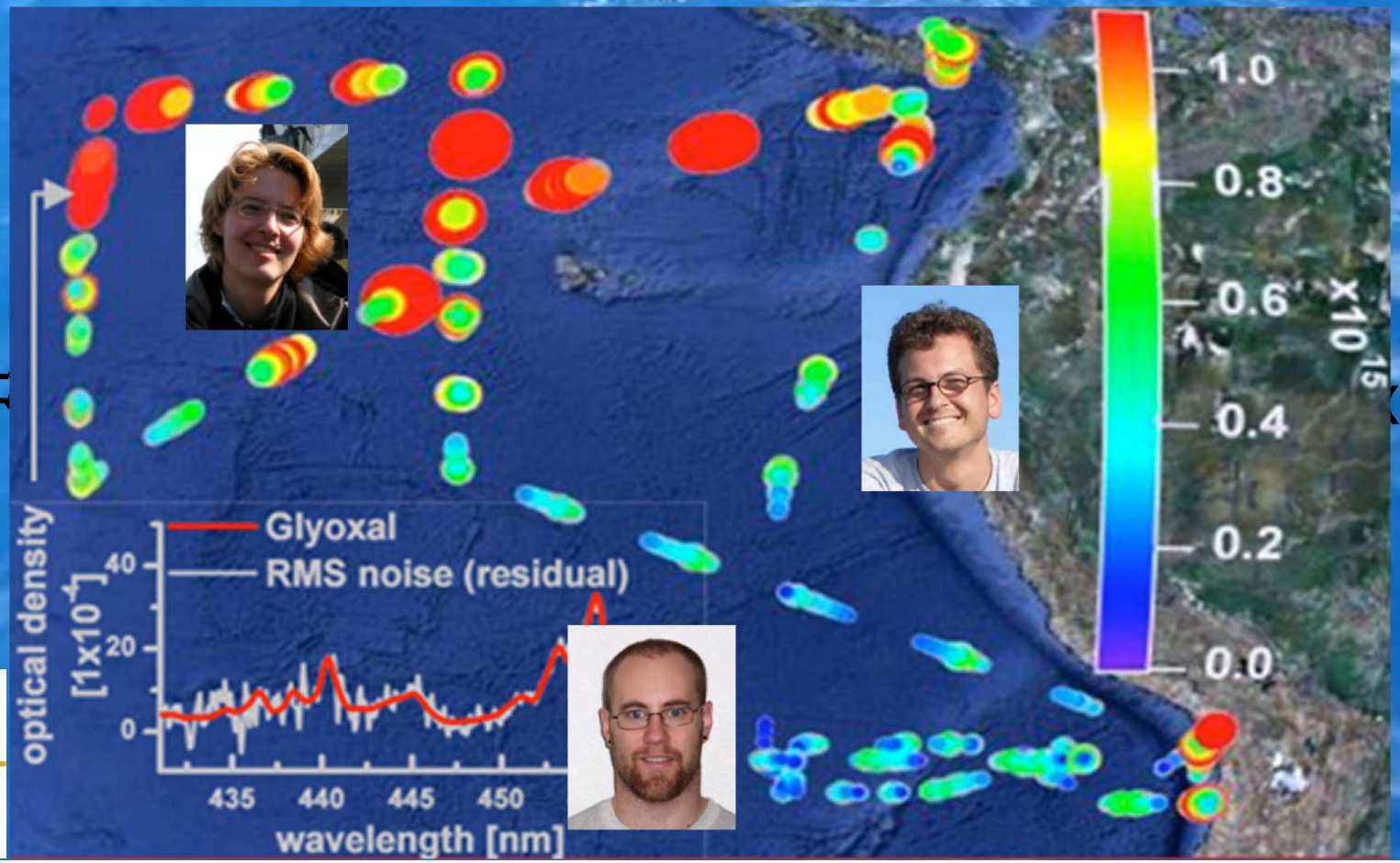
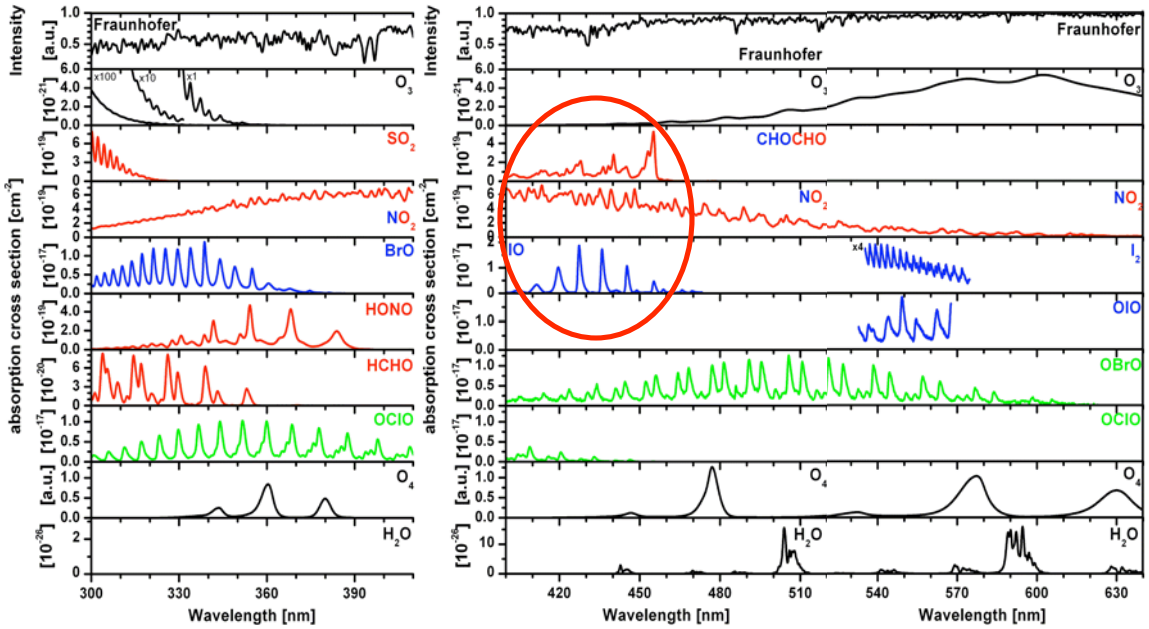
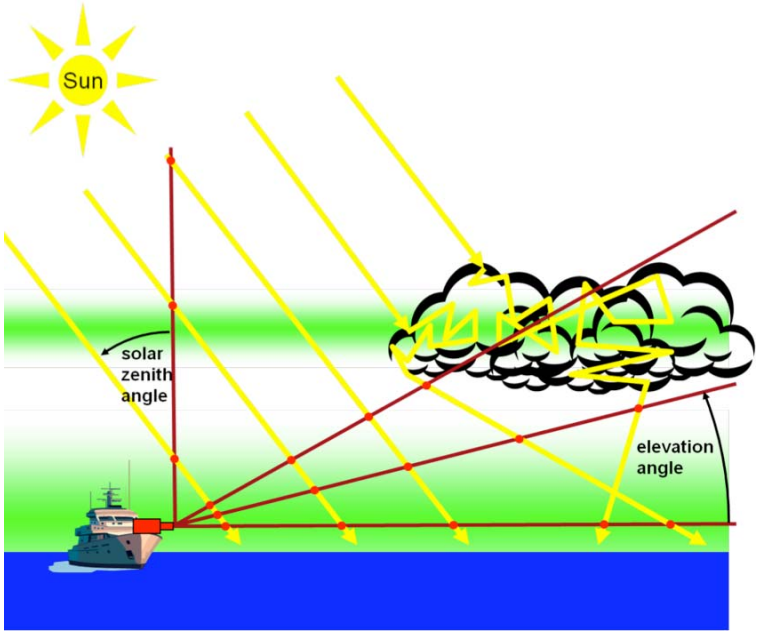
Direct observations of reactive trace gases over the eastern Pacific Ocean



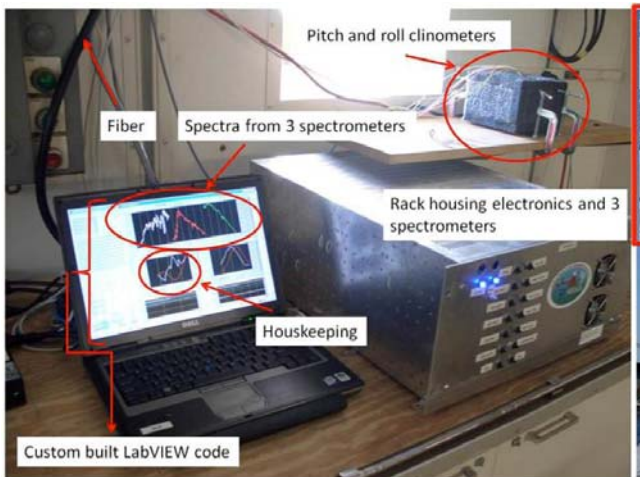
CU Ship MAX-DOAS

target gasses: CHOCHO, IO, HCHO, NO_2 (OIO, I_2, BrO, SO_2)

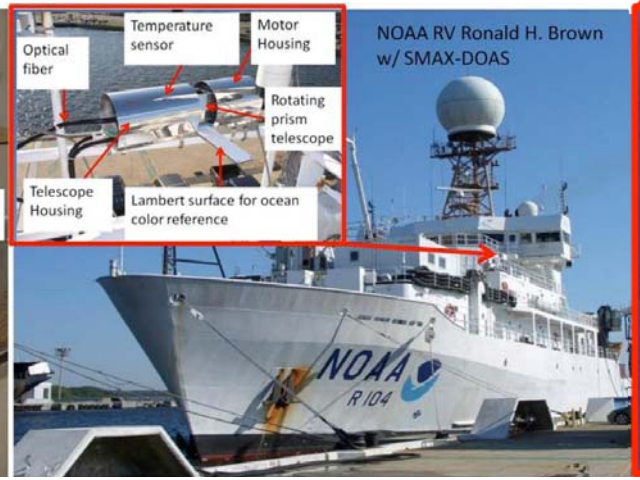




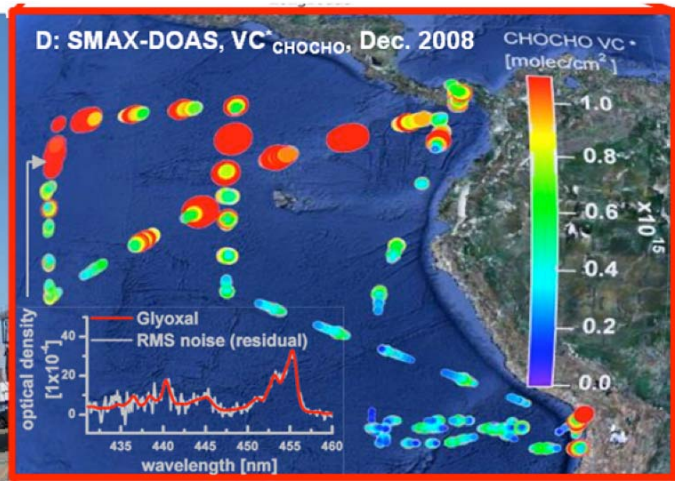
Inside: spectrometers/clinometers



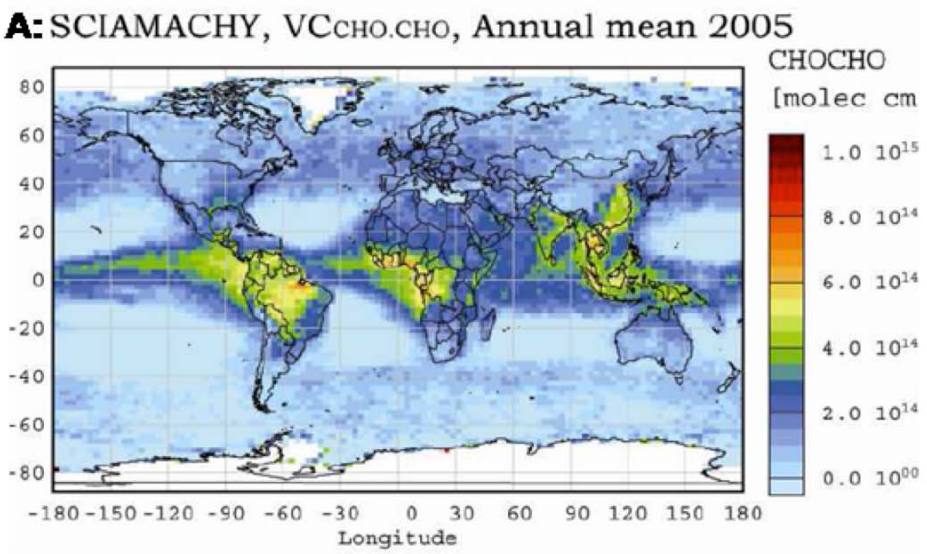
Outside: telescope

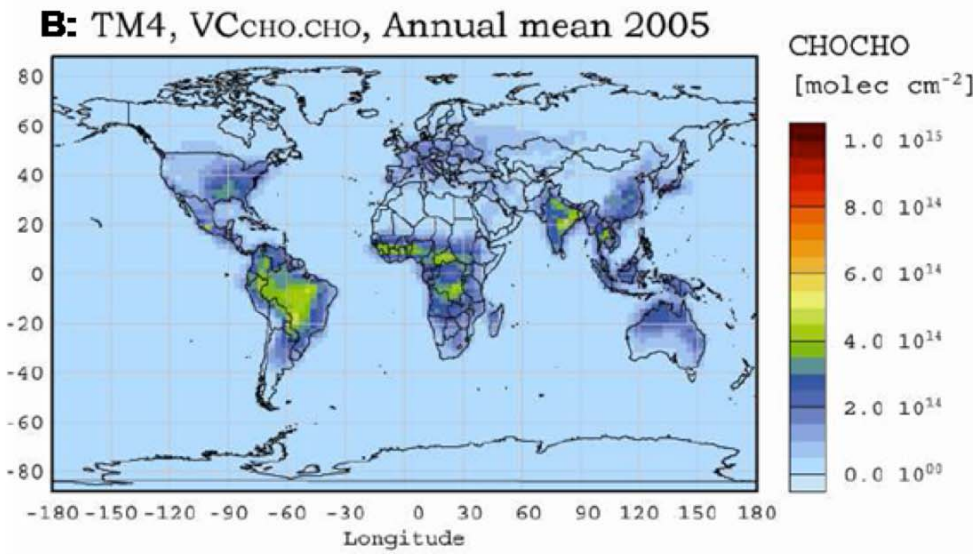


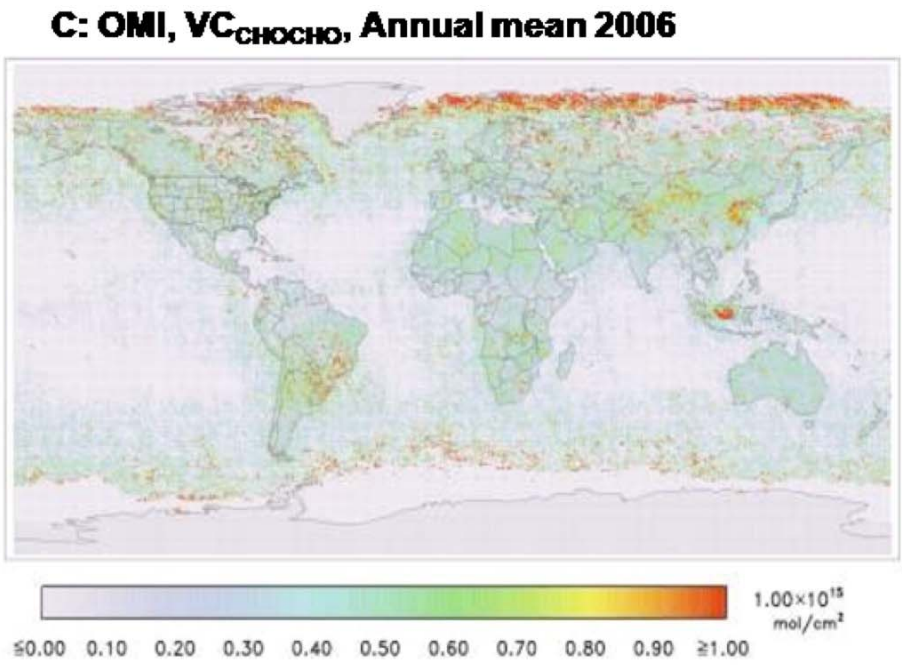
Cruise tracks (Oct08-Dec08)

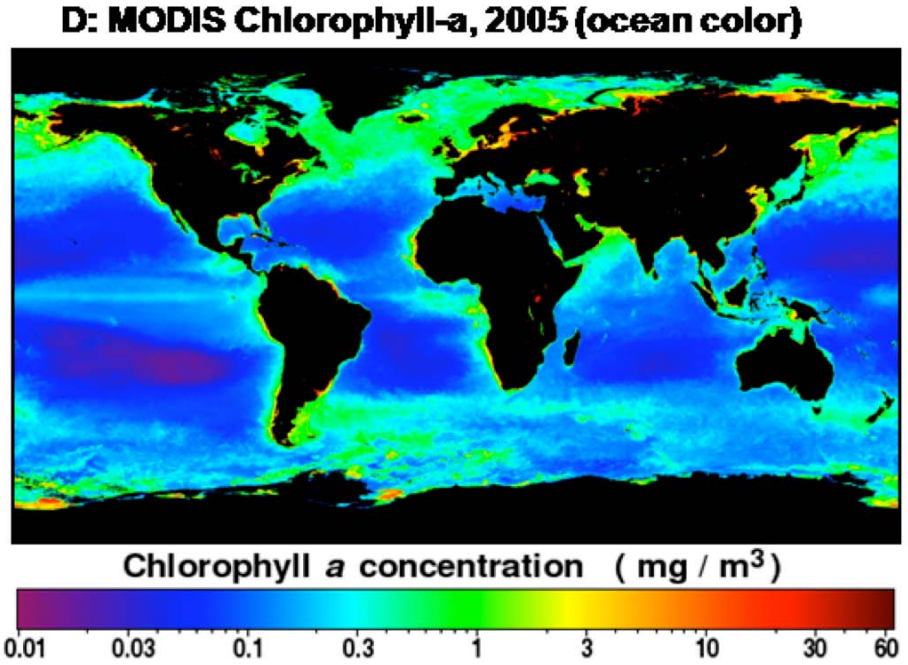


Objective: is there glyoxal over the ocean? Where could it be coming from?









Glyoxal (CHOCHO)

Global source α-dicarbonyls:

- Glyoxal: 40%
- Methylglyoxal: 55%
- Biacetyl: 5%

} > 185 Tg/yr (uncertain by factor 2)

Glyoxal source:

- 30% biogenic VOC (isoprene)
- 20% anthropogenic VOC
- 50% unaccounted land sources

} 108 Tg/yr

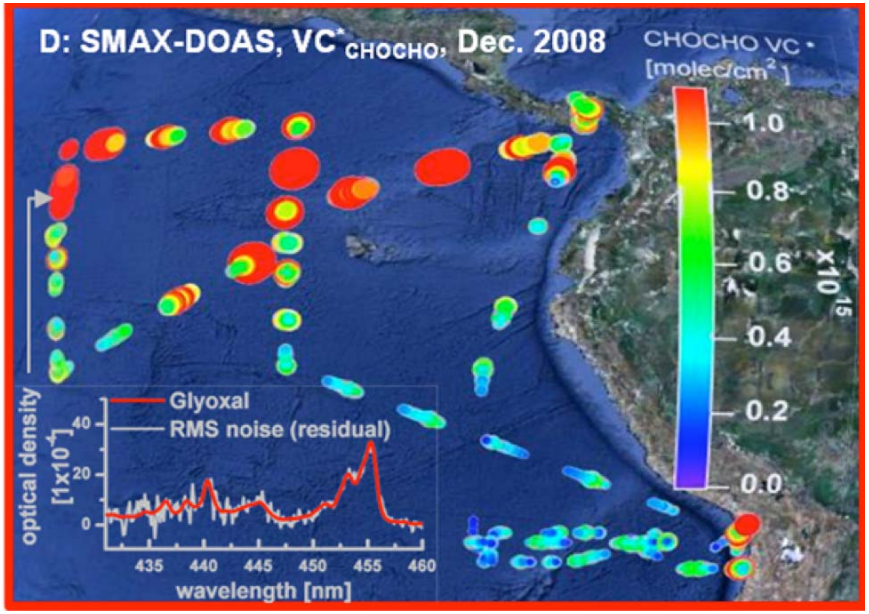
- Secondary sources dominate over primary sources
- biomass burning? (potentially 5-10 Tg/yr)
- ocean sources?
- energy sector, industry?

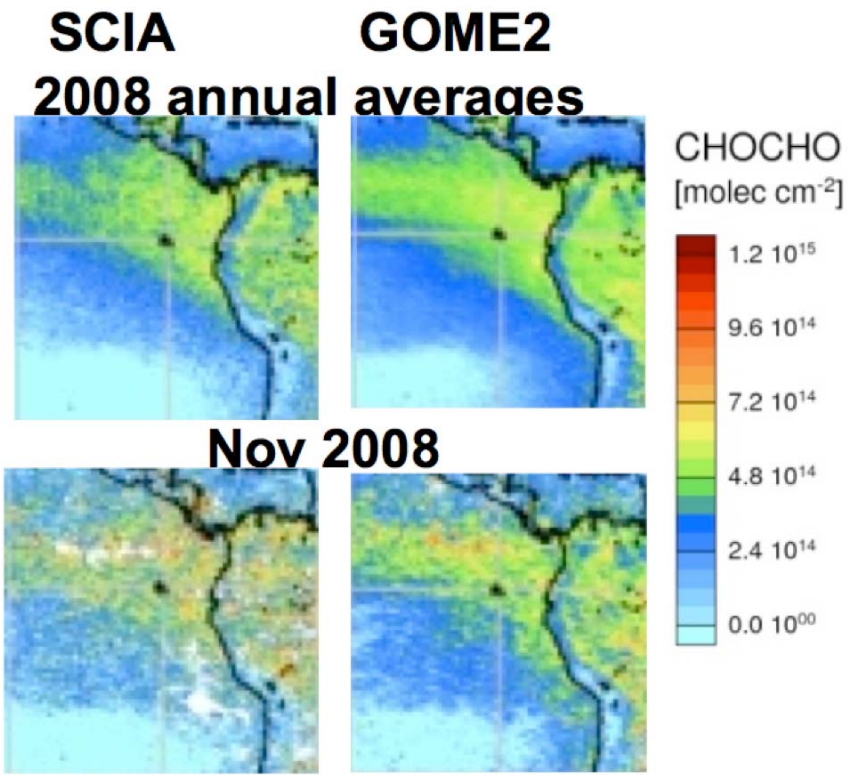
Atmospheric lifetime: <1.2h

- Photolysis (60%)
- OH-radical reaction (40%)
- aerosol loss timescales are uncertain (could determine 75 – 95% of the CHOCHO lifetime
- cloud processing timescales (few hours)
- Source for H_2, CO, HCHO and HO_2-radicals

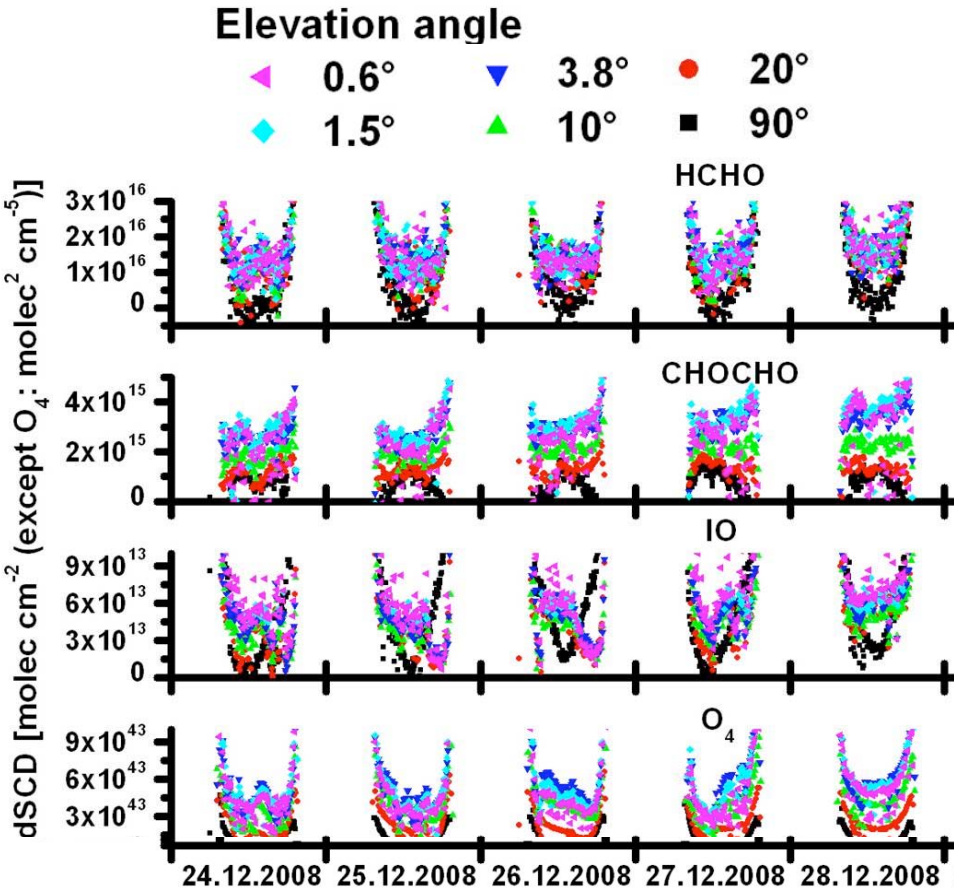
Global SOA source: 5-11 Tg/yr

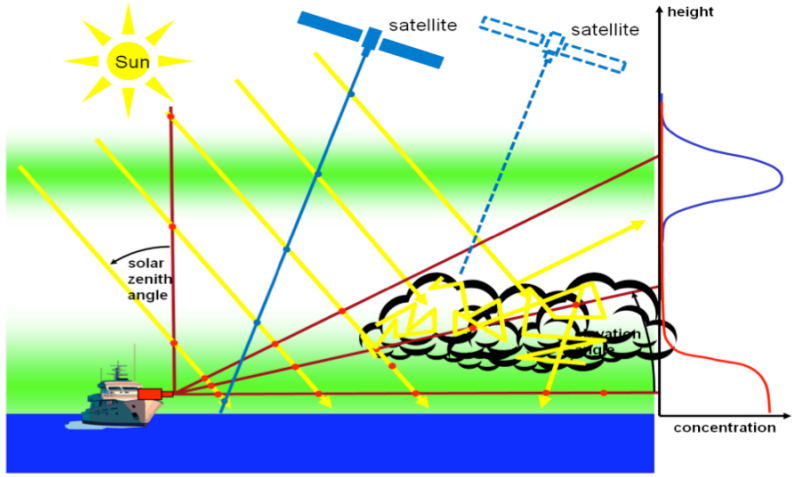
- Potentially comparable to aromatics and terpenes
- 85% deemed to form in clouds (?)
- Lower limit estimate (sources underestimated !)

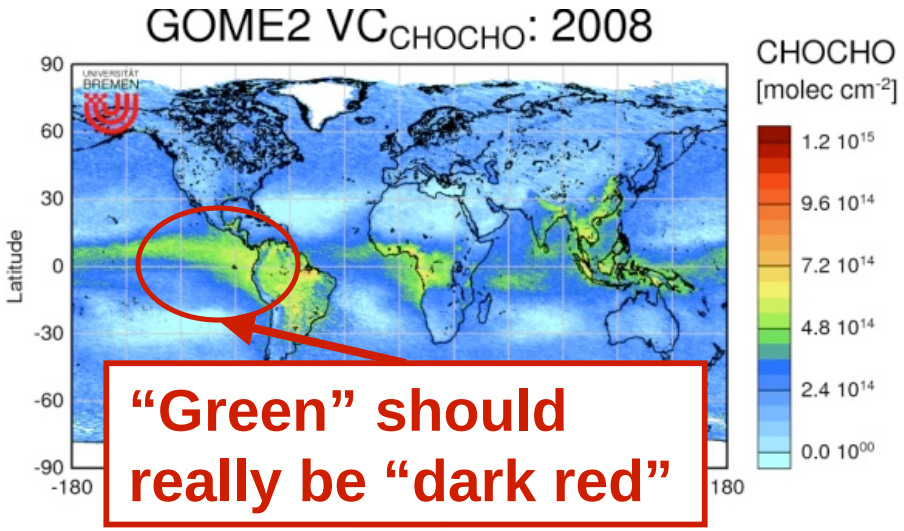




Vertical distribution: CHOCHO in MBL!

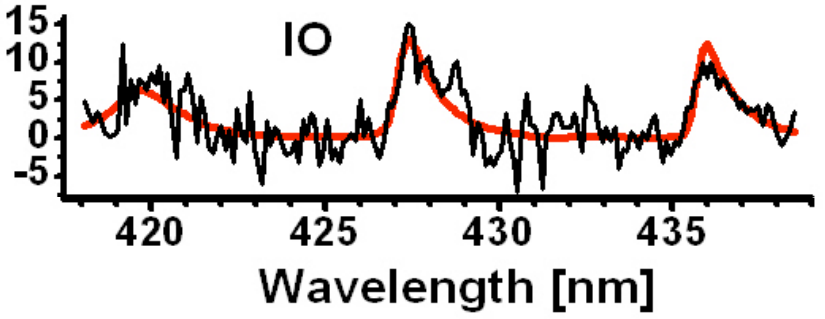






Satellite can not measure the vertical distribution (FT profile)
Higher VC by SMAX-DOAS can be explained by MBL profile
=> 2-4 times higher VC over oceans (largest globally!!)

Iodine oxide (IO)



Iodine sources:

- Highly uncertain on global scales
- Mostly constrained from studies in coastal environments: 1.5 Mg I yr^{-1} km^{-1}
- Very few observations over open ocean

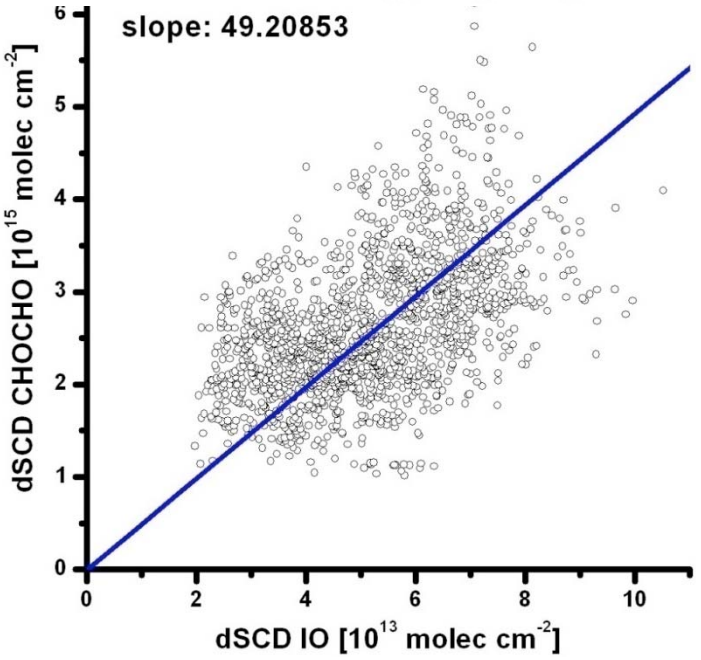
Currently suggested mechanisms:

- Production from alkylhalides
- I_2 from macroalgae (low tide)
- Cape Verde: current mechanisms are insufficient to account for observed IO
- I_2 from microalgae (?)
- Sea salt (?)

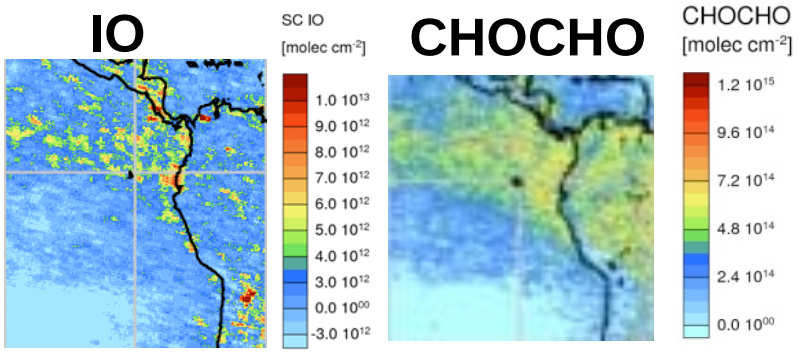
Atmospheric lifetime: sec

Atmospheric relevance:

- Destruction of trop ozone
- Oxidative capacity
- New particle formation/particle growth
- Mercury oxidation?



SCIAMACHY Oct-Dec 2008



Proposed reaction mechanism

Photoenhanced Reaction of Ozone with Chlorophyll at the Seawater Surface (Reeser et al., J. Phys. Chem. C **2009,** 113, 2071–2077):

$$CHL + hv \rightarrow CHL^* \rightarrow CHL^+ + e^-$$

$$CHL+ + Cl^- \rightarrow CHL + Cl$$

$$Cl + RH \rightarrow R + HCl$$

Correlations CHOCHO and IO suggest extended scheme:

$$CHL^+ + I^- \rightarrow CHL + I$$

$$I + I \rightarrow I_2$$

$$I_2 + hv \rightarrow 2I$$

$$I + O_3 \rightarrow IO + O_2$$

$$OH, Cl, Br + RH \rightarrow \rightarrow CHOCHO, HCHO$$

(chemical reason to accumulate I_2, but not Br_2 or Cl_2)

Conclusions

- Spectral proof for elevated glyoxal and IO over the open ocean (3000km from land) !
- Glyoxal and IO are located in the marine boundary layer
- Satellites underestimate VC by factor 2-4
- Tropical ocean is a global hotspot for CHOCHO
- Field evidence compatible with a chemical mechanism for halogen and OVOC release from surface photochemistry
- Tropics are chemically very active atmosphere: destroys ozone (IO), forms/grows aerosols (CHOCHO, IO)
- VOCALS: evidence for aerosol formation/growth from sources other than SO_2 (DMS)

Acknowledgements

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