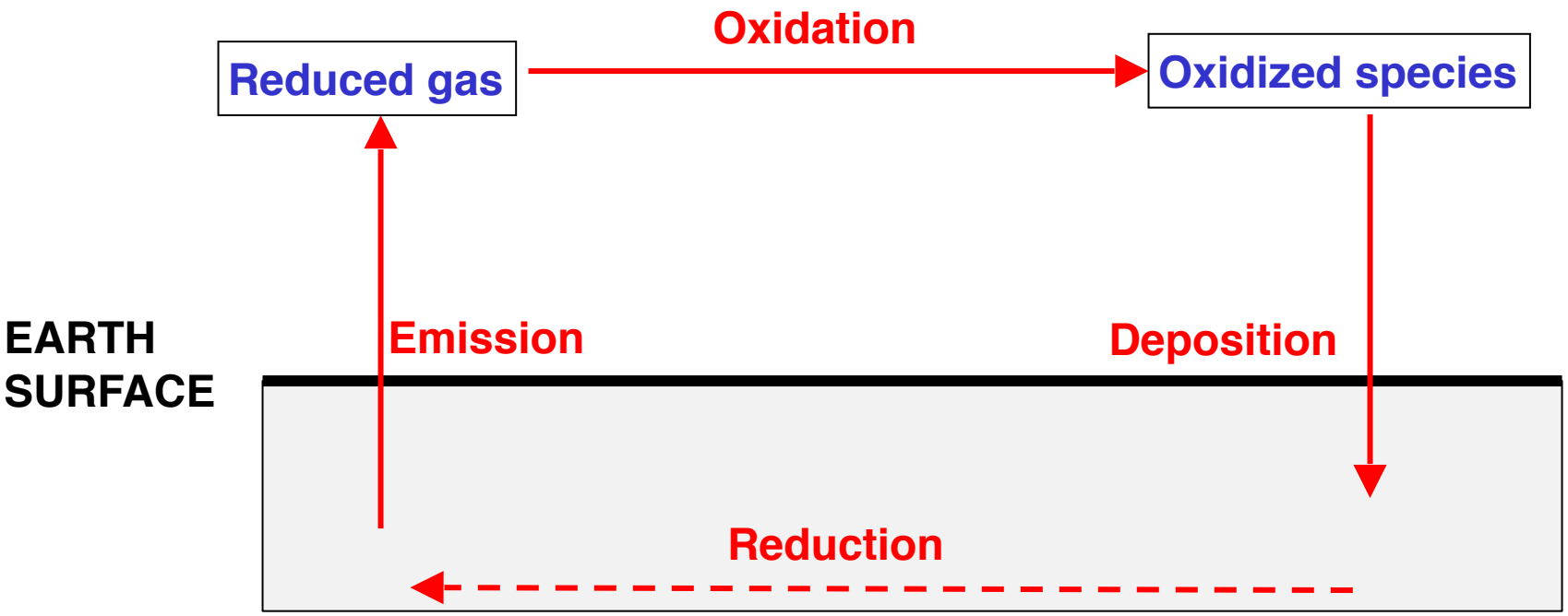
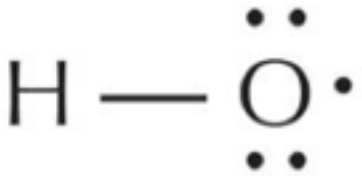
The troposphere as an oxidizing medium



- Oxidation cleans the atmosphere of environmentally harmful gases:
  - Greenhouse gases such as methane, halocarbons
  - Toxic gases such as CO, benzene
  - Ozone-depleting gases such as hydrochlorofluorocarbons (HCFCs)
- Where the oxidation takes place affects patterns of deposition:
  - Acid rain
  - Nitrogen, mercury deposition

Main tropospheric oxidant: the OH radical



Source:

$$O_3 + h\nu \rightarrow O_2 + O(^1D)$$

$$O(^1D) + H_2O \rightarrow 2OH$$

Sink:

$$OH + X \rightarrow \text{products}$$

where X is almost any non-radical reduced species

Lifetime:

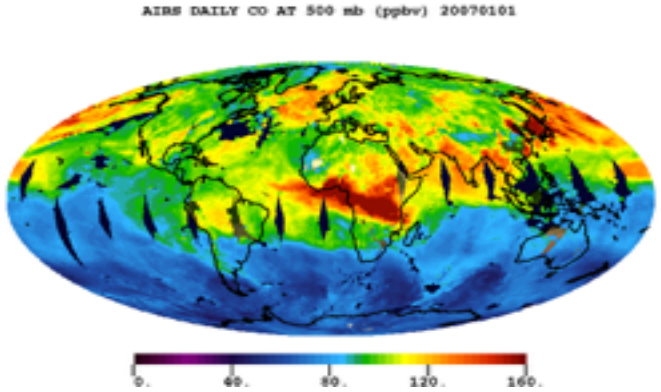
$$\tau_{OH} = \frac{1}{\sum_i k_i[X_i]} \sim 1 \text{ s}$$

➡ concentrations of OH are low, variable

Principal OH sinks:
CO, methane, other volatile organic compounds (VOCs)

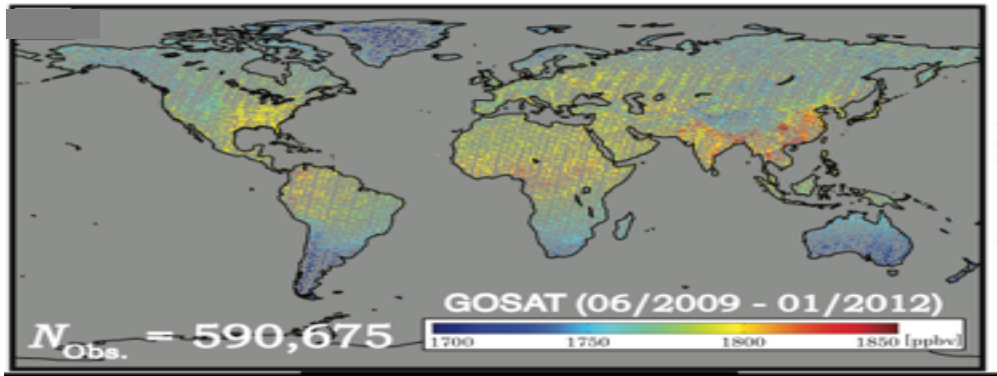
- **CO observed from space: 50-200 ppb**

  Sources: fuel combustion, open fires, VOC oxidation



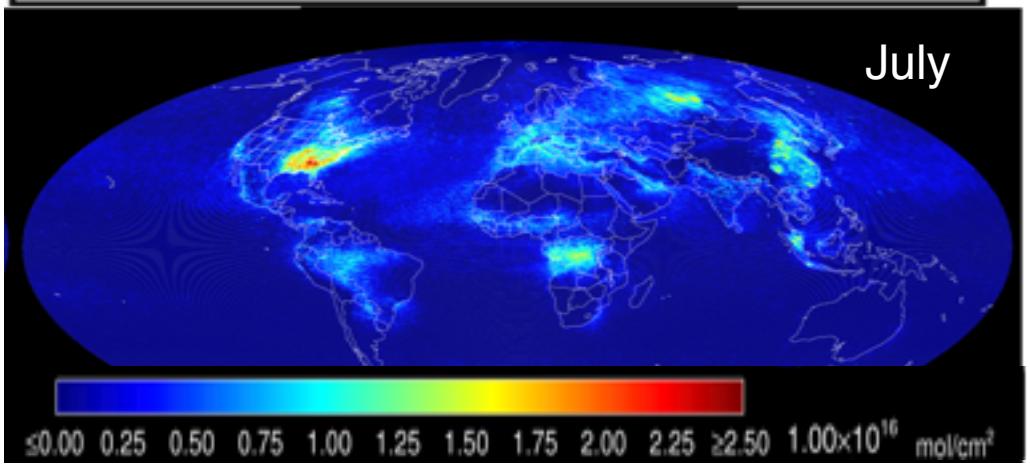
- **Methane observed from space: 1700-1900 ppb**

Sources: wetlands, livestock, oil/gas production, landfills, coal mines…



- **Formaldehyde (HCHO) observed from space: product of VOC oxidation**

Non-methane VOC sources: vegetation, fuel combustion, open fires, industry



Methylchloroform as a proxy for global tropospheric OH

Methylchloroform (CH_3CCl_3):

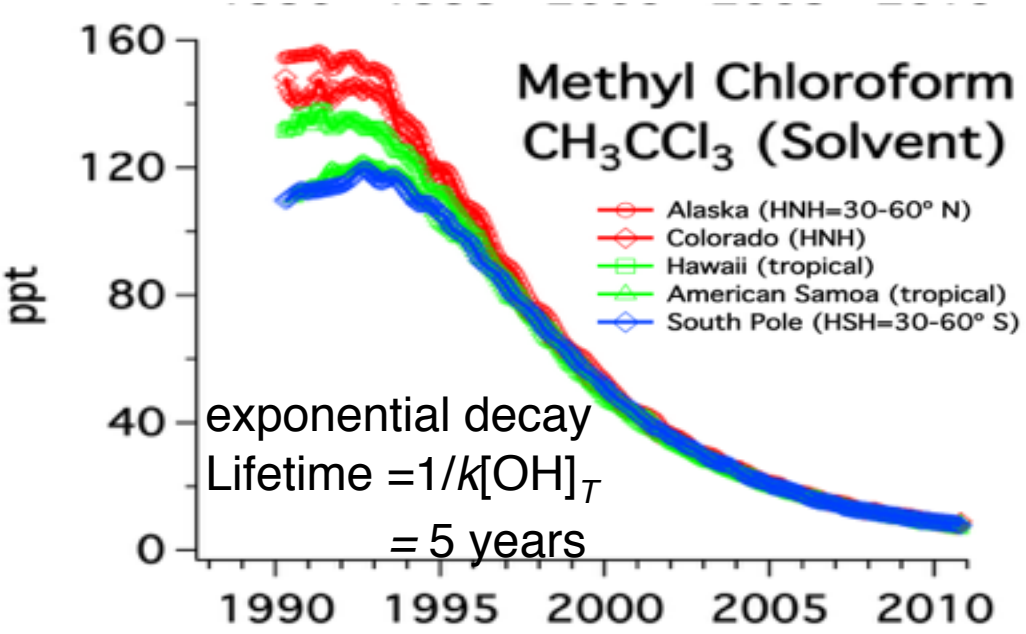
- Uniquely anthropogenic (industrial solvent), banned by Montreal Protocol
- Removed from troposphere by oxidation by OH, transport to troposphere

Mass balance equation for troposphere *(T)*:

Observed decay rate $\frac{dm_T}{dt} = -km_T[OH]_T - k_{TS}m_T + k_{ST}m_S$

loss rate from CH_3CCl_3 + OH

exchange with stratosphere (small)



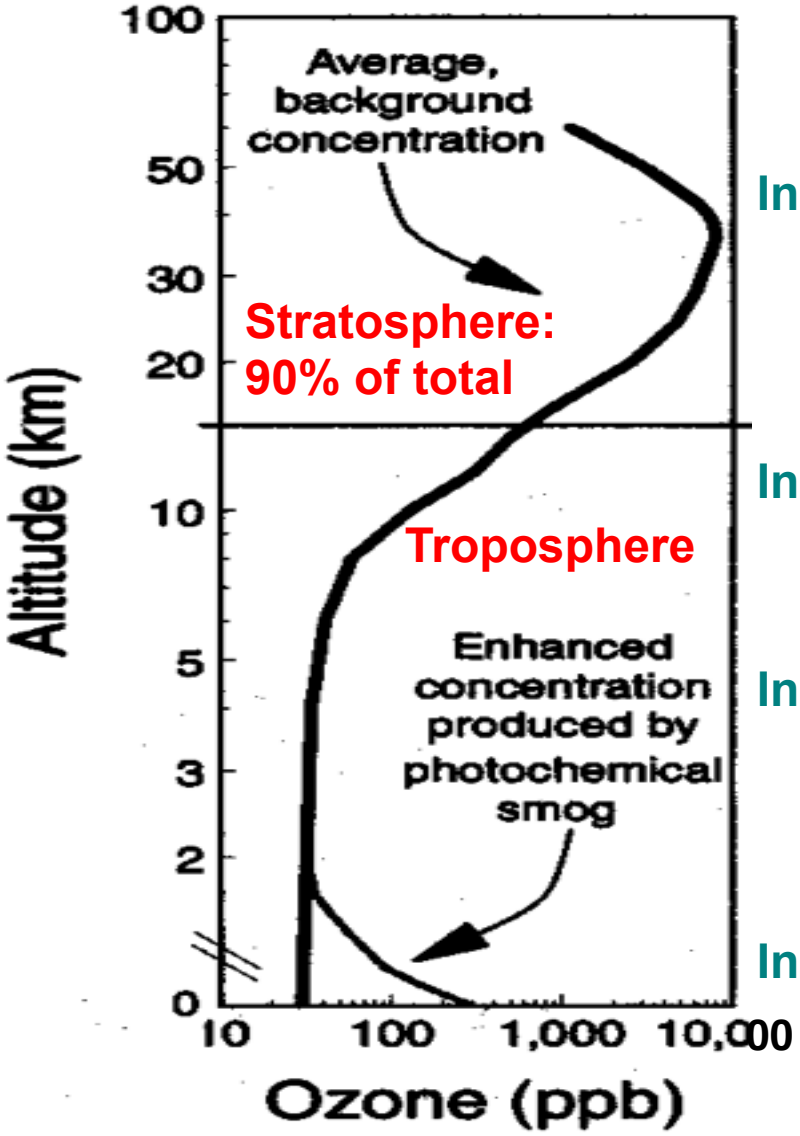
$$[OH]_T = \frac{-dm_T / dt}{km_T}$$

$$= 1.0 \times 10^6 \text{ molecules cm}^{-3}$$

τ_{CO} = 2 months

τ_{CH4} = 10 years

Several reasons to care about tropospheric ozone



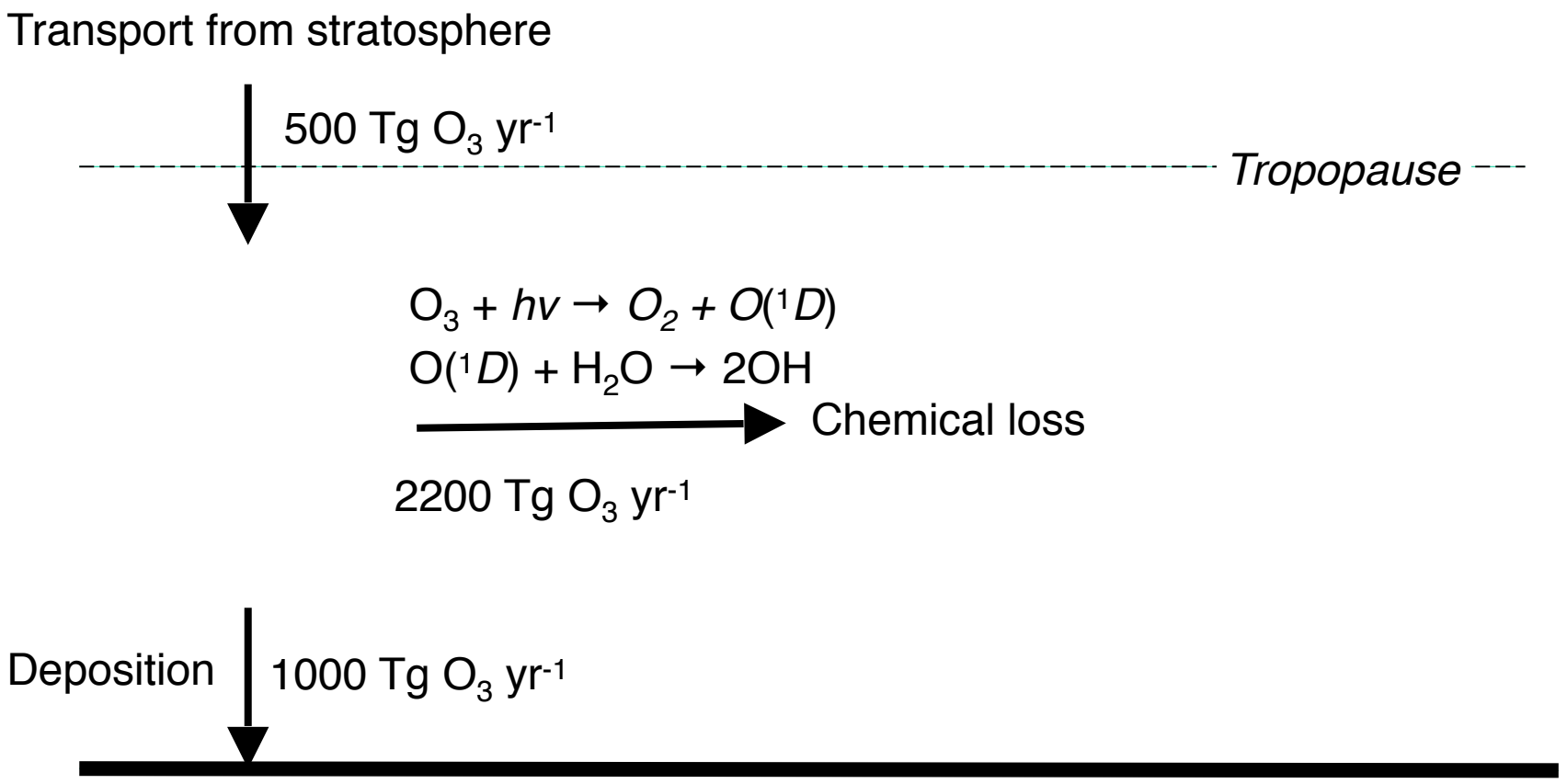
In stratosphere: UV shield

In middle/upper troposphere: greenhouse gas

In troposphere: source of OH

In surface air: toxic to humans and vegetation

Closing the tropospheric ozone budget requires a large chemical source in troposphere

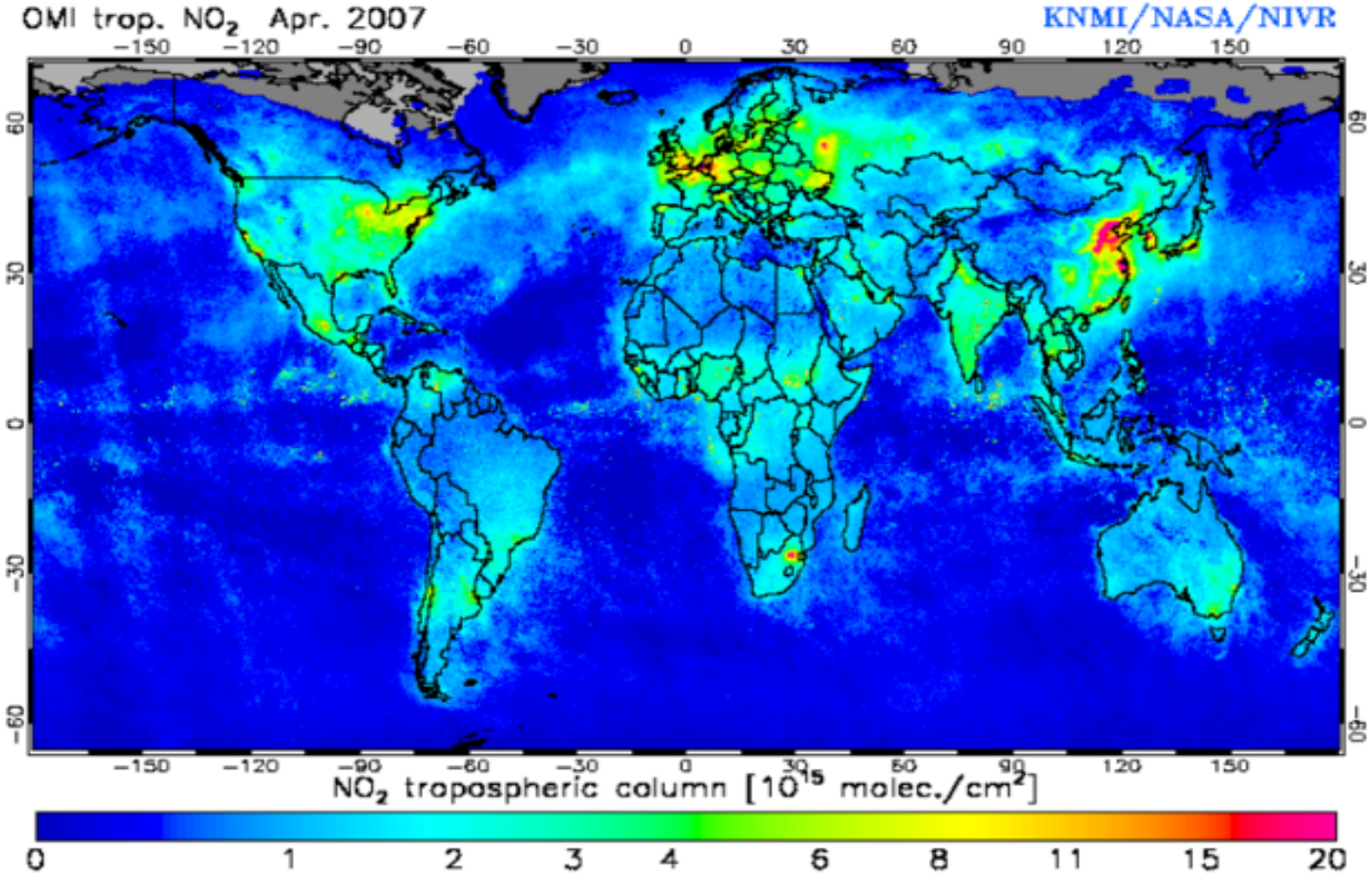


A large tropospheric source is needed to balance the loss

Tropospheric NO_x: critical agent for ozone production

Sources: fuel combustion, open fires, lightning, soils

Tropospheric NO_2 columns measured from satellite



Production of tropospheric ozone by oxidation of CO and VOCs catalyzed by HO_x and NO_x radicals

Initiation: production of HO_x radicals

$$O_3 + h\nu \rightarrow O_2 + O(^1D)$$

$$O(^1D) + H_2O \rightarrow 2OH$$

Propagation: oxidation of CO (simplest case) in presence of NO_x

$$CO + OH \xrightarrow{O_2} CO_2 + HO_2$$

$$HO_2 + NO \rightarrow OH + NO_2$$

$$NO_2 + h\nu \xrightarrow{O_2} NO + O_3$$

Net: $CO + 2O_2 \rightarrow CO_2 + O_3$

Termination: loss of HO_x radicals

$$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$$

$$OH + NO_2 + M \rightarrow HNO_3 + M$$

followed by H_2O_2 and HNO_3 deposition

HO_x and NO_x radicals catalyze ozone production in troposphere, but loss in the stratosphere – why the difference?

In stratosphere,

$$OH + O_3 \rightarrow HO_2 + O_2$$
$$HO_2 + O_3 \rightarrow OH + 2O_2$$
Net: $2O_3 \rightarrow 3O_2$

$$NO + O_3 \rightarrow NO_2 + O_2$$
$$NO_2 + O \rightarrow NO + O_2$$
Net: $O_3 + O \rightarrow 2O_2$

In troposphere,

$$CO + OH \xrightarrow{O_2} CO_2 + HO_2$$
$$HO_2 + NO \rightarrow OH + NO_2$$
$$NO_2 + h\nu \xrightarrow{O_2} NO + O_3$$
Net: $CO + 2O_2 \rightarrow CO_2 + O_3$

- CO/O_3 and NO/O_3 ratios are much higher in troposphere than stratosphere
- O concentrations are very low in troposphere

Methane oxidation cascade follows same schematic as CO

$$CH_4 + OH \xrightarrow{O_2} CH_3O_2 + H_2O$$

$$CH_3O_2 + NO \rightarrow CH_3O + NO_2$$

$$CH_3O + O_2 \rightarrow CH_2O + HO_2$$

$$CH_2O + OH \xrightarrow{O_2} CO + HO_2 + H_2O$$

$$CO + OH \xrightarrow{O_2} CO_2 + HO_2$$

$$HO_2 + NO \rightarrow OH + NO_2$$

$$NO_2 + h\nu \xrightarrow{O_2} NO + O_3$$

$$\text{Net: } CH_4 + 8O_2 \rightarrow CO_2 + 4O_3 + 2H_2O$$

	C oxidation #
CH_4	-4
CH_2O	0
CO	+2
CO_2	+4

- Expanded HO_x family: $HO_x \equiv OH + HO_2 + CH_3O_2 + CH_3O$
- Oxidation of methane by above mechanism produces four ozone molecules

Questions

1. How do you expect recovery of the stratospheric ozone layer to affect tropospheric OH concentrations?

2. Maximum photon flux during summer results in a seasonal maximum of ozone in polluted regions but a seasonal minimum of ozone in very clean regions. Why is that?

Same basic mechanism for higher VOCs but many branches

RO_2 can also isomerize, or react with HO_2 or RO_2, producing peroxides, epoxides, alcohols, carboxylic acids…

OH can also add to double bonds of unsaturated VOCs, producing hydroxyorganics

$$RH + OH \xrightarrow{O_2} RO_2 + H_2O$$

$$RO_2 + NO \rightarrow RO + NO_2$$

NO can also add to produce organic nitrates

$$RO + O_2 \rightarrow R'CHO + HO_2$$

$$HO_2 + NO \rightarrow OH + NO_2$$

$$NO_2 + h\nu \xrightarrow{O_2} NO + O_3$$

$$\text{Net: } RH + 4O_2 \rightarrow R'CHO + 2O_3 + H_2O$$

RO can also decompose or isomerize to produce a range of aldehydes, ketones, dicarbonyls…

Oxidation product goes on to react with OH, adding functionality and making more ozone

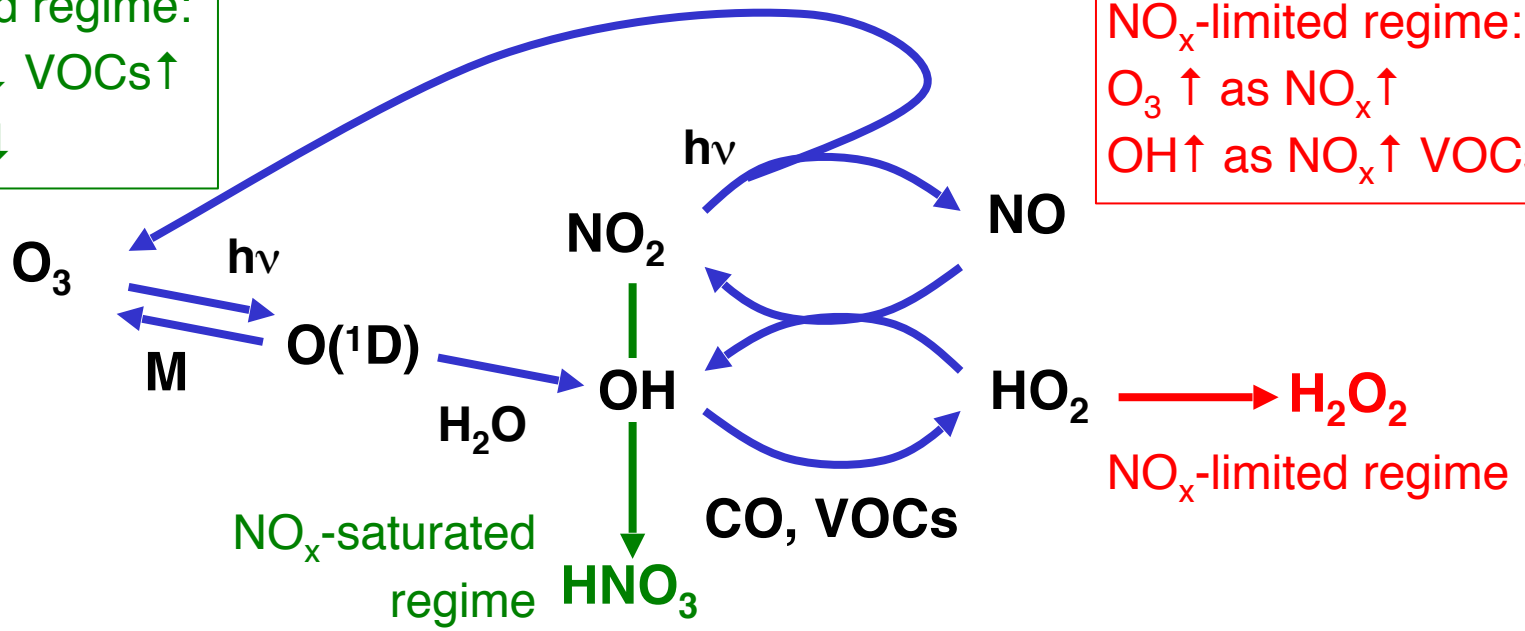
A brief cheat sheet for organic functions

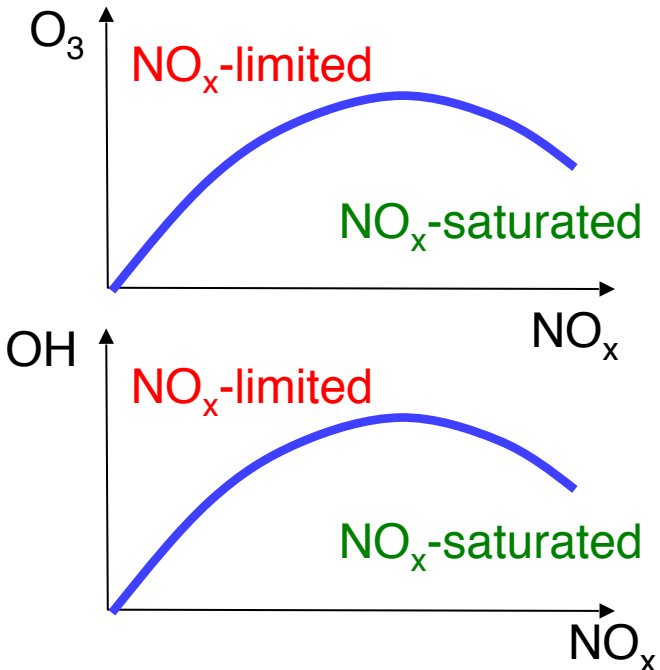
RCHO	aldehyde
RC(O)R’	ketone
RC(O)-	acyl group
RC(O)C(O)R’	dicarbonyl
RO_2	peroxy radical
ROOR’	peroxide
ROOH	hydroperoxide
ROH	hydroxy, alcohol
RC(O)CR’	epoxide (cyclic ether)
RC(O)OH	carboxylic acid
RC(O)OR’	ester
$RONO_2$	nitrate

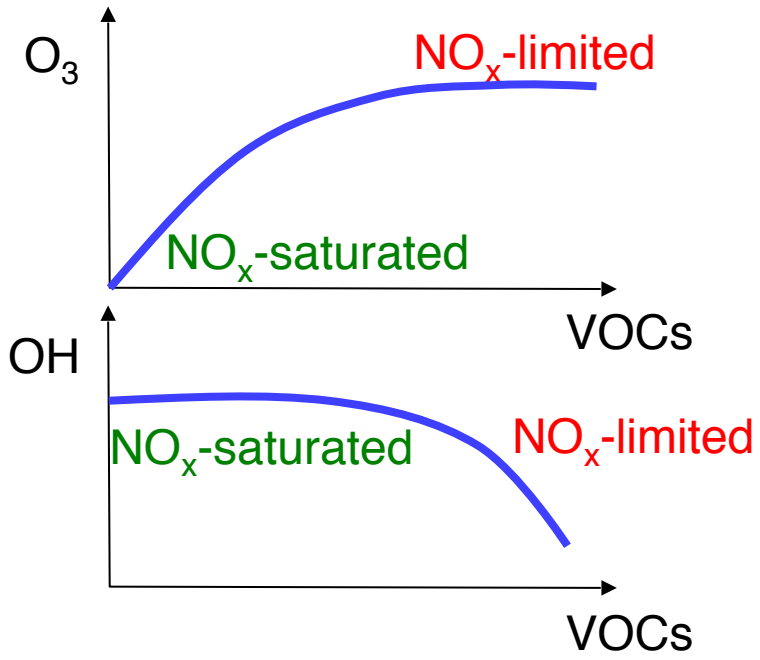
Dependence of ozone production and OH on NO_x and VOCs

NO_x-saturated regime:
O_3 ↑ as NO_x↓ VOCs↑
OH↑ as NO_x↓

NO_x-limited regime:
O_3 ↑ as NO_x↑
OH↑ as NO_x↑ VOCs↓







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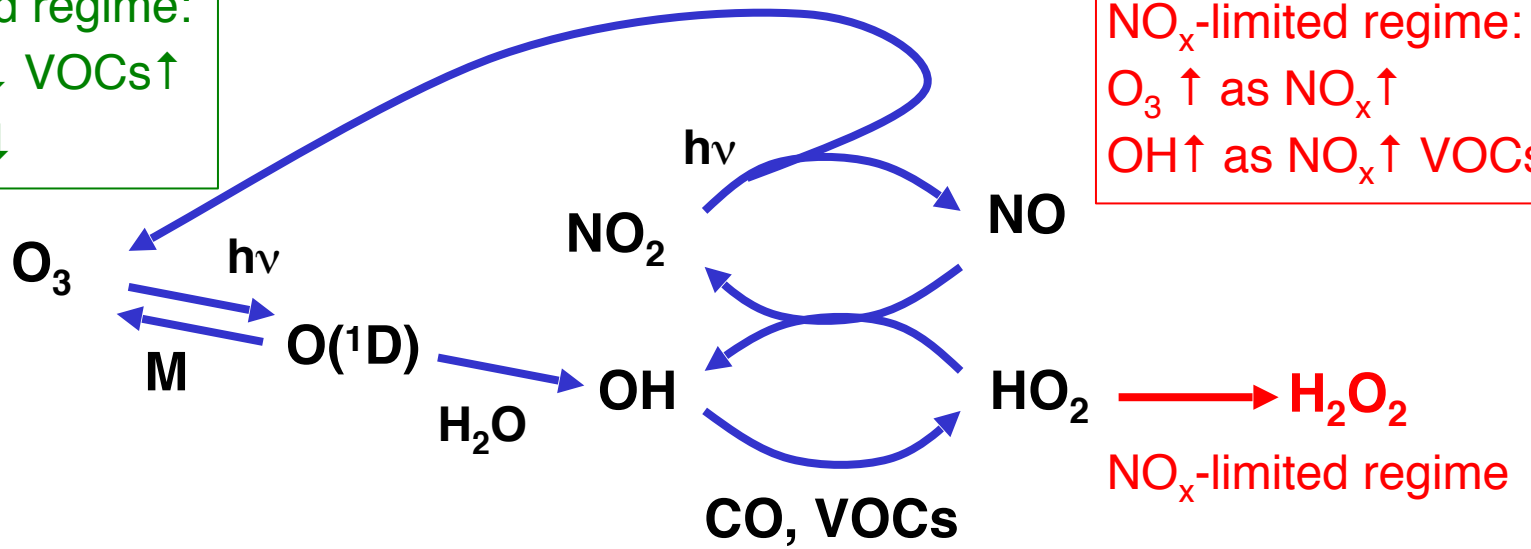

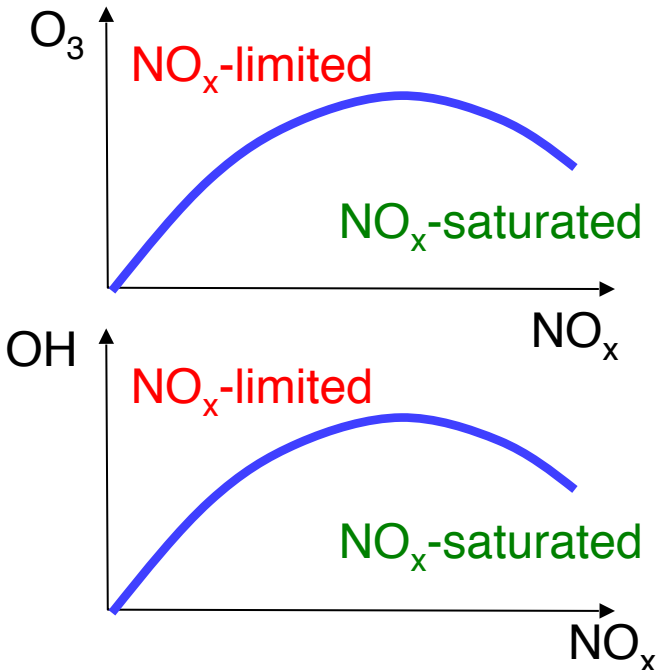

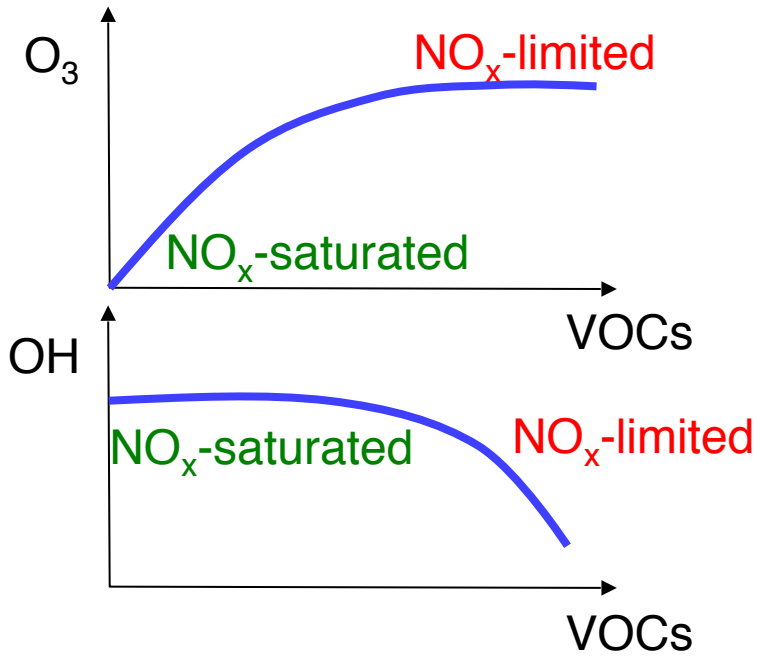

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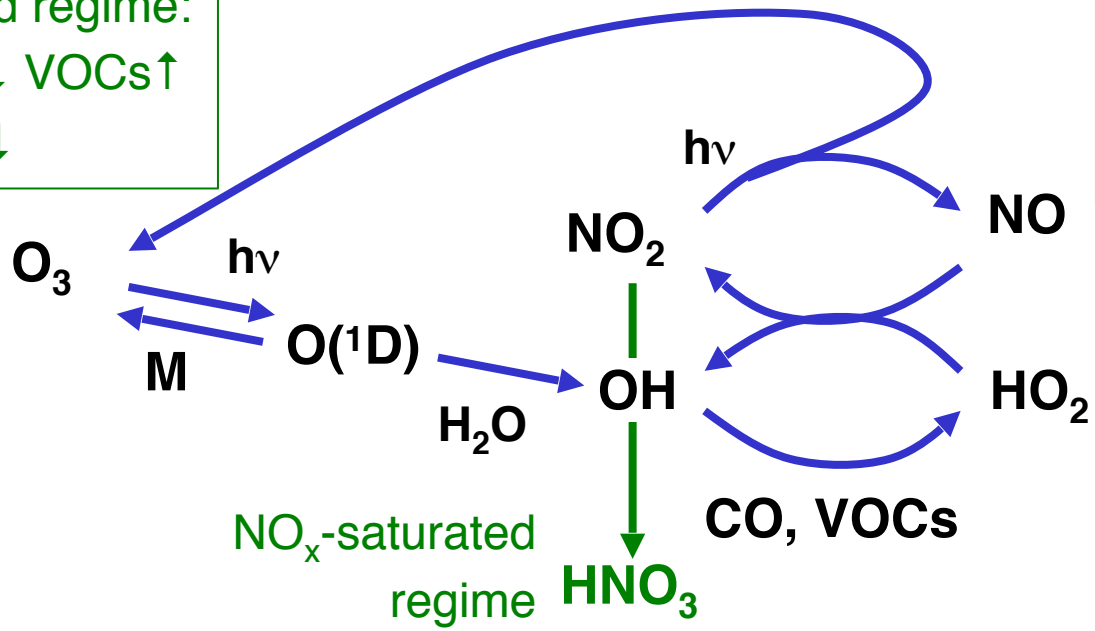
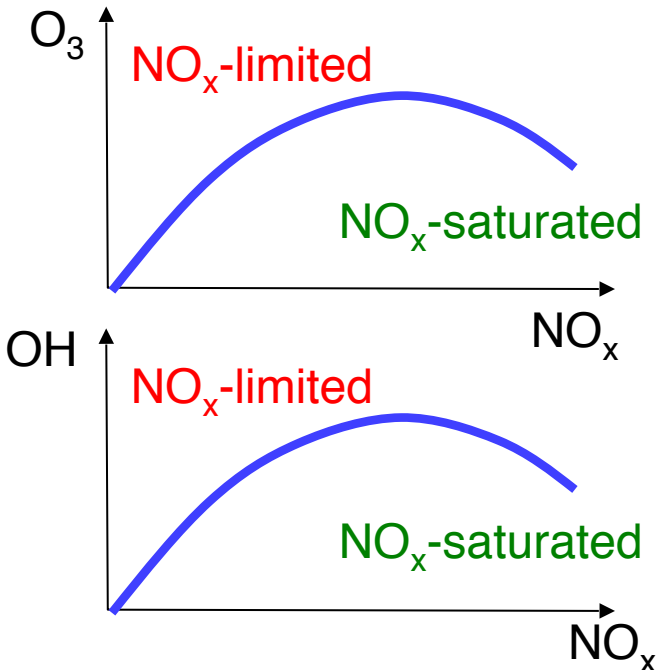
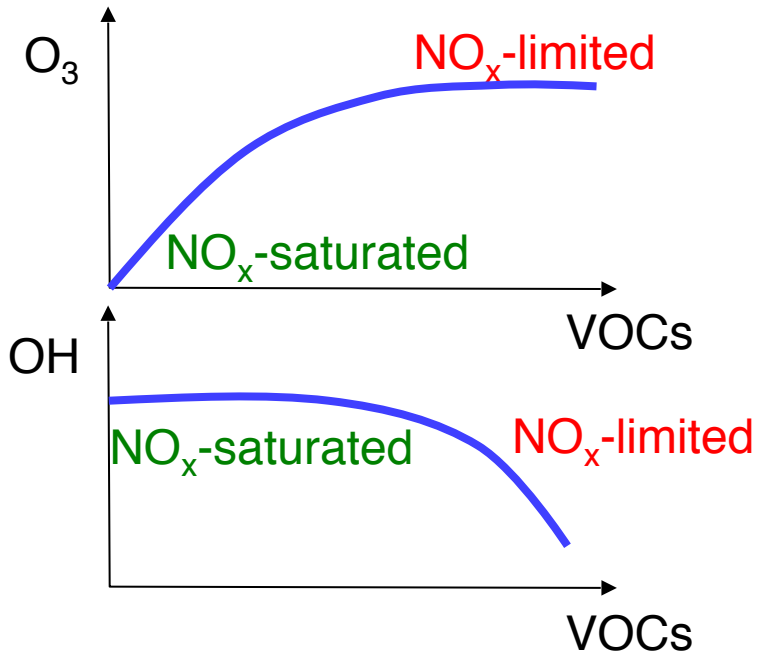
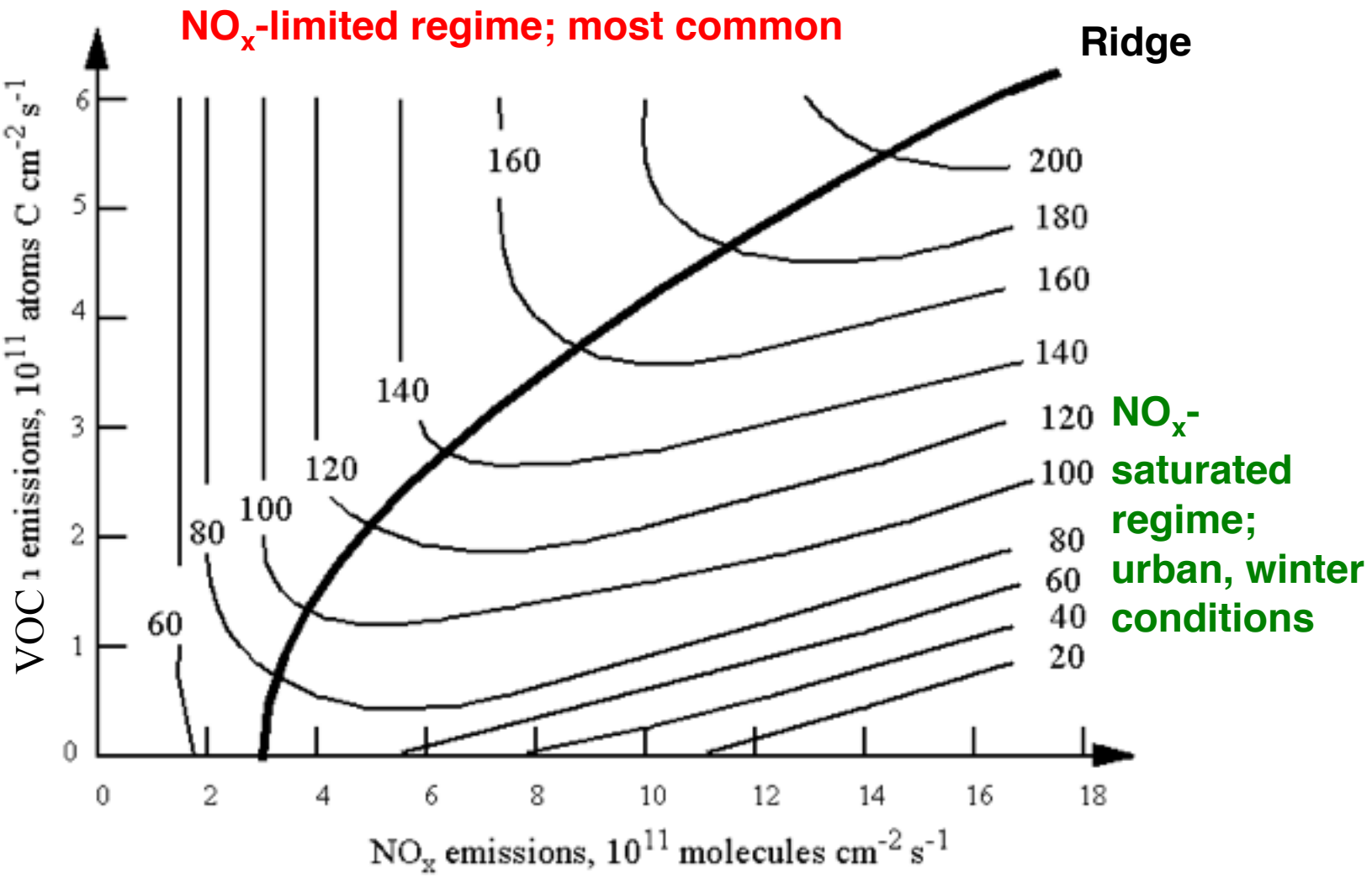






OZONE CONCENTRATIONS vs. NO_x AND VOC EMISSIONS

Sample box model calculation with detailed mechanism

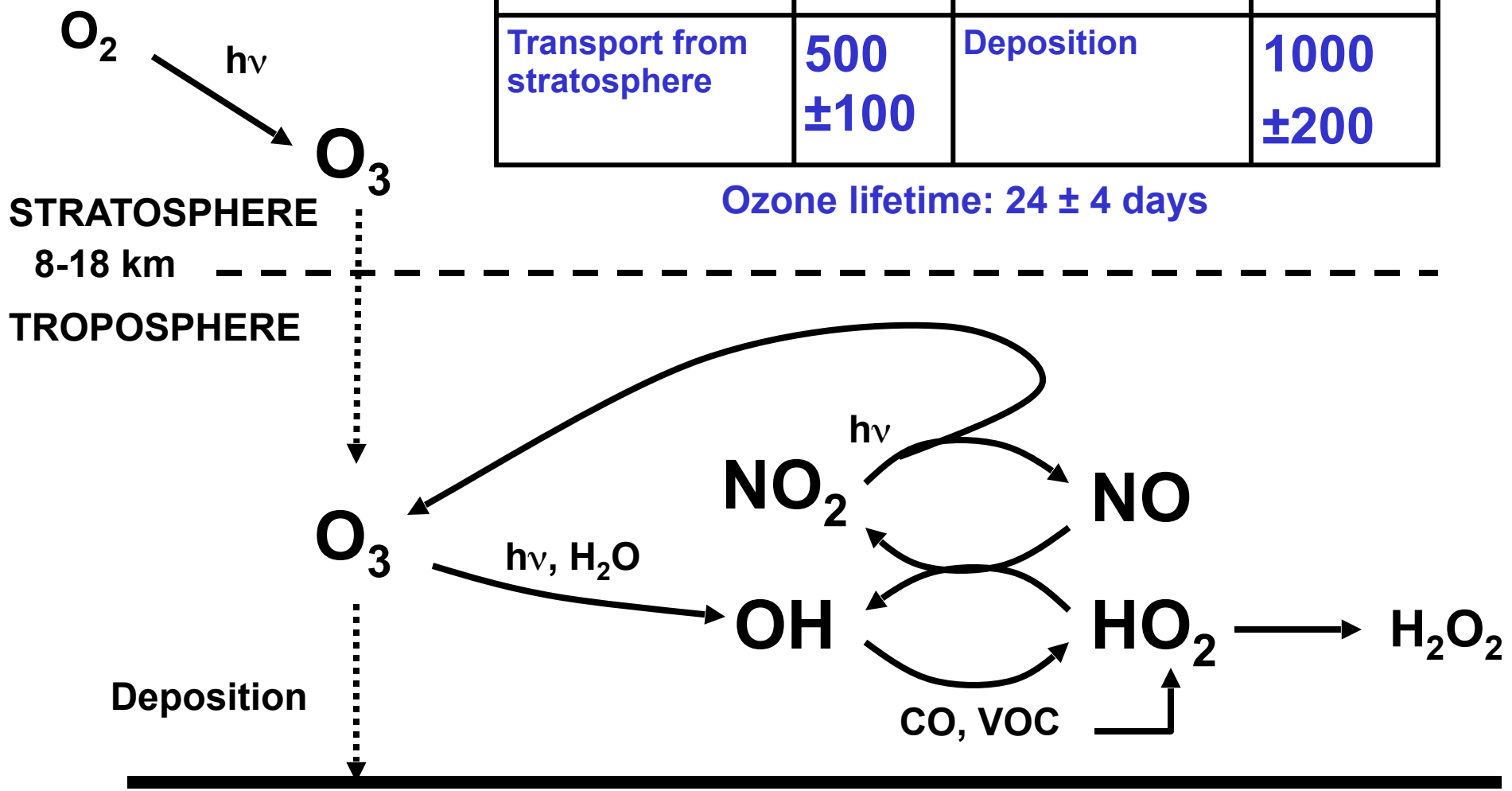


GLOBAL BUDGET OF TROPOSPHERIC OZONE (Tg O_3 yr^{-1})

IPCC (2007) average of 12 models

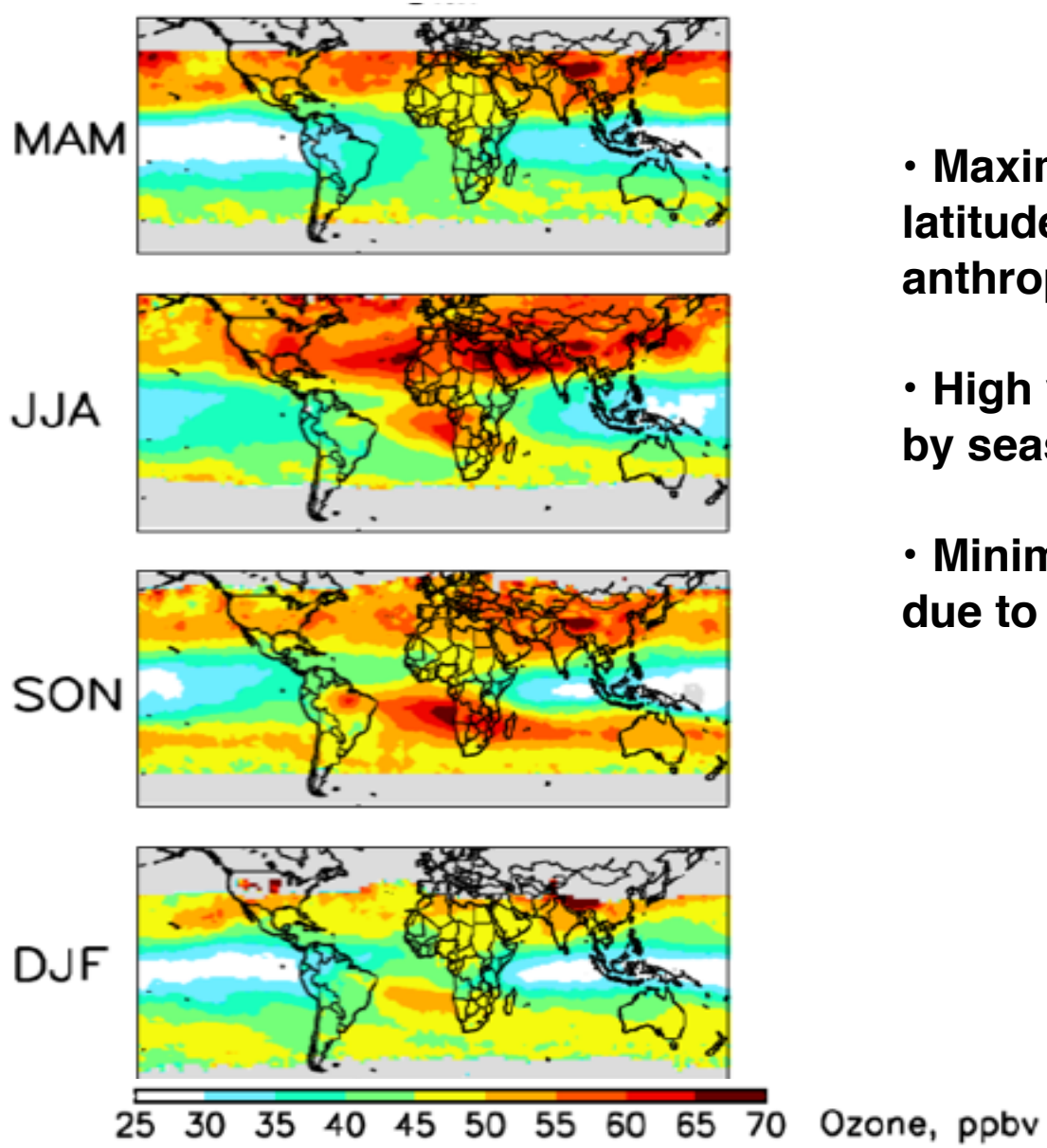
Chem prod in troposphere	4700 ±700	Chem loss in troposphere	4200 ±500
Transport from stratosphere	500 ±100	Deposition	1000 ±200

Ozone lifetime: 24 ± 4 days



GLOBAL DISTRIBUTION OF TROPOSPHERIC OZONE

OMI satellite observations at 700-400 hPa

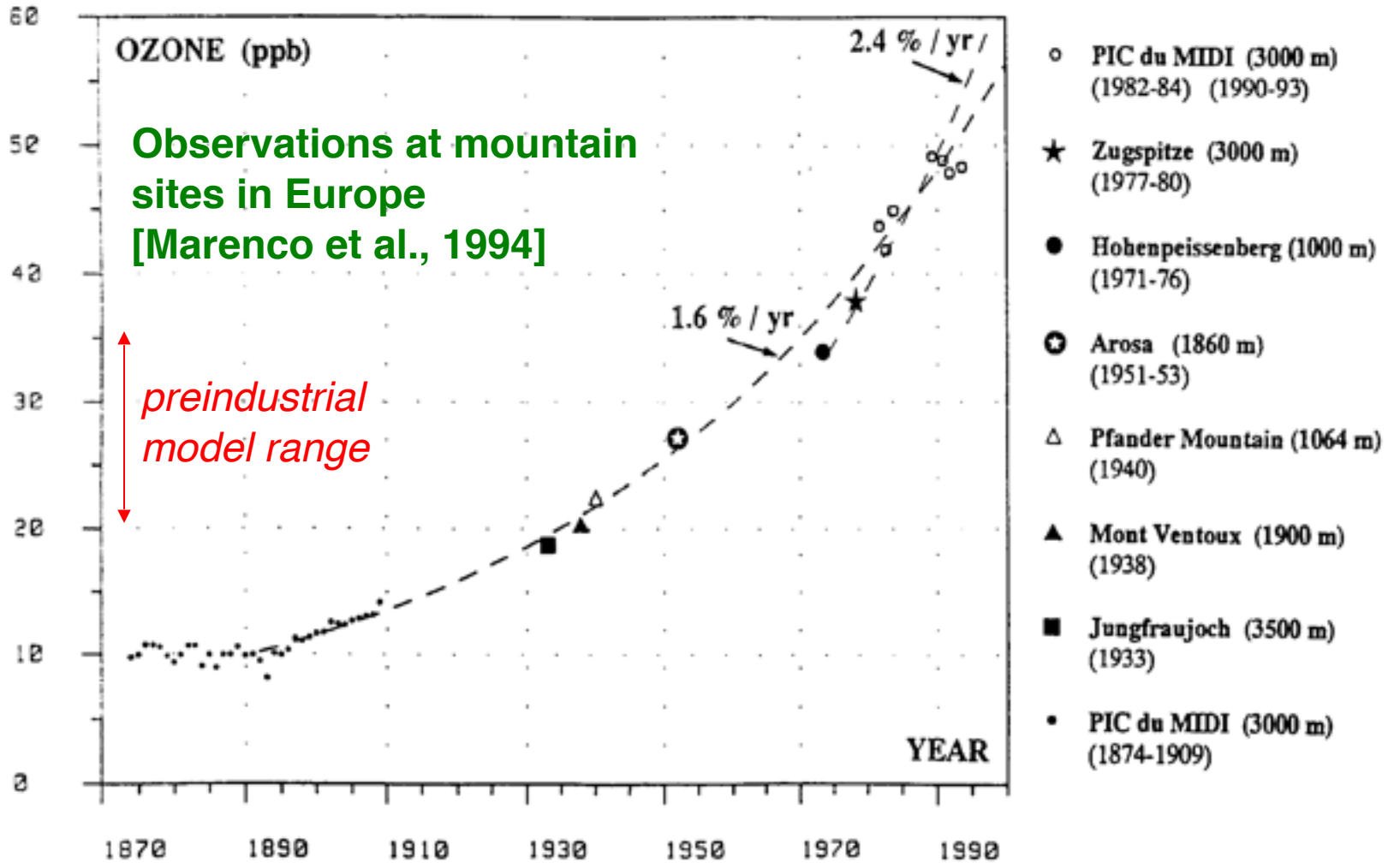


- **Maximum values at northern mid-latitudes in spring-summer due to anthropogenic pollution;**
- **High values in tropical regions affected by seasonal biomass burning;**
- **Minimum values over tropical oceans due to chemical loss**

Hu et al. [2017]

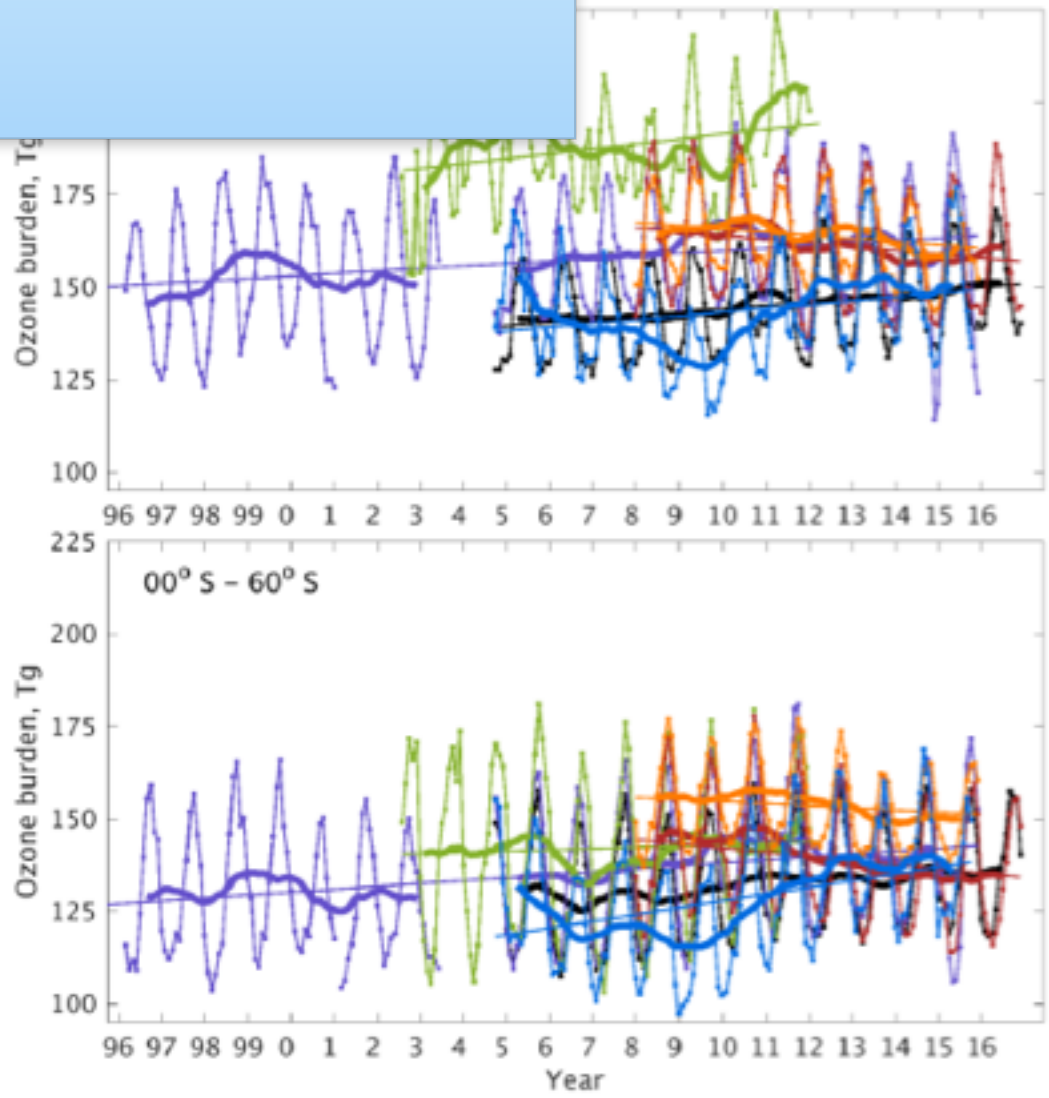
Observed rise of tropospheric ozone in 20th century

thought to be due mostly to anthropogenic NO_x and methane but this is uncertain



tropospheric ozone seen from satellites

se in ozone that models cannot explain

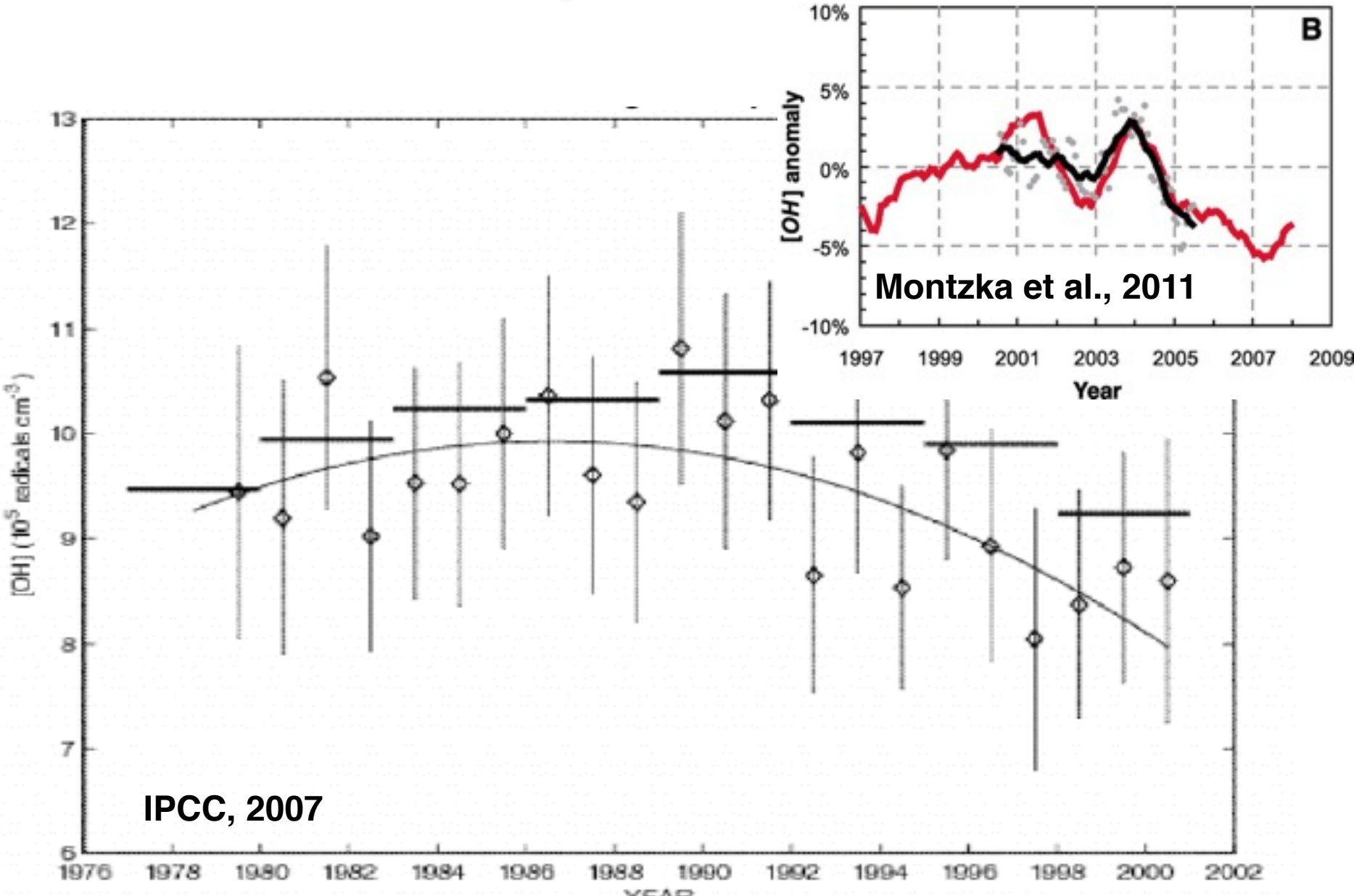


	change, Tg yr^{-1}	p-value
Black: OMI/MLS	0.95 +/- 0.55	0.00
Brown: IASI-FORLI	-1.01 +/- 1.17	0.09
Orange: IASI-SOFRID	-0.86 +/- 0.95	0.07
Purple: GOME/OMI	0.68 +/- 0.39	0.00
Blue: OMI-RAL	1.02 +/- 0.79	0.01
Green: SCIAMACHY	1.33 +/- 1.04	0.01

	change, Tg yr^{-1}	p-value
Black: OMI/MLS	0.83 +/- 0.64	0.01
Brown: IASI-FORLI	-1.14 +/- 1.14	0.05
Orange: IASI-SOFRID	-0.56 +/- 0.97	0.26
Purple: GOME/OMI	0.80 +/- 0.40	0.00
Blue: OMI-RAL	1.83 +/- 0.84	0.00
Green: SCIAMACHY	0.34 +/- 1.48	0.65

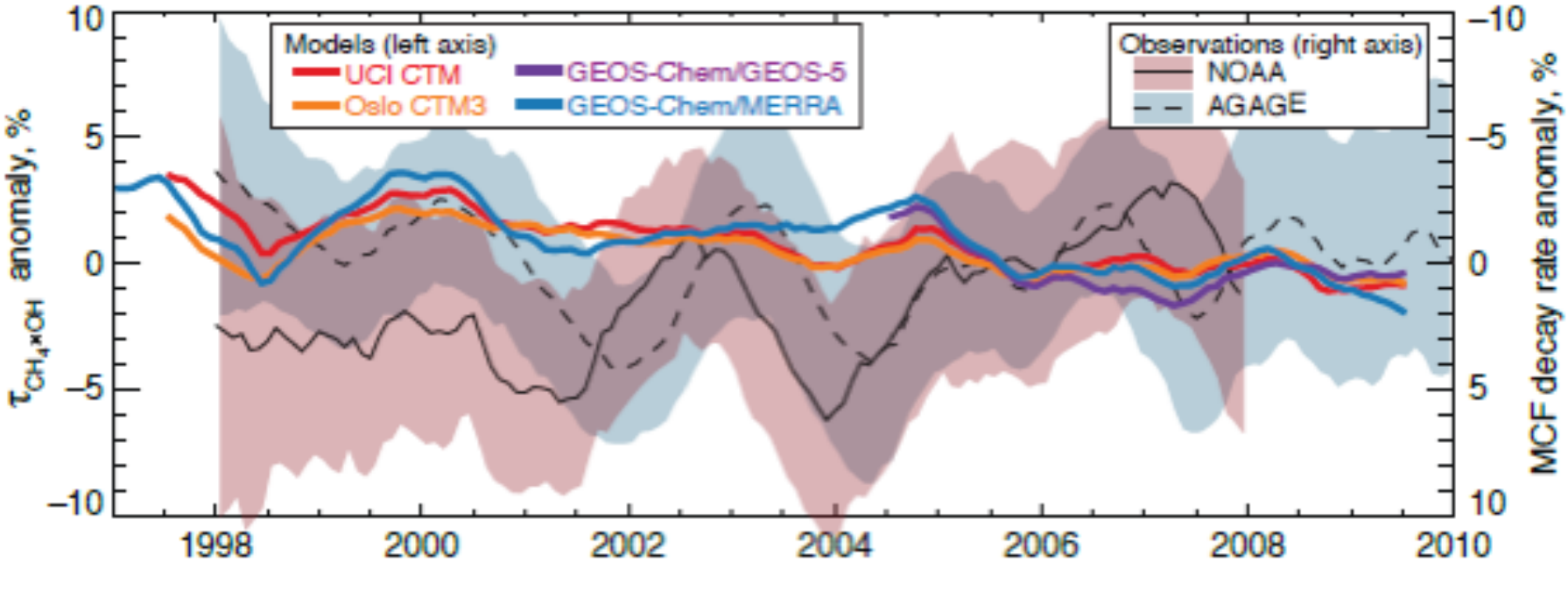
Cooper et al. [2017]

TRENDS IN GLOBALTROPOSPHERIC OH
inferred from methylchloroform observations



But current models have no skill in simulating observed OH trends

Lightning NO_x is the dominant factor of interannual variability in models



Better understanding of OH changes is needed!

Holmes et al., ACP2013

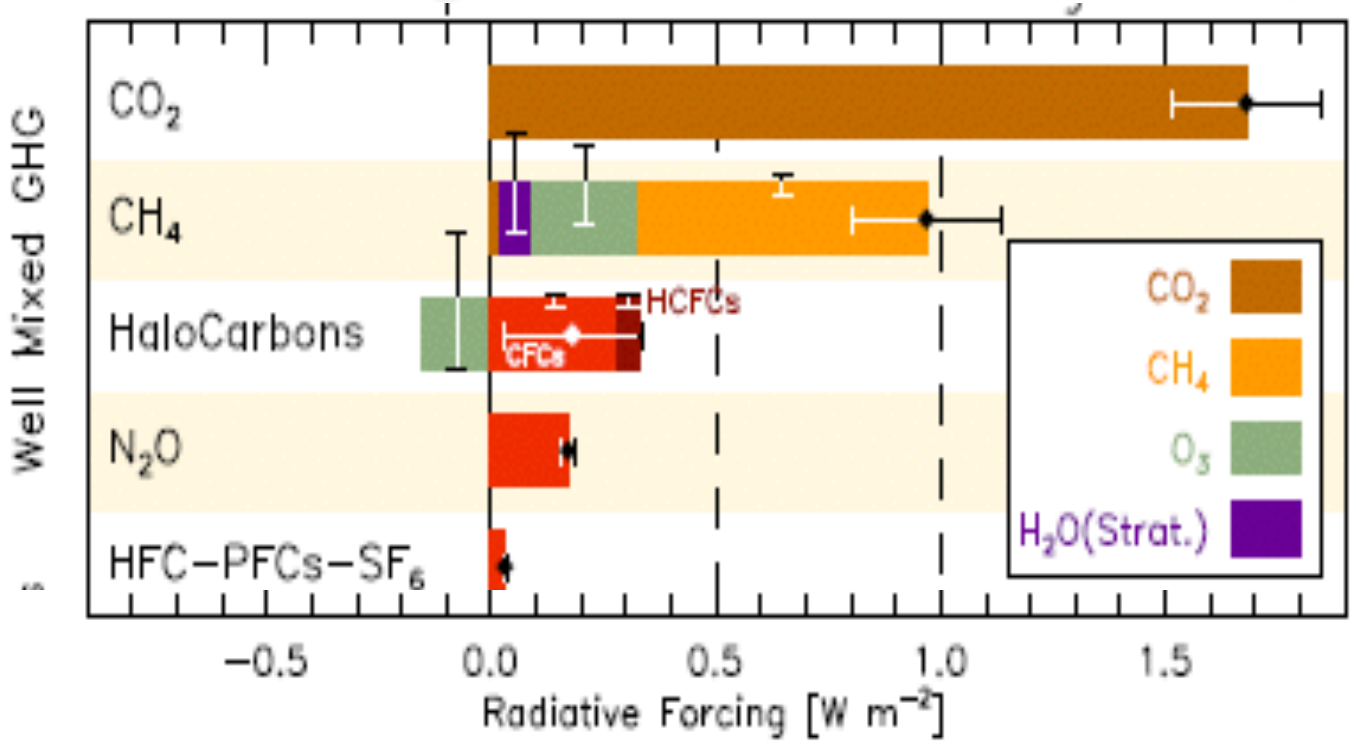
Questions

1. If the methane source to the atmosphere were to double, would the methane concentration (a) double, (b) less than double, (c) more than double?

2. Atmospheric measurements of the H_2O_2/HNO_3 concentration ratio offer a simple diagnostic of whether ozone production in a polluted environment is NO_x-limited or NO_x-saturated. Why?

Methane: 2nd anthropogenic greenhouse gas after CO_2

Radiative forcing of climate referenced to emissions, 1750-2011



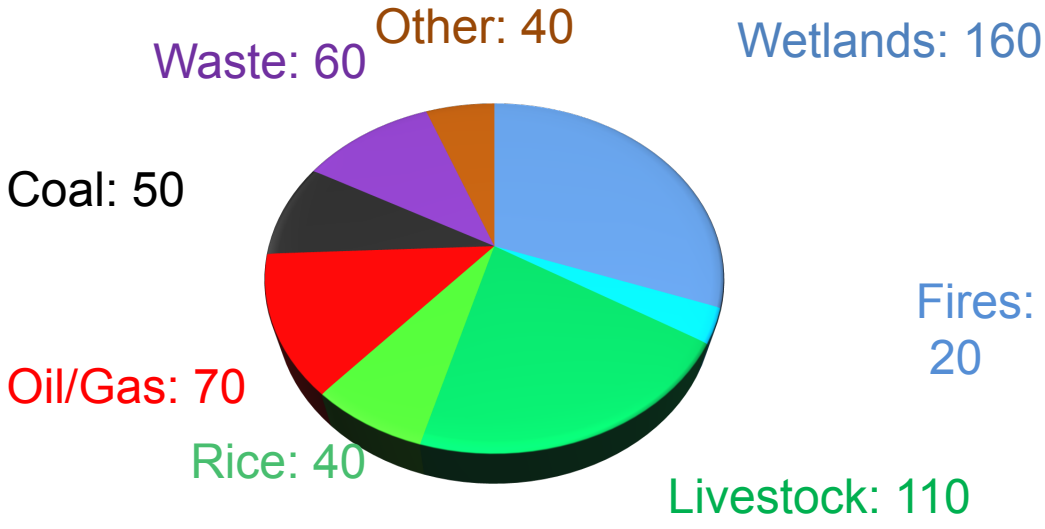
[IPCC, 2014]

- Methane is 60% as important as CO_2 in explaining past warming
- Atmospheric lifetime of methane is 9 years, much shorter than CO_2 (> 100 years)
  - ⇒ Methane is most relevant as a near-term (~20 years) climate forcer
  - ⇒ Methane and CO_2 emissions should not be "equivalent" in climate policy
- Reducing methane emissions has air quality co-benefits and can make money

Complexity of methane sources

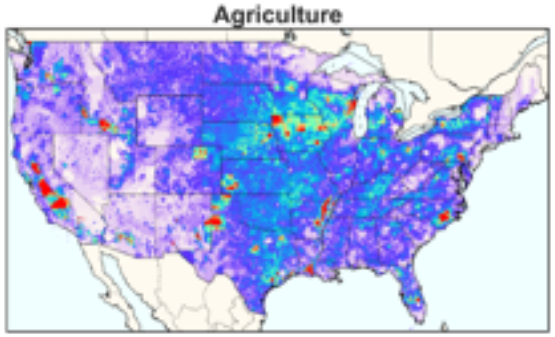
CH_4 —Oxidation by OH radical, Lifetime 9 years→ CO_2

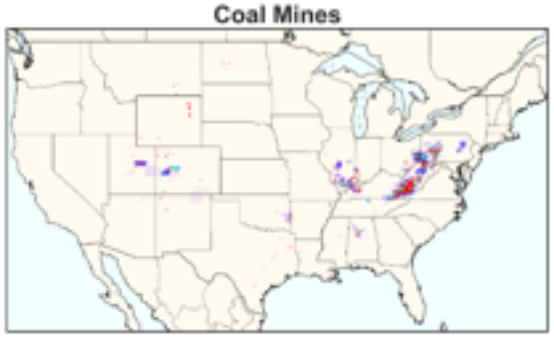
Emission
550 ± 60 Tg/year

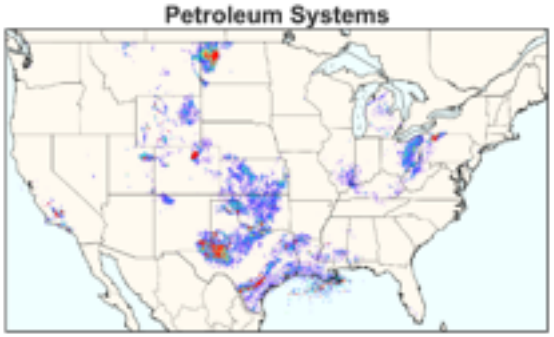


Global totals (Tg/y), EDGAR4.2 and LPJ wetlands

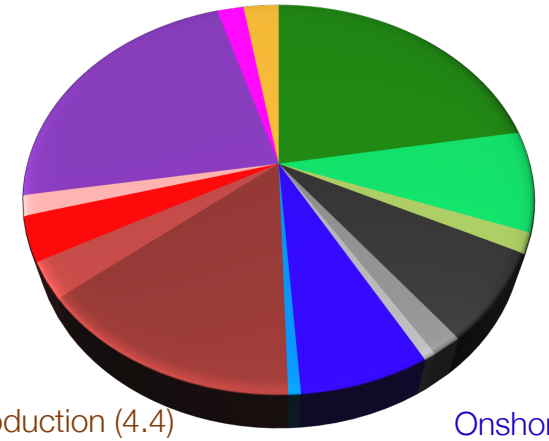
EPA anthropogenic methane inventory for the US







EPA US inventory (2012) submitted to UNFCCC



Other 0.8

Wastewater (0.6)

Waste 7.6

Landfills (6.9)

Distribution (0.5)

Transmission (1.1)

Processing (0.9)

Natural gas 6.9

Production (4.4)

(All values in Tg a^{-1})

Agriculture 9.7

Enteric fermentation (6.7)

Manure (2.5)

Rice (0.5)

Coal 2.9

Underground (2.2)

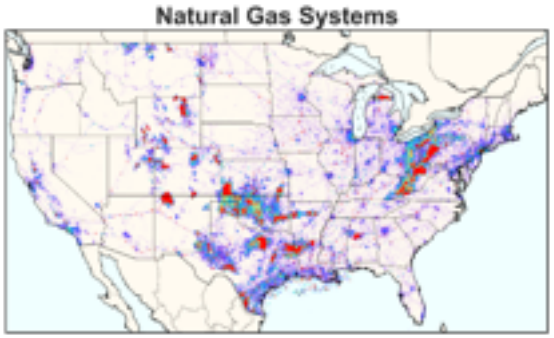
Surface (0.5)

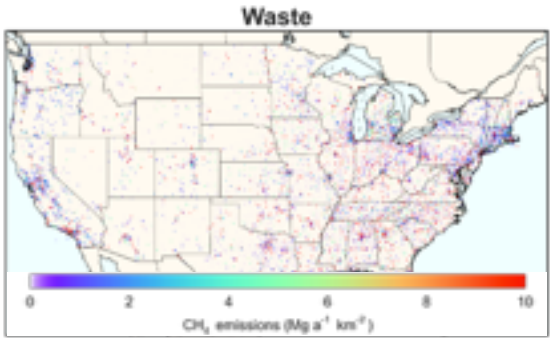
Abandoned (0.2)

Onshore (2.1)

Petroleum 2.3

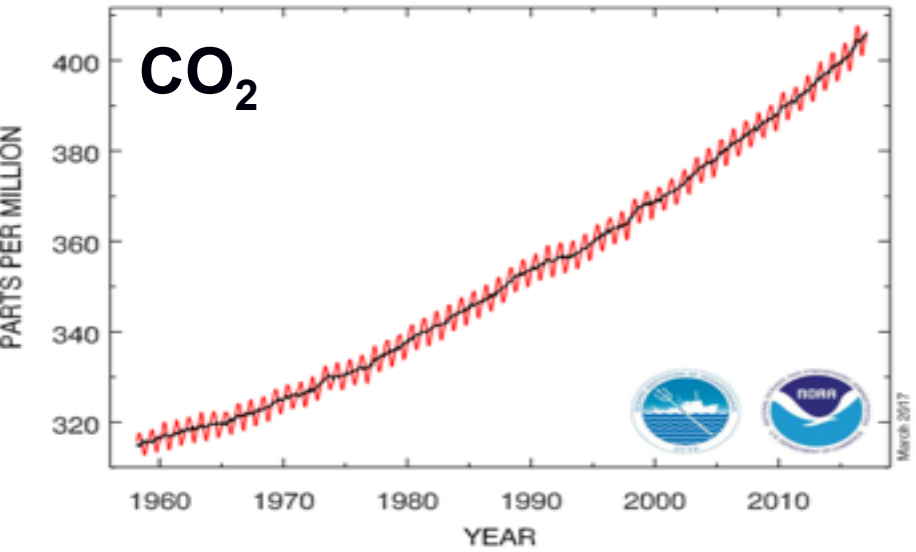
Offshore (0.2)

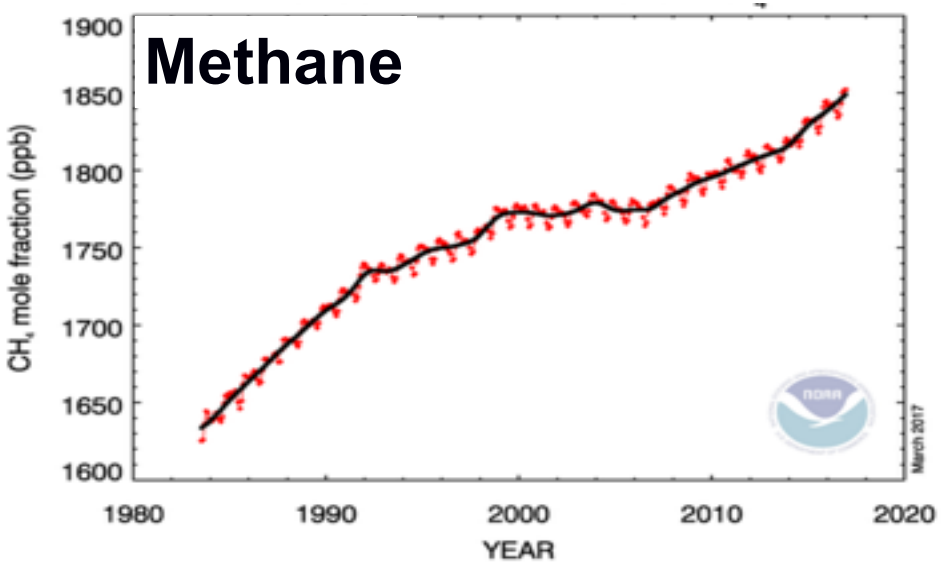




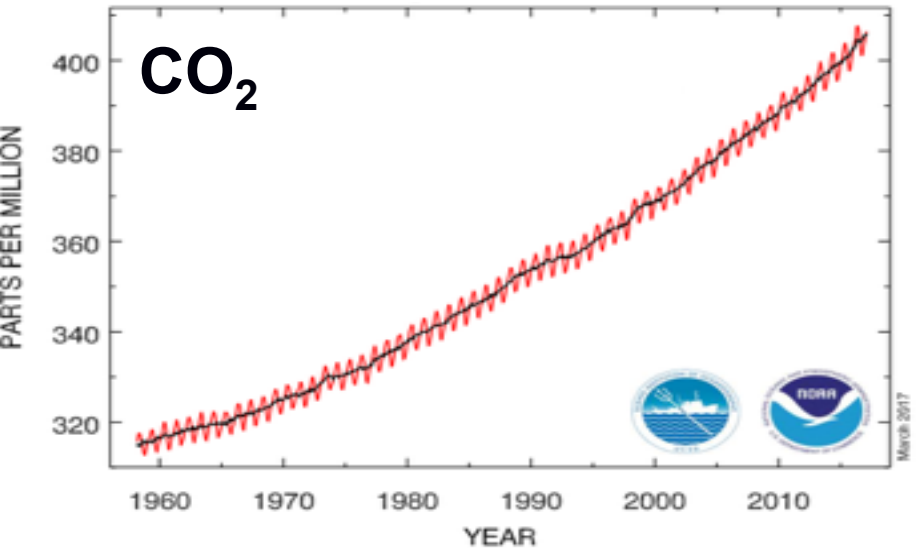
Maasakkers et al. [2016]

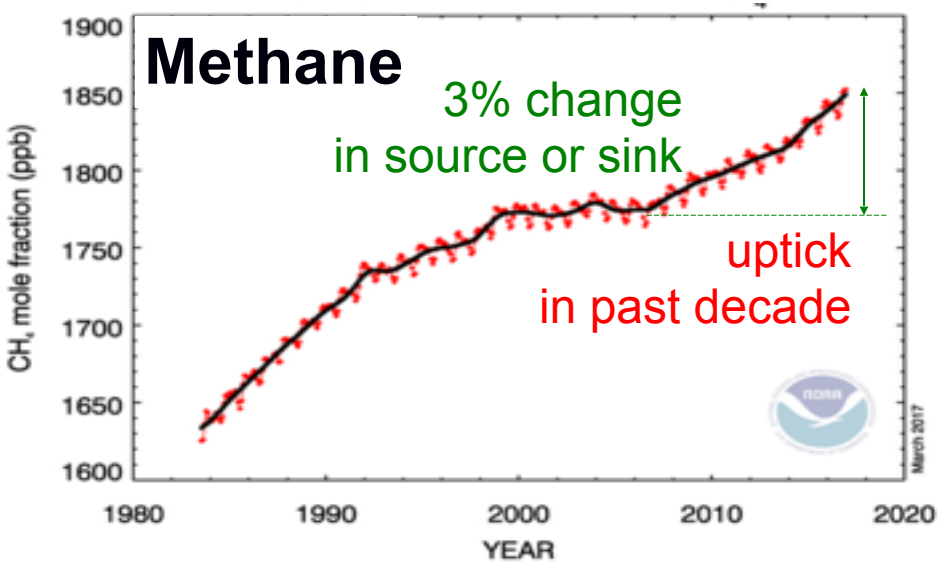
Methane fits and starts over past 40 years





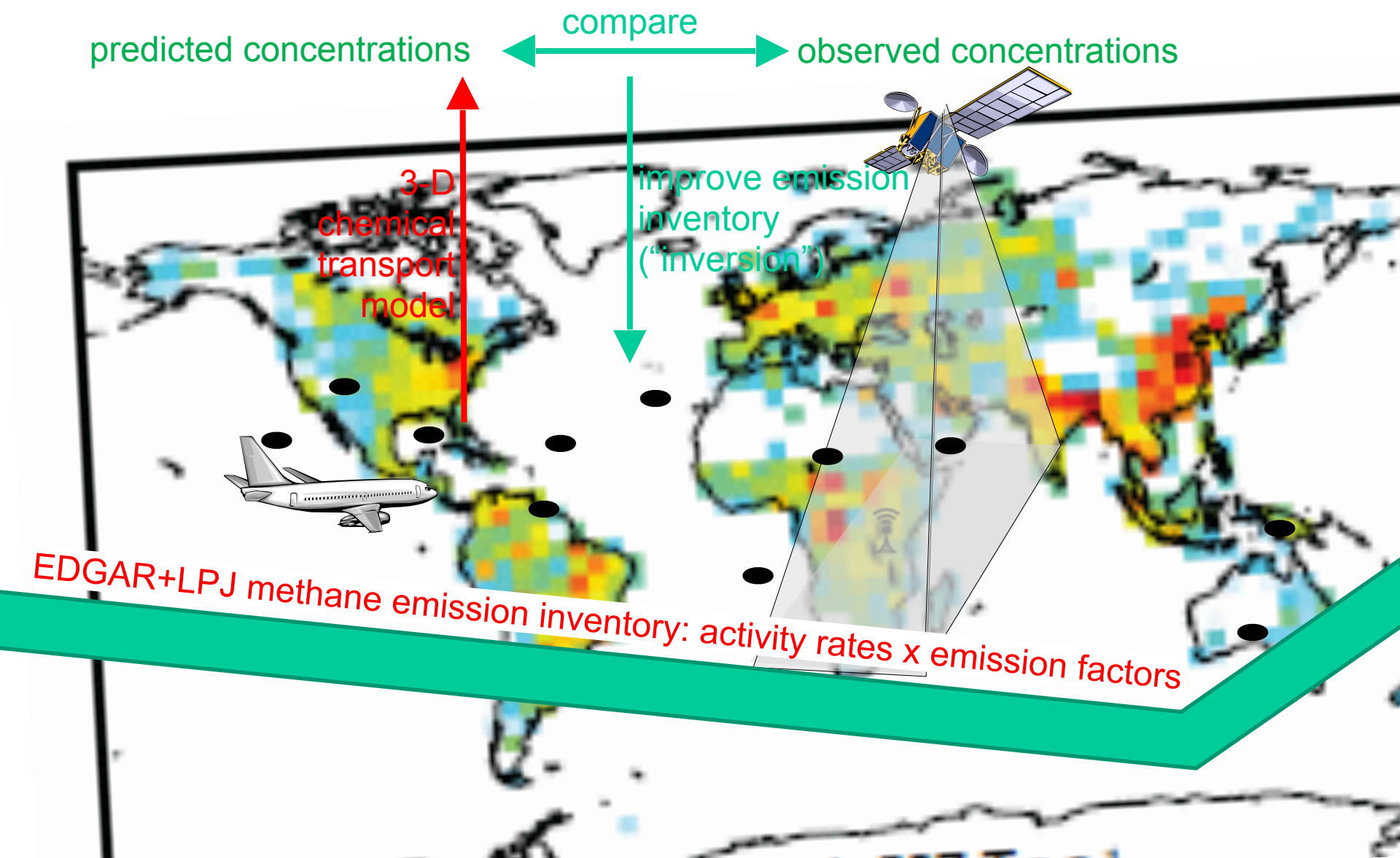
Methane fits and starts over past 40 years





- Uptick since 2006 has been attributed to oil/gas, livestock, wetlands, OH…
- …but it represents only 3% change in sources or sinks,
  on top of a factor 2.5 increase since preindustrial times that we don't understand!

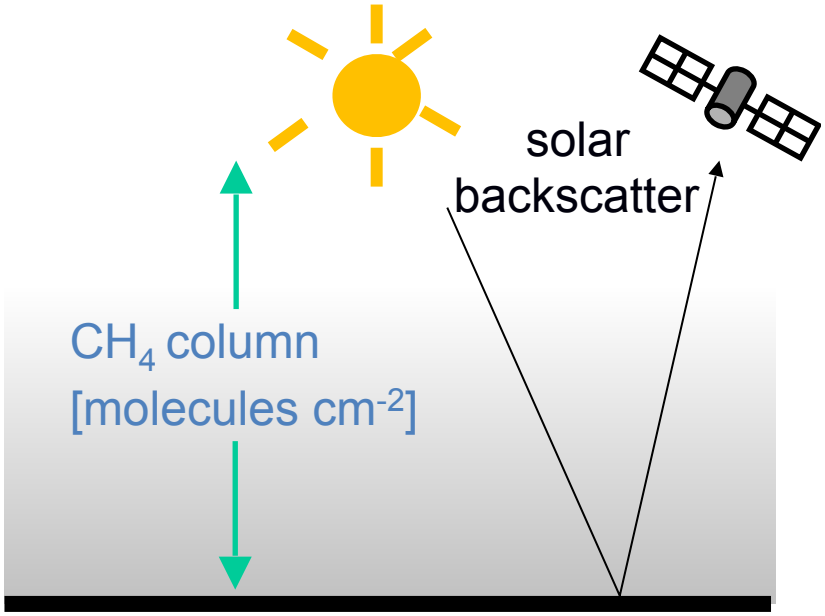
Using atmospheric methane observations to improve emission inventories



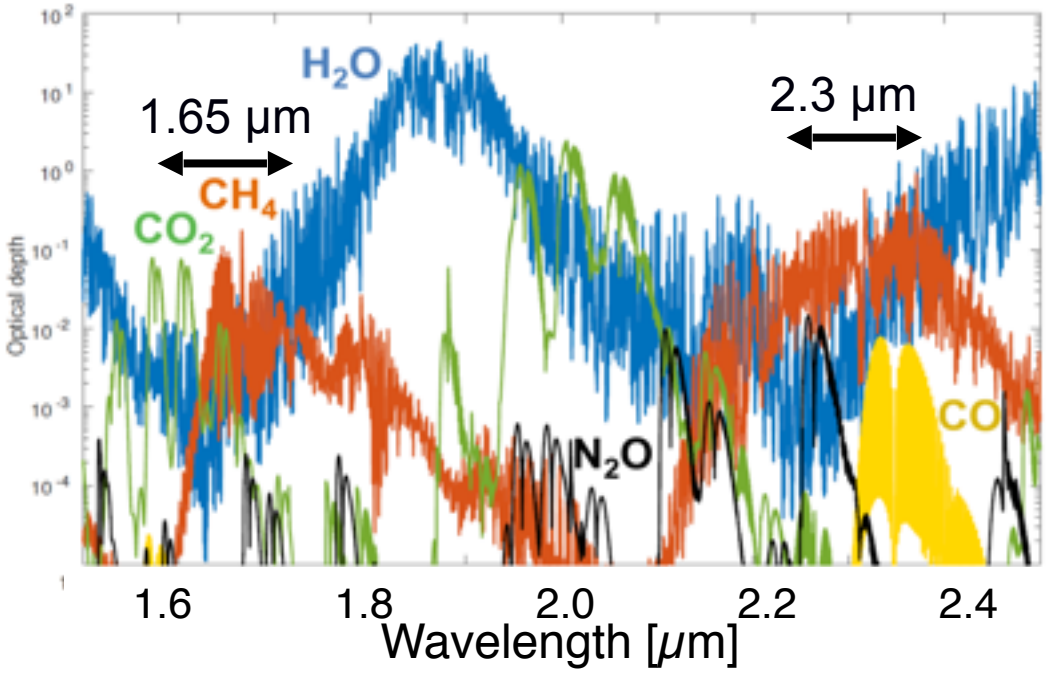
Sometimes methane is easy to observe by remote sensing…

…but generally it's much harder!

Observing methane atmospheric columns from space

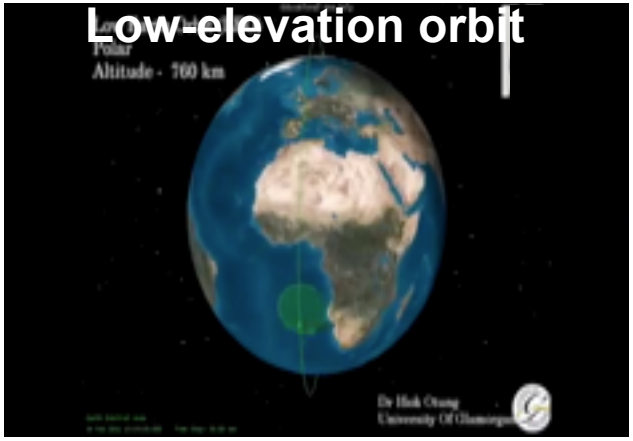


Atmospheric optical depths



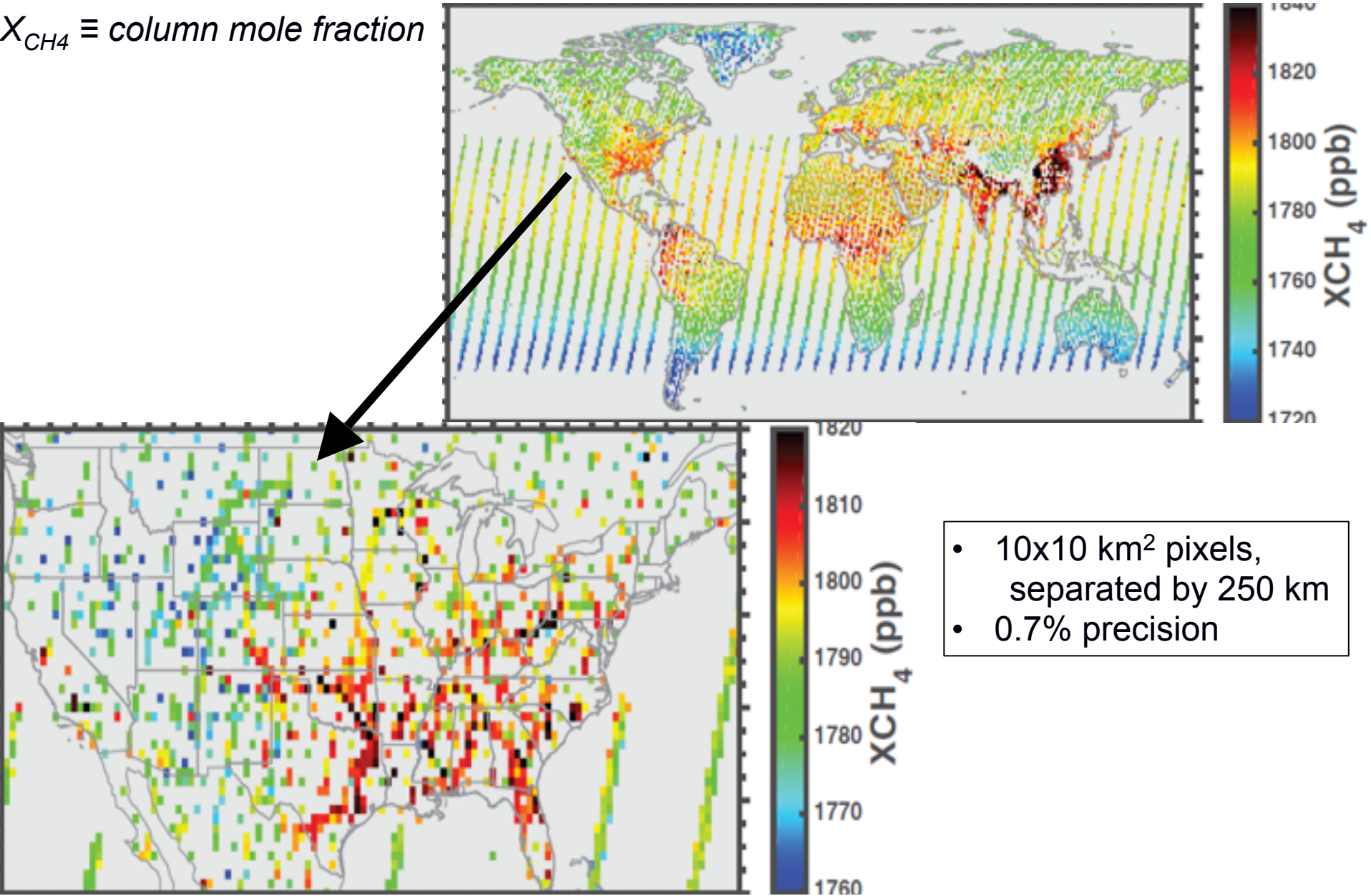
GOSAT (JAXA), 2009- ;
TROPOMI (ESA), 2017 launch

geoCARB (NASA), in formulation



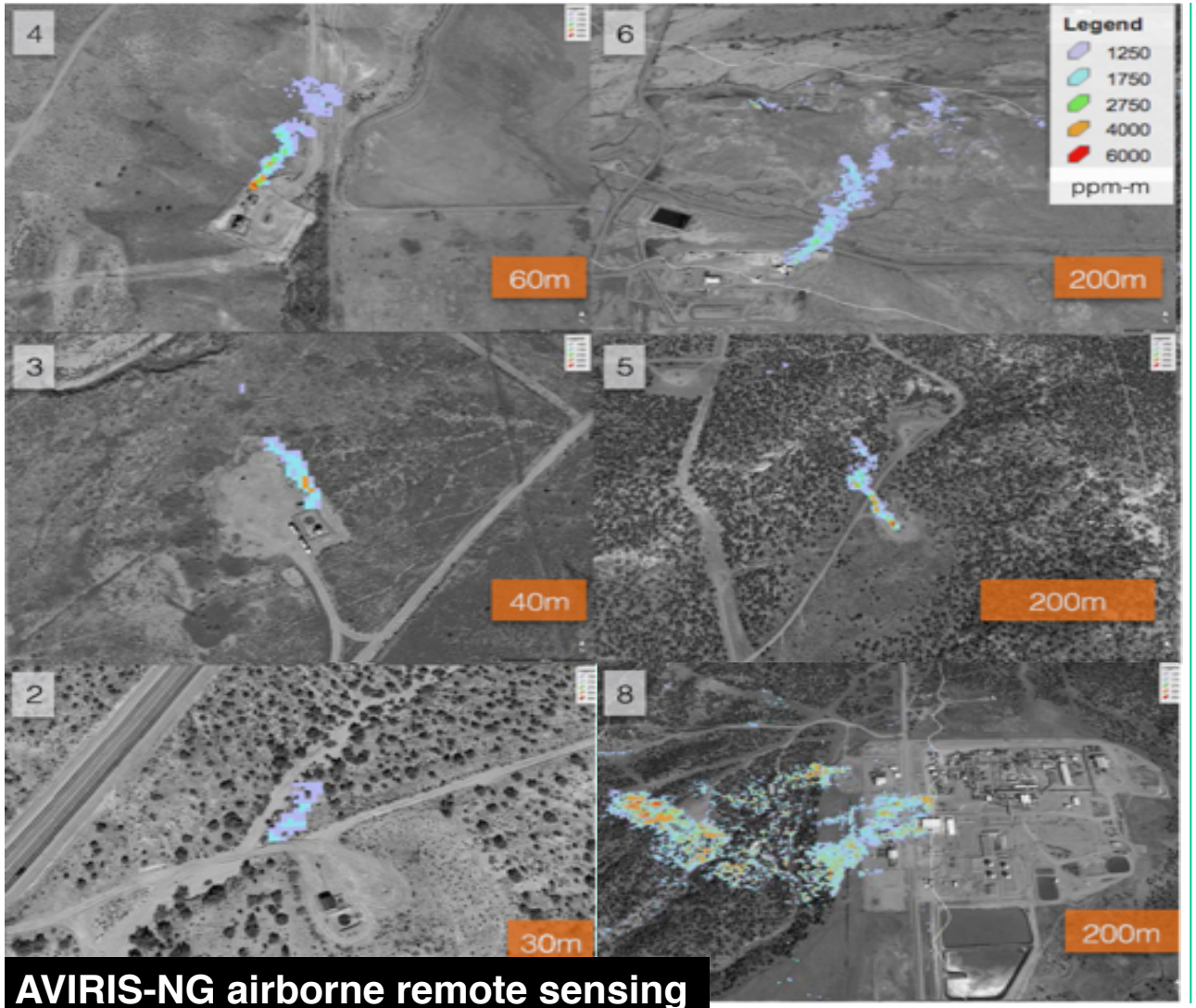
GOSAT satellite methane observations (2010-2013)

X_{CH4} ≡ *column mole fraction*



- 10x10 km^2 pixels, separated by 250 km
- 0.7% precision

Challenge of observing methane point sources at the facility scale: they are many and small and variable



AVIRIS-NG airborne remote sensing of methane plumes in Four Corners Frankenberg et al. [2016]

GHGSat space-based observation of point sources

Effective pixel resolution of 50x50 m^2 over selected 12x12 km^2 scenes

First microsatellite launched in June 2016

Smaller pixel resolution causes loss in precision…
but this is more than offset by lower dilution over pixel

GHGSat
GLOBAL EMISSIONS MONITORING

Lom Pangar Dam, Cameroon
April 20th, 2017
GHGSat-D excess CH_4 column measurement

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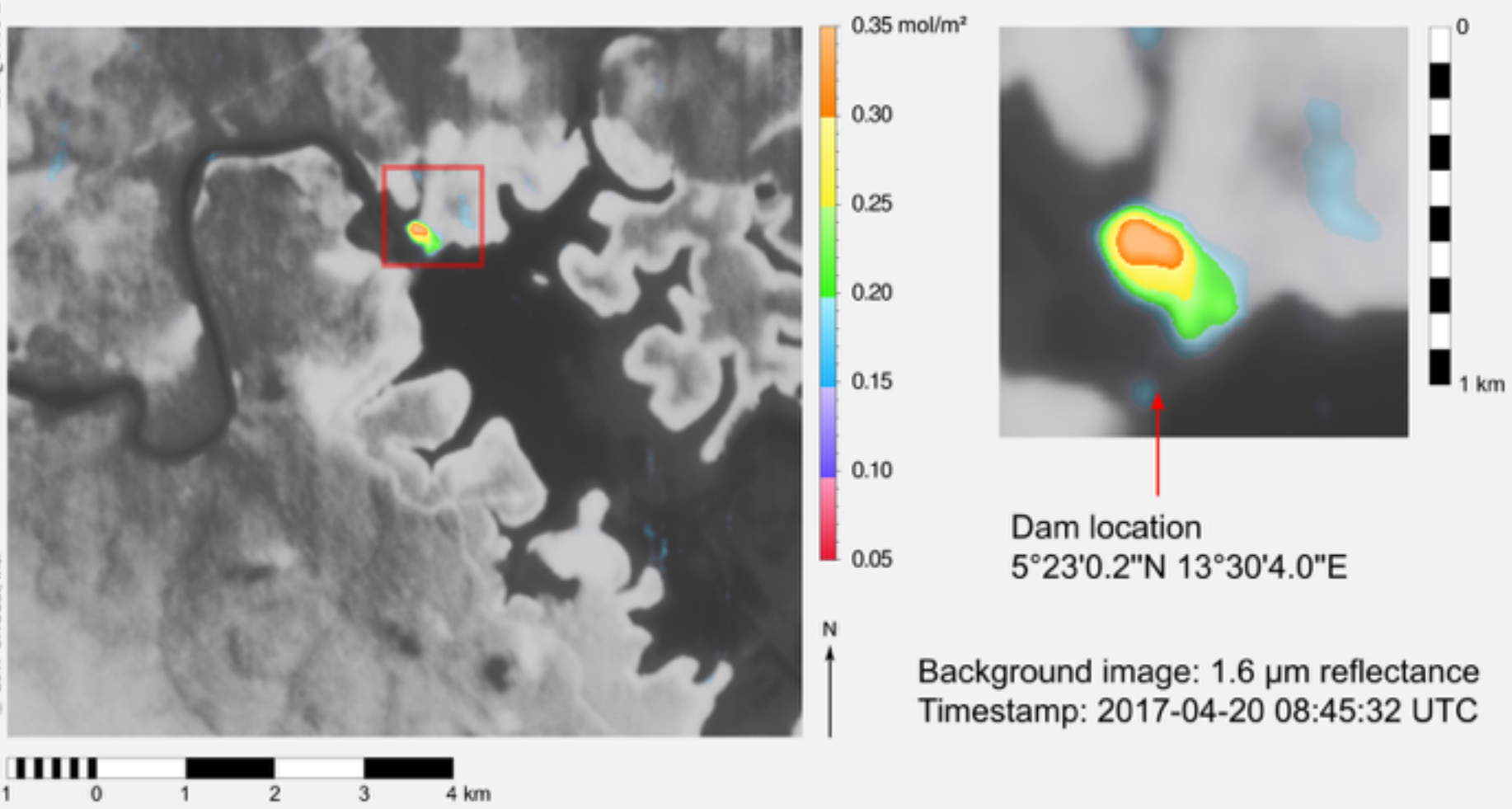

Background image: 1.6 µm reflectance
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