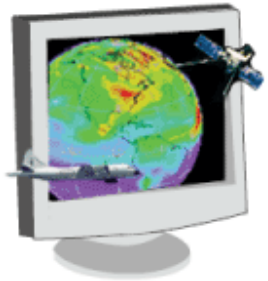
Oxidant chemistry in the tropical troposphere: role of oxygenated VOCs and halogens, and implications for mercury

Daniel J. Jacob

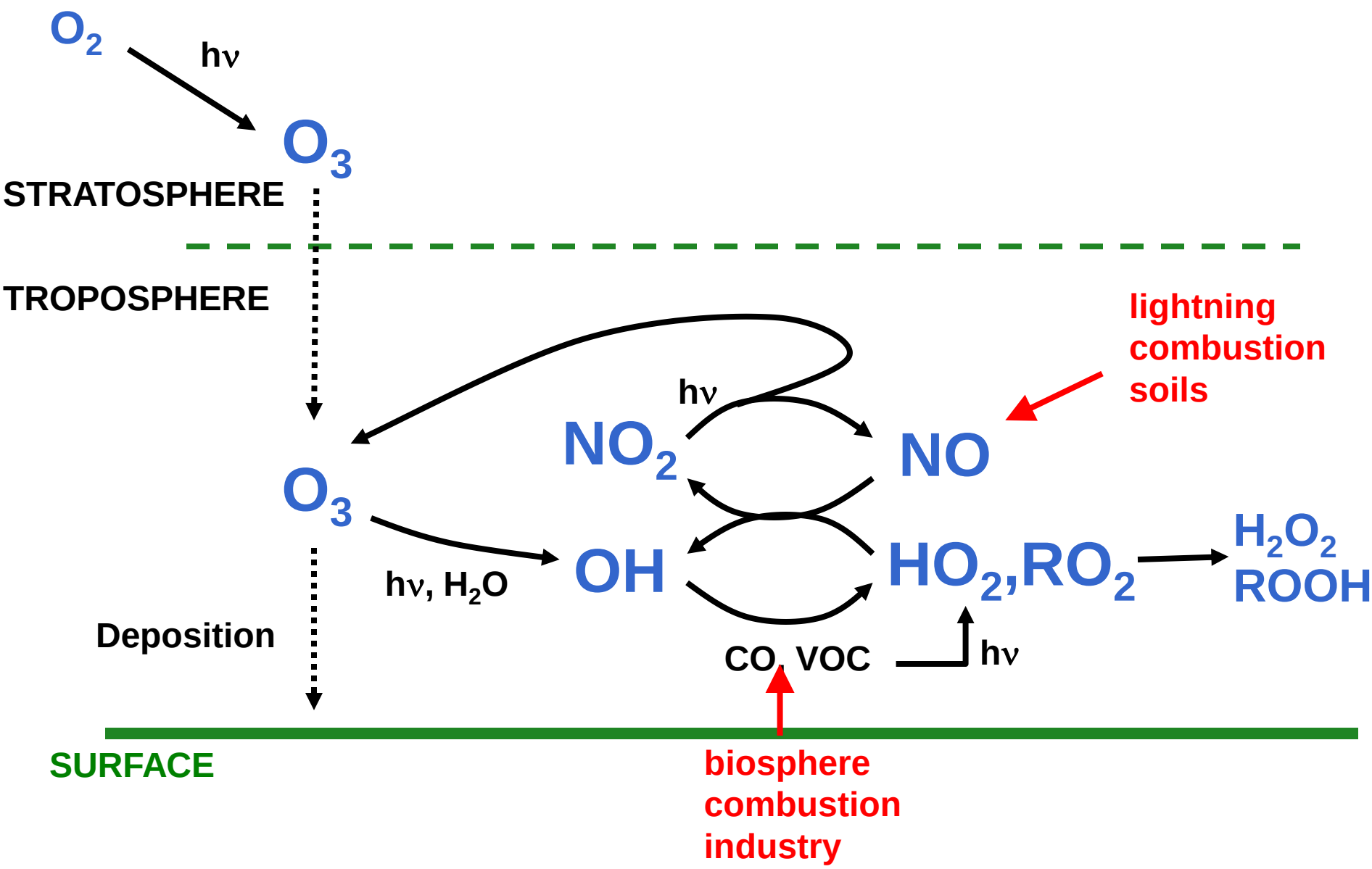
with Kevin J. Wecht, Lee T. Murray, Emily V. Fischer, Justin P. Parrella, Anne L. Soerensen, Helen M. Amos

HARVARD UNIVERSITY

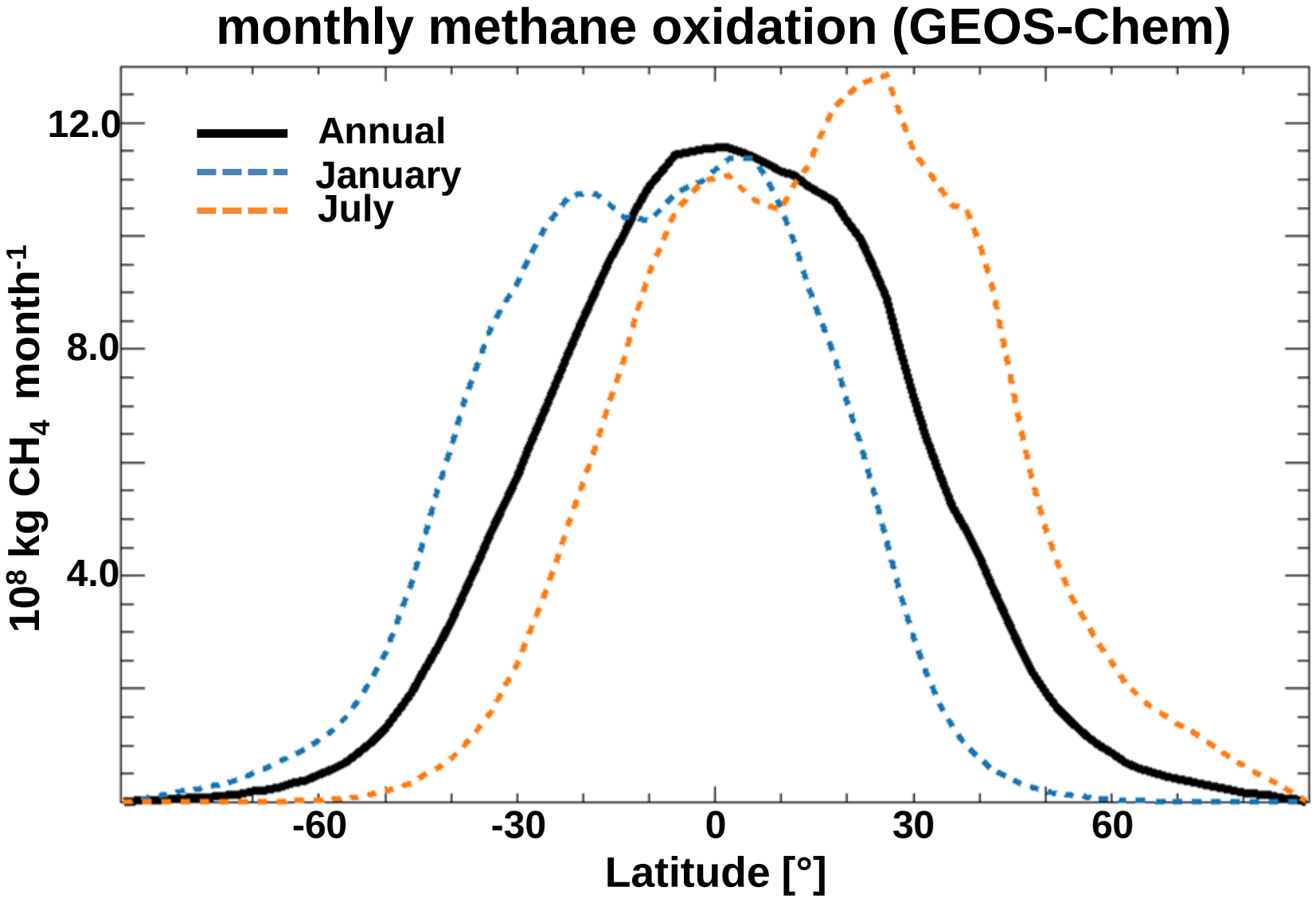


ATMOSPHERIC CHEMISTRY MODELING GROUP

Radical cycle controlling tropospheric ozone and OH



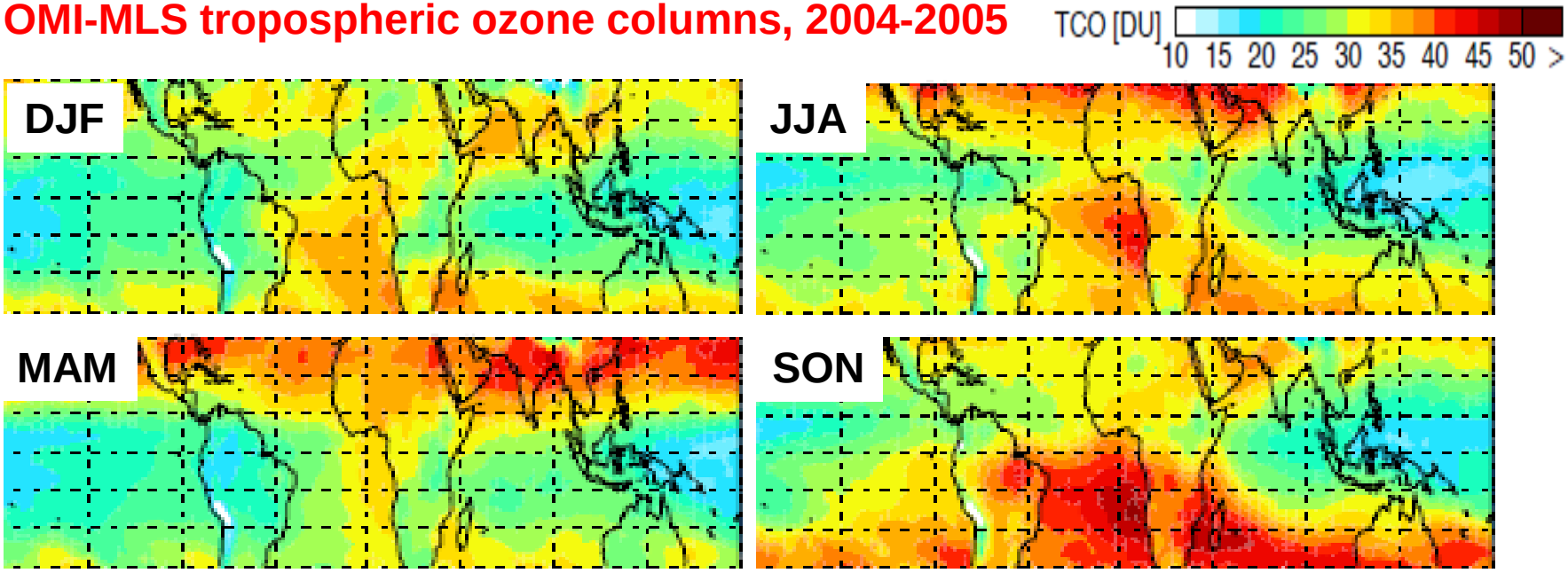
Oxidation of long-lived gases by OH is mostly in tropics



Kevin Wecht, Harvard

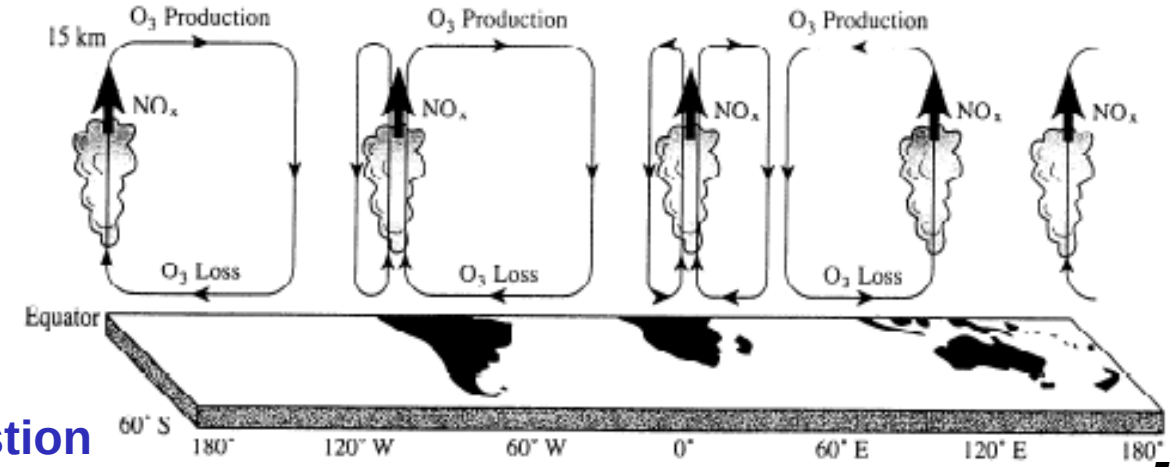
Ozone distribution in tropical troposphere

OMI-MLS tropospheric ozone columns, 2004-2005



Murray et al. [2012]

Ozone budget schematic (Walker circulation):

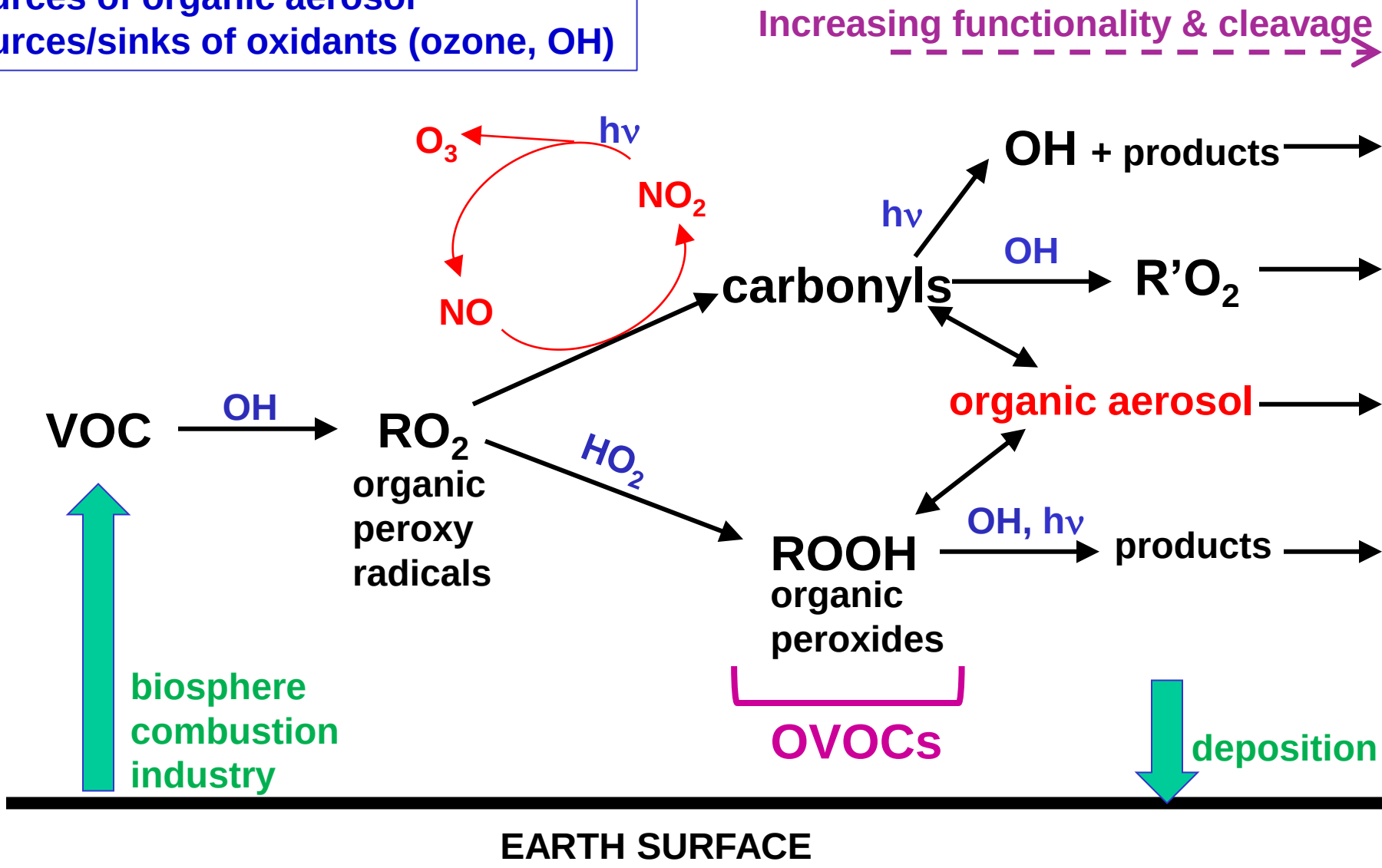


NO_x from
- lightning
- open fires
- soils
- fuel combustion

Jacob et al. [1996]

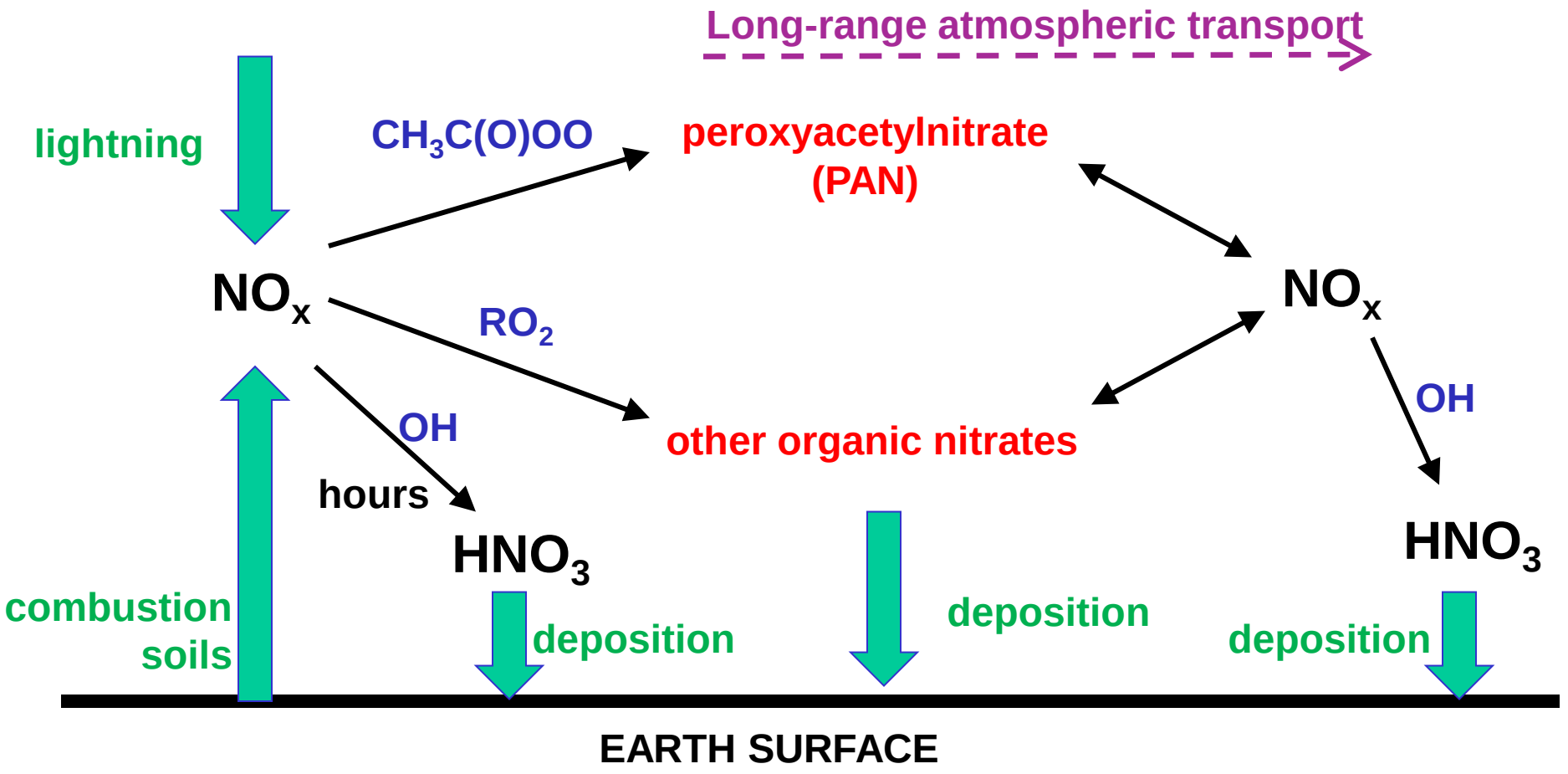
Volatile organic compounds (VOCs) in the atmosphere: carbon oxidation chain

- sources of organic aerosol
- sources/sinks of oxidants (ozone, OH)



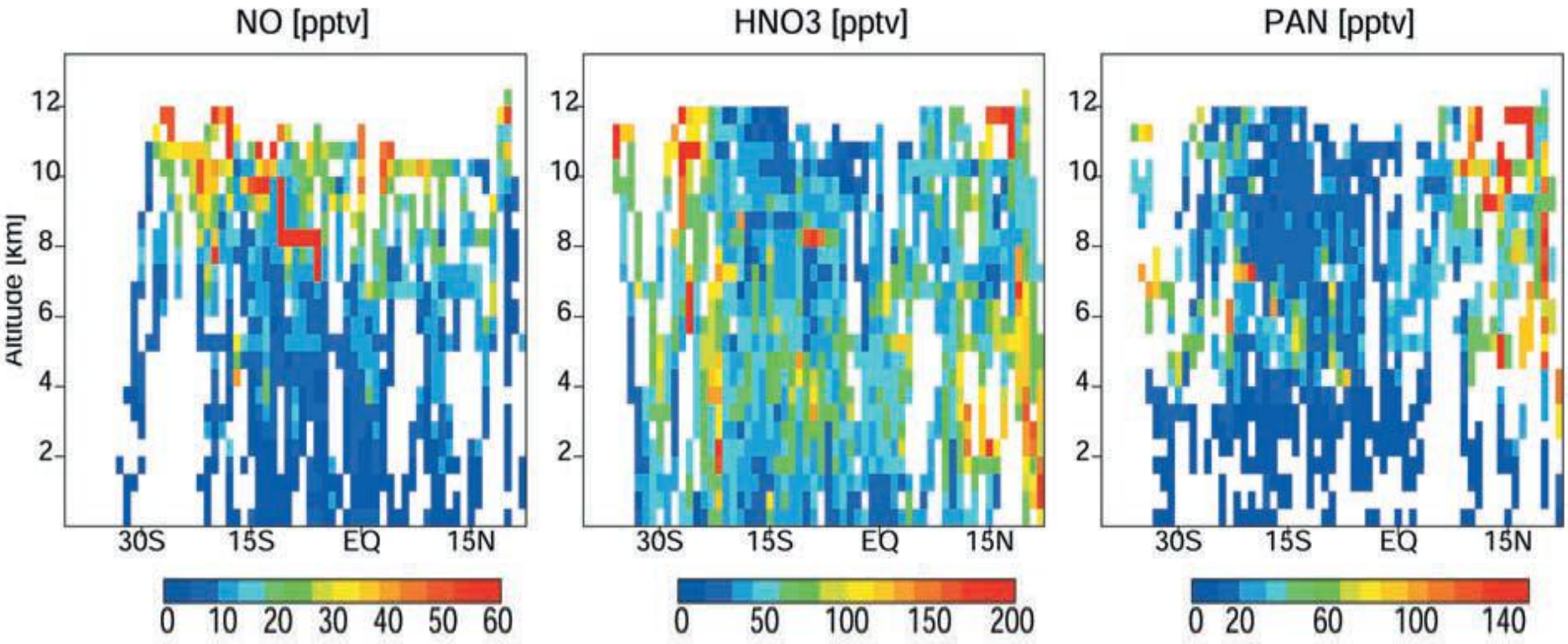
Volatile organic compounds (VOCs) in the atmosphere: effect on nitrogen cycle

Reservoirs for long-range transport of NO_x



Distributions of NOx, HNO_3, and PAN over Pacific

PEM-Tropics B aircraft campaign (Mar-Apr 1999): latitude-altitude x-sections

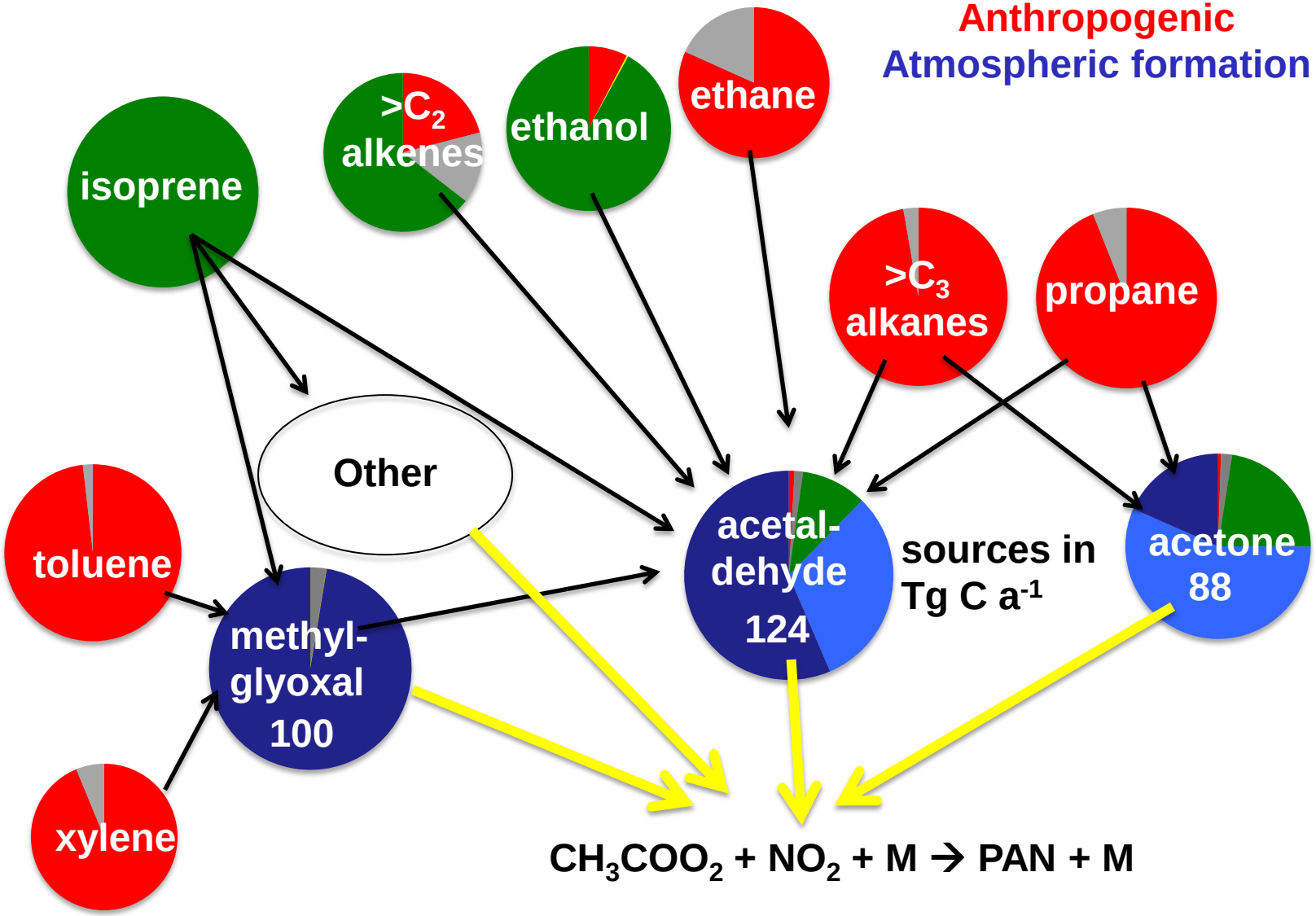


NO_x below 6 km over Pacific is mainly from PAN decomposition

Staudt et al. [2003]

Global sources of PAN

Terrestrial
Marine
Open fires
Anthropogenic
Atmospheric formation



Emily Fischer, Harvard

PAN precursors over Pacific

January mean GEOS-Chem results

0 – 3 km

Above 3 km

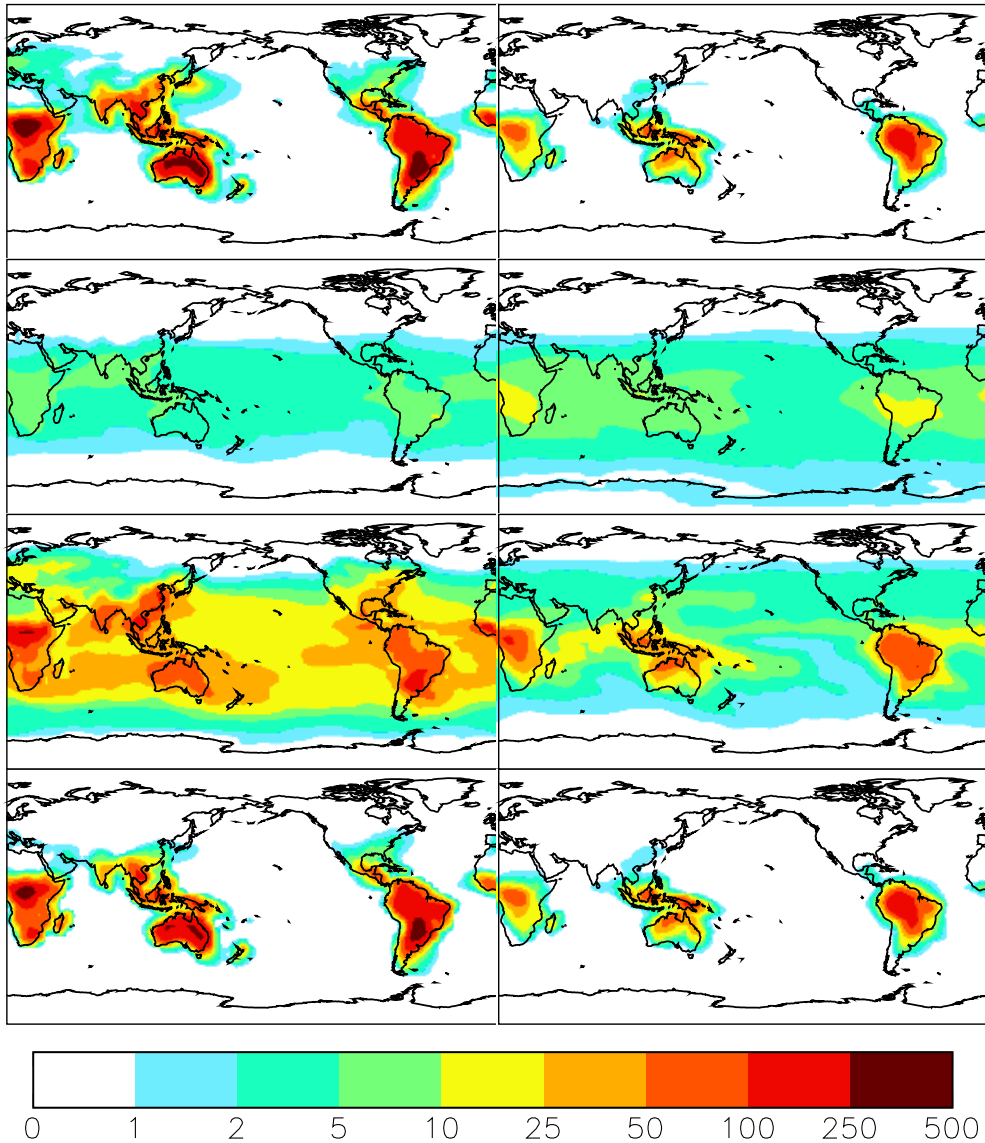
Methylglyoxal

Acetone

Acetone and acetaldehyde are the main precursors

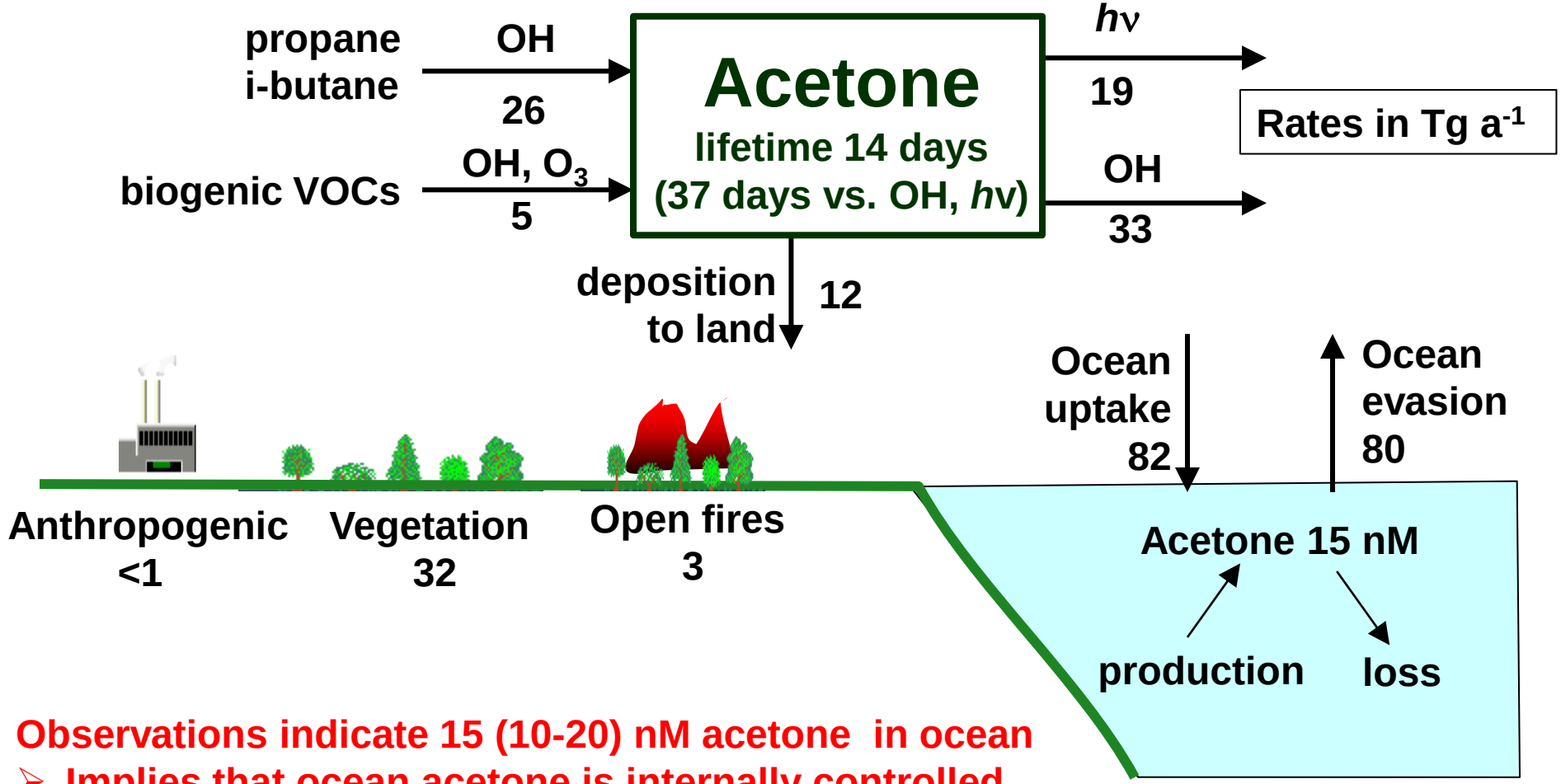
Acetaldehyde

Other (isoprene)



Emily Fischer, Harvard

Global budget of acetone

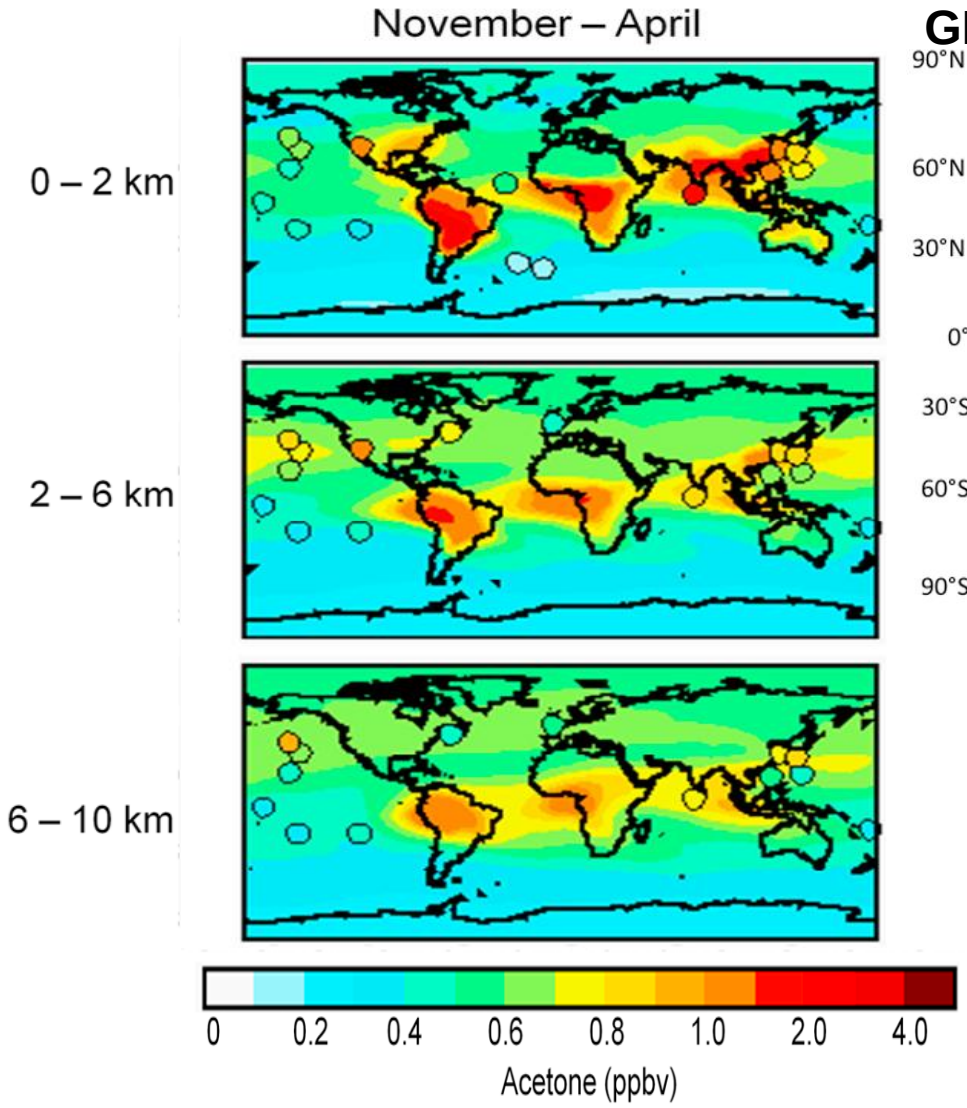


Observations indicate 15 (10-20) nM acetone in ocean

- **Implies that ocean acetone is internally controlled**
- **Implies that ocean is dominant source to the atmosphere**

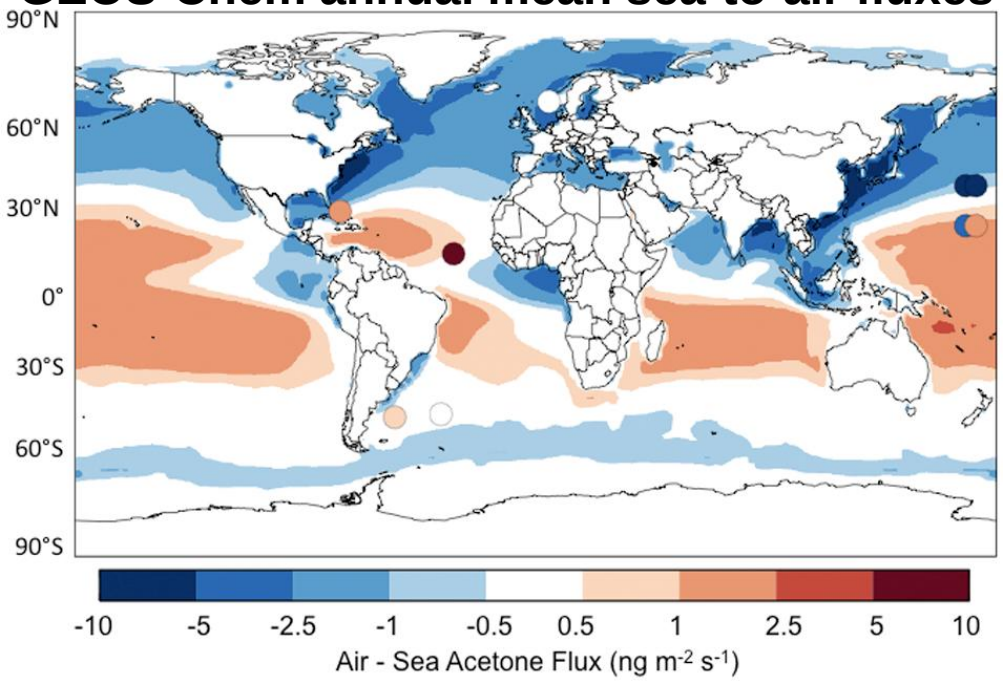
Fischer et al. [2012]

Global distribution of acetone and net air-sea fluxes



Circles: mean obs from aircraft campaigns
Background: GEOS-Chem model

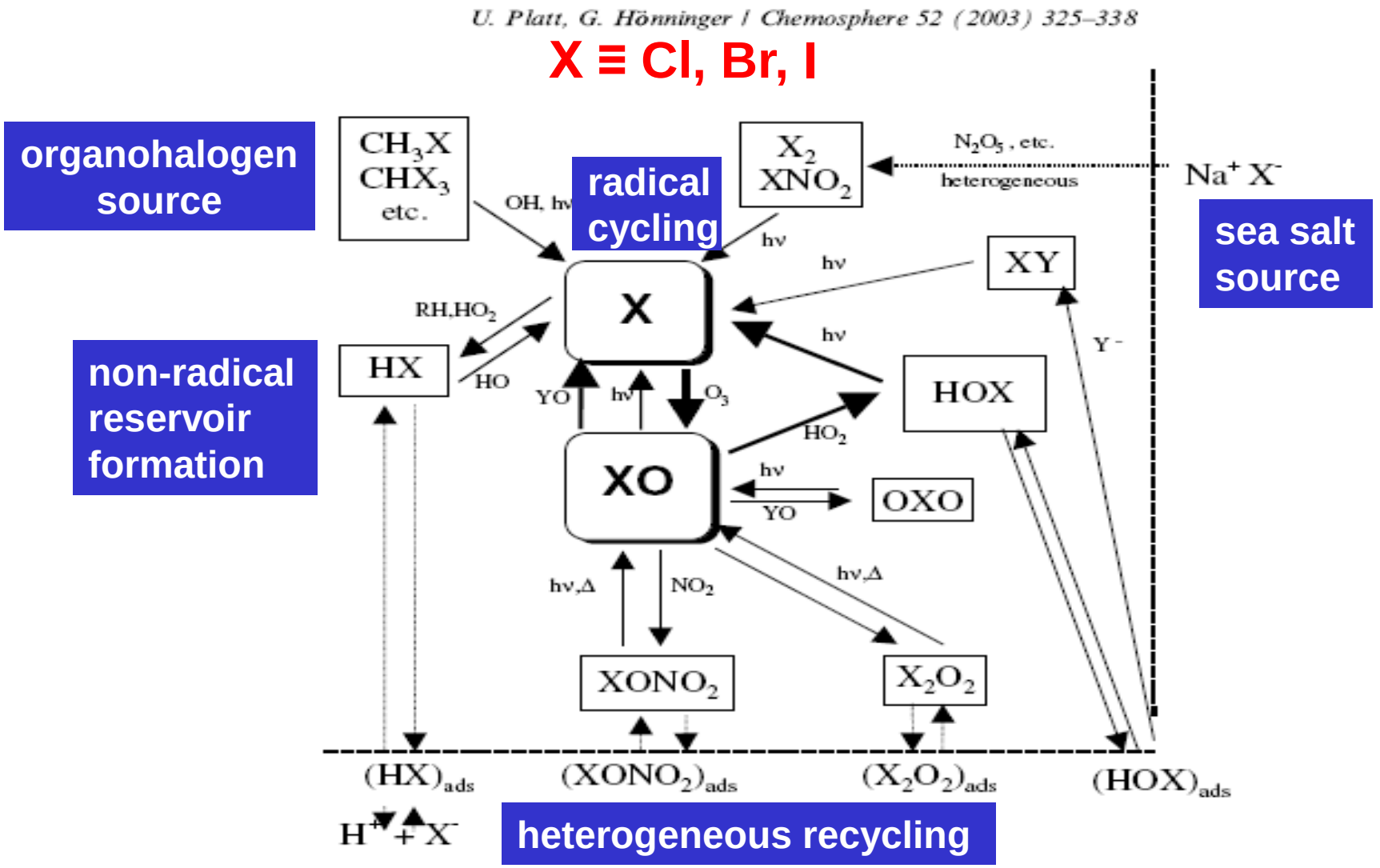
GEOS-Chem annual mean sea-to-air fluxes



- **Ocean is net source in tropics (except coastal), sink in northern extratropics**
- **Remote atmospheric background is determined by ocean control, long photochemical lifetime**

Fischer et al. [2012]

Halogen radical chemistry in troposphere: sink for ozone, NO_x, VOCs, mercury



Bromine chemistry in the atmosphere

Inorganic bromine (Br_y)

O_3

Halons — hv → Br ⇄ BrO ⇄ $BrNO_3$

hv, NO

OH → HBr, HOBr

CH_3Br

VSLS

Stratosphere

Tropopause (8-18 km)

Troposphere

$CHBr_3$, CH_2Br_2 — OH, $h\nu$ → Br_y

debromination

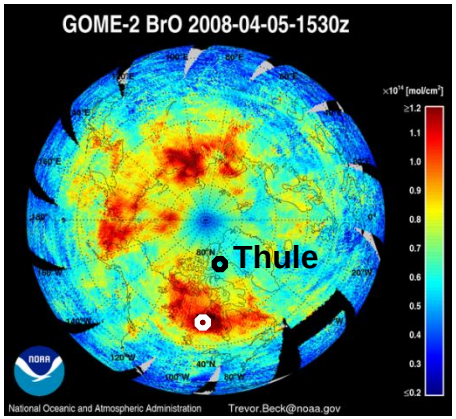
deposition

Sea salt

industry

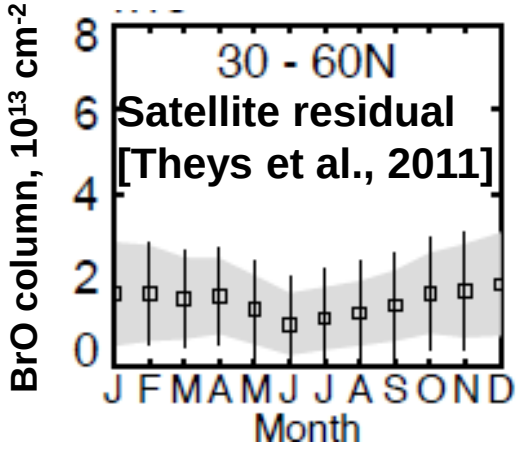
plankton

GOME-2 BrO columns



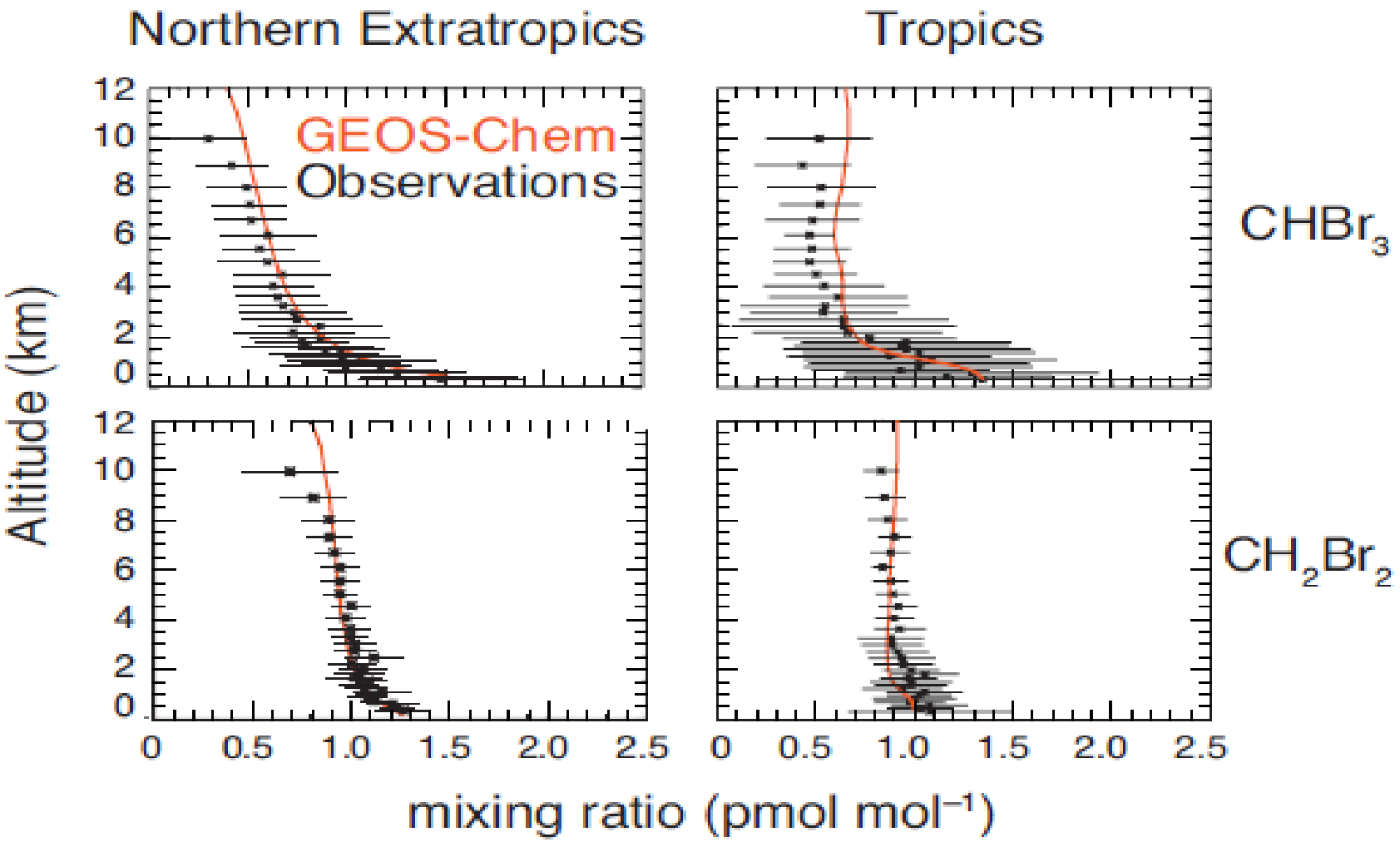
Stratospheric BrO: 2-10 ppt

Tropospheric BrO: 0.5-2 ppt



Mean vertical profiles of $CHBr_3$ and CH_2Br_2

From NASA aircraft campaigns over Pacific in April-June

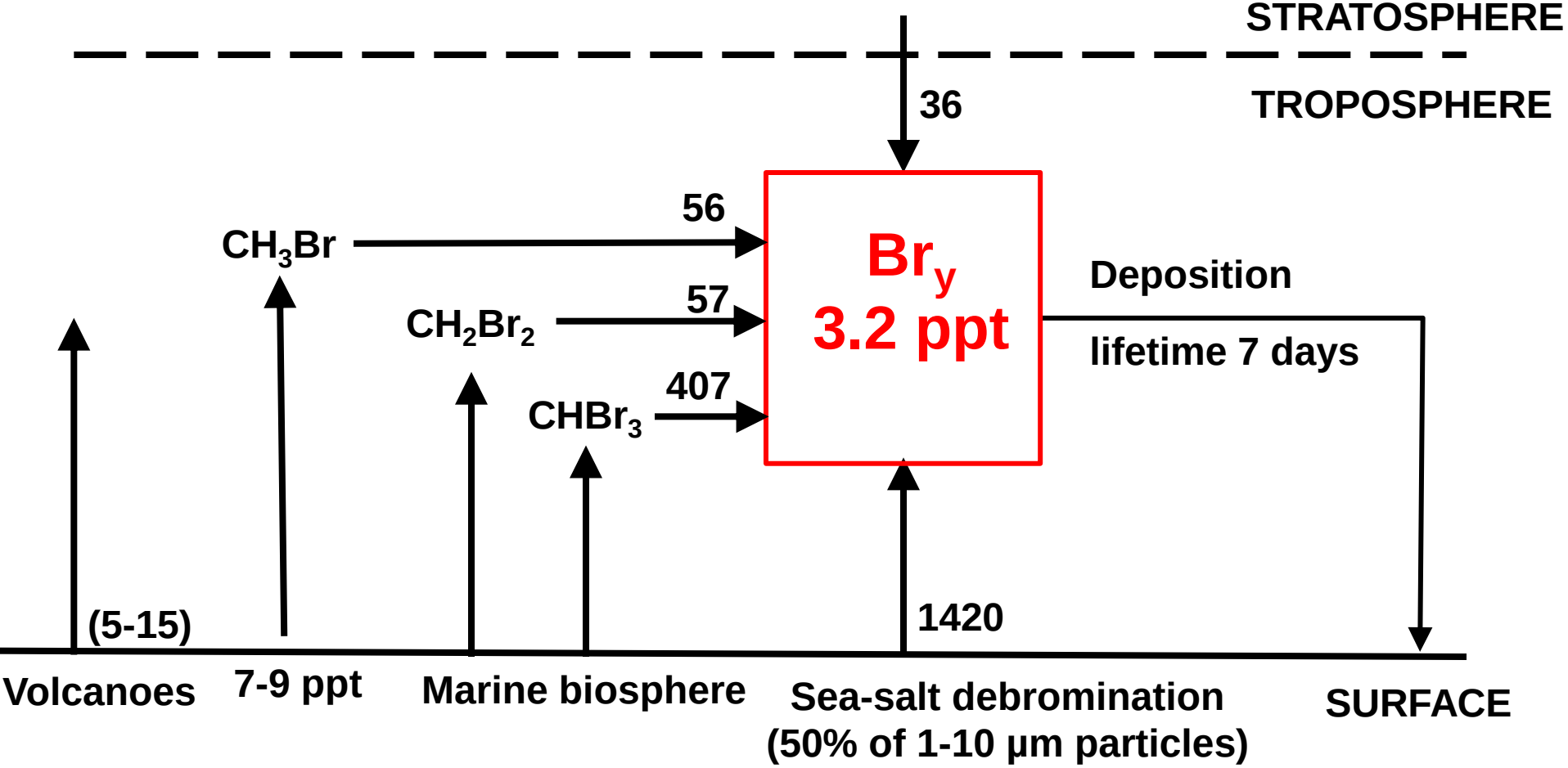


Vertical profiles steeper for $CHBr_3$ (mean lifetime 21 days) than for CH_2Br (91 days), steeper in extratropics than in tropics

Parrella et al. [2012]

Global tropospheric Br_y budget in GEOS-Chem (Gg Br a^{-1})

Liang et al. [2010] stratospheric Bry model (upper boundary conditions)

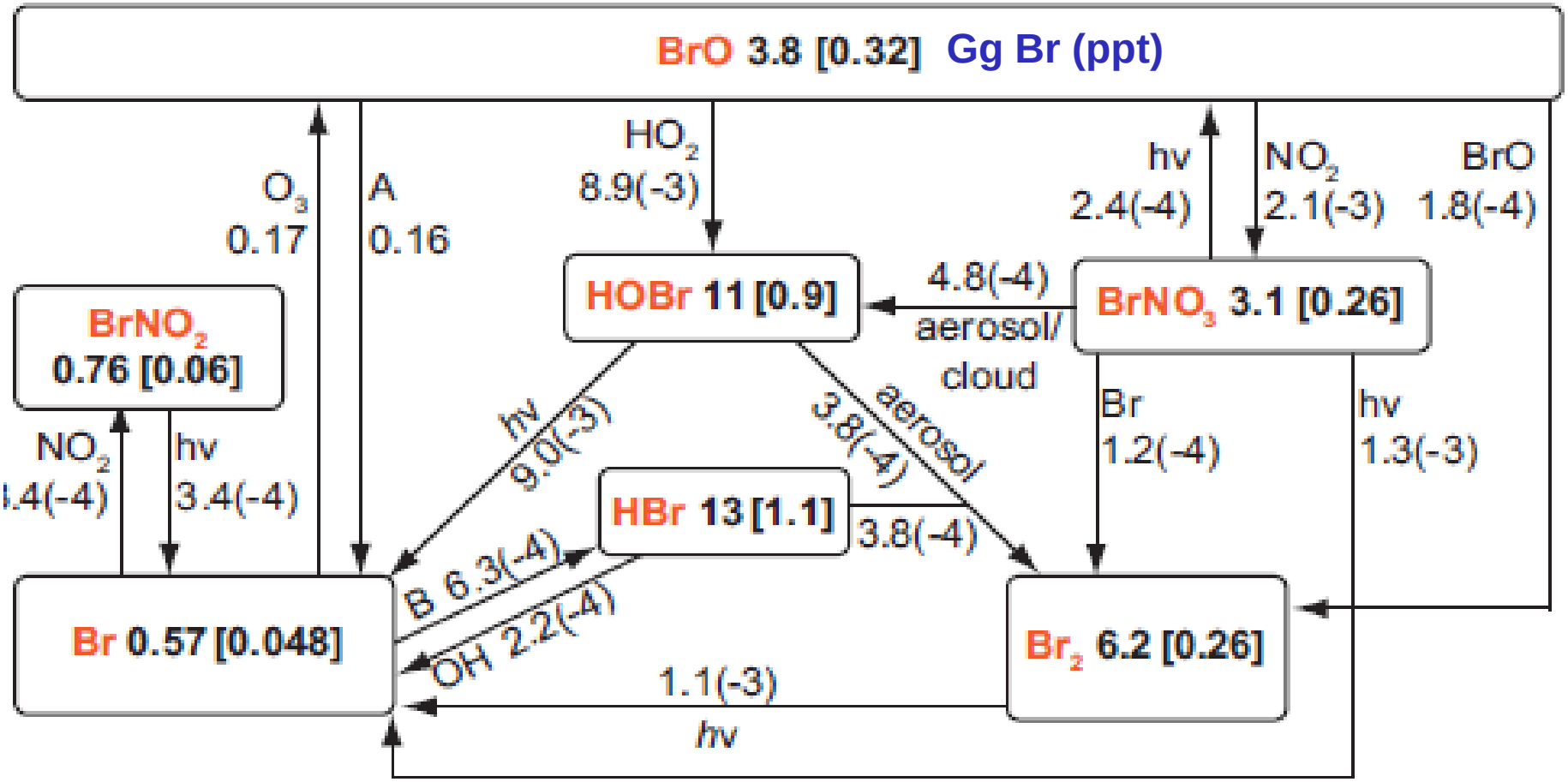


Sea salt is the dominant global source but is released in marine boundary layer where lifetime against deposition is short; $CHBr_3$ is major source in the free troposphere

Parrella et al. [2012]

Tropospheric Br_y cycling in GEOS-Chem

Global annual mean concentrations in Gg Br (ppt), rates in Gg Br s^{-1}

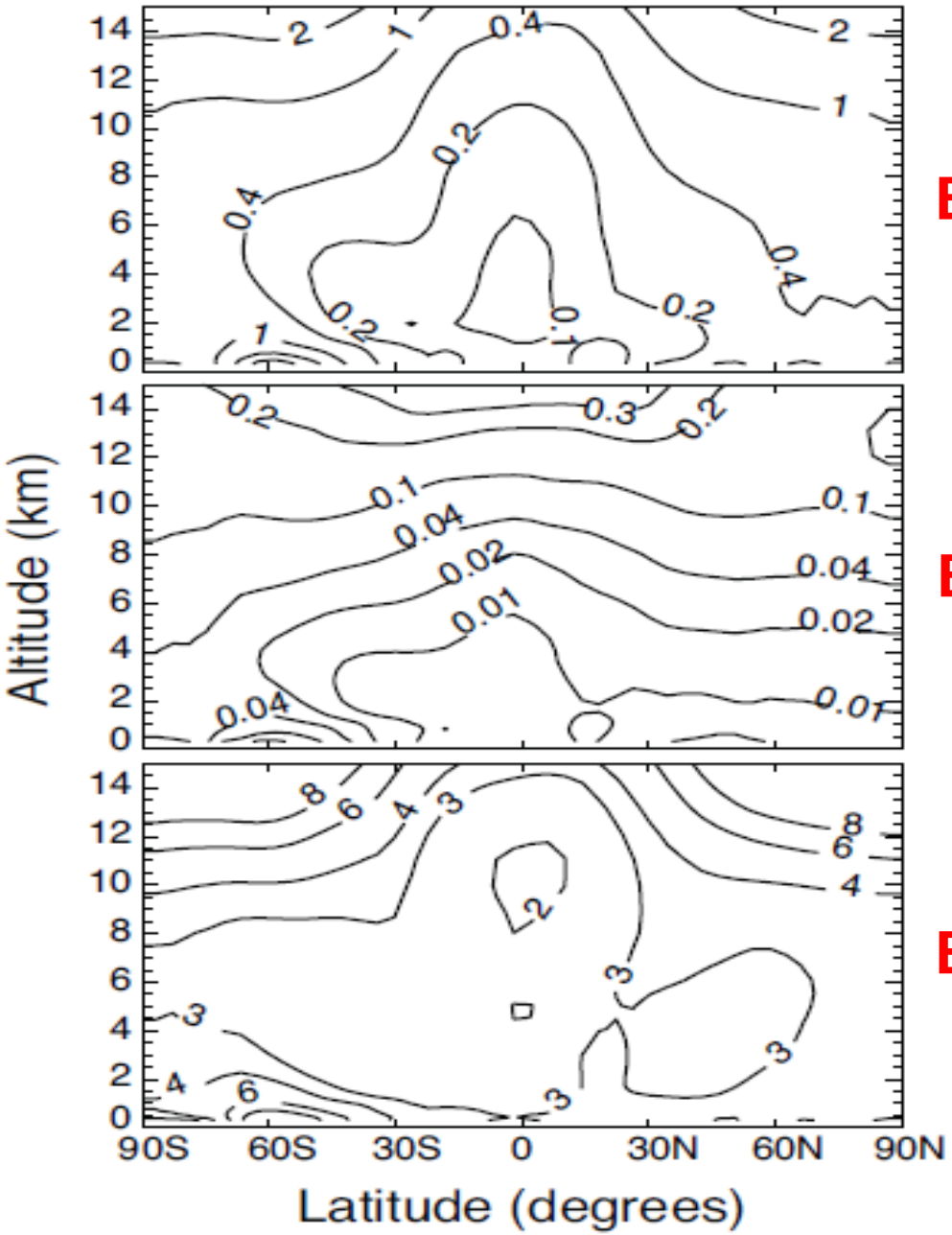


- Model includes HOBr+HBr in aq aerosols with $\gamma = 0.2$, ice with $\gamma = 0.1$
- Mean daytime BrO = 0.6 ppt; would be 0.3 ppt without HOBr+HBr reaction

Parrella et al. [2012]

Zonal annual mean concentrations (ppt) in GEOS-Chem

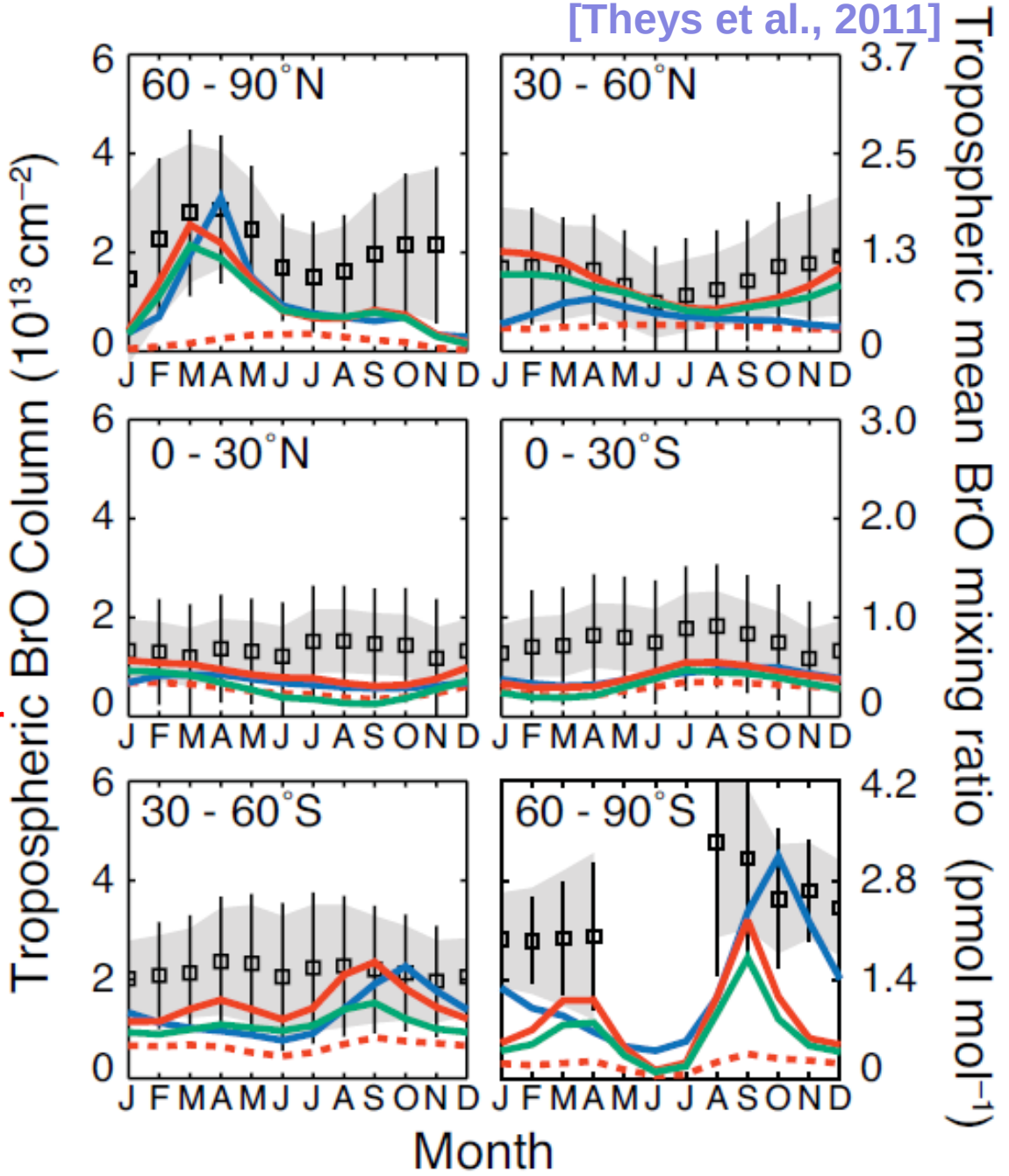
- Br_y is 2-4 ppt, highest over Southern Ocean (sea salt)
- BrO increases with latitude (photochemical sink)
- Br increases with altitude (BrO photolysis)



Parrella et al. [2012]

Comparison to seasonal satellite data for tropospheric BrO

[Theys et al., 2011]

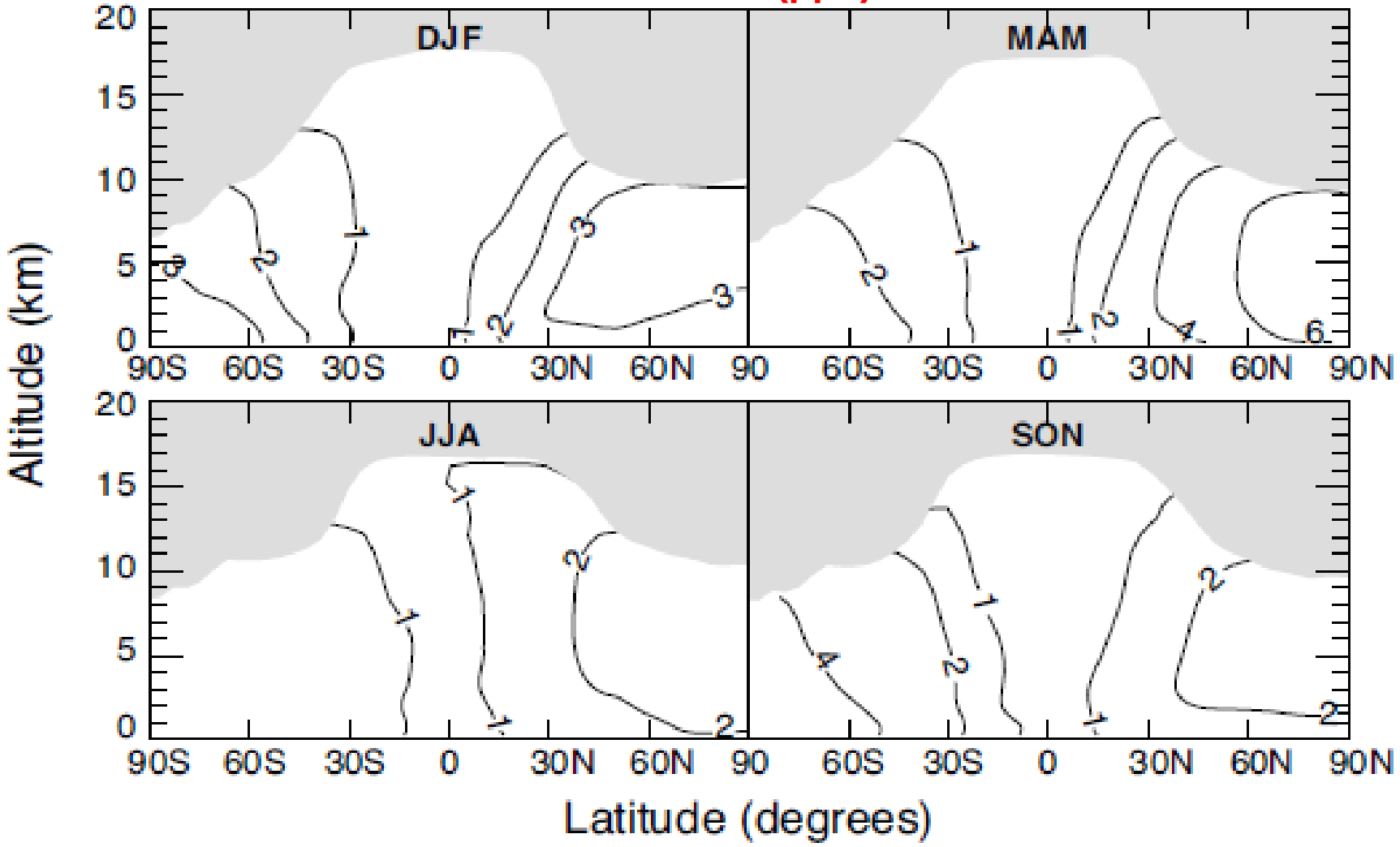


- **TOMCAT has lower γ=0.02 for HOBr+HBr than GEOS-Chem, large polar spring source from blowing snow**
- **HOBr+HBr reaction critical for increasing BrO with latitude, winter/spring NH max in GEOS-Chem**

Parrella et al. [2012]

Effect of Br chemistry on tropospheric ozone

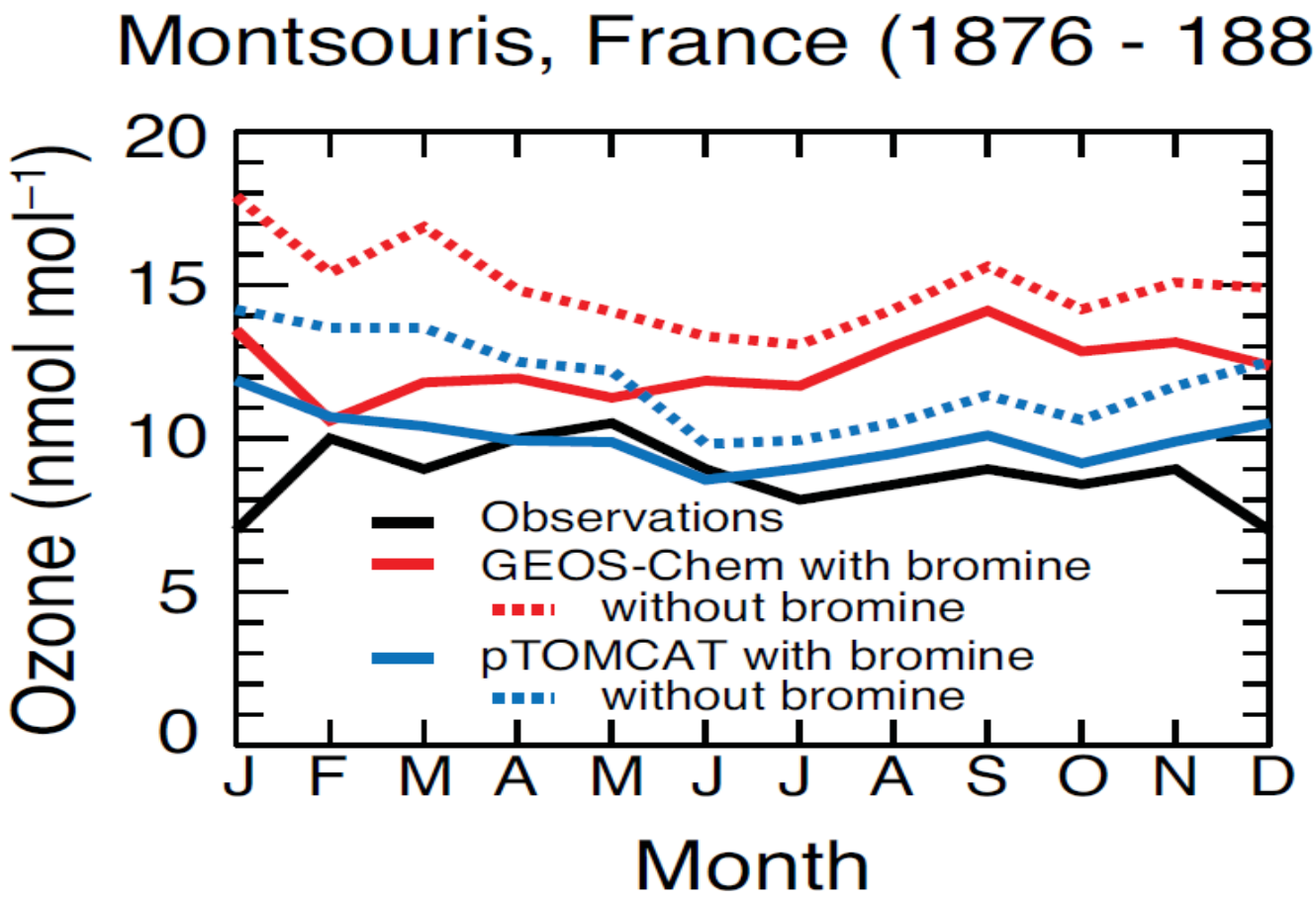
Zonal mean ozone decreases (ppb) in GEOS-Chem



- **Two processes: catalytic ozone loss via HOBr, NO_x loss via $BrNO_3$**
- **Global OH also decreases by 4% due to decreases in ozone and NO_x**

Parrella et al. [2012]

Bromine chemistry improves simulation of 19th century surface ozone

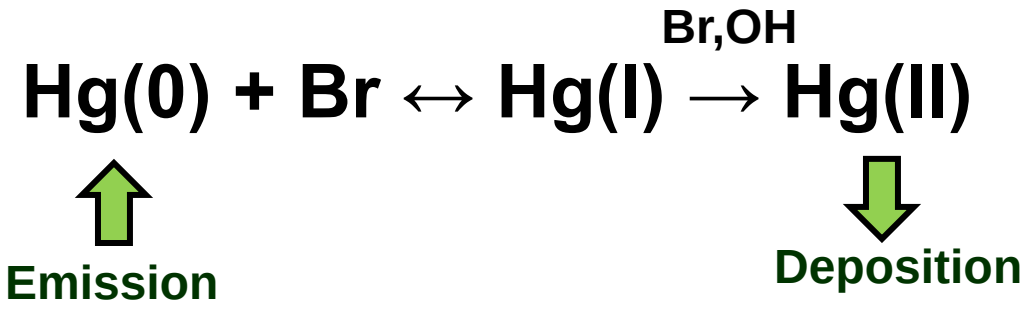


- **Standard models without bromine are too high, peak in winter-spring; bromine chemistry corrects these biases**
- **Model BrO is similar in pre-industrial and present atmosphere (canceling effects)**

Parrella et al. [2012]

Atmospheric lifetime of Hg(0) against oxidation to Hg(II) by Br

- 2-step Hg(0) oxidation (Goodsite et al., 2004; Donohoue et al., 2006)



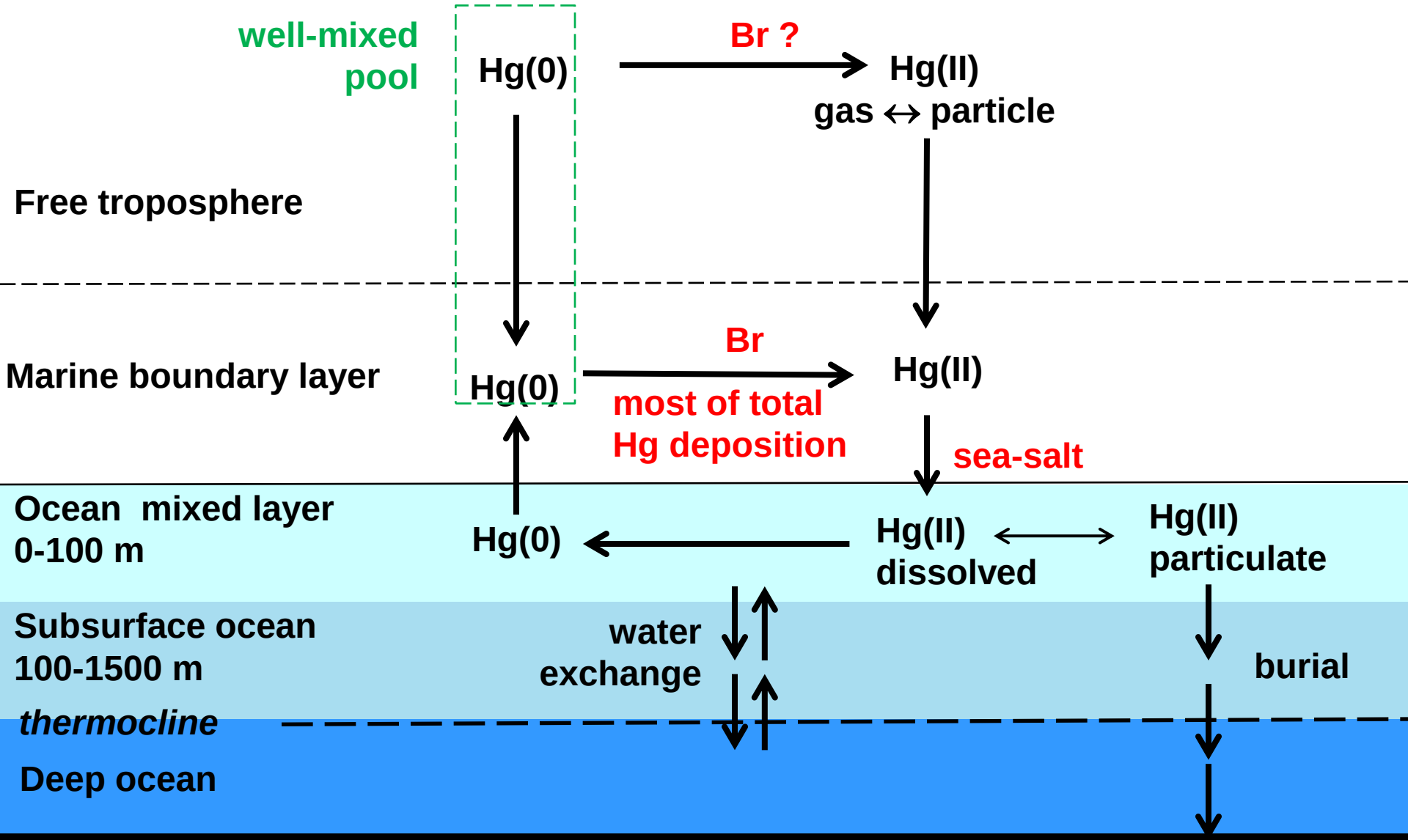
- GEOS-Chem Br yields Hg(0) global mean tropospheric lifetime of 4 months, consistent with observational constraints

- Br in pre-industrial atmosphere was 40% higher than in present-day (less ozone), implying a pre-industrial Hg(0) lifetime of only 2 months
  ⇒ Hg could have been more efficiently deposited to northern mid-latitude oceans in the past

Parrella et al. [2012]

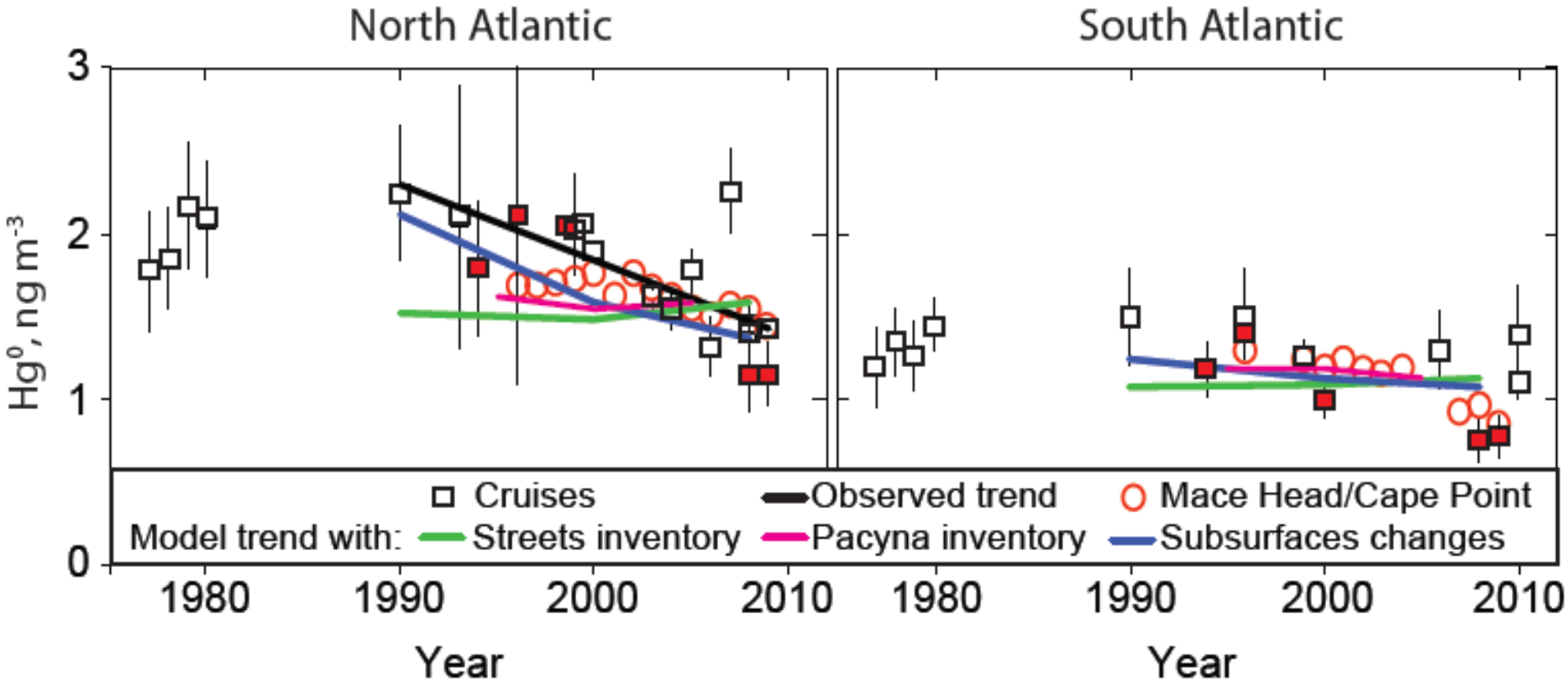
Mechanism for uptake of atmospheric Hg by ocean

as implemented in GEOS-Chem model



Hg(0) decreasing trend in North Atlantic surface air

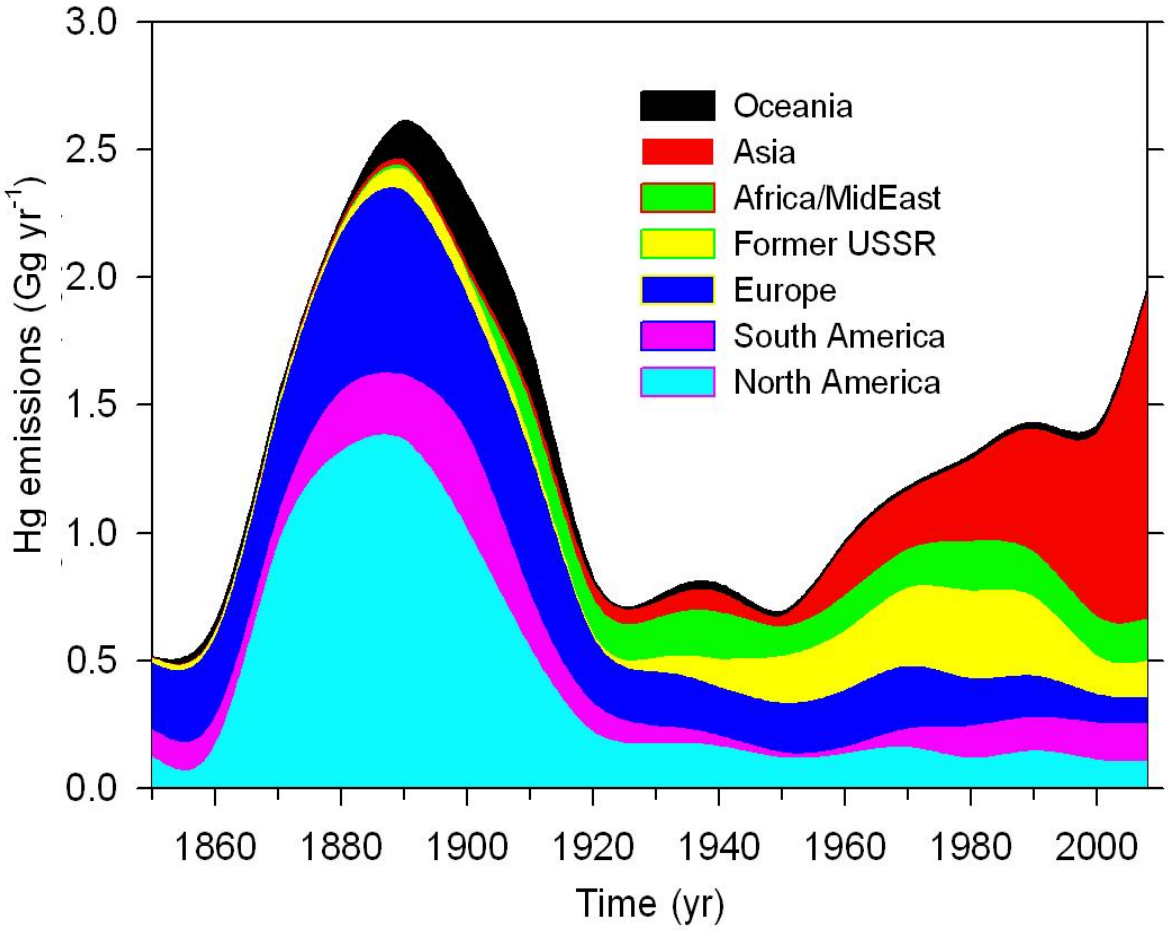
Ensemble of cruise data, 1977-present



- **Large decrease observed since 1990 in N Atlantic, not in S Atlantic**
- **Model can reproduce this decrease based on 80% observed decrease of dissolved Hg in subsurface N Atlantic since 1990**
- **Why this large subsurface ocean decrease? Increasing MBL ozone, decreasing coastal inputs from rivers/wastewater, missing historical Hg sources?**

Soerensen et al. [2012]

Historical inventory of global anthropogenic Hg emissions

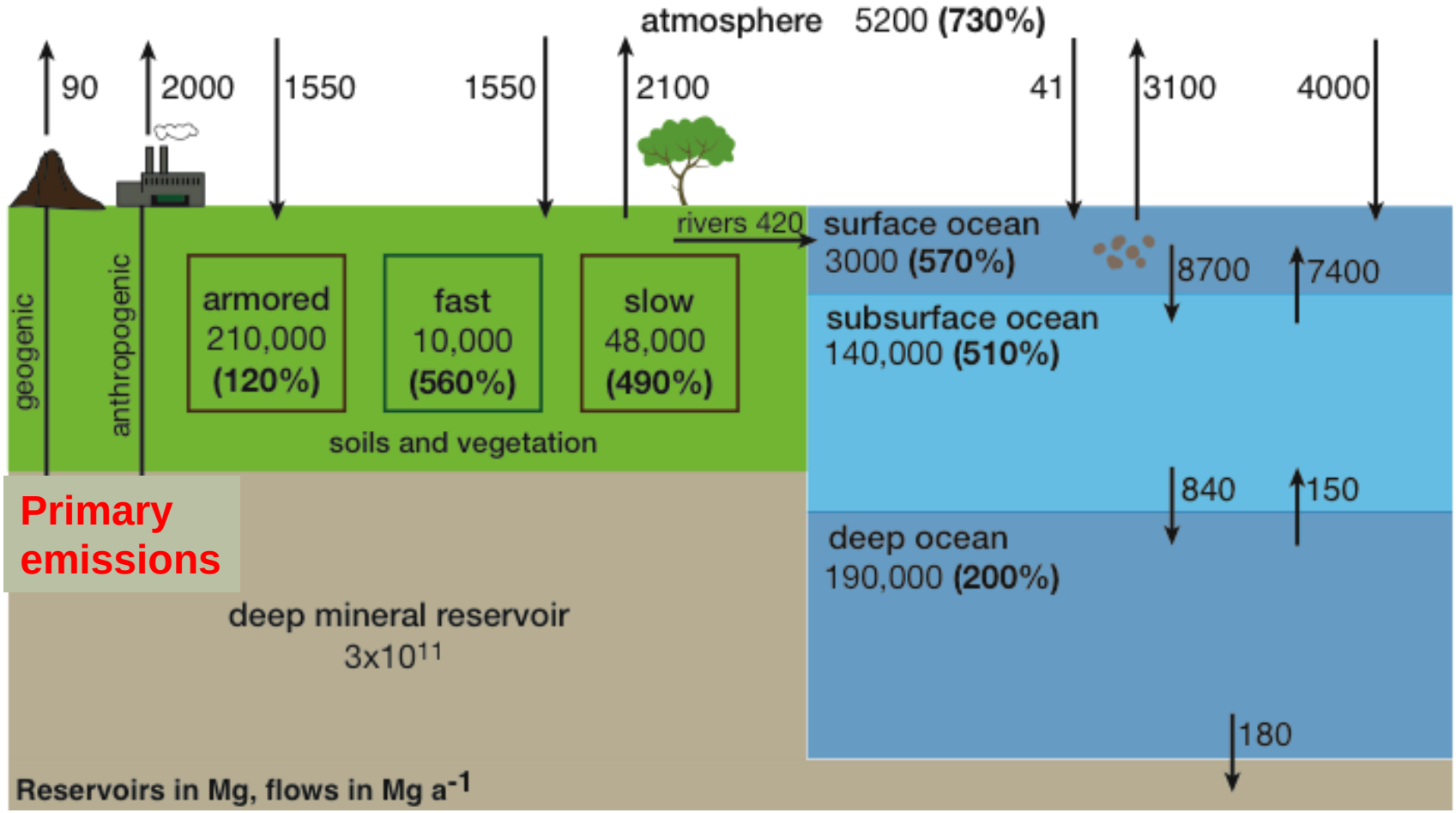


- **Large legacy contribution from N. American and European emissions; Asian dominance is a recent phenomenon**
- **Pre-1850 releases from mining account for 40% of all-time anthropogenic emissions**

Streets et al. , 2012

Global biogeochemical model for mercury

7-box model with 7 coupled ODEs *dm/dt = s(t) – km* where *s* is primary emission (atmosphere only)

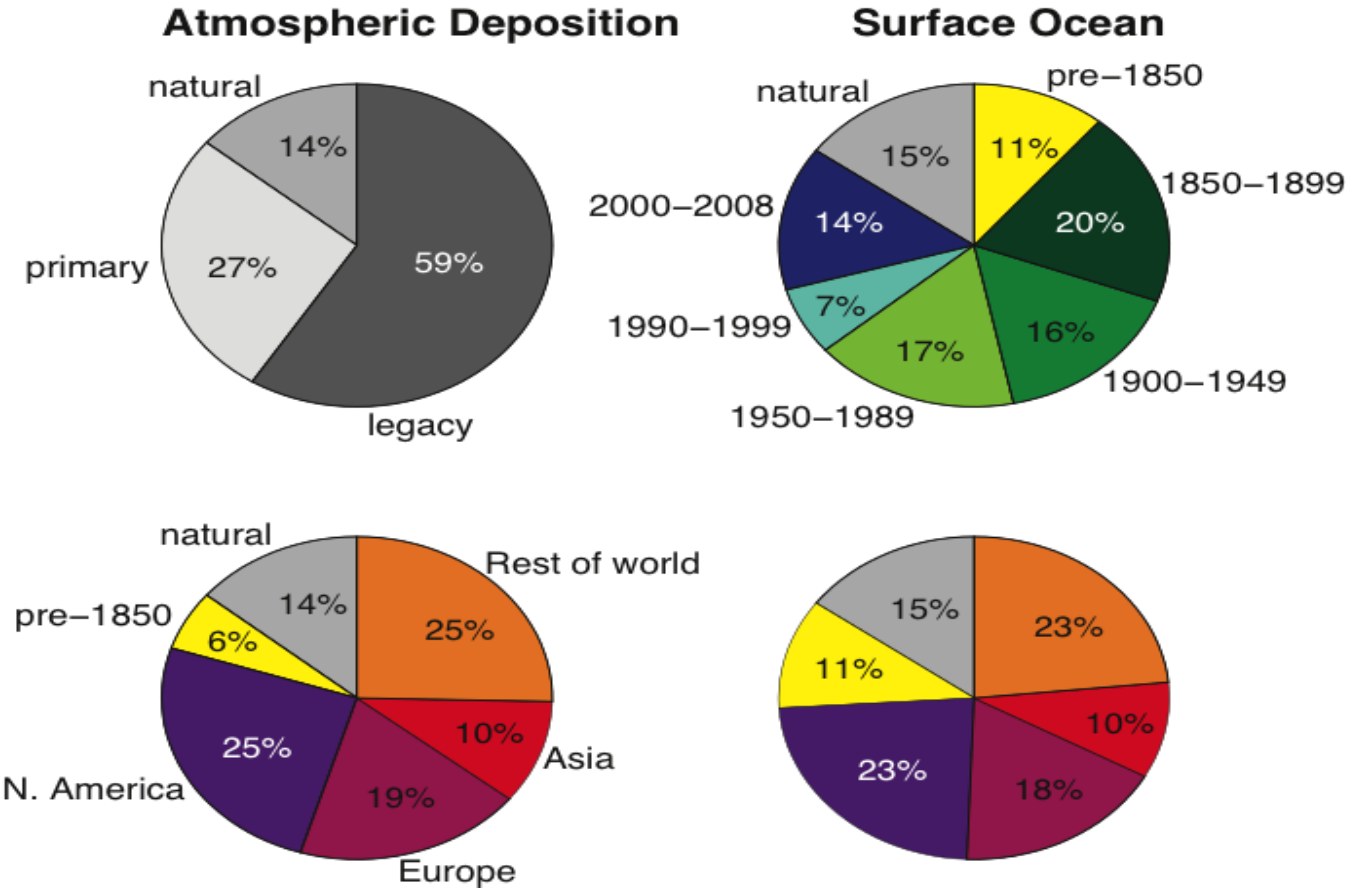


Model is initialized at natural steady state, forced with historical anthropogenic emissions for 2000 BC – present; % present-day enrichments are indicated

Helen Amos, Harvard

Contribution of old anthropogenic (legacy) mercury to global atmospheric deposition and surface ocean

GEOS-Chem based global biogeochemical model of mercury cycling



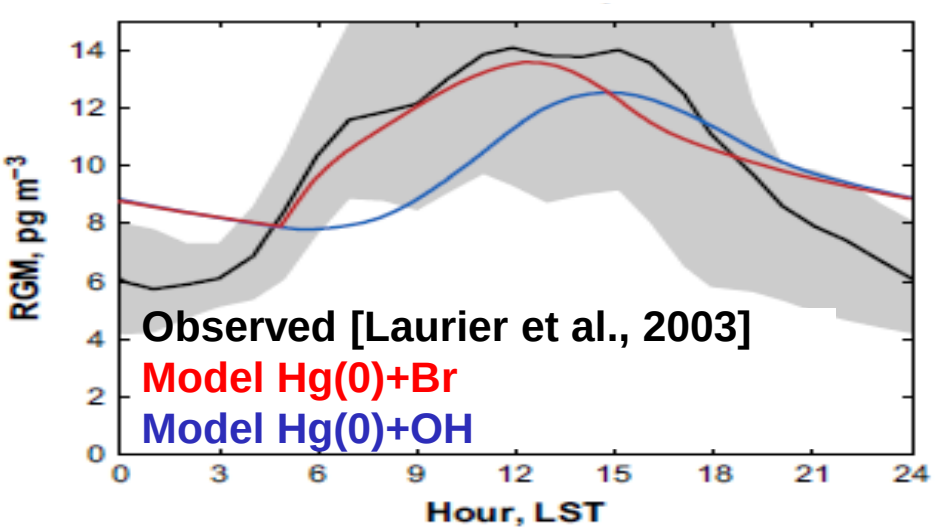
Mercury pollution is mainly a legacy problem that will take centuries to fix; all we can do in short term is prevent it from getting worse

Helen Amos, Harvard

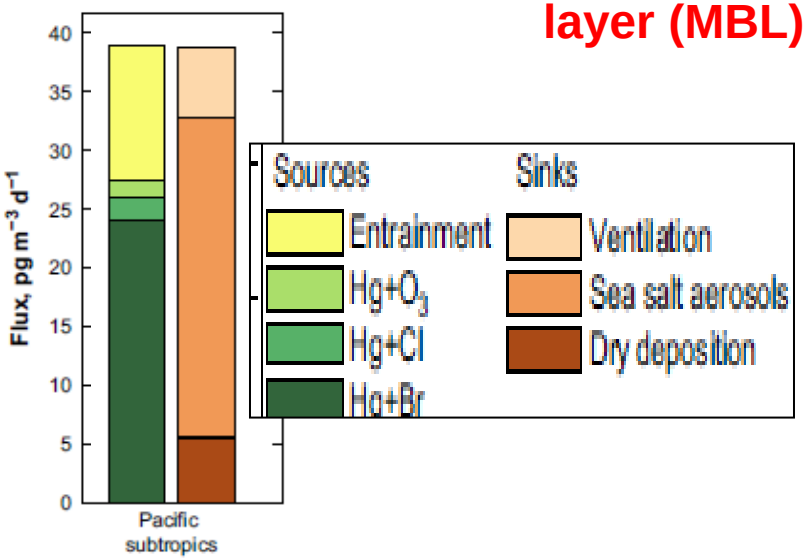
Importance of MBL chemistry for Hg deposition to oceans

Observed RGM diurnal cycle suggests Br chemistry, deposition via sea salt uptake

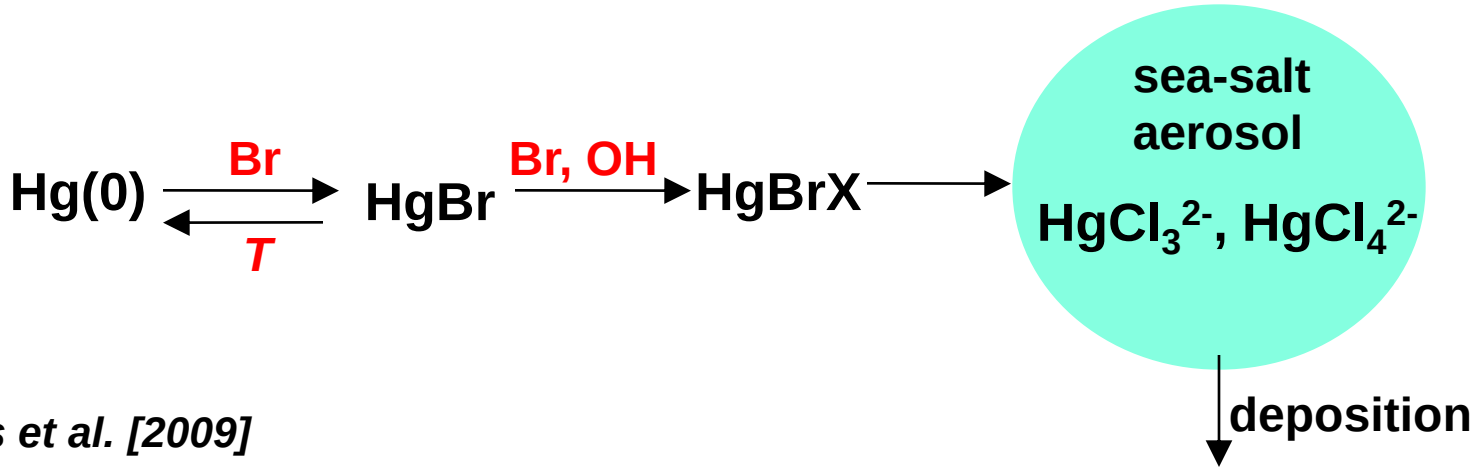
Subtropical Pacific cruise data



Box model budget for marine boundary layer (MBL)



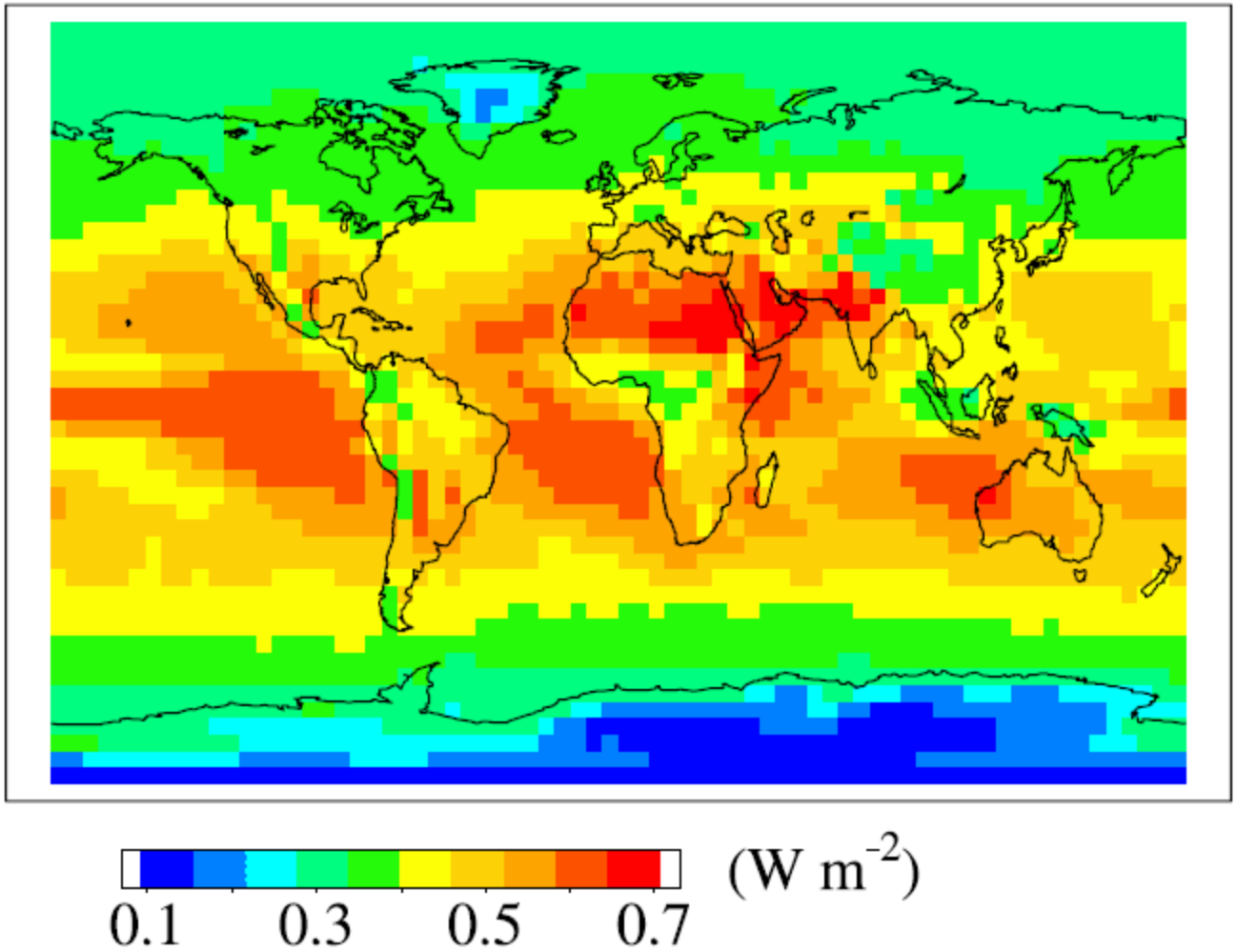
Box model predicts that ~80% of Hg(II) in MBL should be in sea salt aerosol:



Holmes et al. [2009]

Radiative forcing efficiency from tropospheric ozone is strongest in tropics and particularly in TORERO region

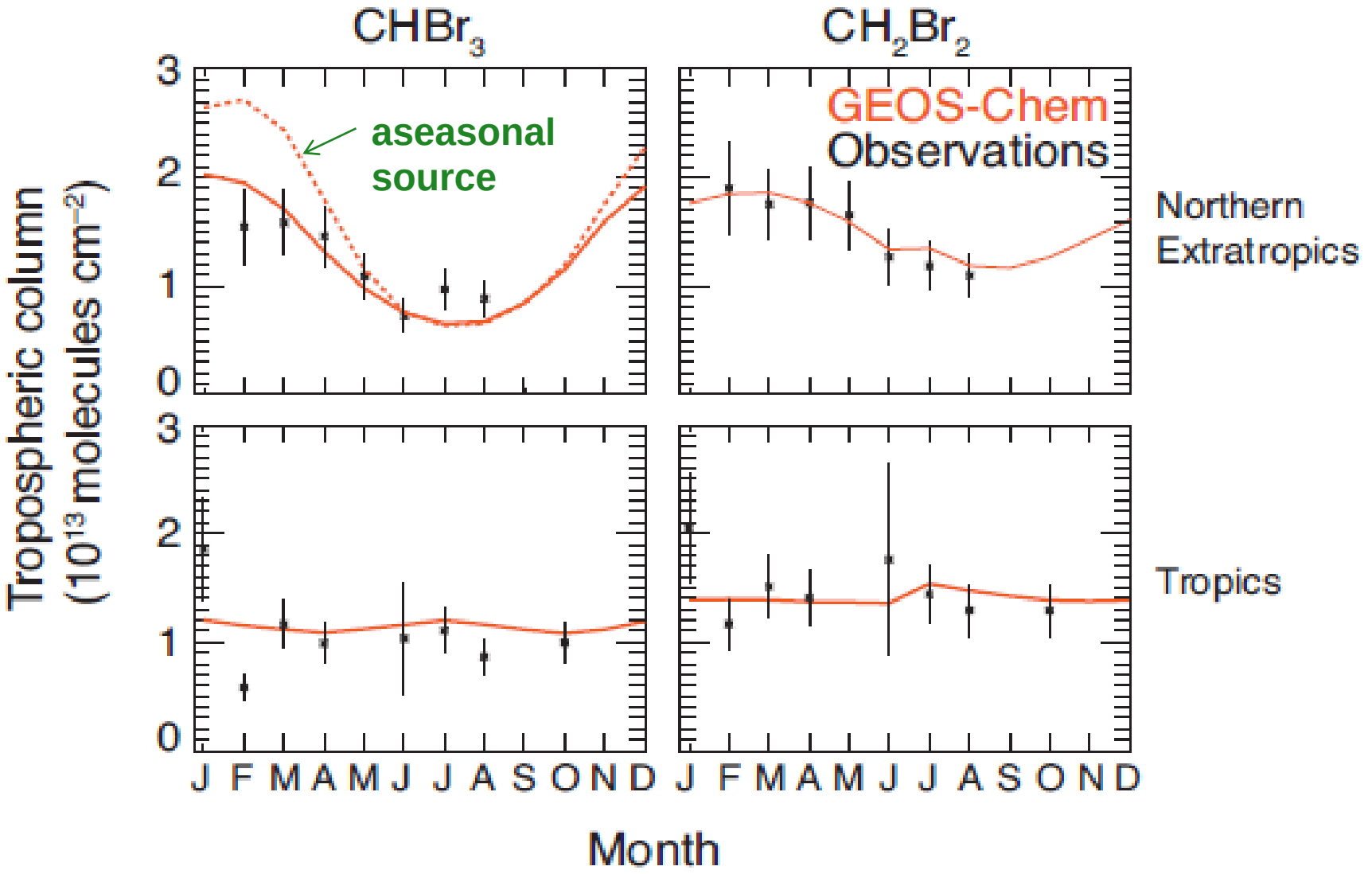
Radiative forcing from uniform ΔO_3 = 18 ppb in troposphere (GISS GCM)



Mickley et al. [2004]

Seasonal variation of $CHBr_3$ and CH_2Br_2 tropospheric columns

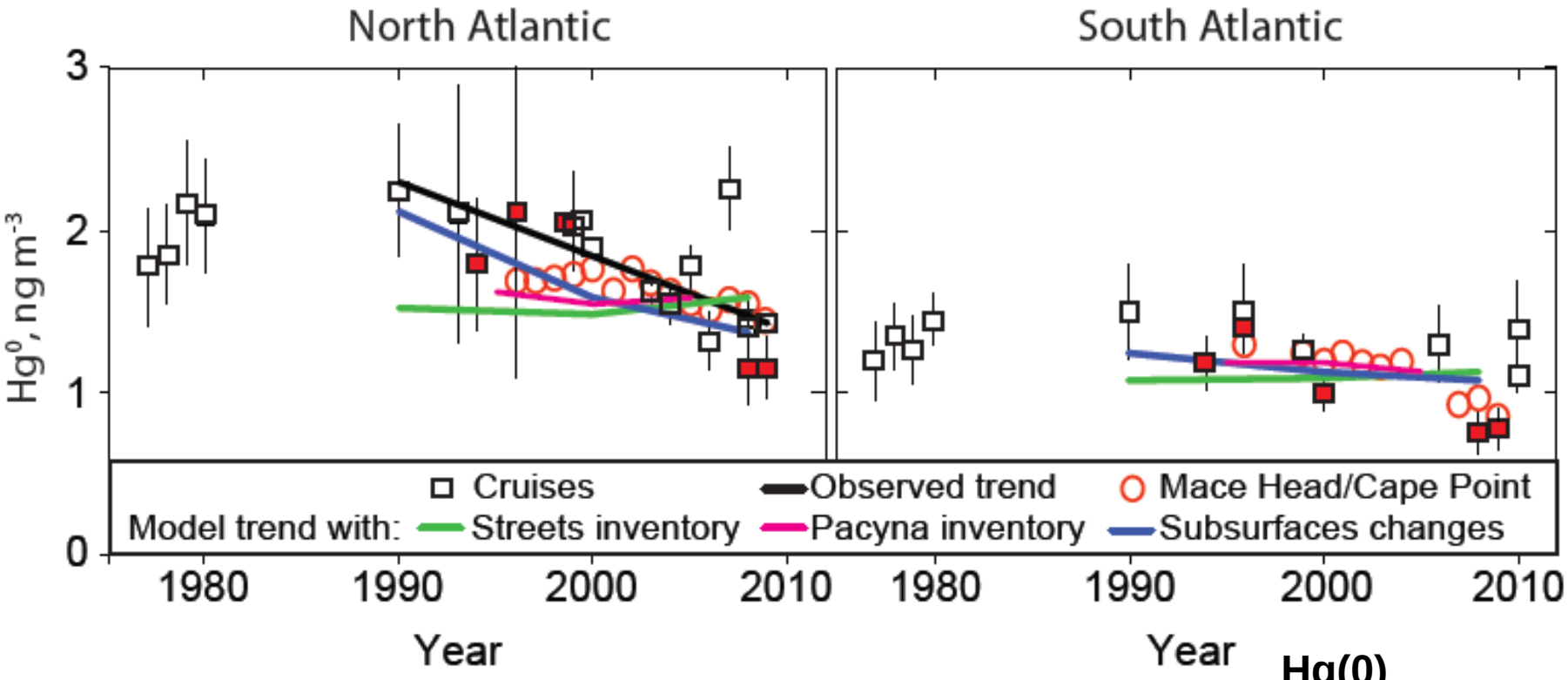
Marine sources from Liang et al. [2010] with seasonality for $CHBr_4$ in extratropics



Tests magnitude of model sources

Parrella et al. [2012]

Hg(0) decreasing trend in North Atlantic surface air



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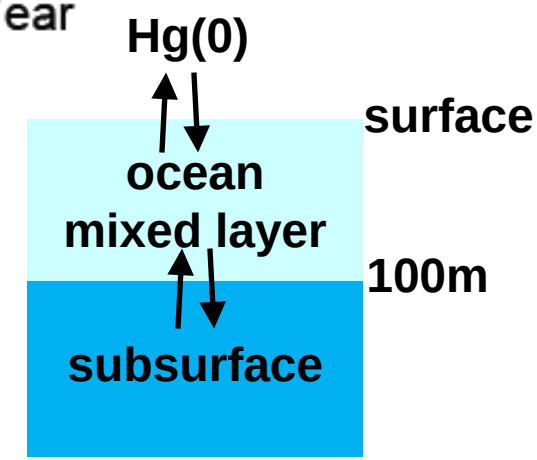

Soerensen et al. [2012]