chem configuration

CAM-Chem: CESM 1_0_1 with offline meteorology and full tropospheric chemistry

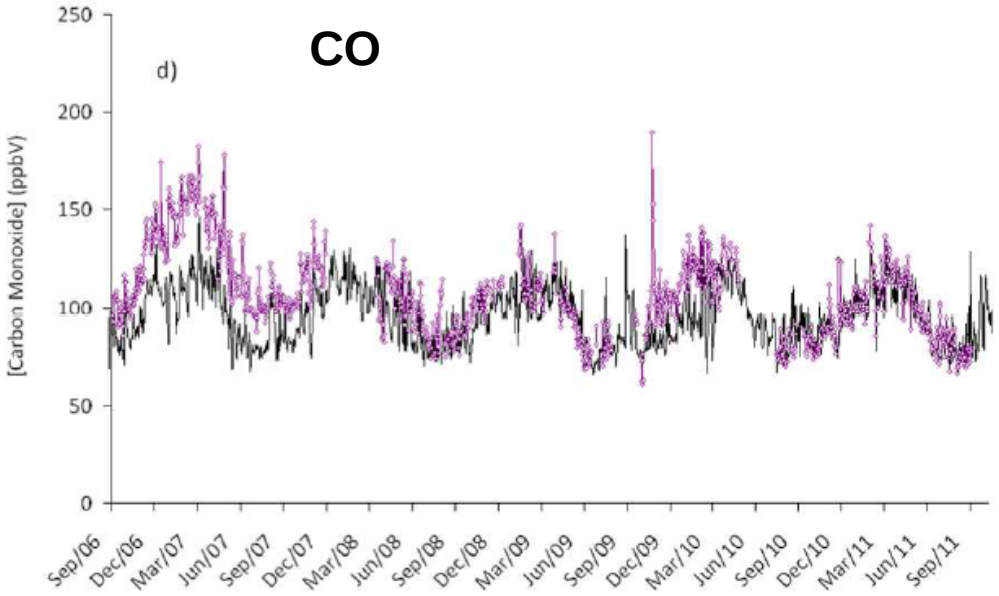
- MOZART 4 tropospheric chemistry scheme.

- 2.5^{O} x 1.9^{O} horizontal resolution, L56, GEOS-5 meteorology

- 2006 – 2010 multiannual simulation

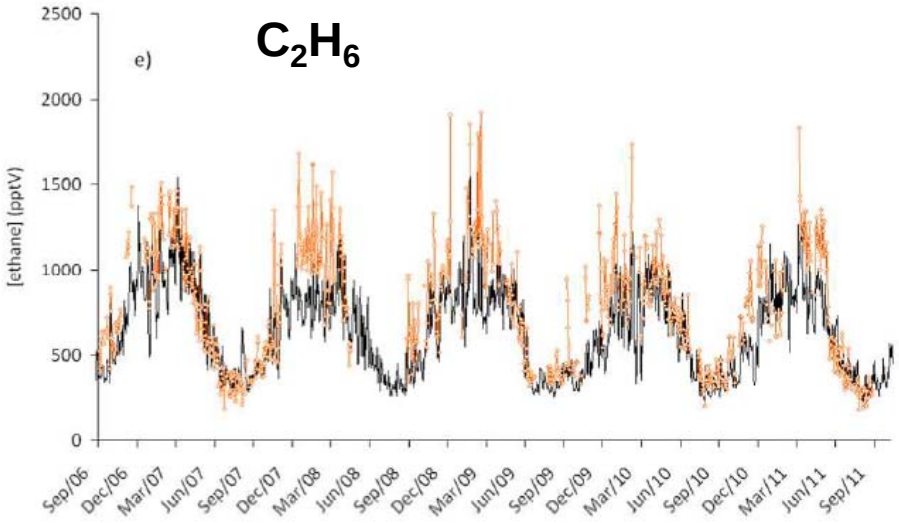
- Surface emissions from POET database + REAS anthropogenic emissions for Asia (non-varying). Monthly GFED2 (yearly-varying) biomass burning emissions.

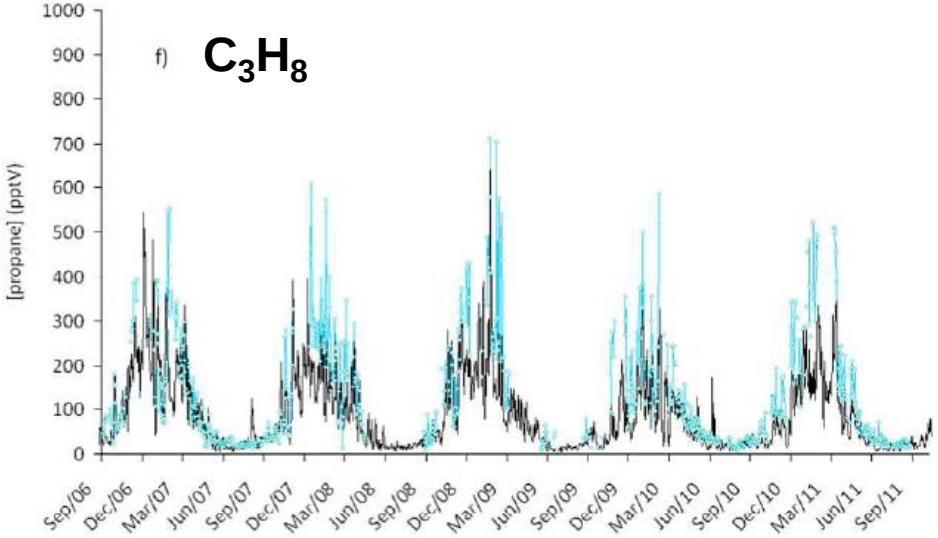
Model performance at Cape Verde



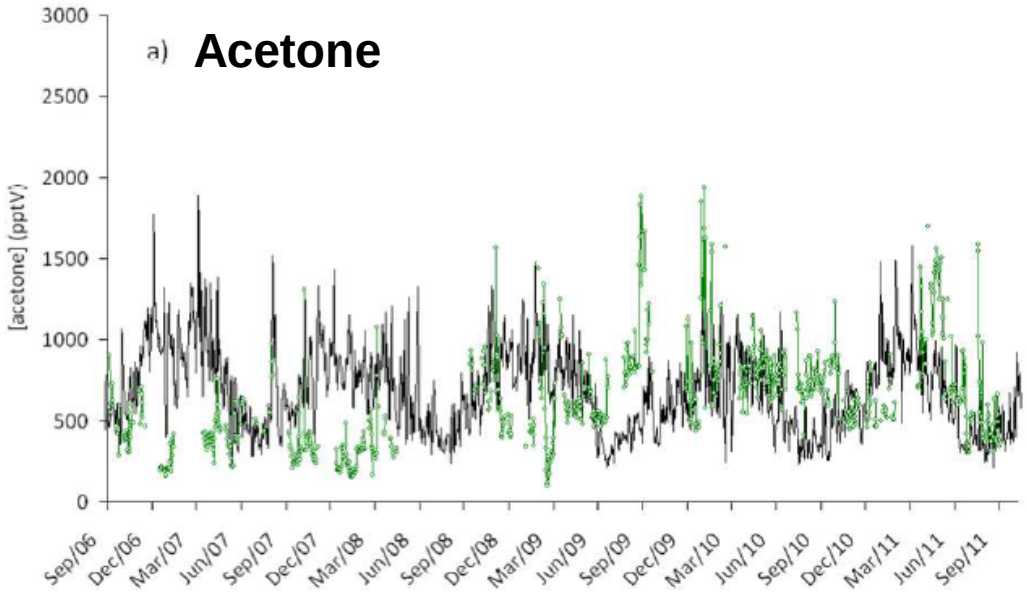
Colour: obs

Black: model





Model performance at Cape Verde



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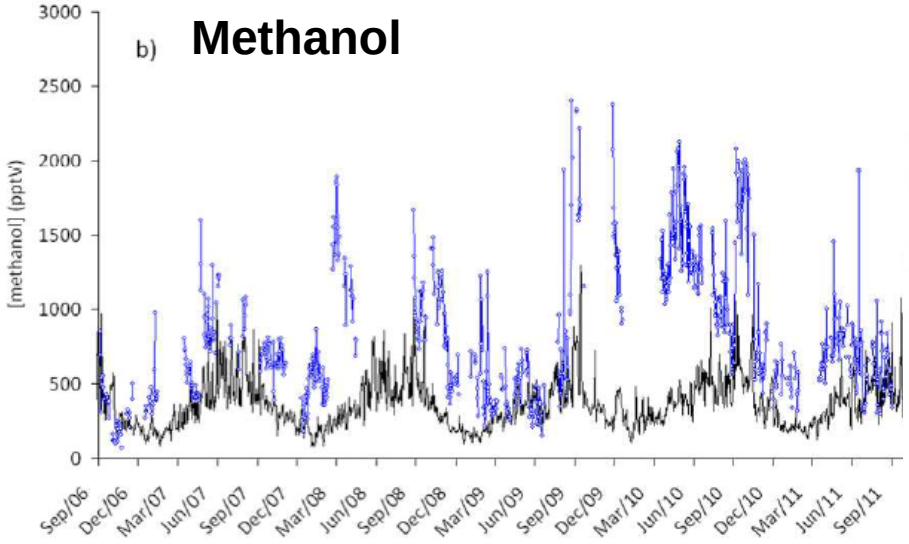
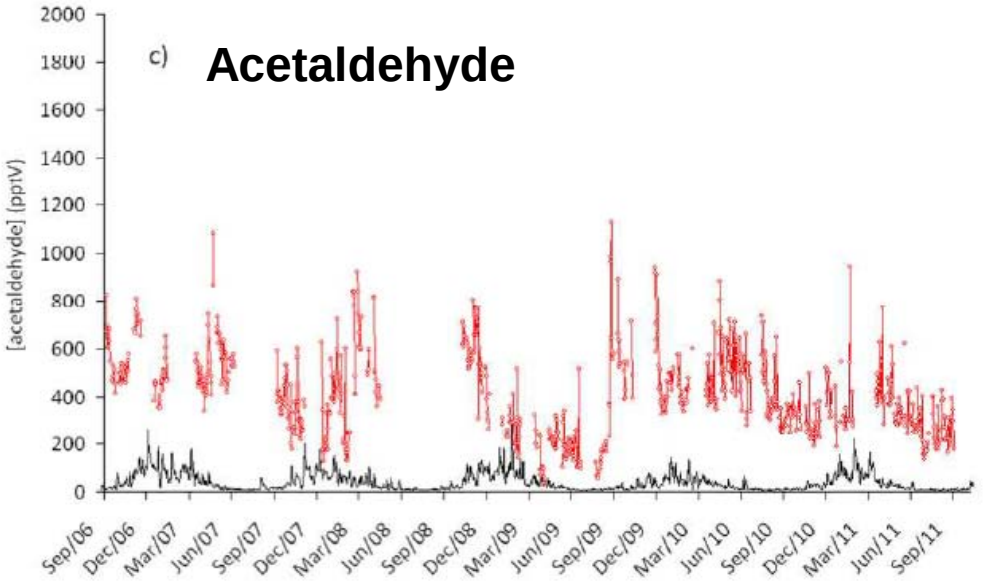
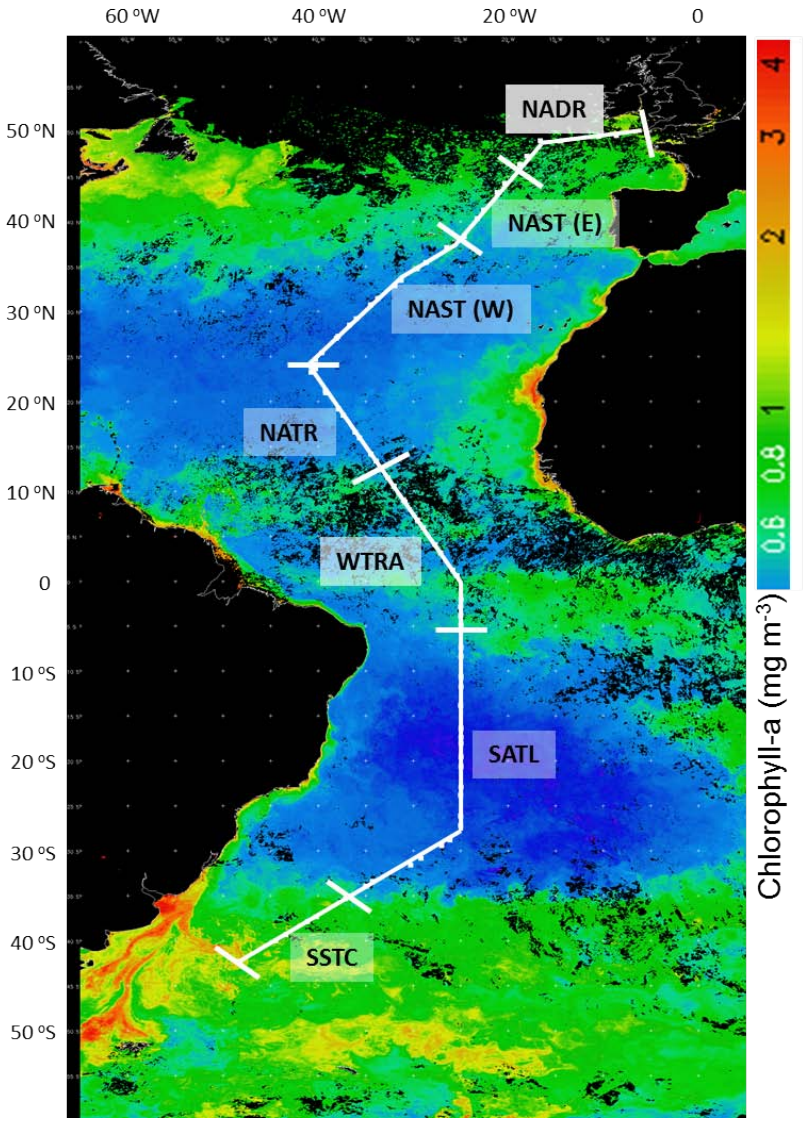




Ocean flux implementation



- Based on observed latitudinal distribution of seawater oVOC concentrations through Atlantic [Beale et al., *submitted*].

-Air-side and water-side transport velocities based on model surface layer wind speed scaled to 10 m.

-Schmidt numbers for each oVOC calculated using kinematic viscosity of water & temperature-dependent diffusivities of each gas in water.

- Bi-directional fluxes for the OVOCs dependent on oceanic and atmospheric concentrations, sea-surface temperature and wind speed.

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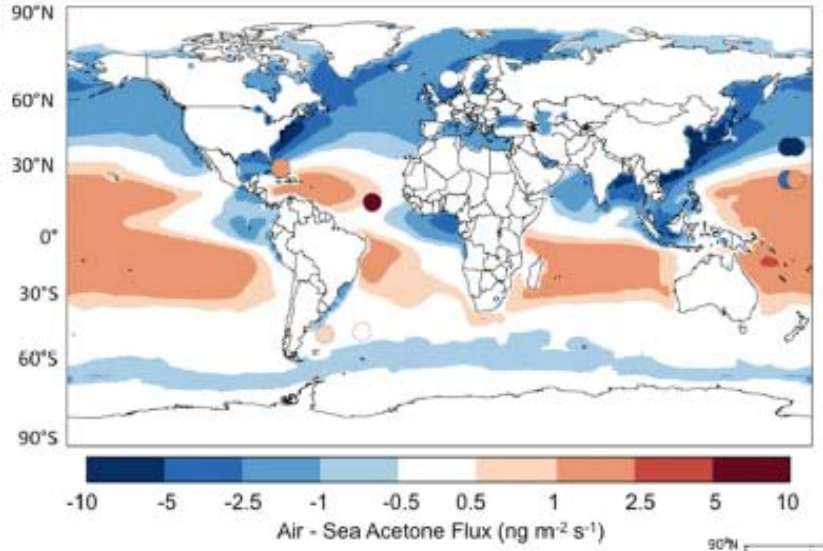
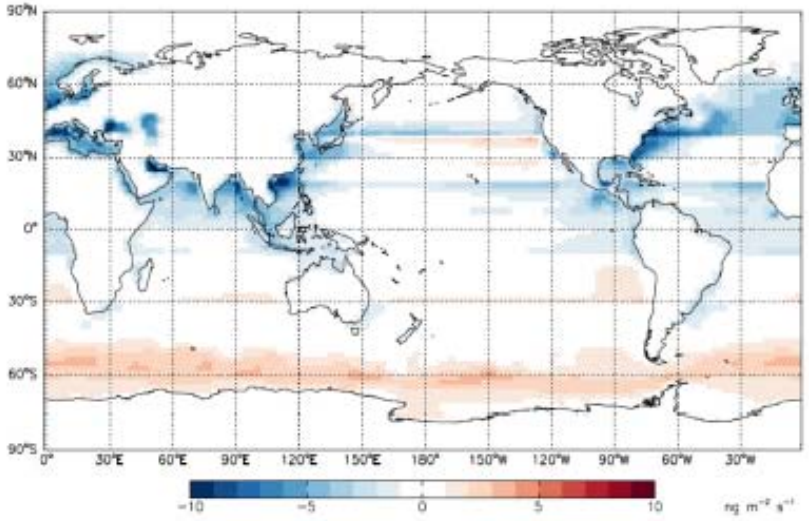
Ocean fluxes

Annual net acetone ocean fluxes



Fischer et al., (2012)
Net: -2 Tg / yr (ocean sink)

Based on single global seawater concentration



CAM-chem
Net: -2.8 Tg / yr (ocean sink)

Model flux calculations suggest that tropical Atlantic region is a net sink for acetone but a net source for methanol and acetaldehyde.

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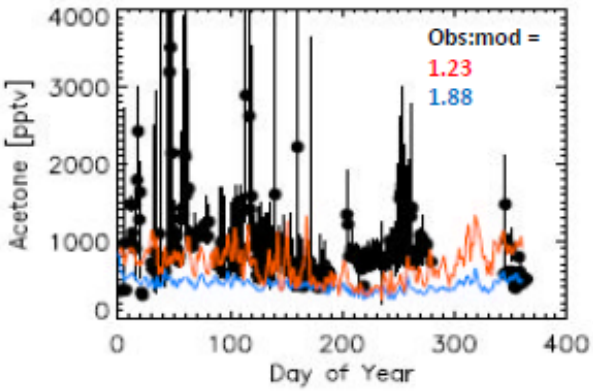
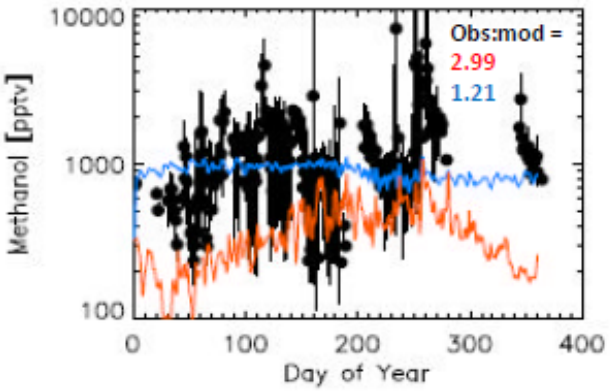
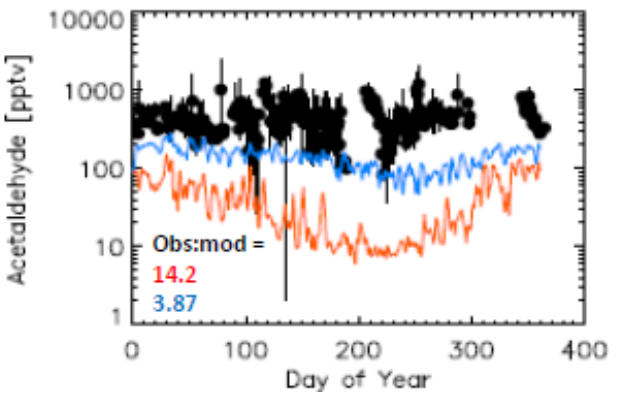
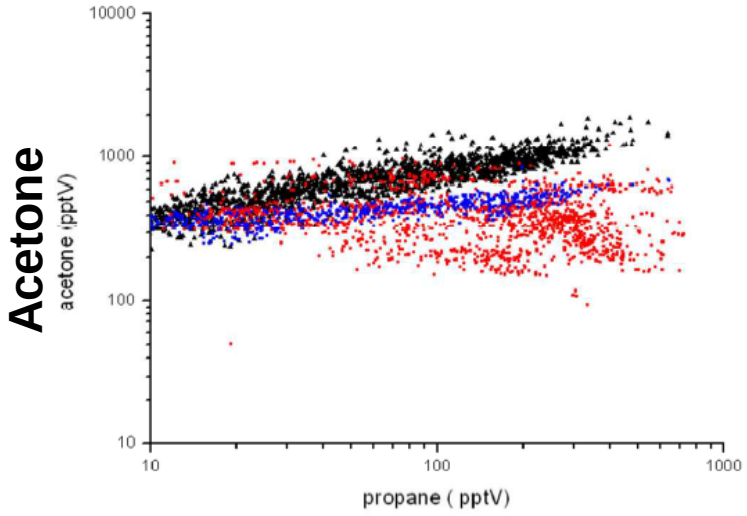
Model sensitivity to ocean fluxes

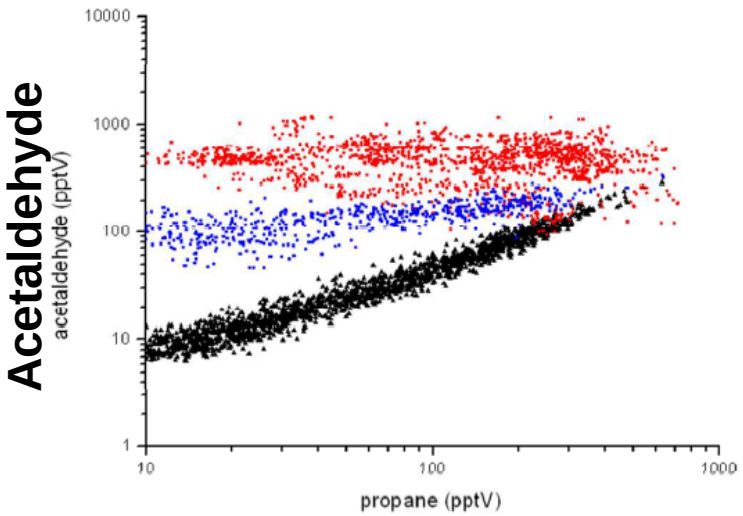








Propane



Propane

Std model

Ocean flux

Obs

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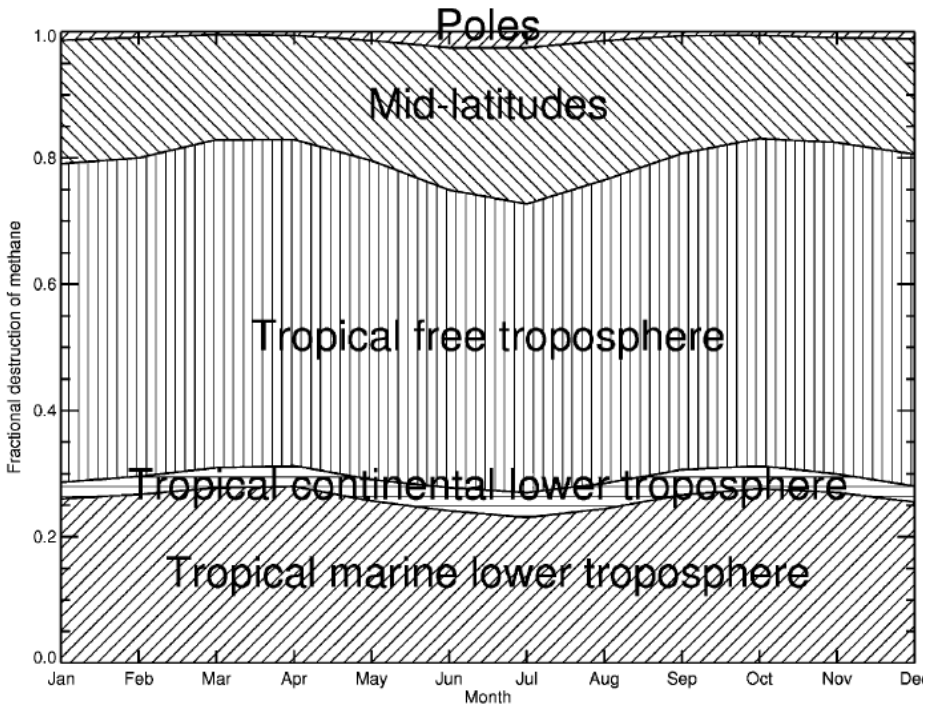
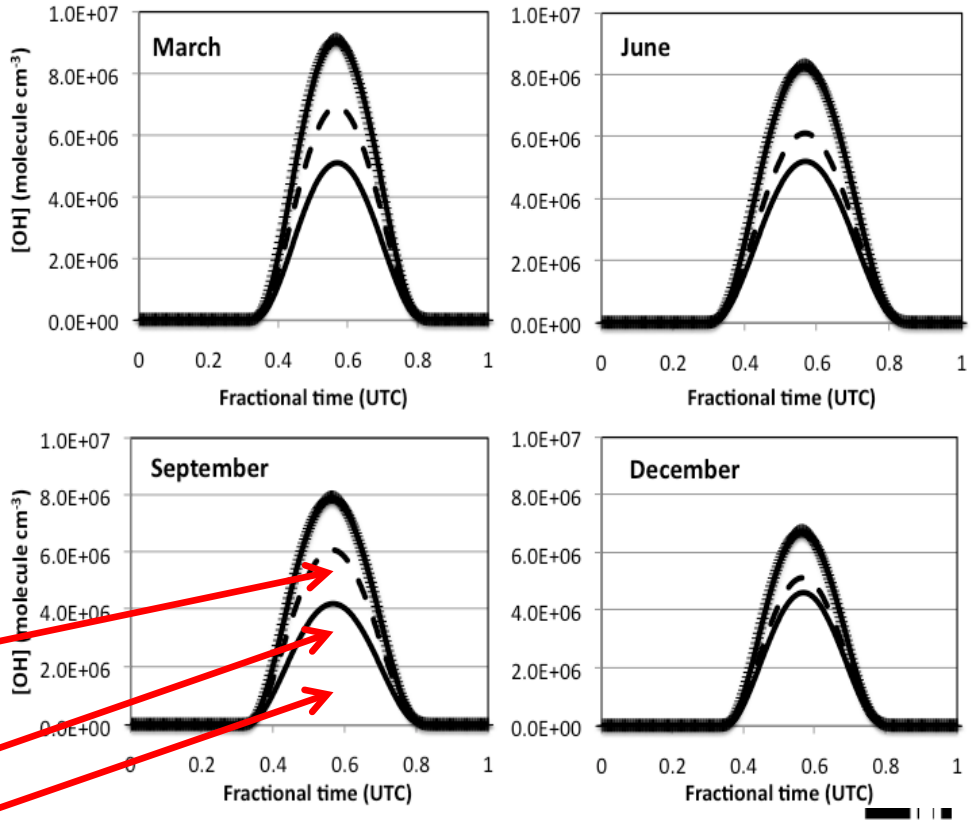
Impacts on oxidising capacity

20-25% of methane oxidation occurs in the tropical marine lower troposphere.



Bloss et al., (2005)

If assume oVOC model bias is consistent across marine tropics, then model methane lifetime may be underestimated by up to 8%.



Zero oVOCs

CAM-Chem oVOCs

Observed oVOCs

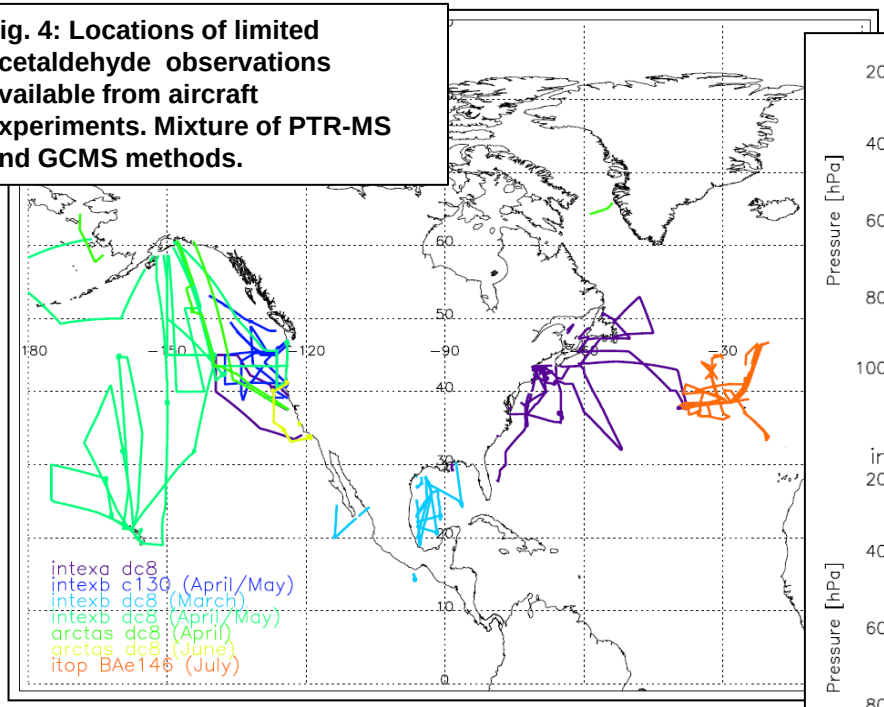
Read et al., (*submitted*)

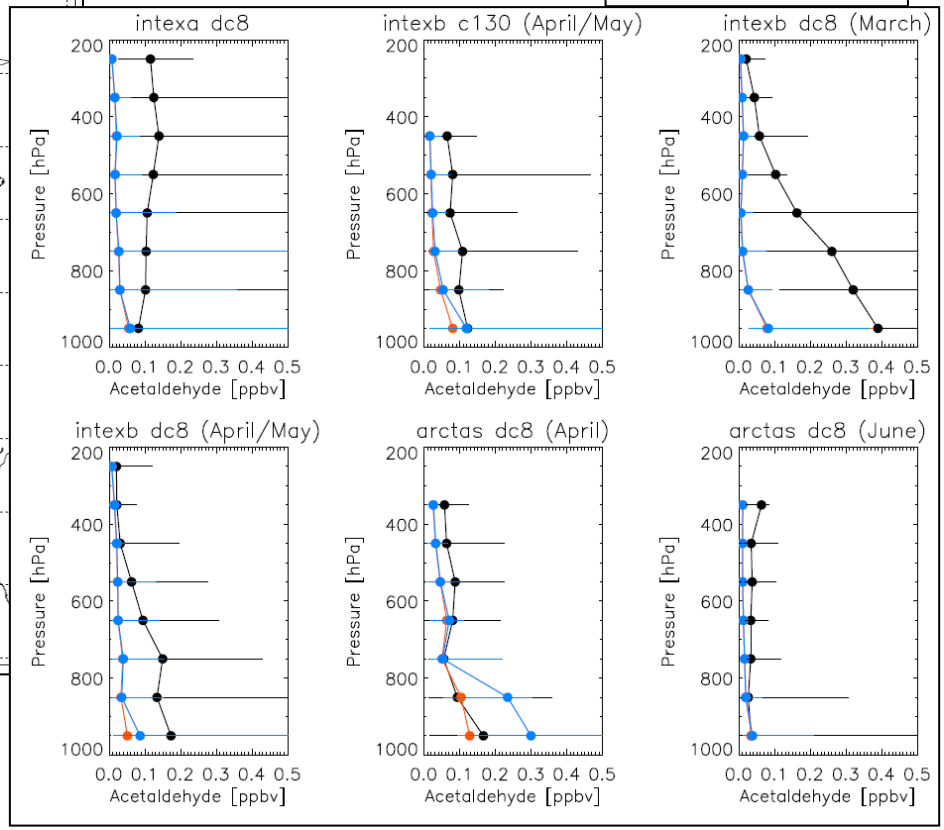
Acetaldehyde bias

Evaluation of remote marine acetaldehyde

Obs
CAM-chem (std)
CAM-chem with oVOC ocean fluxes

Fig. 4: Locations of limited acetaldehyde observations available from aircraft experiments. Mixture of PTR-MS and GCMS methods.





- **Large model bias through whole depth of marine troposphere (as seen by Millet et al., 2010).**
- **Ocean fluxes improve marine BL bias in some regions.**
- **Short CH_3CHO lifetime means free troposphere is unaffected by ocean fluxes.**

Fig. 5: Aircraft observations and model output both filtered for oceanic model grid-boxes only. Symbols indicate median binned values and lines are min/max ranges.

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Why does the model underestimate acetaldehyde?

1. **VOC 'lumping' / mechanism reduction?**

True chemical evolution of emitted VOC mixture likely not well represented.

2. Biogenic emissions?

Model biogenic emissions invariable with year. Simplified chemistry.

Addressing this now with updated online MEGAN model in CESM.

3. Indirect ocean source?

e.g. Monoterpenes & other hydrocarbons as CH_3CHO source

New NERC project (ORC^3) on marine VOC emissions at Cape Verde.

4. Is it a real bias?

Can we (the community) measure acetaldehyde?

Summary

CAM-Chem underestimates oVOCs over 5 year period at Cape Verde.

Implemented bidirectional sea-air flux parameterisation for VOCs in CESM.

Ocean fluxes improve model bias for acetaldehyde and methanol.

Model oVOC bias may constitute an OH bias and underestimate in model methane lifetime.

Acetaldehyde bias appears widespread & large through depth of remote atmosphere. Similarities to e.g. glyoxal [TORRERO, Volkamer et al.]

Model chemistry and / or biogenic sources and / or difficulties in measurement may contribute to bias.

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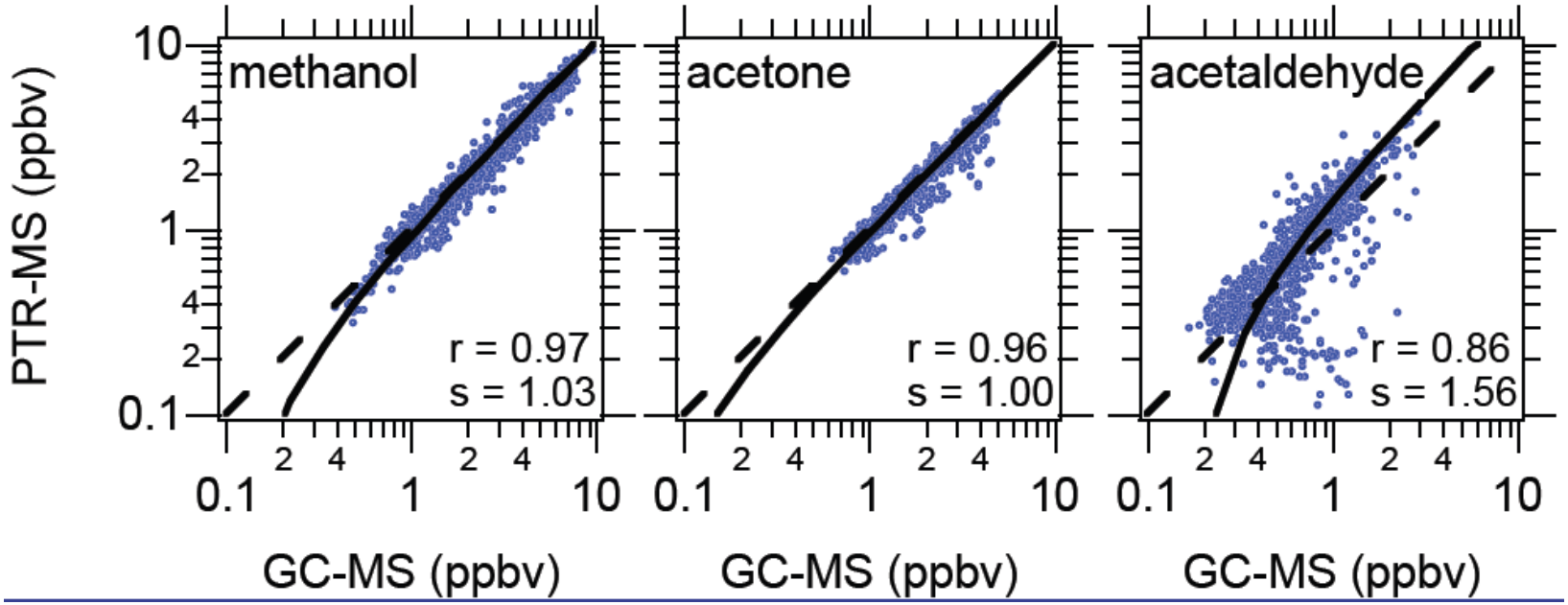
Instrument comparison (NEQS 2002)



De Gouw et al., (2003)

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