Future directions for SOLAS Core Theme 5:

Ocean biogeochemical controls on atmospheric chemistry

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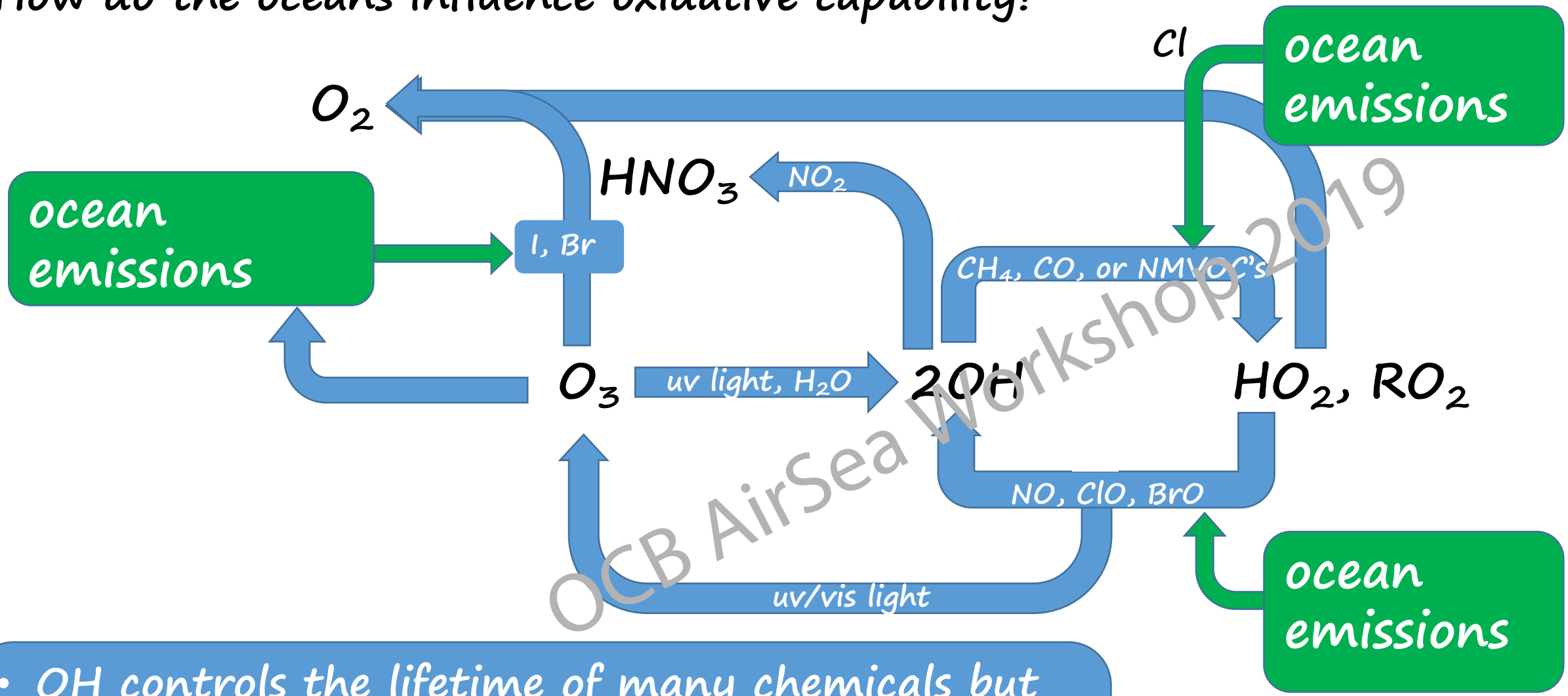
OCB Ocean-atmosphere interactions
scoping directions for US research
Arlington, VA, Oct. 2019

"Ocean emissions of reactive gases and aerosols influence *atmospheric photochemistry, air quality, and stratospheric ozone*"

- what are marine biogeochemical controls on *release of photochemically reactive gases into the atmosphere*?
- how will *future changes in ocean biogeochemistry and anthropogenic emissions* interact to influence tropospheric chemistry and stratospheric ozone?

influence on climate is implicit:
tropospheric chemistry and stratospheric ozone impact radiative forcing in many ways

How do the oceans influence oxidative capability?

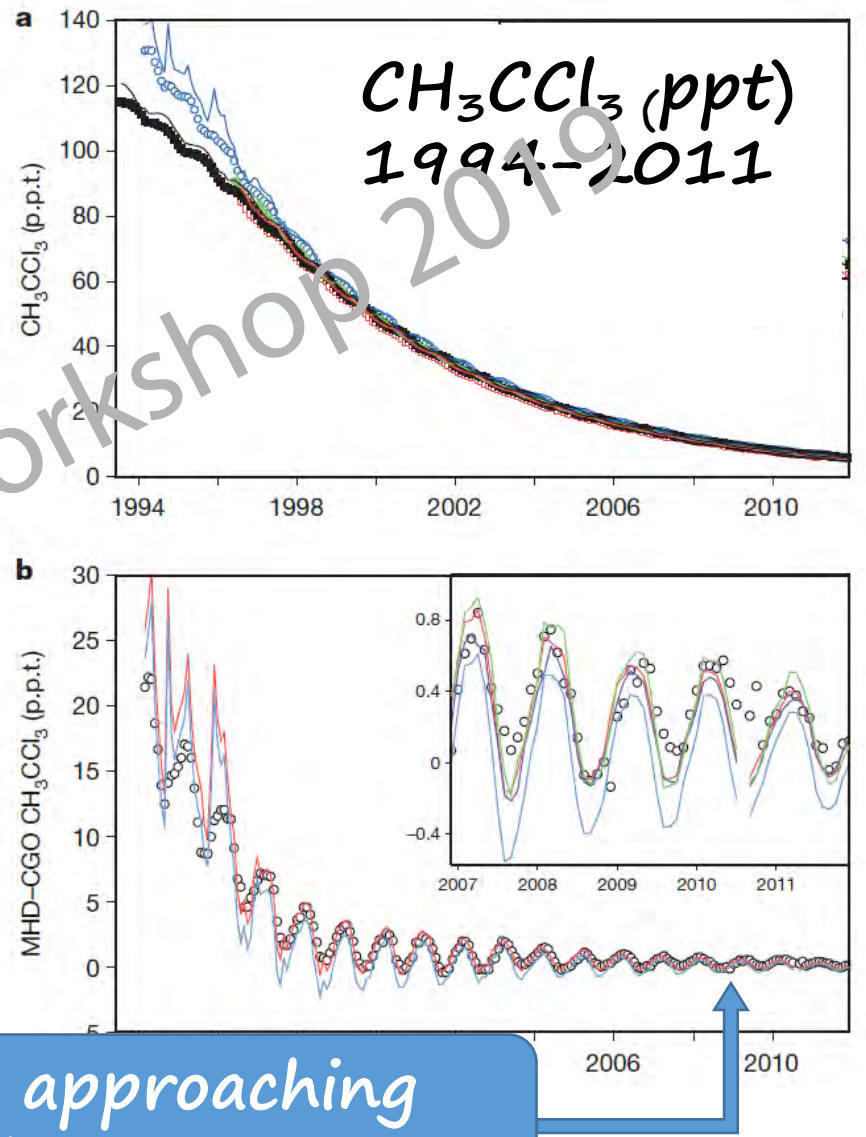


- OH controls the lifetime of many chemicals but only a few control OH levels
- How does the ocean impact atmospheric OH levels and how will OH evolve in the future?

How do we know it? ...methyl chloroform (CH_3CCl_3)

industrial emissions declining rapidly ✓✓
atmospheric distribution well known
lifetime ~5 years ✓

Patra et al., 2014



25 years of <u>really</u> good measurements show:

consistent with OH models

OH constant to within about 10%

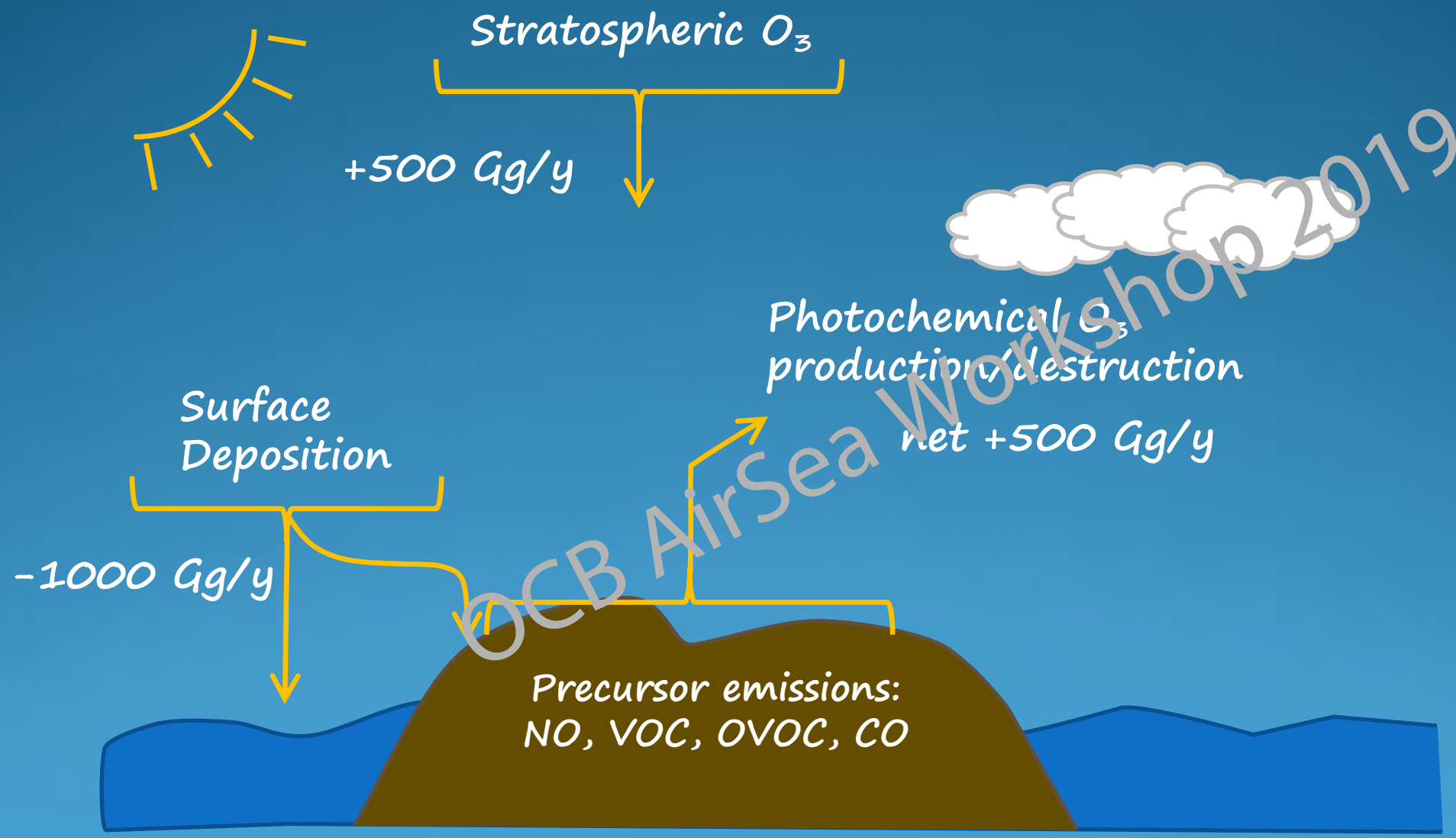
some evidence for impact of ENSO (tires)

$\frac{k_{gN}}{k_{gS}} \cong 1$ but models say $\frac{k_{gN}}{k_{gS}} = 1.2\text{–}1.3$

what's up with that?

N–S approaching zero!

Tropospheric ozone (and strat/trop coupling)

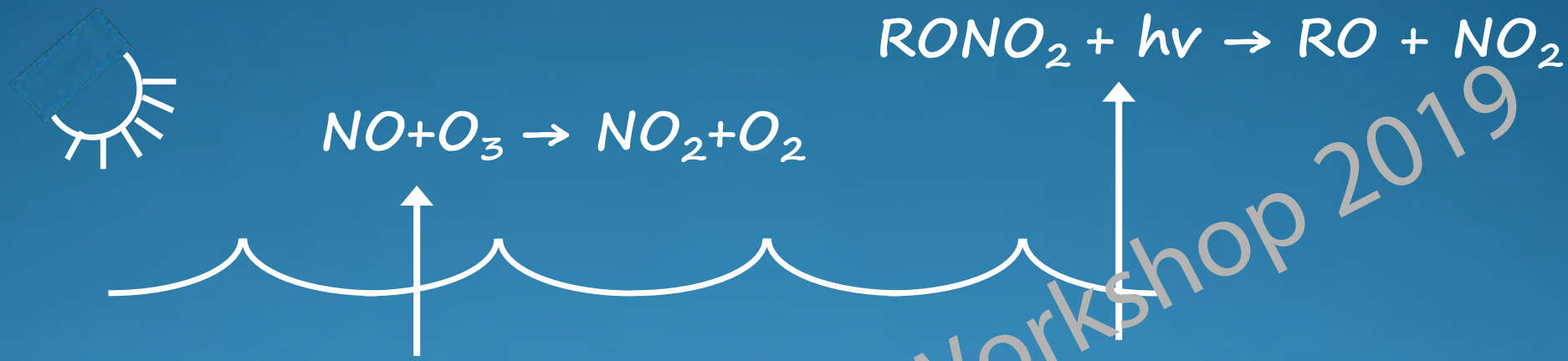


note: Δstrat O_3 affects trop O_3 (but not vice versa)

How does ocean biogeochemistry influence atmospheric oxidative capability and stratospheric ozone?

Oceanic emissions/uptake	Effect	Impact
CO, CH_4 emissions	Reduce OH, partially offset by O_3 production	↑↓
alkyl nitrate, NO emissions	Produce NOx, generate O_3 and OH	↑
emissions/uptake of OVOC's (acetone, acetaldehyde, …)	Produce/destroy trop O_3	↑↓
reactive iodine precursor emissions	Destroy trop O_3	↓
emissions of reactive bromine precursors	Destroy trop and strat O_3	↓
emissions of reactive chlorine precursors	Reduce methane lifetime, partially offset by O_3 destruction	↑↓

Cartoon #1: NO and alkyl nitrates



NO_2^- ⟶ $NO + ROO\cdot$ ⟶ $[ROONO]$ ⟶ $RONO_2$

nitrite — alkylperoxynitrite — alkyl nitrate

$CDOM + h\nu$ ⟶ $R\cdot + O_2$ organoperoxy radicals

direct biological production?

Dahl et al., 2003

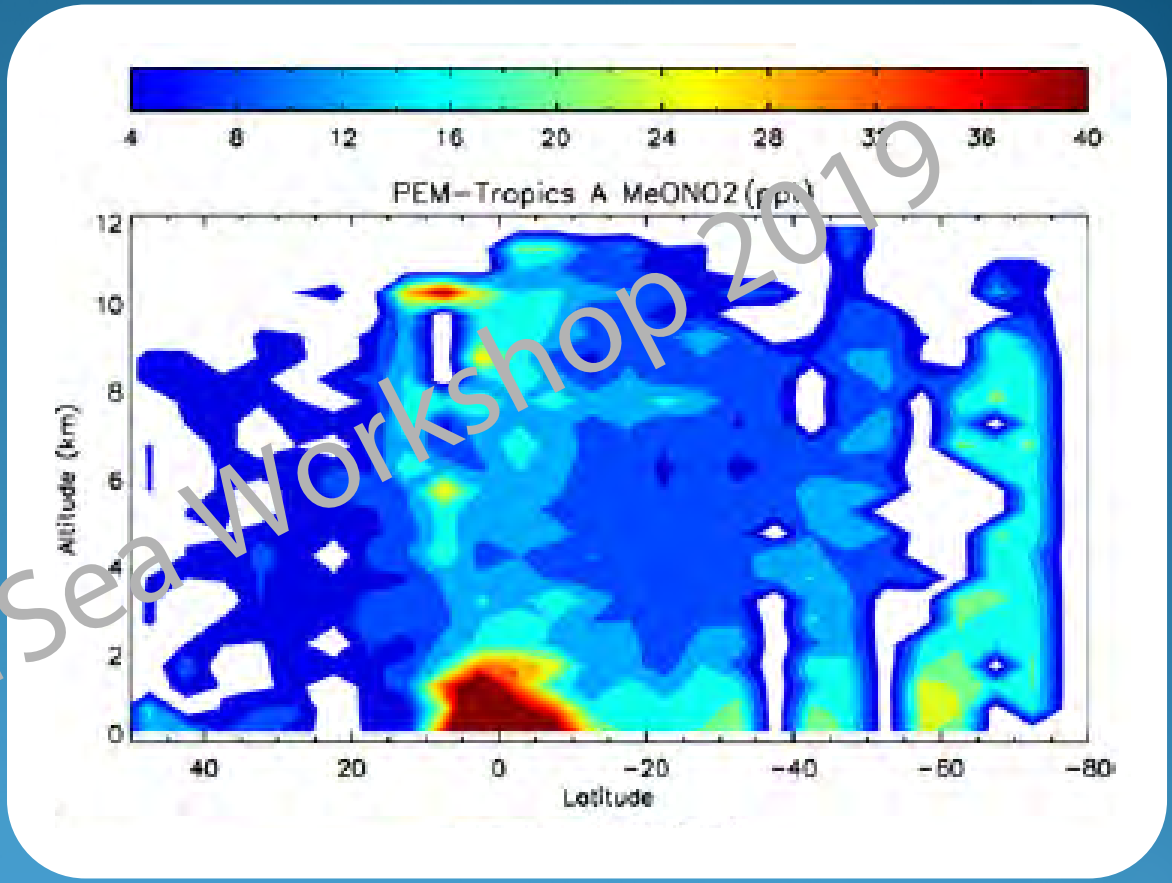
Methyl nitrate (CH_3ONO_2) over the equatorial Pacific

>30 ppt over equatorial upwelling

typically found in urban smog

$$RO + NO_2 \rightarrow RONO_2$$

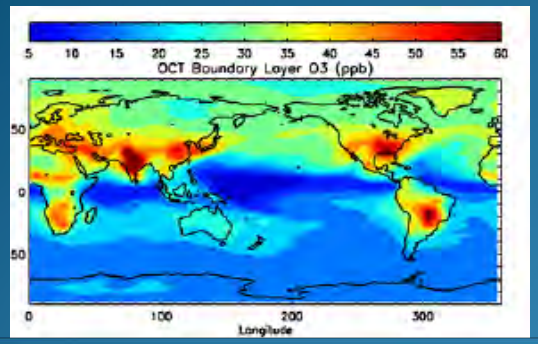
What are these compounds doing here?



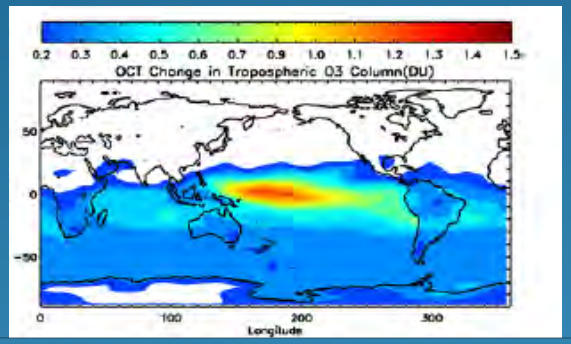
Blake et al., 2003
Chuck et al., 2002

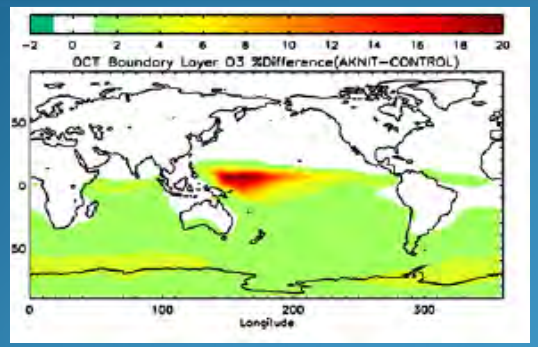
Alkyl nitrates and global oxidizing capability

Boundary layer O_3

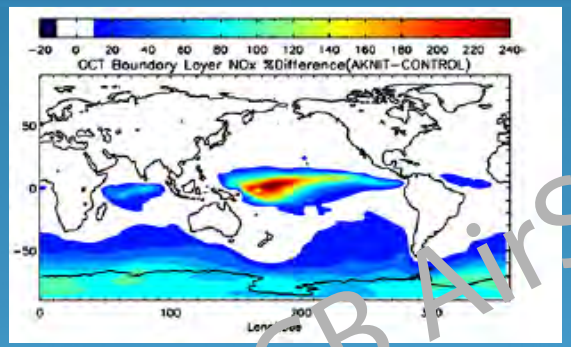


Δ Column O_3





Boundary layer Δ O_3



Boundary layer ΔNO_x

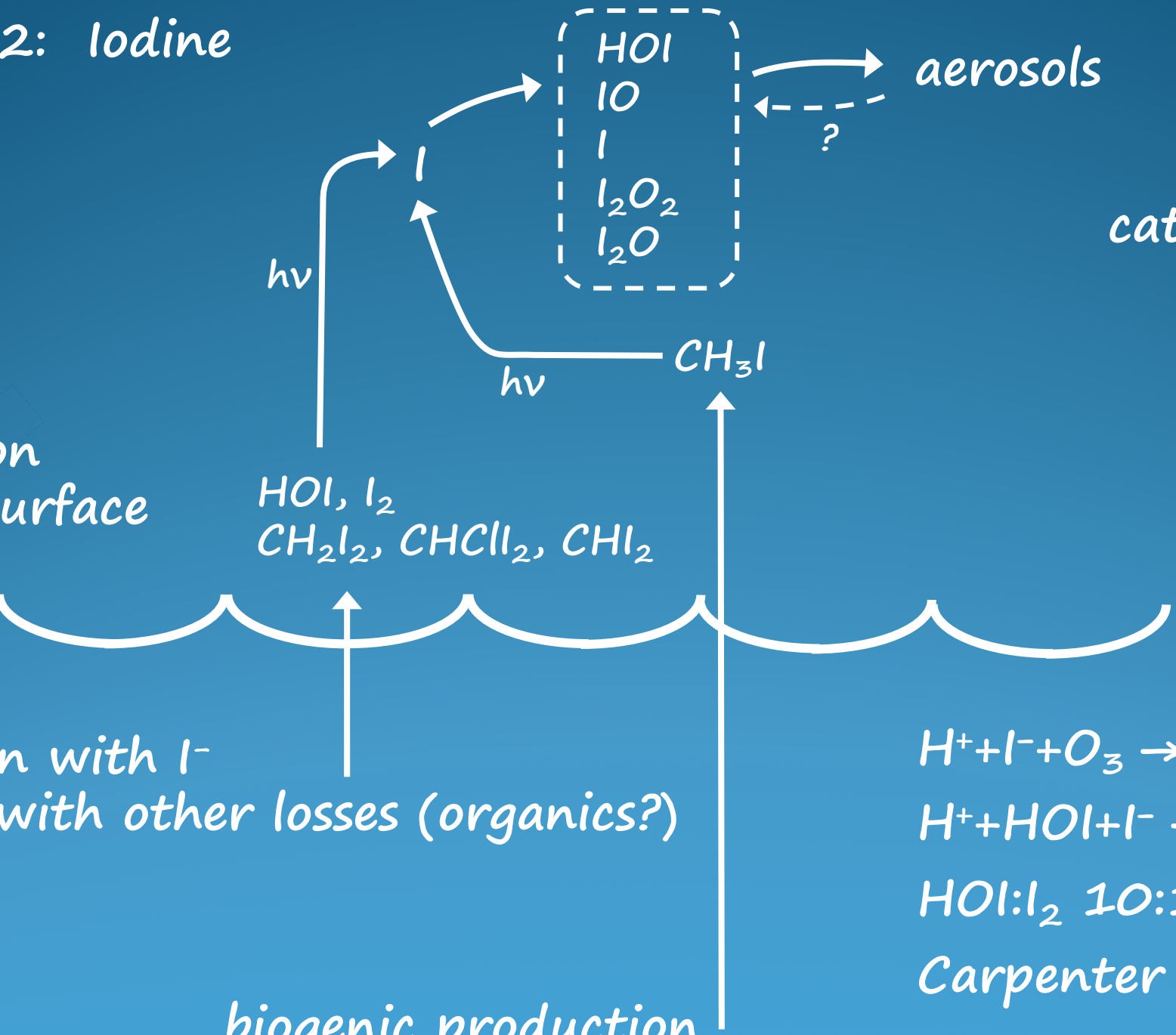
- 0.35 Tg N/year (global is ~46)
- 3D chemical transport model
- +1 DU tropospheric ozone
- 2-3% of global oxidative capability
- more O_3 per molecule than aircraft NOx

Future research:

- Atlantic vs Pacific... ATom?
- Process understanding... direct biological production?

Neu et al., 2008

Cartoon #2: Iodine



catalytic ozone loss:

$I+O_3 \rightarrow IO+O_2$

$IO+IO \rightarrow 2I+O_2$

$H^+ + I^- + O_3 \rightarrow HOI + O_2$

$H^+ + HOI + I^- \rightarrow I_2 + H_2O$

$HOI:I_2$ 10:1

Carpenter et al., 2013

Iodine (cont'd)...

many field obs. for iodomethanes

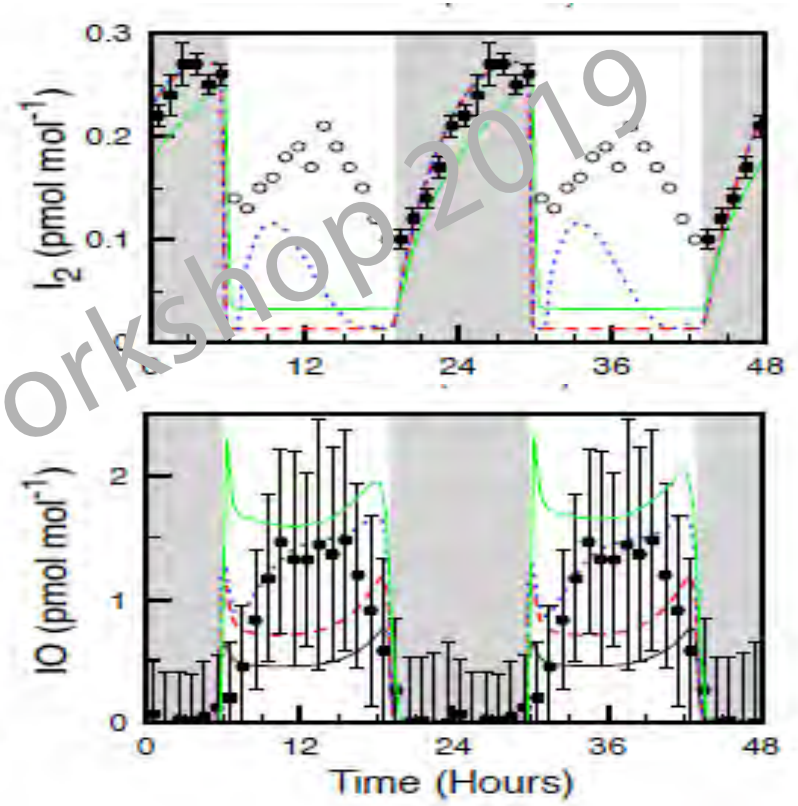
some field obs. for IO (a few for OIO)

very few for I_2 (1?)

none for HOI ... the major source!

models estimate 15-30% of O_3 loss in tropics

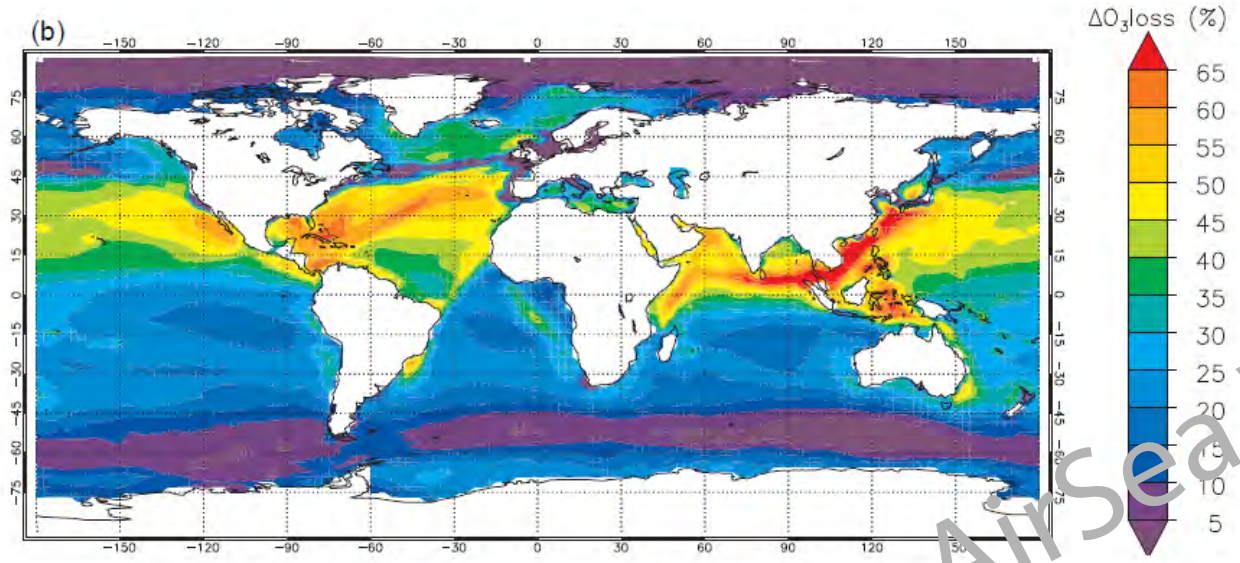
climate forcing

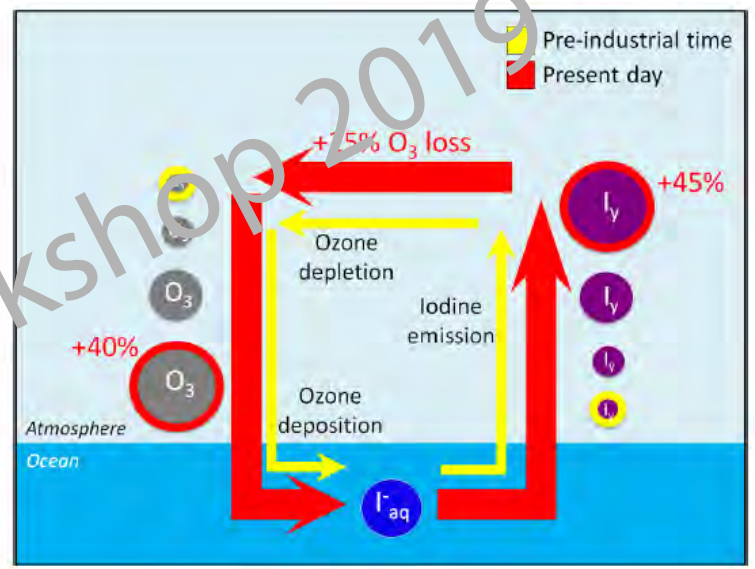


Cape Verde observations

Lawler et al., 2014

Proposed iodine/O_3 feedback loop





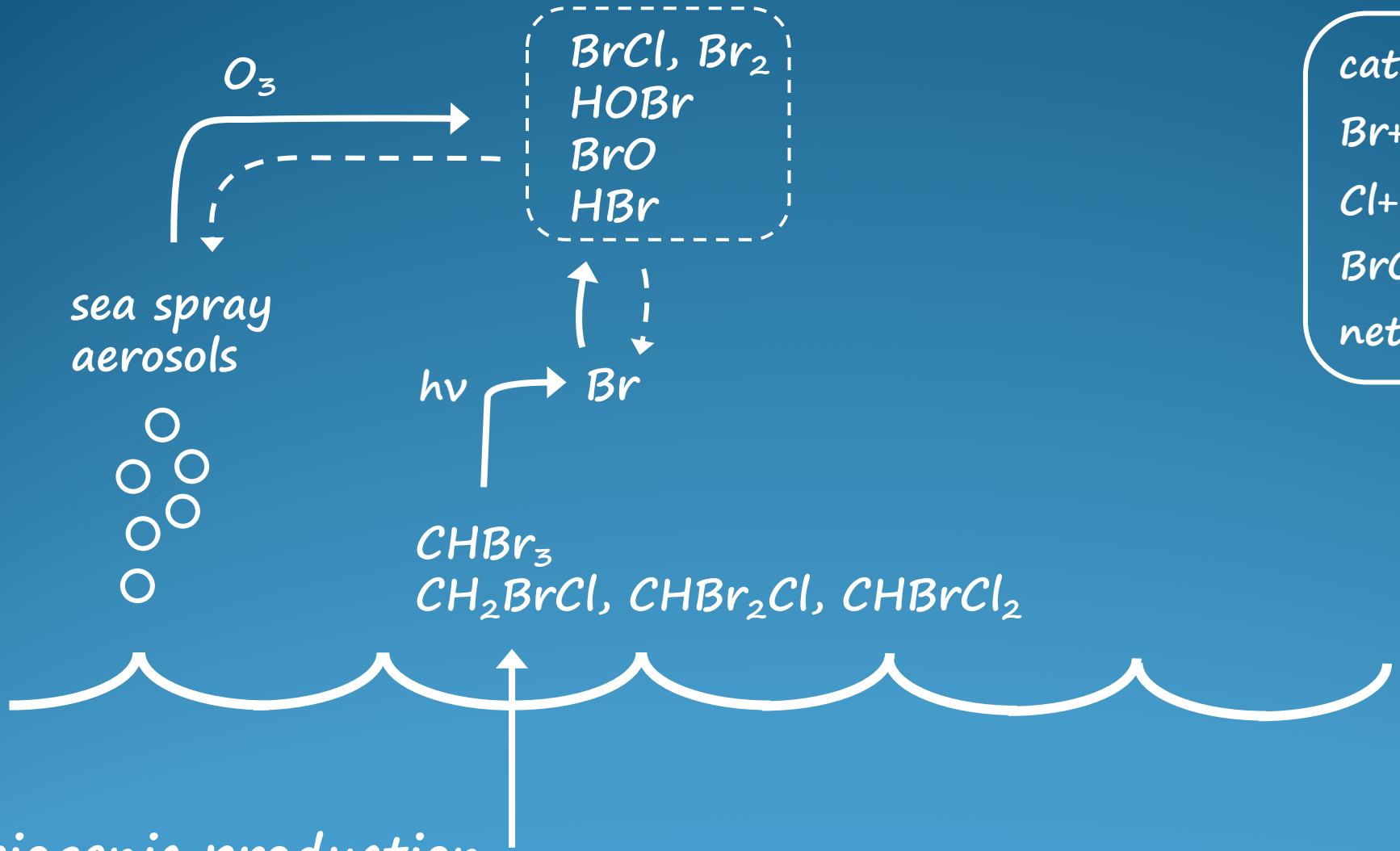
- I emissions doubled due to anthropogenic O_3
- negative feedback on trop O_3
- largely in tropics

Prados-Roman et al. 2015

Research agenda for iodine…

- large-scale biogeochemical controls on surface ocean iodide/iodate cycling
- explore I chemistry in the upper meter, what limits emissions?
- validate the HOI model of I ocean emissions with observations
- …do aerosols "recycle" iodine oxides? i.e. is aerosol uptake a one-way trip?
- …future changes?

Cartoon #3: seasalt and VSLS bromine



catalytic ozone loss

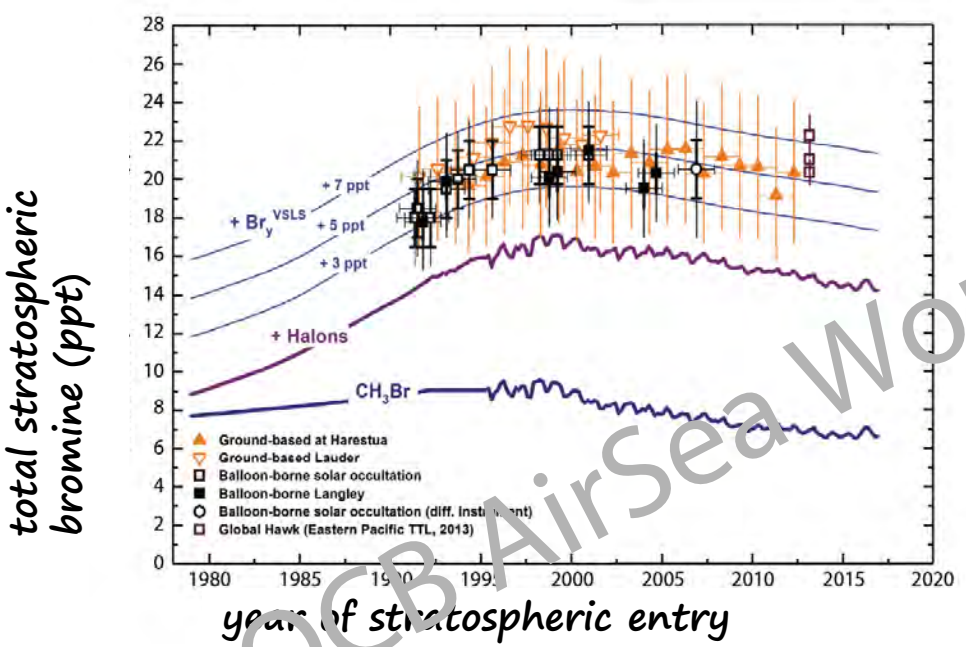
$Br + O_3 \rightarrow BrO + O_2$

$Cl + O_3 \rightarrow ClO + O_2$

$BrO + ClO \rightarrow Br + Cl + O_2$

net: $2O_3 \rightarrow 3O_2$

Bromine and stratospheric ozone depletion…



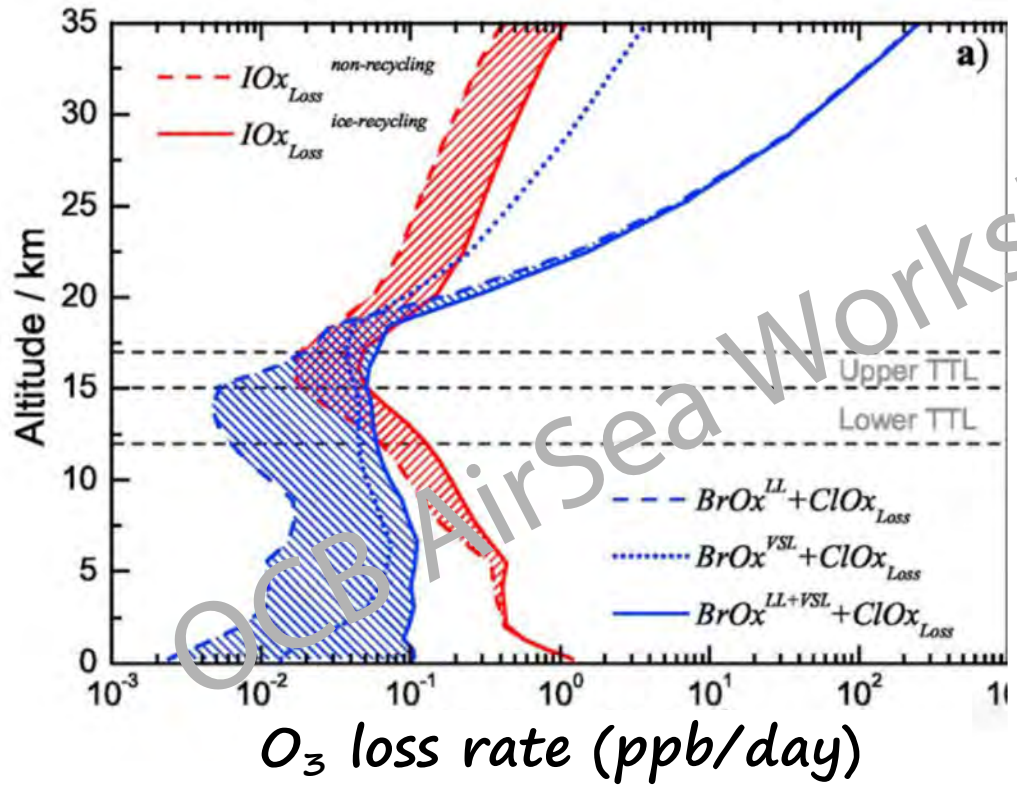
VSLS ($CHBr_3$ etc.)

Halons

CH_3Br

Engel and Rigby, 2018

Bromine and stratospheric ozone depletion...



Longer-lived

VSLS ($CHBr_3$ etc.)

Saiz-Lopez et al., 2014

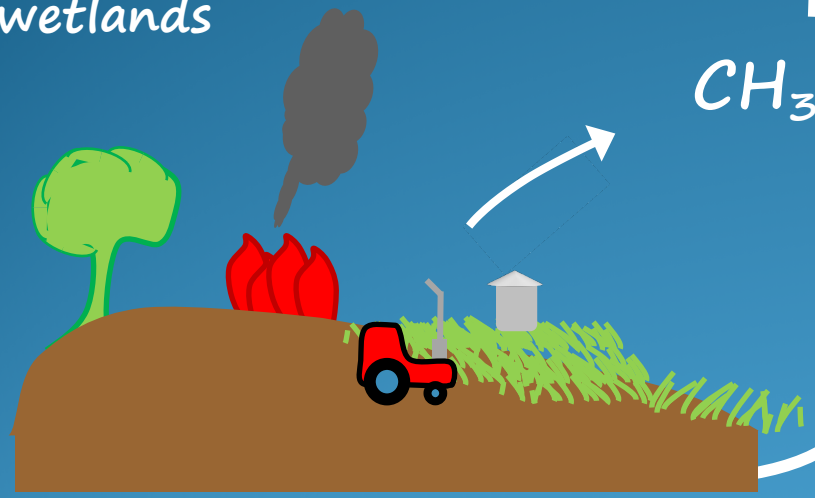
Research questions for seasalt and VSLS bromine...

- atmospheric impact of Br on O_3 ... sensitivity to aldehydes
- need for Br lifetime studies?
- bromination of marine aerosol organics?
- large-scale biogeochemical controls on VSLS Br... future changes?

Cartoon #4: methyl bromide

stratosphere catalytic O_3 loss

Terrestrial emissions:
- fumigation
- biofuels
- biomass burning
- wetlands



hν → Br ⇄ HOBr, BrO, HBr, BrCl → aerosols

CH_3Br

reaction with OH
photolysis
0.9 year lifetime

air/sea gas exchange

oceanic production
phytoplankton, bacteria, fungi?

oceanic loss
hydrolysis, chloride substitution
bacteria

oceanic uptake and emissions
~1/2 CH_3Br produced is emitted
1990's Ocean was net sink

Methyl bromide …

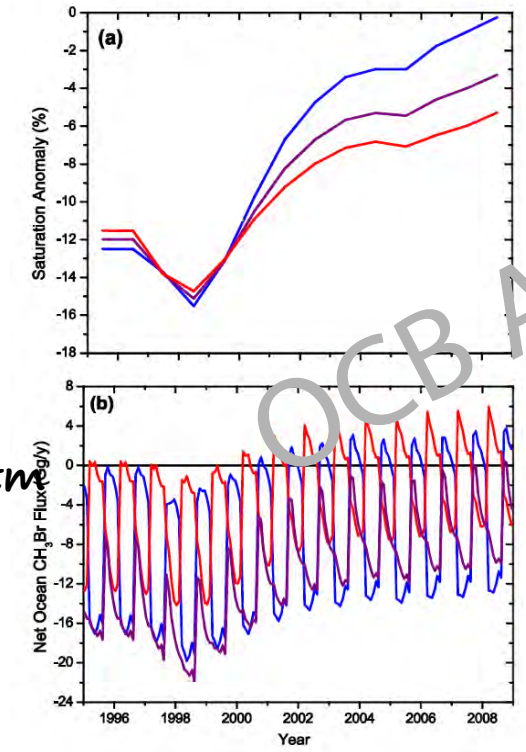
- atmospheric levels declining following Montreal Protocol phaseout
- ocean response/feedback predicted
- is the ocean supersaturated yet?

real data!

model

N, S, Global saturation anomaly (%)

net ocean/atm flux Gg/y

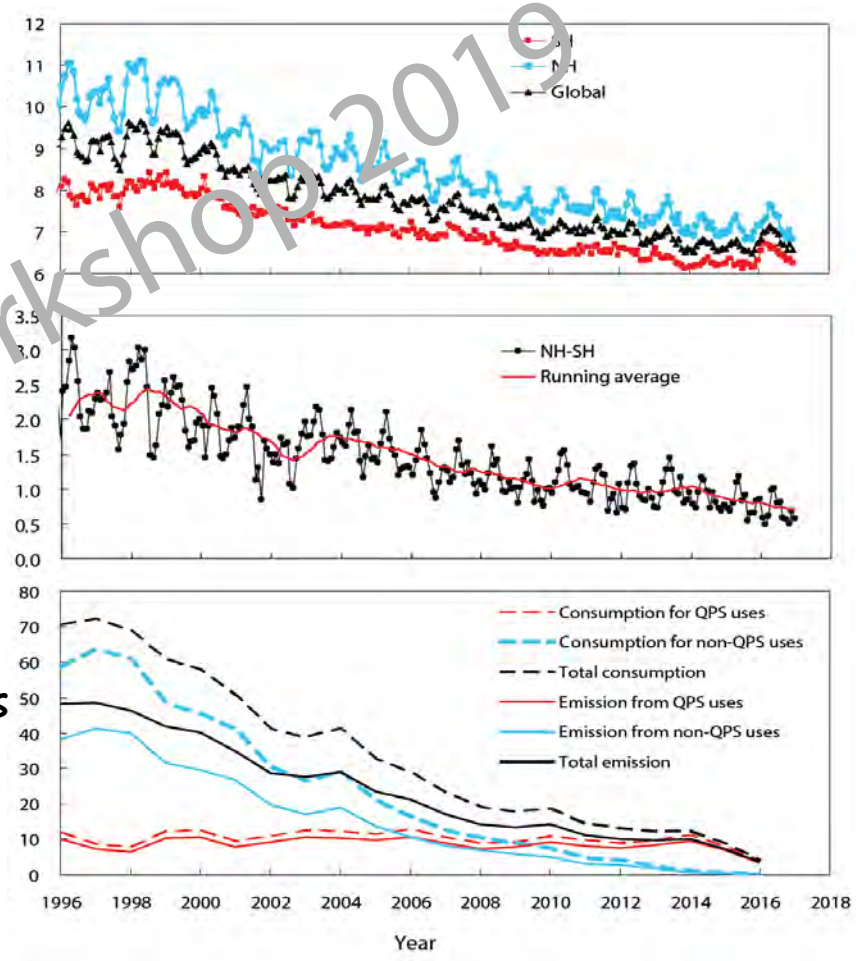


Yvon-Lewis et al., 2009

CH_3Br (ppt)

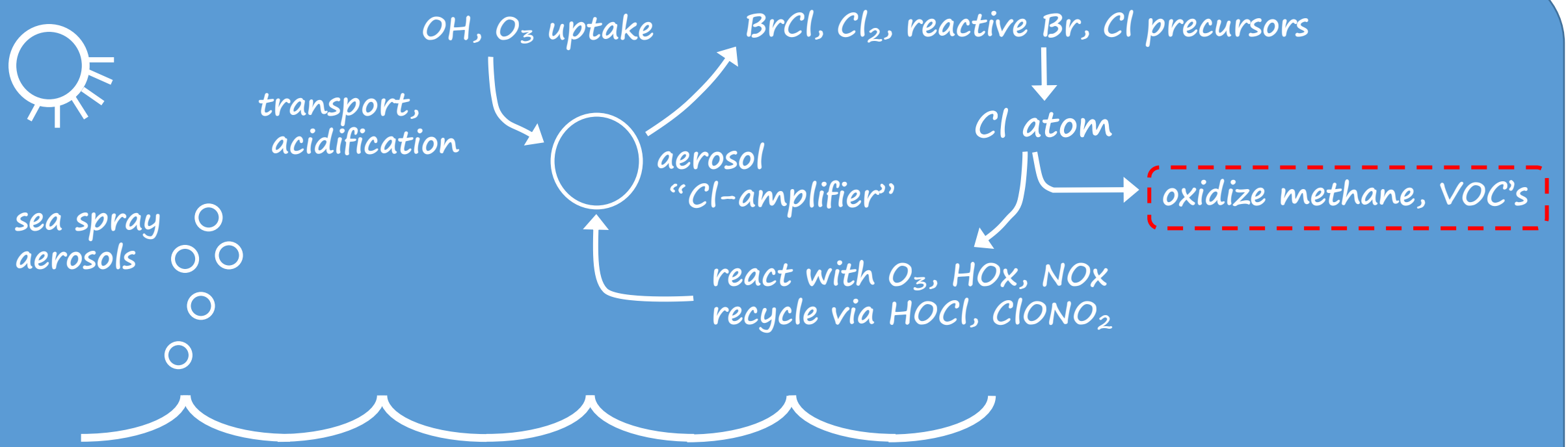
N-S (ppt)

QPS Emissions (Gg/y)



Engel and Rigby, 2018 (WMO)

Cartoon #5 Reactive Cl...



Indirect estimates .... 10^3–10^5 Cl atoms/cm^3

at 6×10^4 cm^{-3} Cl, 10^6 cm^{-3} OH (T 298K)

$L_{CH4\_Cl} = L_{CH4\_OH}$!

such reactivity would not be detected in the methylchloroform budget

Three Cl chemistry regimes …

Highly polluted regions ✓

acidic aerosols, high NOx

$N_2O_5 + Cl^-_{aerosols} \rightarrow \rightarrow ClNO_2$

Continental outflow regions ?

seasalt + acidity + moderate NOx

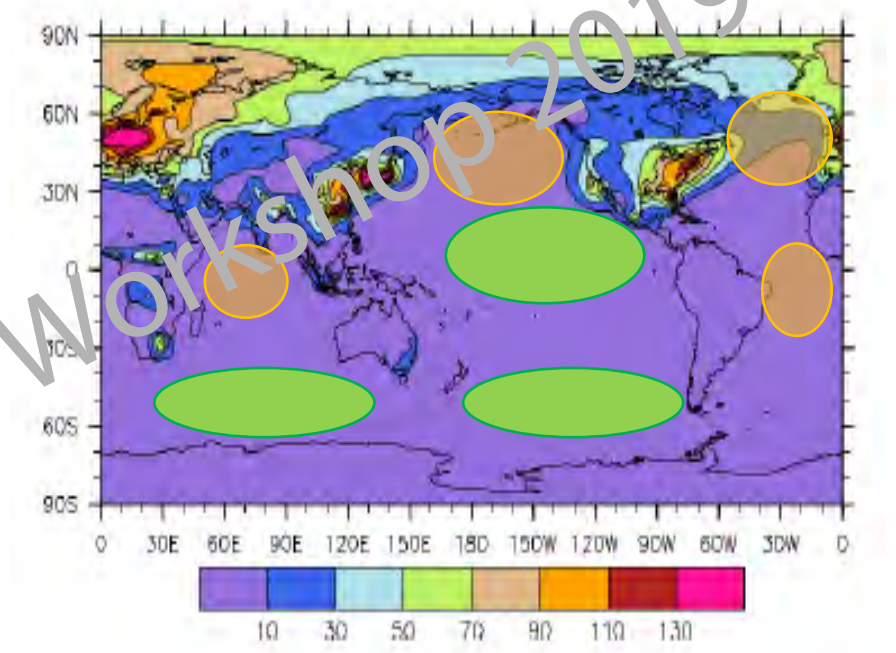
$ClO + NO_2 \rightarrow ClONO_2$

$ClO + HO_2 \rightarrow HOCl$

Remote ocean regions ?

seasalt + natural acidity + low NOx

$ClO + HO_2 \rightarrow HOCl$



$ClNO_2$ (pmol mol^{-1})

Long et al., 2013

Three Cl chemistry regimes …

Highly polluted regions ✓

acidic aerosols, high NOx

$N_2O_5 + Cl^-_{aerosols} \rightarrow \rightarrow ClNO_2$

Continental outflow regions… maybe?

seasalt + acidity + moderate NOx

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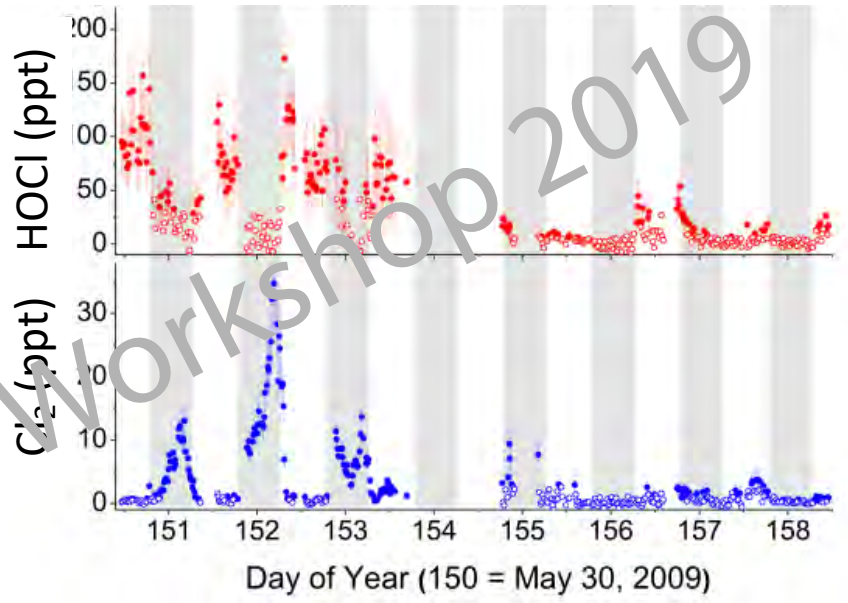

Cape Verde

daytime 60-120 ppt HOCl

nighttime 15-30 ppt Cl_2

Lawler et al., 2011

Research questions for reactive Cl

- does Cl in outflow and remote regions significantly impact global methane lifetime?
- generation/cycling mechanisms…identify the Cl atom precursor, quantify controls on the marine aerosol "amplifier gain"?
- is Cl activated by natural acidity over phytoplankton blooms?
- has Cl reactivity changed over the 20th century due to aerosol acidification?

Some final thoughts:

- How will warming/stratification impact all of these issues in the long term?
- How will oxidation capability change post-fossil fuels?
- Can/should we observe interannual or decadal variability in atmospheric chemistry due to changes in ocean biogeochemistry?
- Is the scale of our research sufficient to answer such questions?

The end.