

THE NITROGEN CYCLE

TOPICS FOR TODAY

1. **The Nitrogen Cycle**
2. Fixed Nitrogen in the Atmosphere
3. Sources of NO_x
4. What about N₂O?
5. Nitrogen Cycle: on the particle side
6. How might the nitrogen cycle be affected by climate change?


Nitrogen:

Nitrogen is a major component of the atmosphere, but an essential nutrient in short supply to living organisms.

OXIDATION STATES OF NITROGEN

N has 5 electrons in valence shell \square 9 oxidation states from -3 to $+5$

Increasing oxidation number (oxidation reactions)

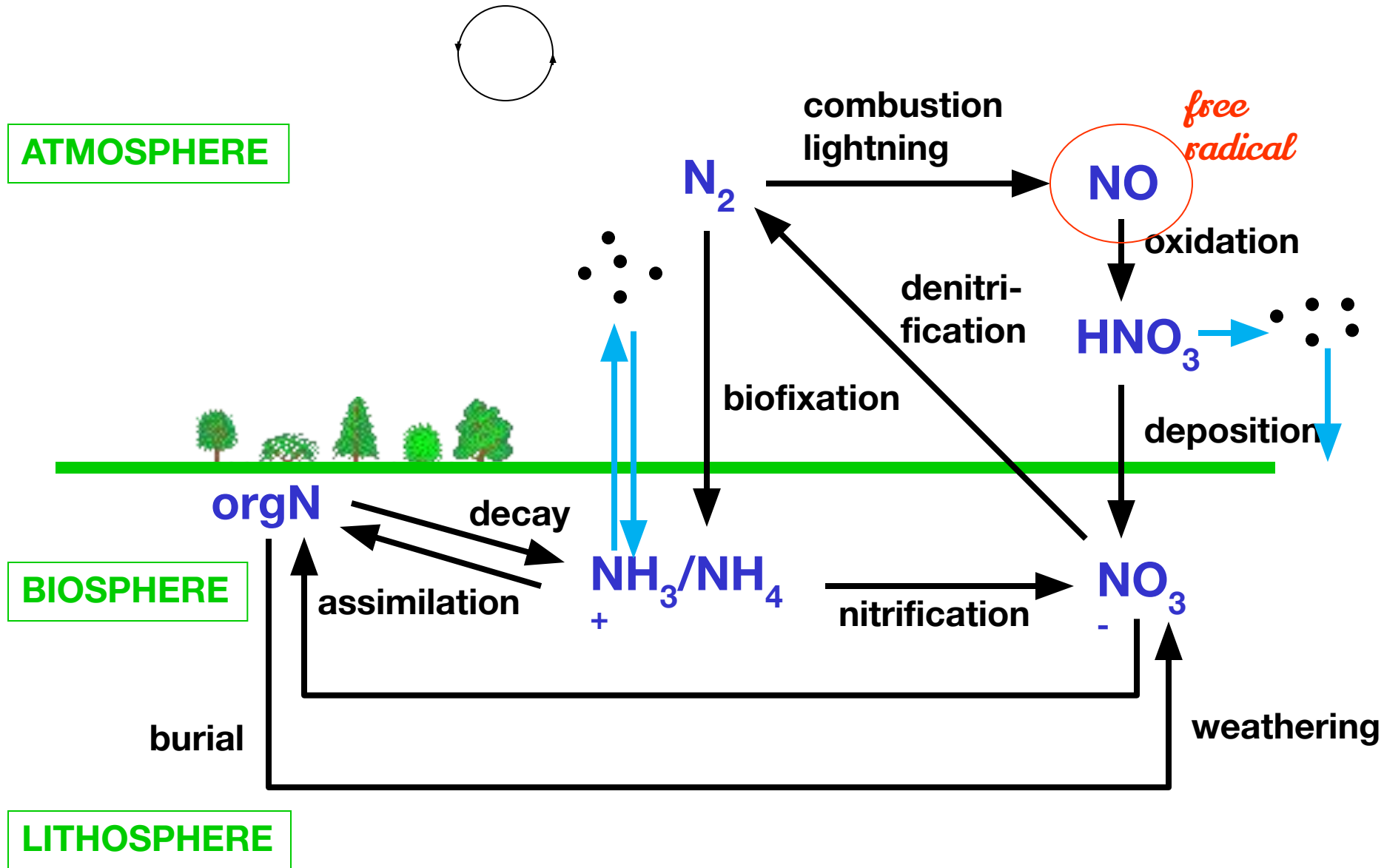


-3	0	+1	+2	+3	+4	+5
NH₃ Ammonia	N₂	N₂O Nitrous oxide	NO Nitric oxide	HONO Nitrous acid	NO₂ Nitrogen dioxide	HNO₃ Nitric acid
NH₄⁺ Ammonium				NO₂⁻ Nitrite		NO₃⁻ Nitrate
R₁N(R₂)R₃ Organic N			<i>free radical</i>		<i>free radical</i>	N₂O₅ Nitrogen pentoxide



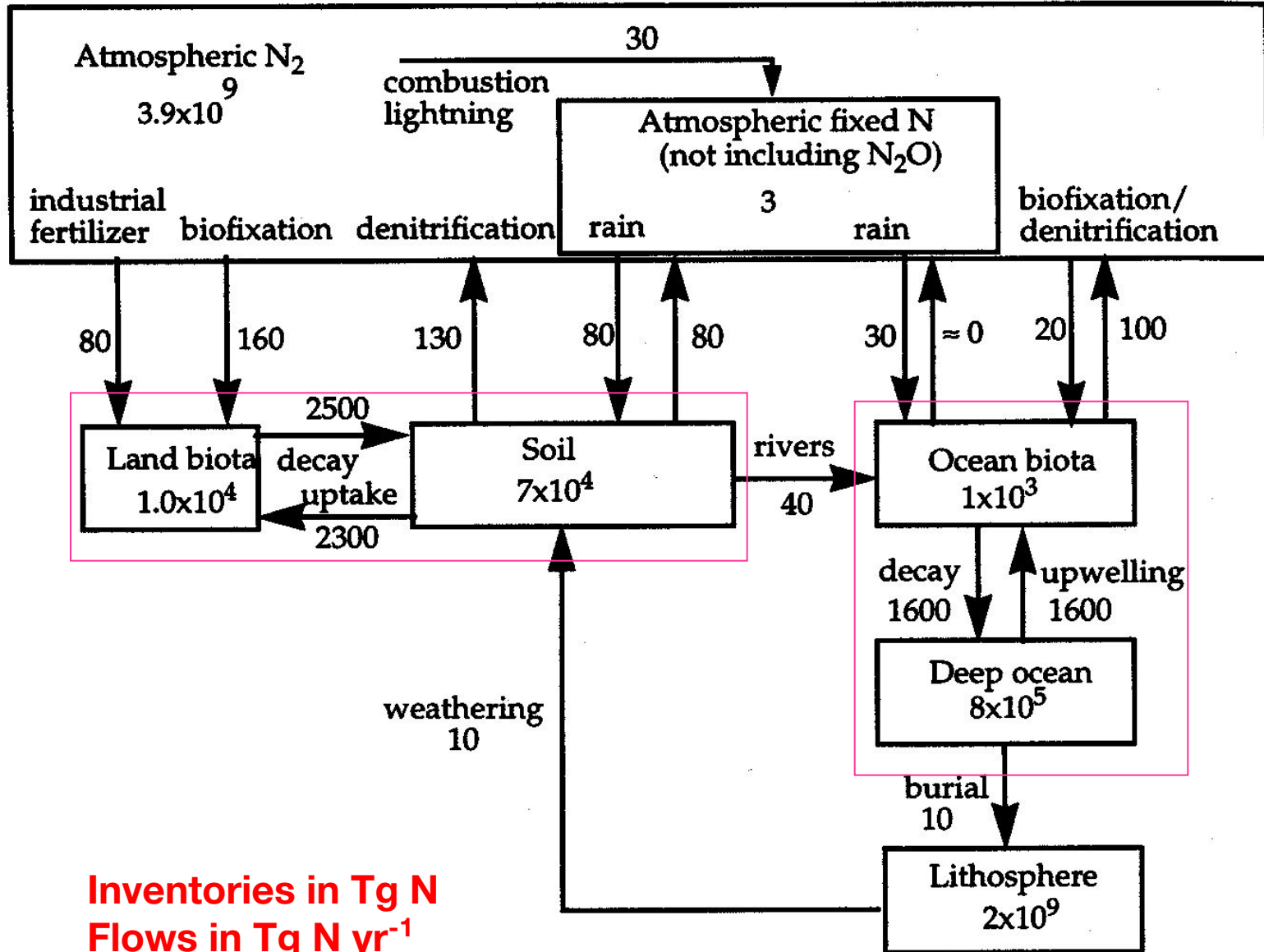
Decreasing oxidation number (reduction reactions)

THE NITROGEN CYCLE: MAJOR PROCESSES



"fixed" or "odd" N is less stable globally => N_2

BOX MODEL OF THE NITROGEN CYCLE



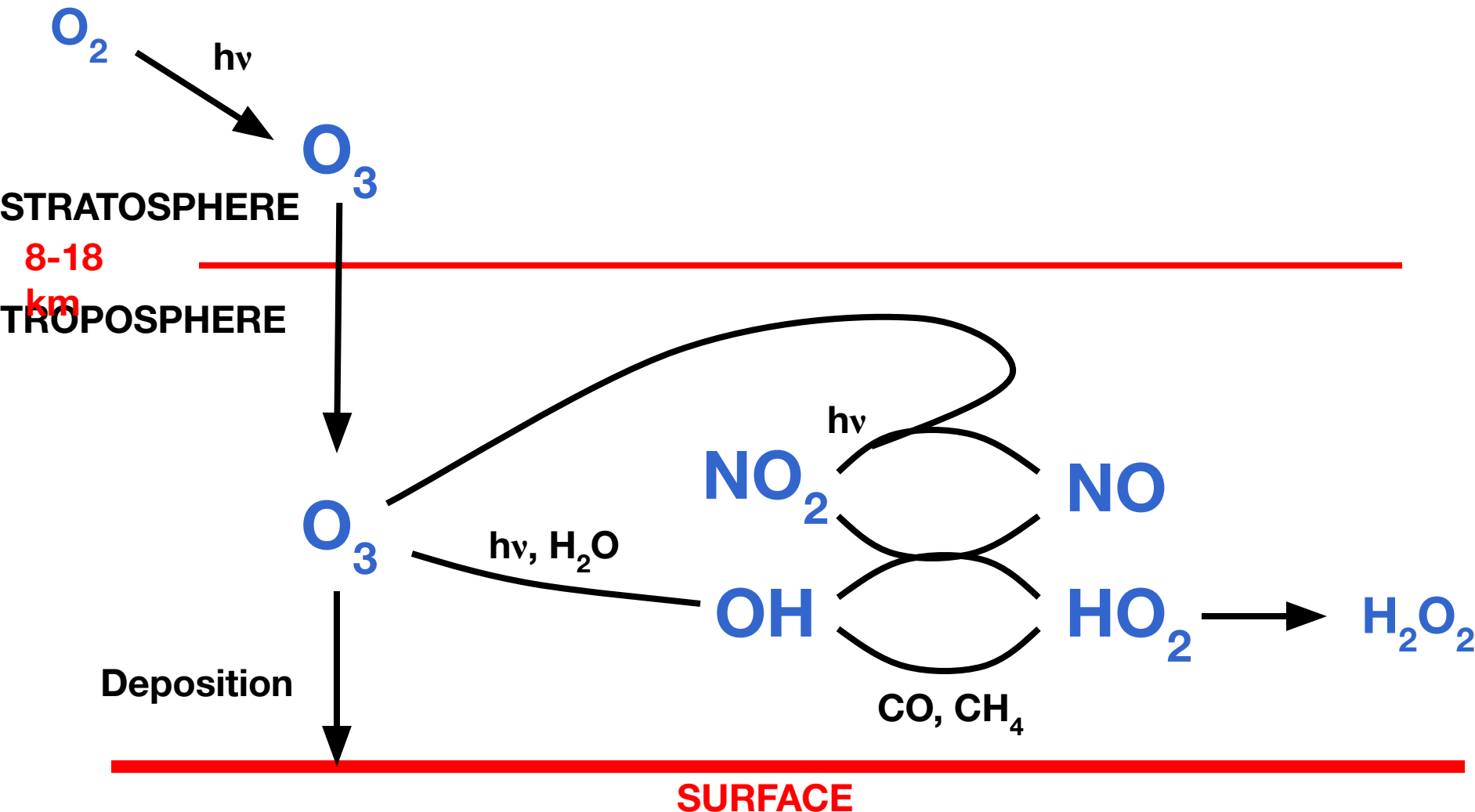
Inventories in Tg N
Flows in Tg N yr⁻¹

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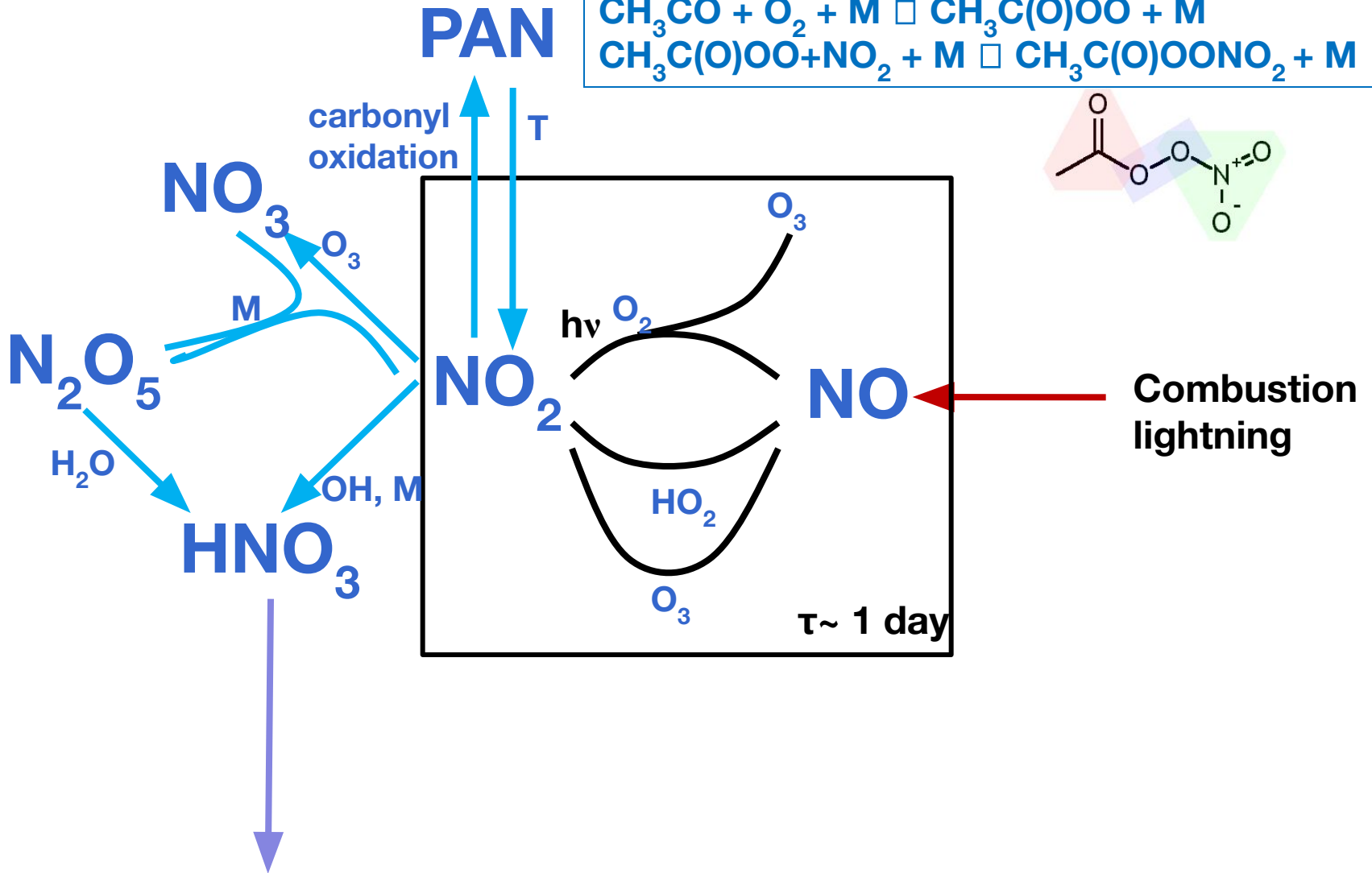
NO_x: KEY TO MAINTAINING THE OXIDIZING POWER OF THE TROPOSPHERE

•ALSO key player in stratospheric O₃ loss

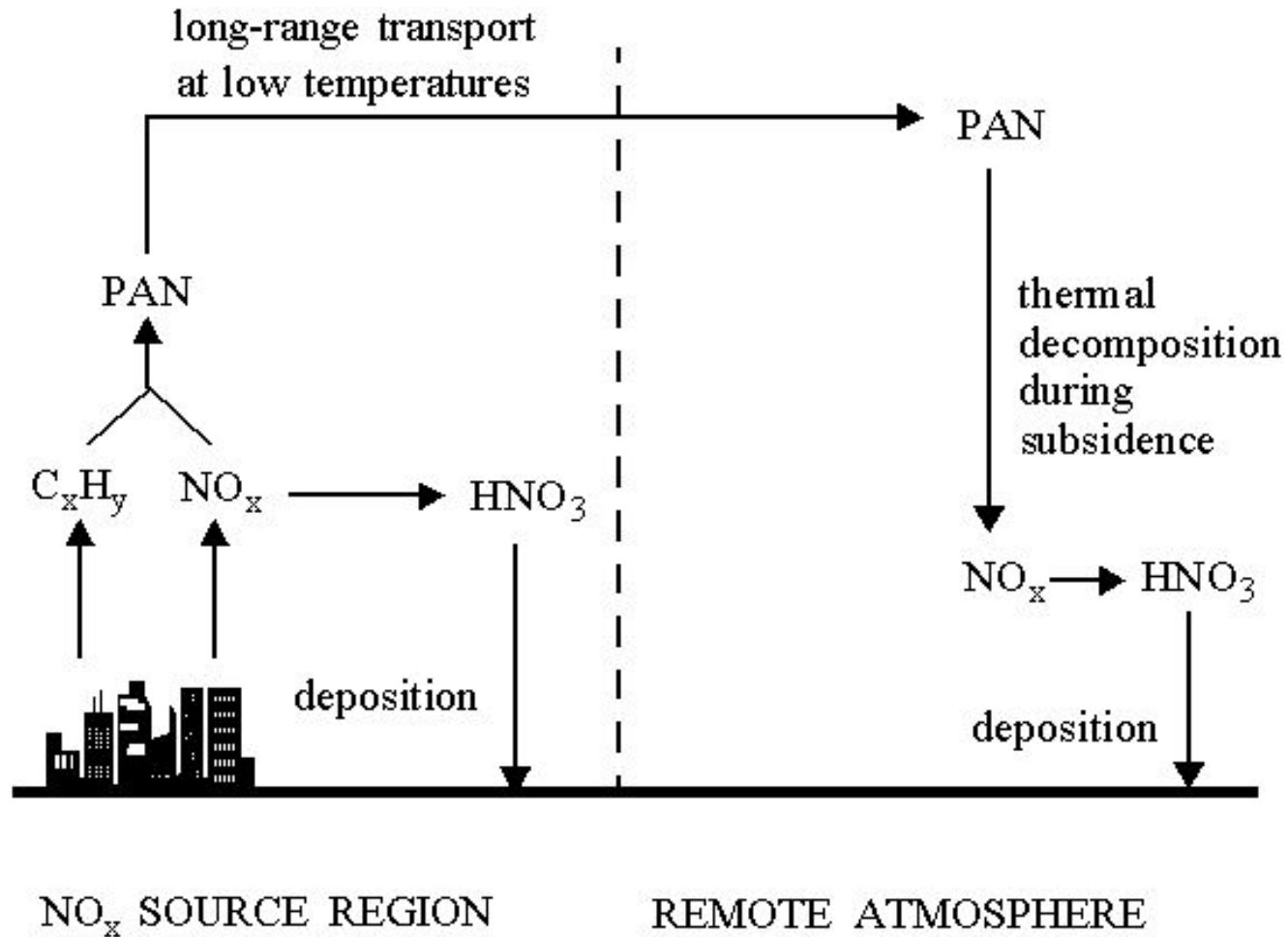


NO_y CYCLING

Example of PAN formation from acetaldehyde:



PEROXYACETYLNITRATE (PAN) AS RESERVOIR FOR LONG-RANGE TRANSPORT OF NO_x



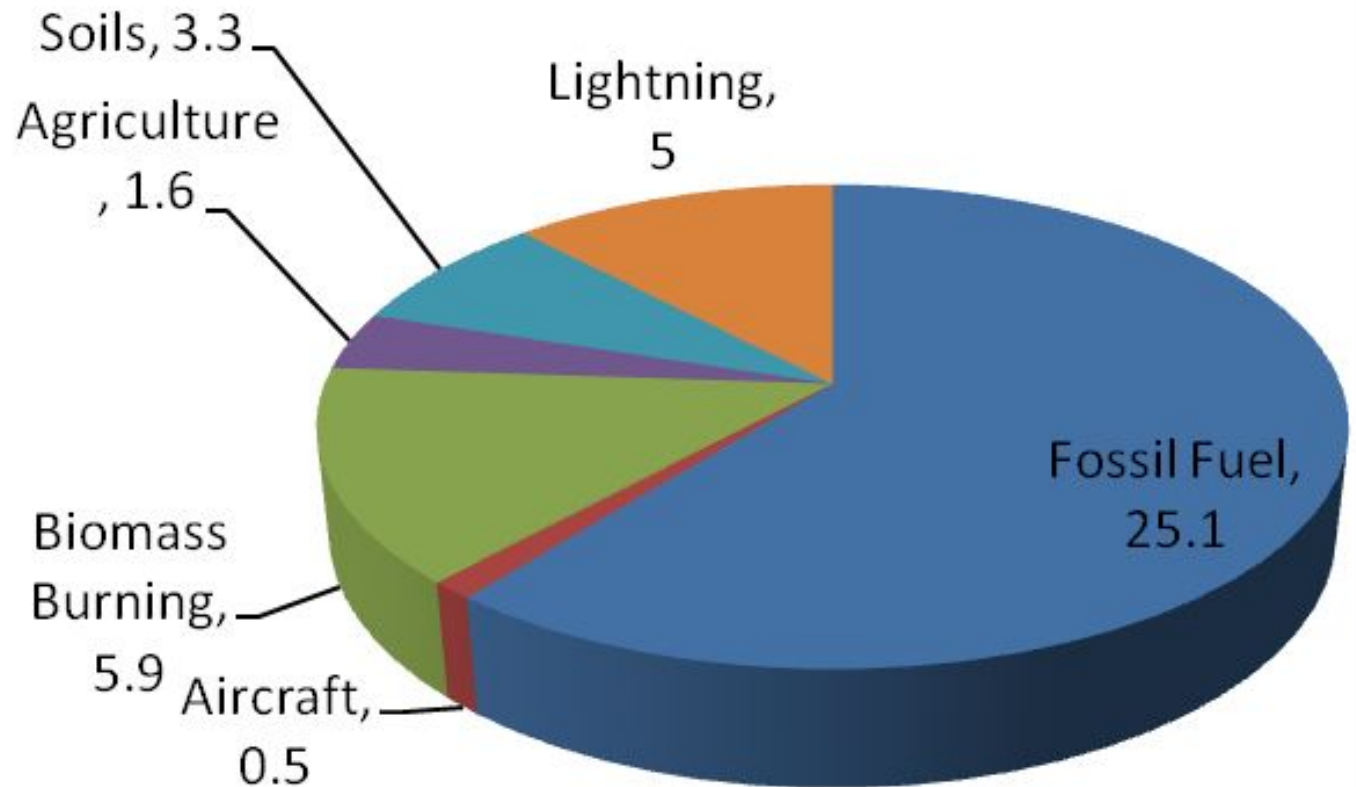
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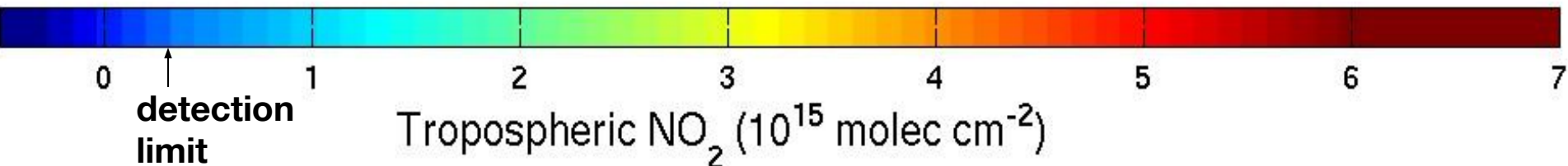
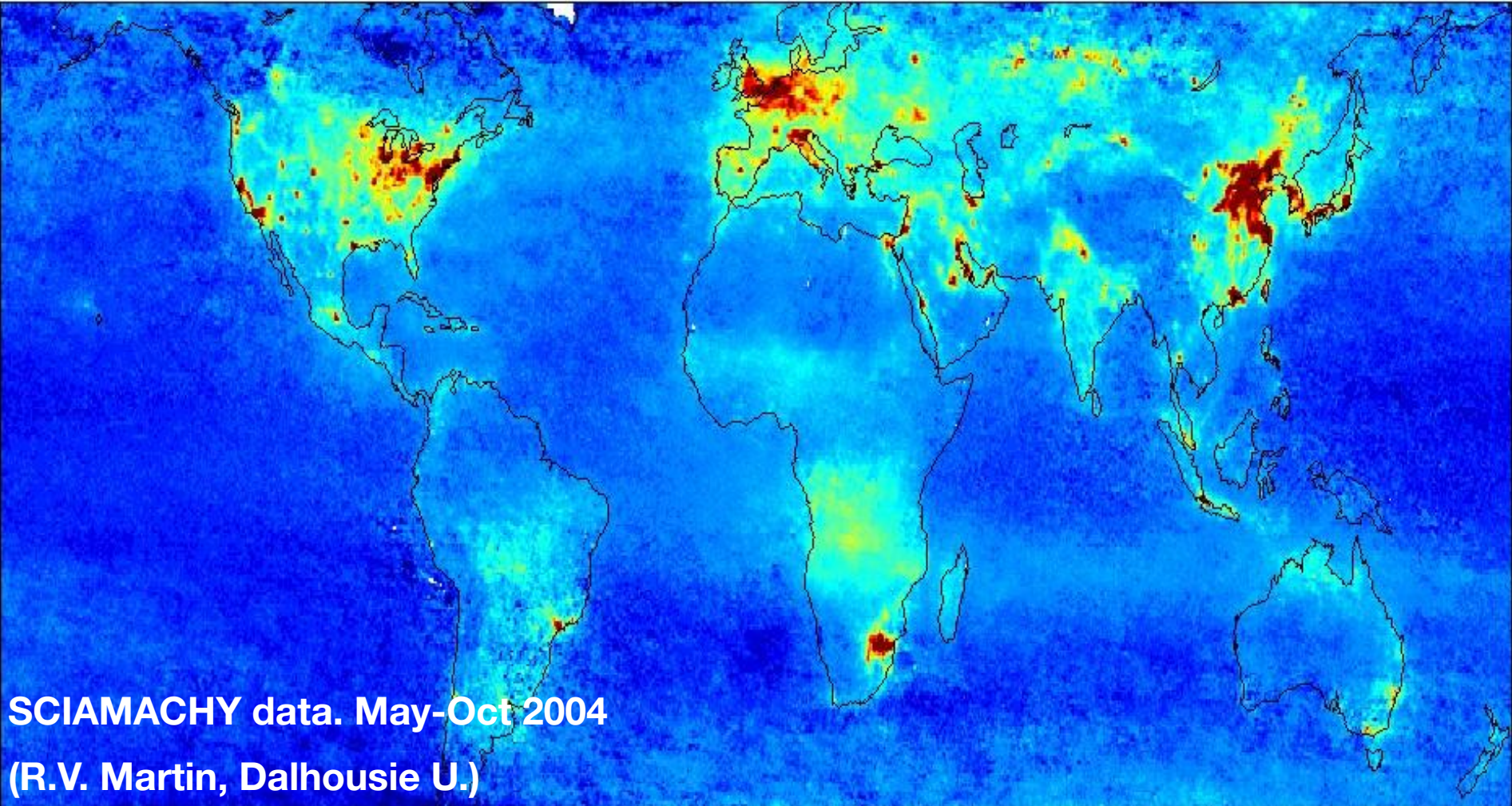
NO_x EMISSIONS (Tg N yr⁻¹) TO TROPOSPHERE

Zeldovich Mechanism: combustion and lightning

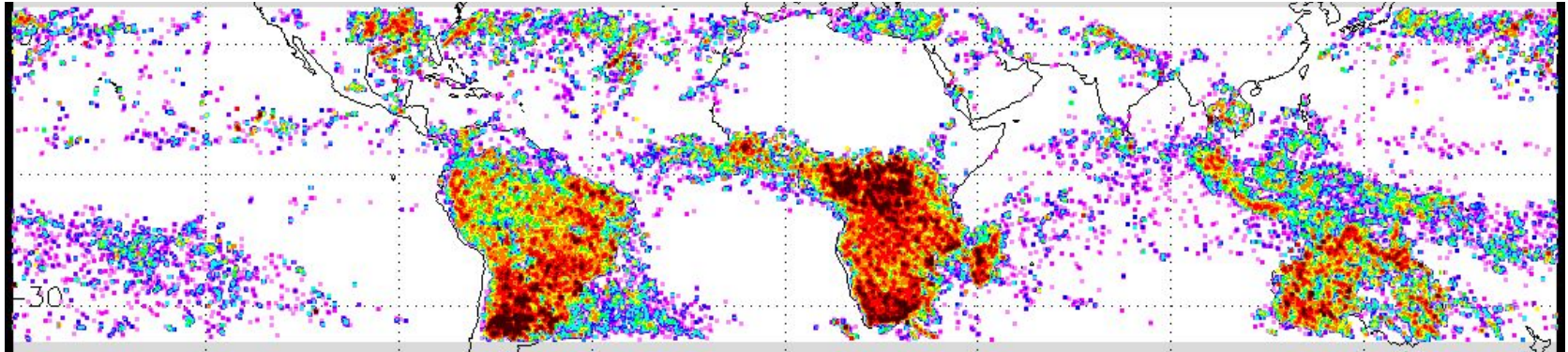
At high T (~2000K) oxygen thermolyzes:



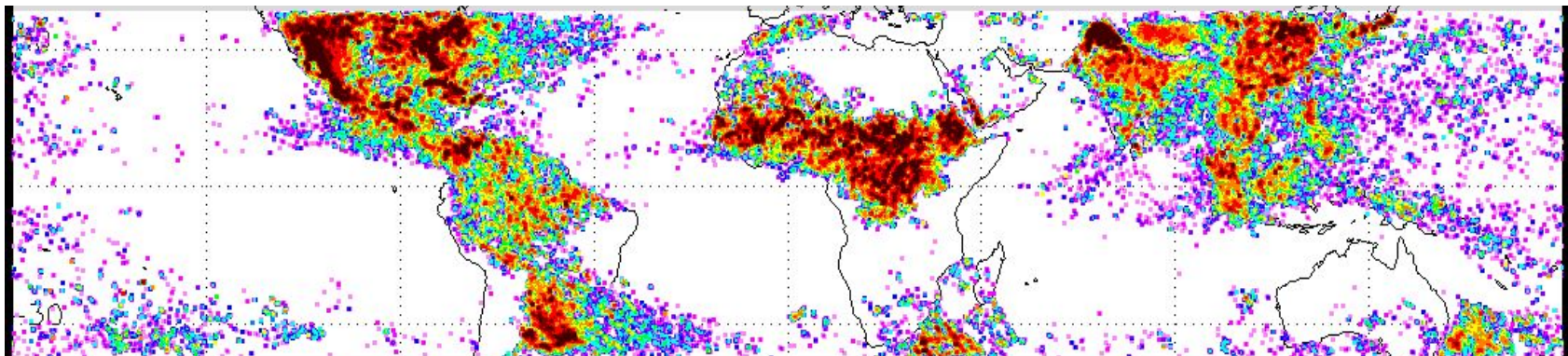
USING SATELLITE OBSERVATIONS OF NO₂ TO MONITOR NO_x EMISSIONS



LIGHTNING FLASHES SEEN FROM SPACE (2000)



DJF



JJA

Bottom-up Emission Estimate:

$$\text{Emission} = (\# \text{ flashes}) \times (\text{NO}_x \text{ molecules /flash})$$



IC or CG flash?
Length of flash?

HIGHLY
UNCERTAIN

TOP-DOWN ESTIMATES OF GLOBAL LIGHTNING NO_x EMISSIONS

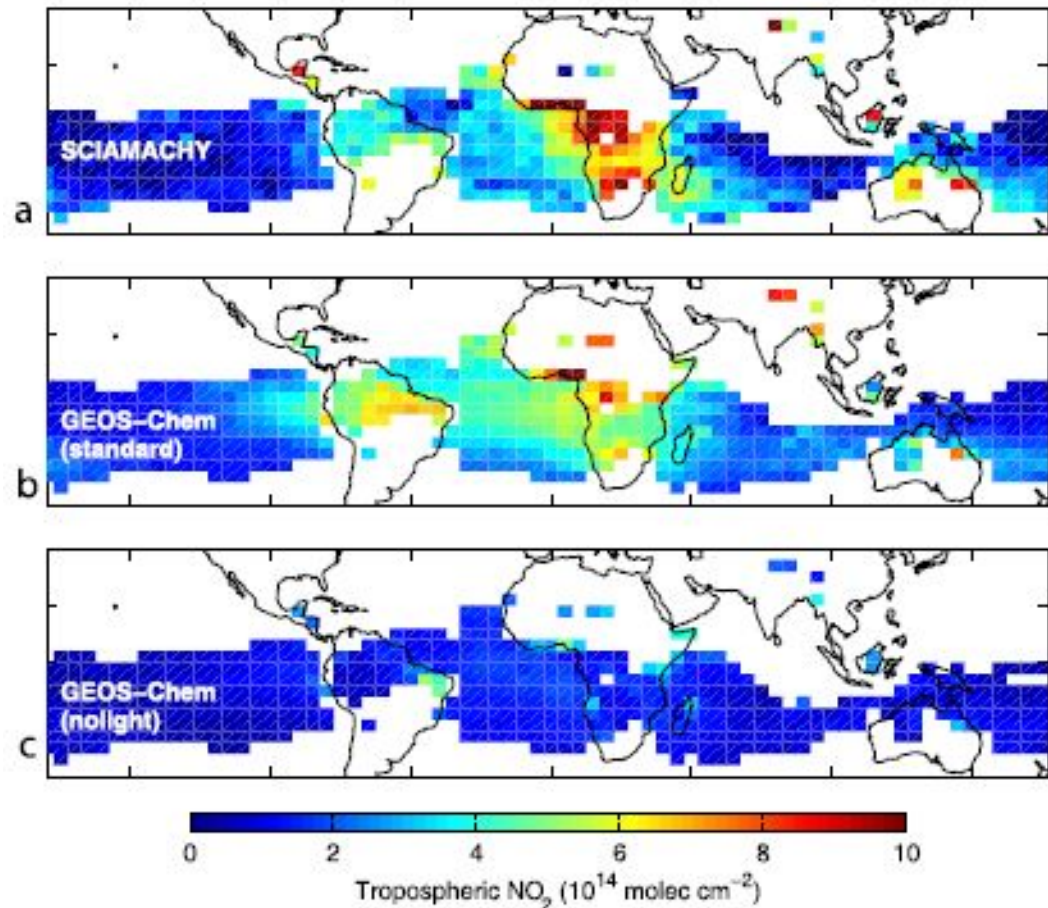
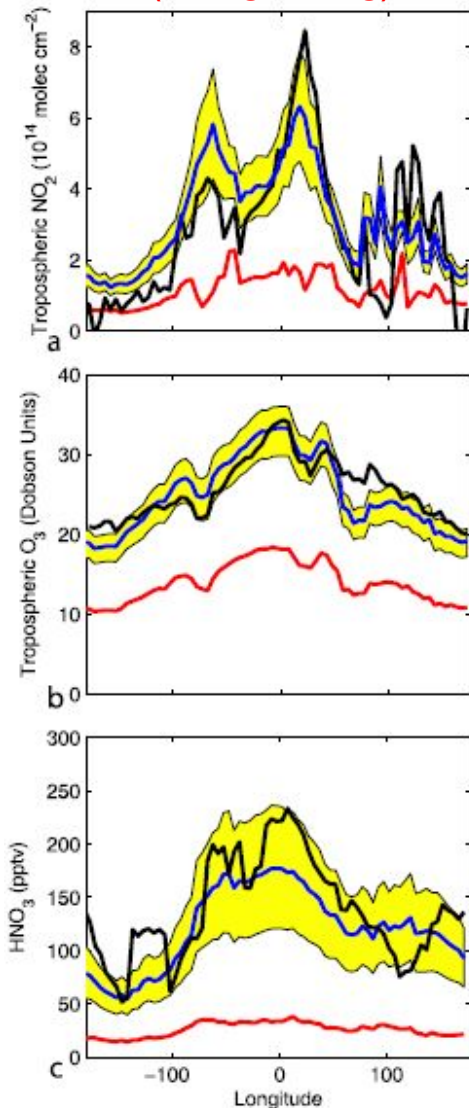
Obs (satellite)

Model (6 TgN/yr)

Model (4-8 TgN/yr)

Model (no lightning)

Using SCIAMACHY (NO₂), OMI (O₃), ACE-FTS (HNO₃): Target locations/times where NO₂ column is dominated by lightning source

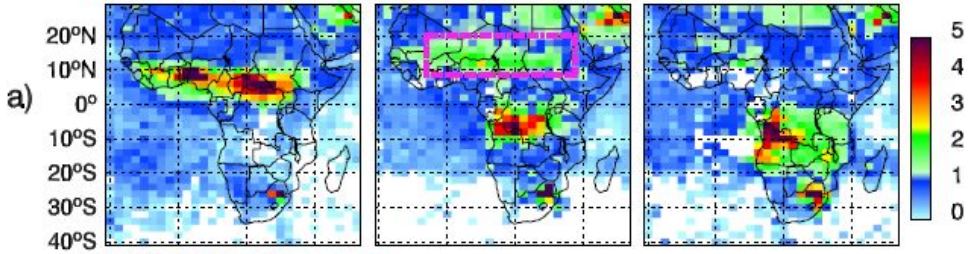


Global source of 6 ± 2 TgN/yr from lightning

[Martin et al., 2007]

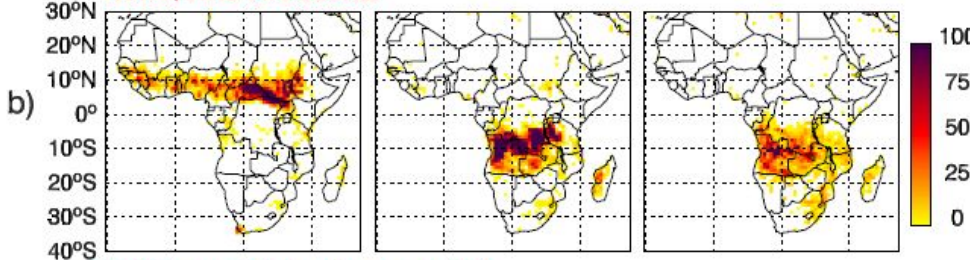
USING SATELLITE OBSERVATIONS TO ESTIMATE SOIL NO_x EMISSIONS

January 2000 June 2000 August 2000
 GOME NO₂ (10¹⁵ molecules cm⁻²)



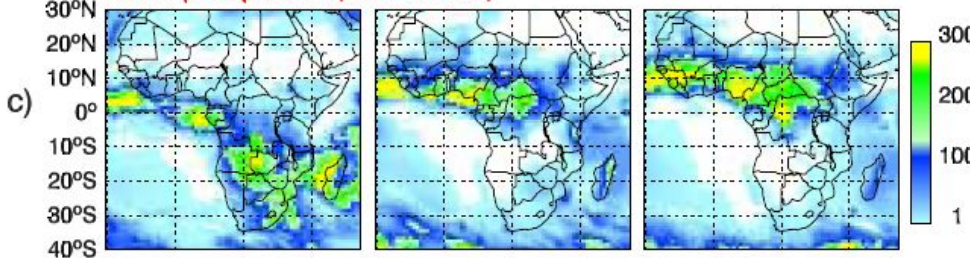
Use GOME observations over Africa:
 Soils: 3.3 TgN/year
 Biomass Burning: 3.8 TgN/year
 □ 40% of surface NO_x emissions!

TRMM/VIRS Fire counts

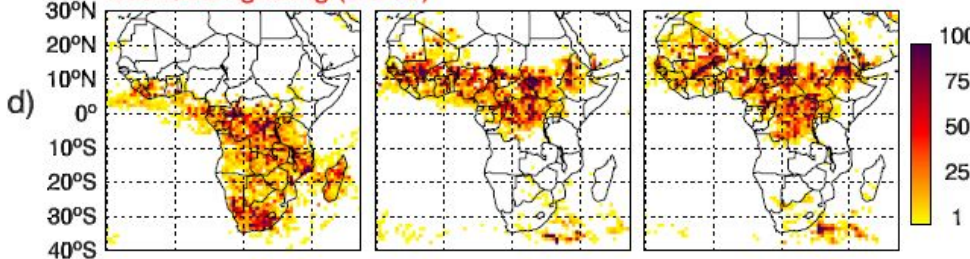


Extrapolating to all the tropics:
7.3 TgN/year biogenic soil
 (twice the IPCC value)

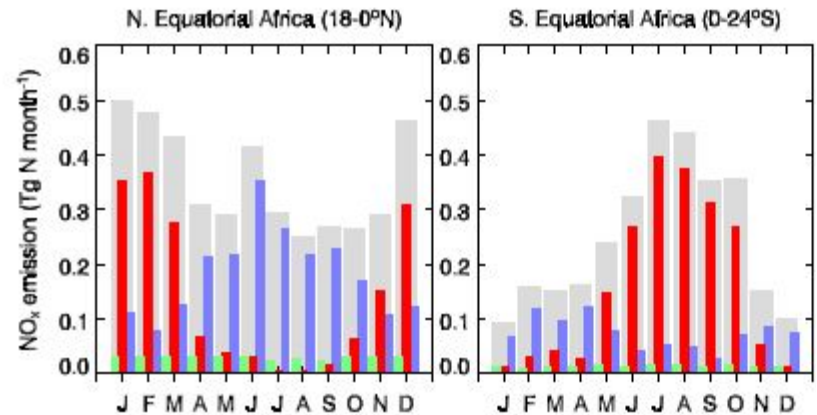
TRMM precipitation (mm month⁻¹)



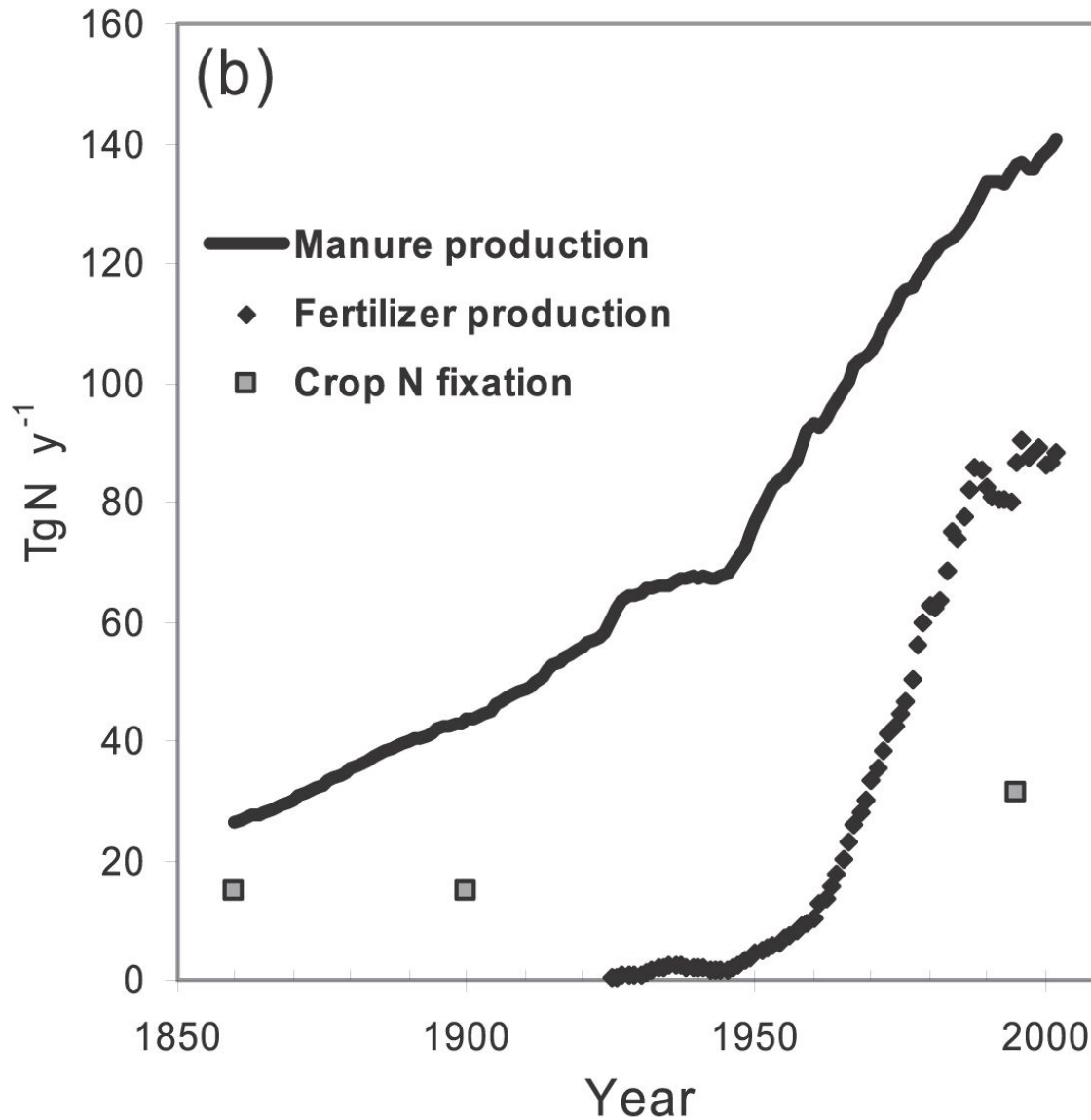
TRMM/LIS lightning (events)



Biomass Burning
Soils
Fossil + biofuels



GROWING CONTRIBUTION OF AGRICULTURE TO N CYCLE



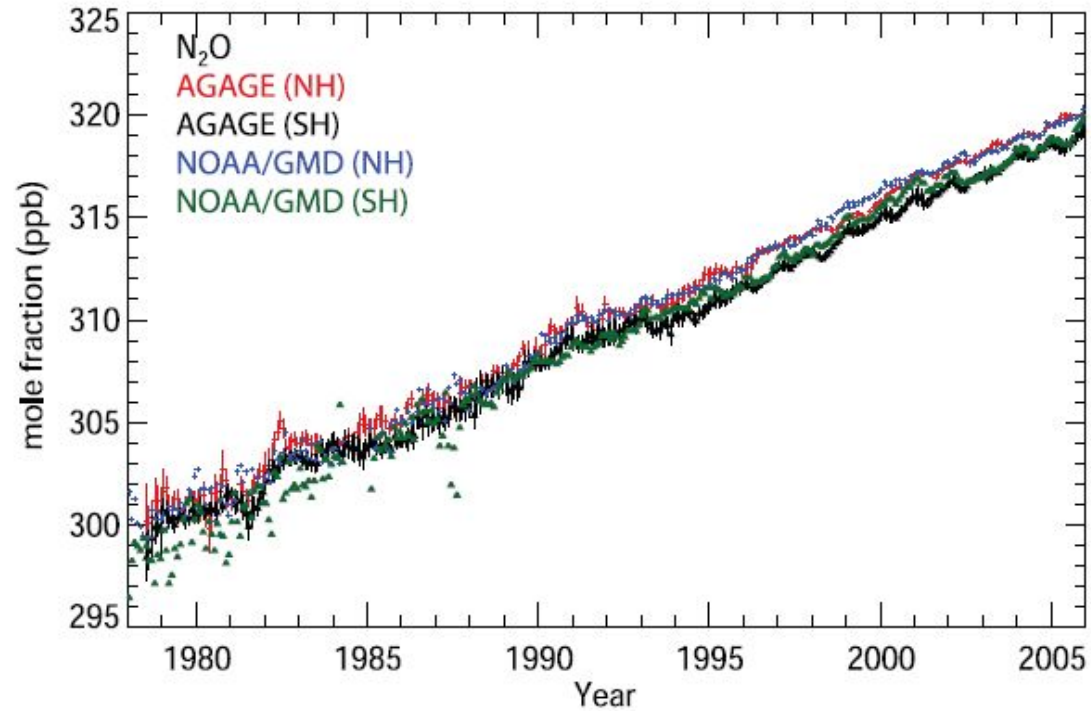
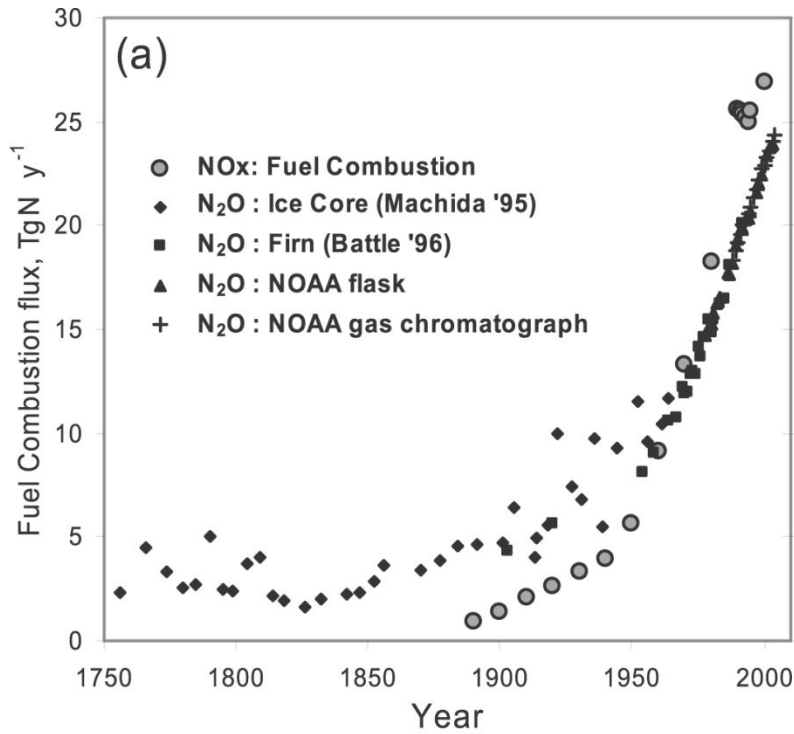
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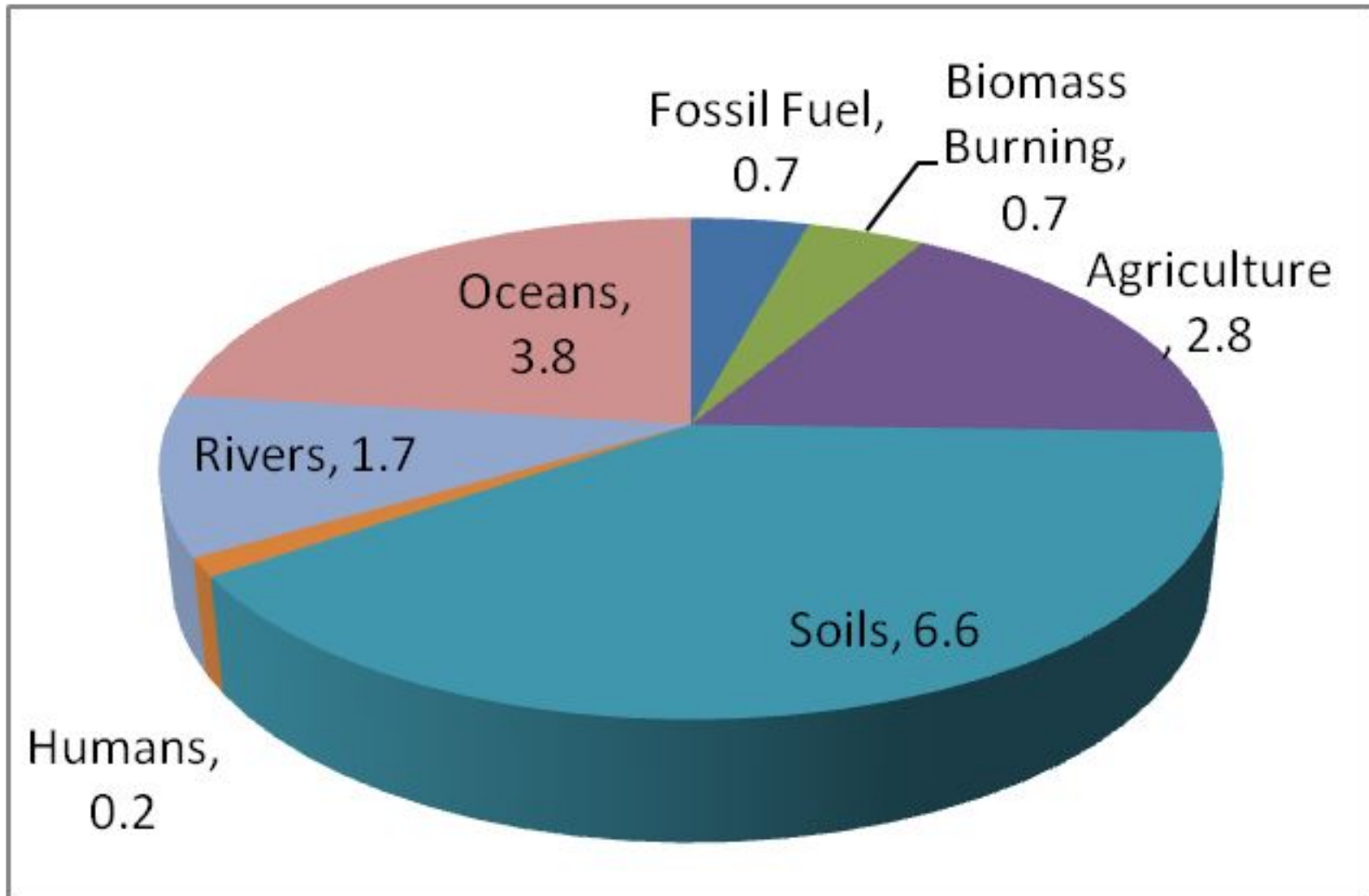
N₂O: LOW-YIELD PRODUCT OF BACTERIAL NITRIFICATION AND DENITRIFICATION

Important as

- source of NO_x radicals in stratosphere
- greenhouse gas

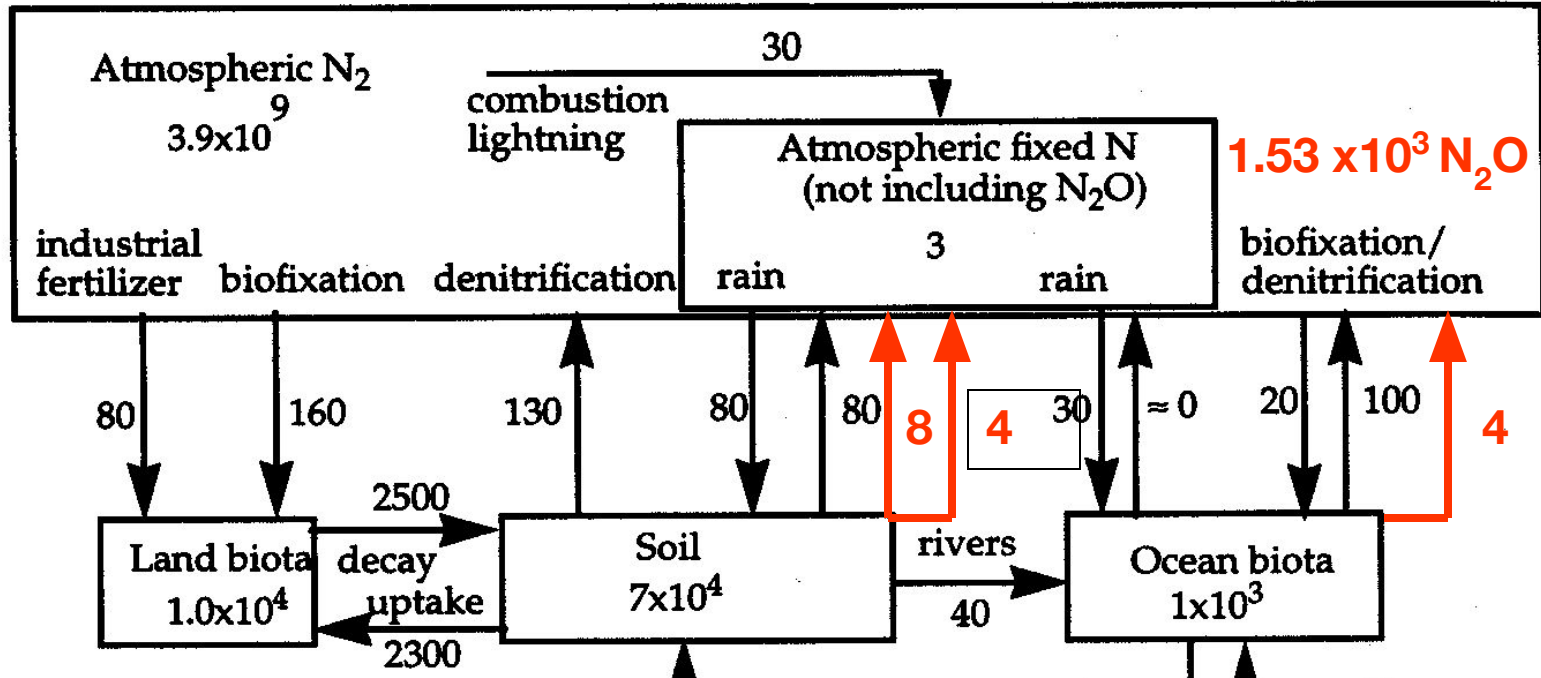


N₂O EMISSIONS (Tg N yr⁻¹) TO TROPOSPHERE



Source is **MOSTLY** (~75%) natural

ADDING N₂O TO THE NITROGEN BOX MODEL



Inventories in Tg N
Flows in Tg N yr⁻¹

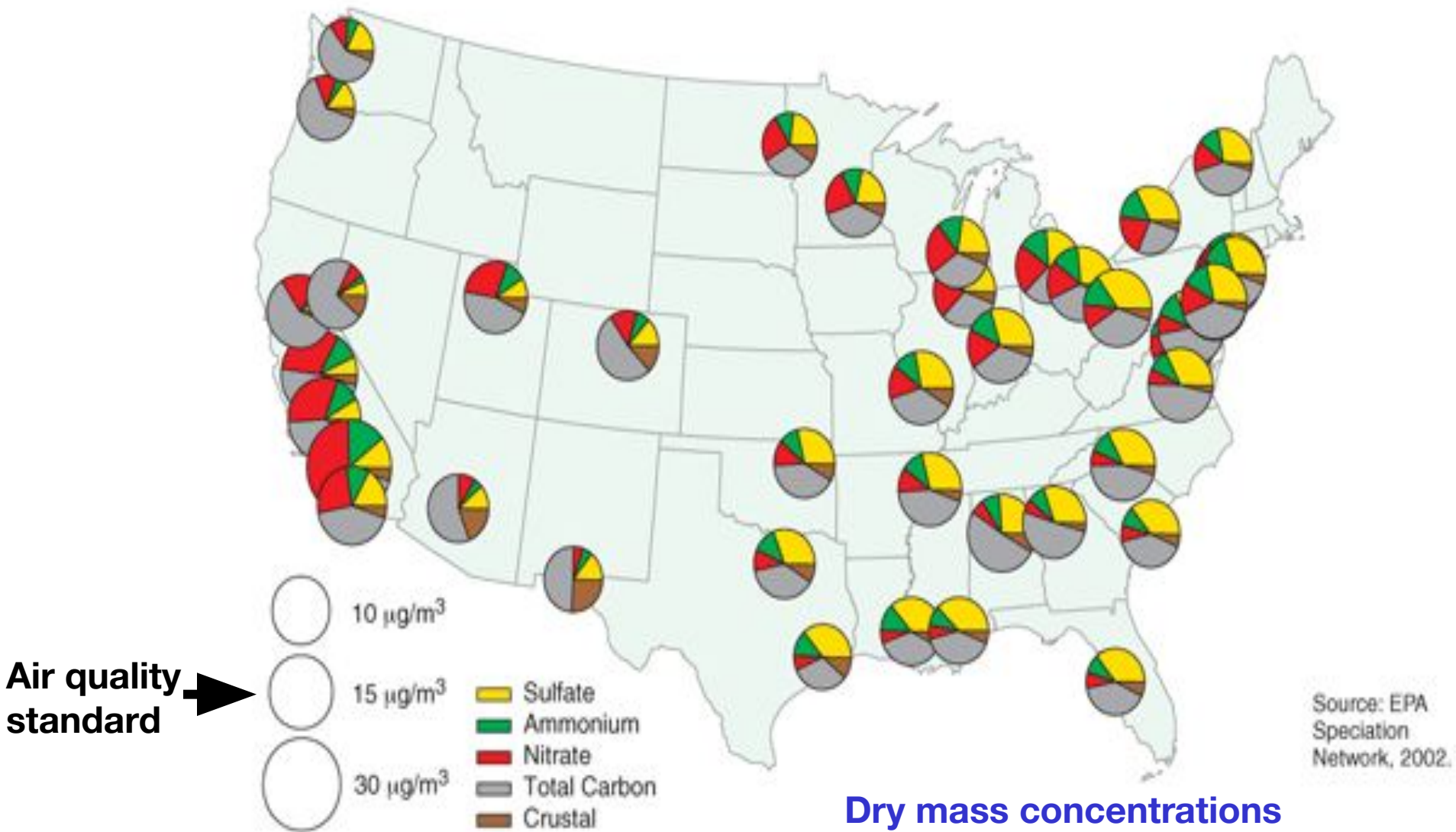
Although a closed budget can be constructed, uncertainties in sources are large!
 (N₂O atm mass = 5.13×10^{18} kg \times 3.1×10^{-7} \times $28/29$ = 1535 Tg)

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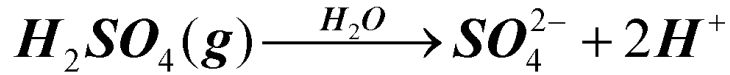
ANNUAL MEAN PM_{2.5} CONCENTRATIONS AT U.S. SITES

Figure 2-47. Annual average PM_{2.5} concentrations ($\mu\text{g}/\text{m}^3$) and particle type in urban areas, 2002.

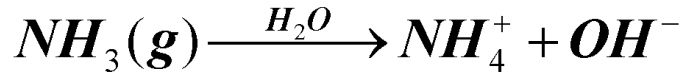


FORMATION OF SULFATE-NITRATE-AMMONIUM AEROSOLS

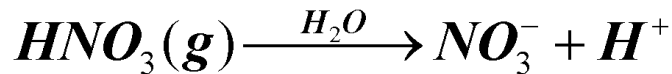
Thermodynamic rules:



Sulfate always forms an aqueous aerosol



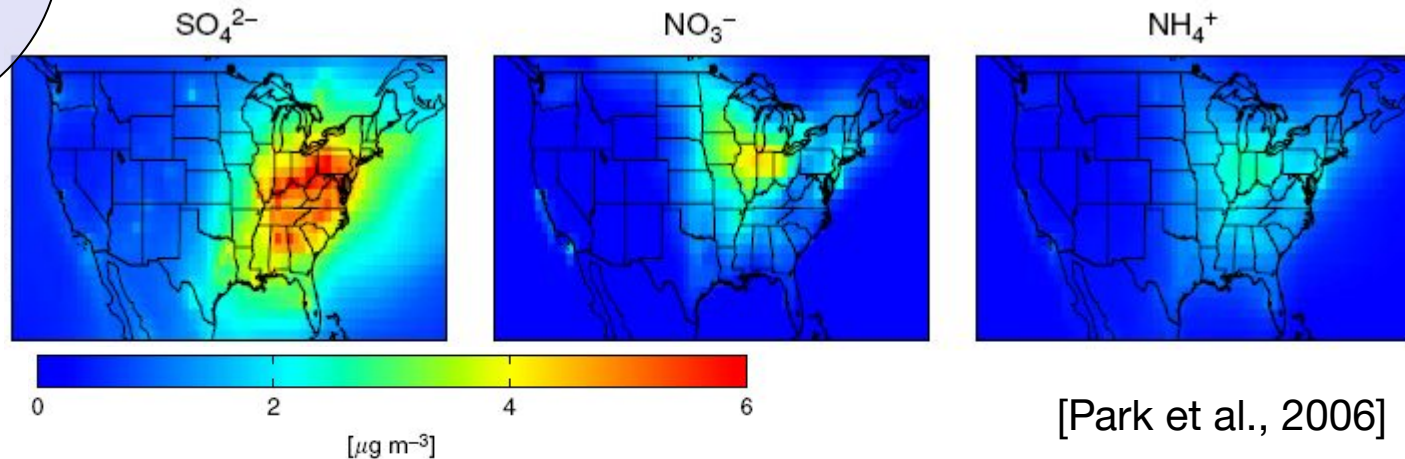
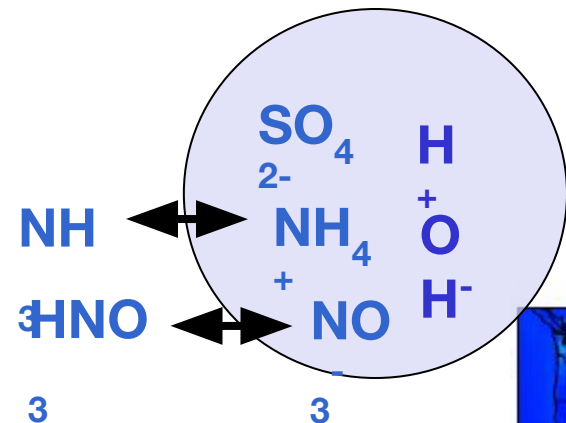
Ammonia dissolves in the sulfate aerosol totally or until titration of acidity, whichever happens first



Nitrate is taken up by aerosol if (and only if) excess NH_3 is available after sulfate titration

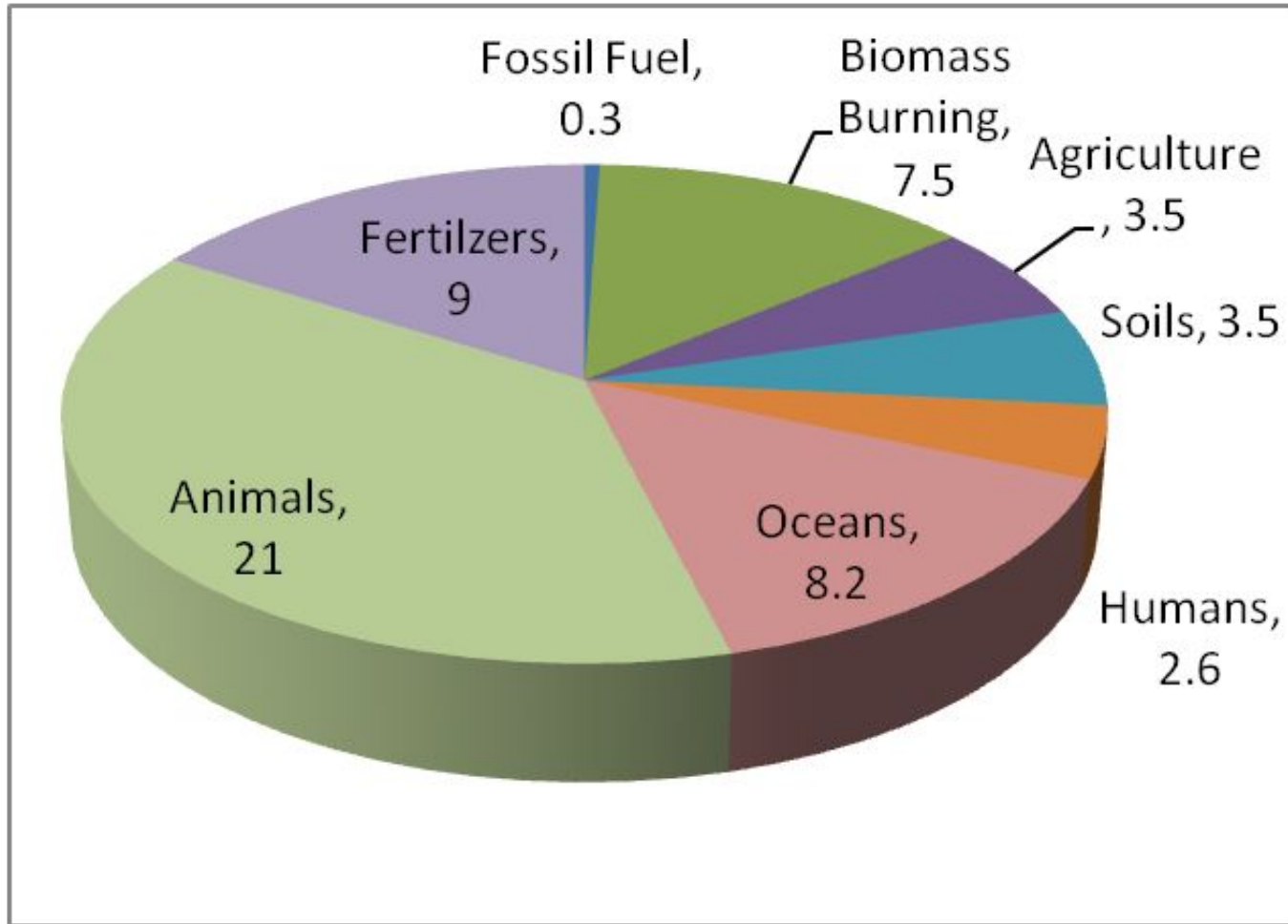


HNO_3 and excess NH_3 can also form a solid aerosol if RH is low



[Park et al., 2006]

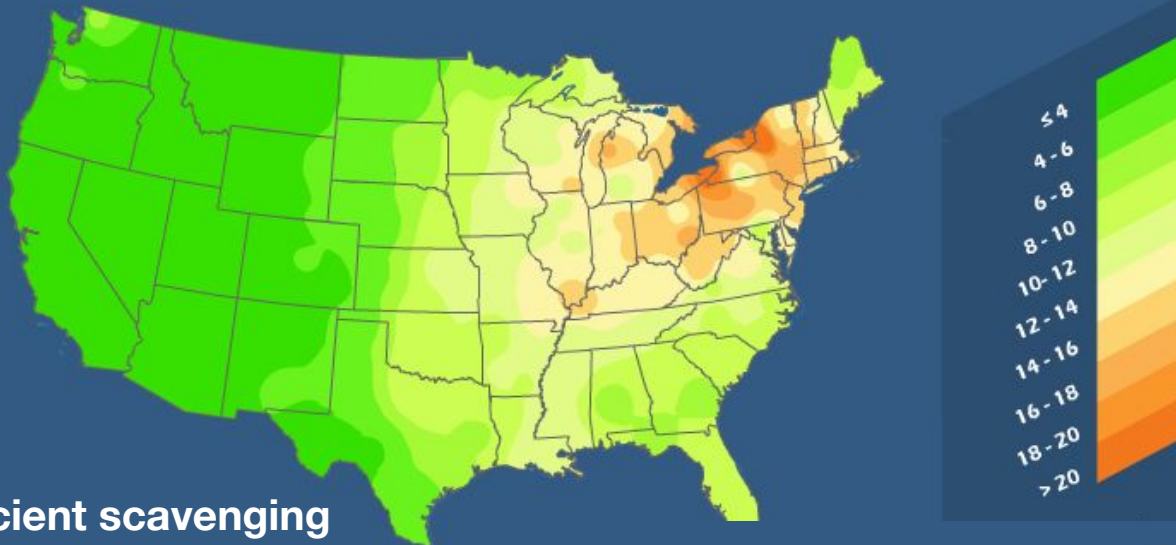
GLOBAL SOURCES OF AMMONIA



VERY UNCERTAIN!

Measurements are tough, so hard to verify regional estimates.

Nitrate Ion Wet Deposition 1985 - 2001

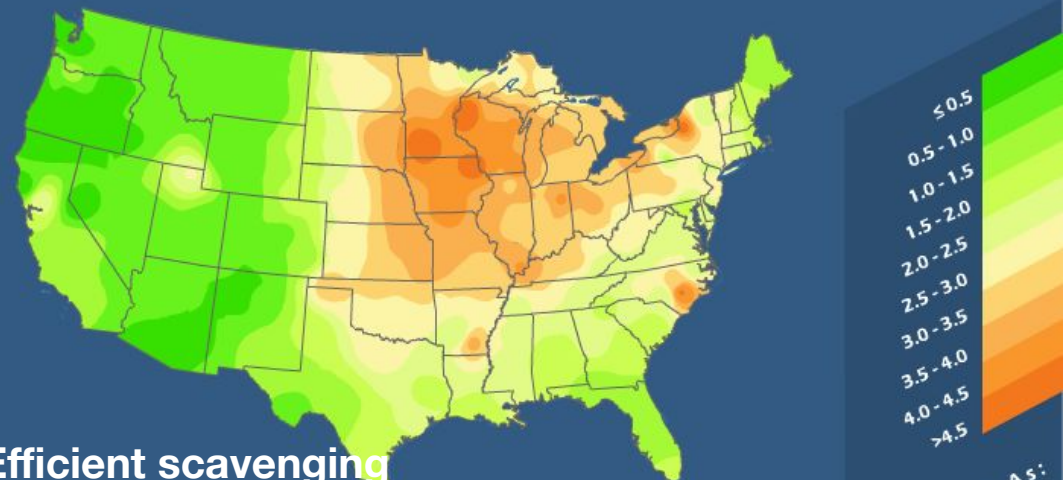


Efficient scavenging
of both $\text{HNO}_3(\text{g})$ and nitrate aerosol

85 86 87 88 89 90 91 92 93 94 95 96 97

National Atmospheric Deposition Program / National Trends Network

Ammonium Ion Wet Deposition 1985 - 2001



Efficient scavenging
of both $\text{NH}_3(\text{g})$ and ammonium aerosol

85 86 87 88 89 90 91 92 93 94 95 96 97 98 99 00 01 02

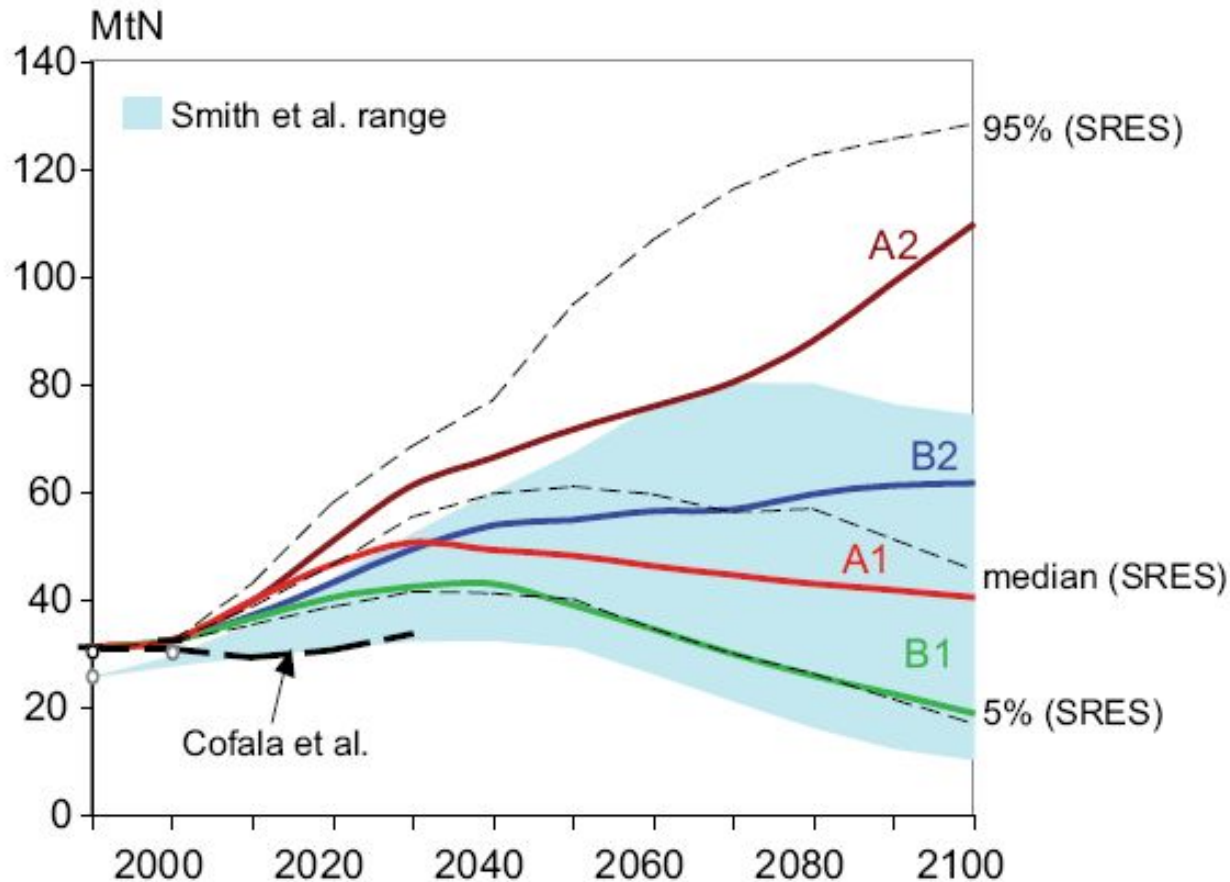
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Ammonium As:
 NH_4^+ (kg/ha)

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PREDICTED CHANGES IN ANTHROPOGENIC NO_x EMISSIONS



Emissions declining in NA, EU, growing in AS (transportation), but predicted to level off (may peak as early as 2015). What about natural sources?

Note: this include aviation NO_x sources which are small but in UT and have grown from 0.55 to 0.7 Tg/yr from 1992-2002 (may double in next 20 years)

[IPCC 2007 (WG3)]

CHANGING LNO_x?



Warmer climate = more thunderclouds = more lightning

Impact:

- (1) increasing UT ozone formation (positive forcing)
- (2) Increasing OH leads to small reductions in CH₄ (negative forcing)

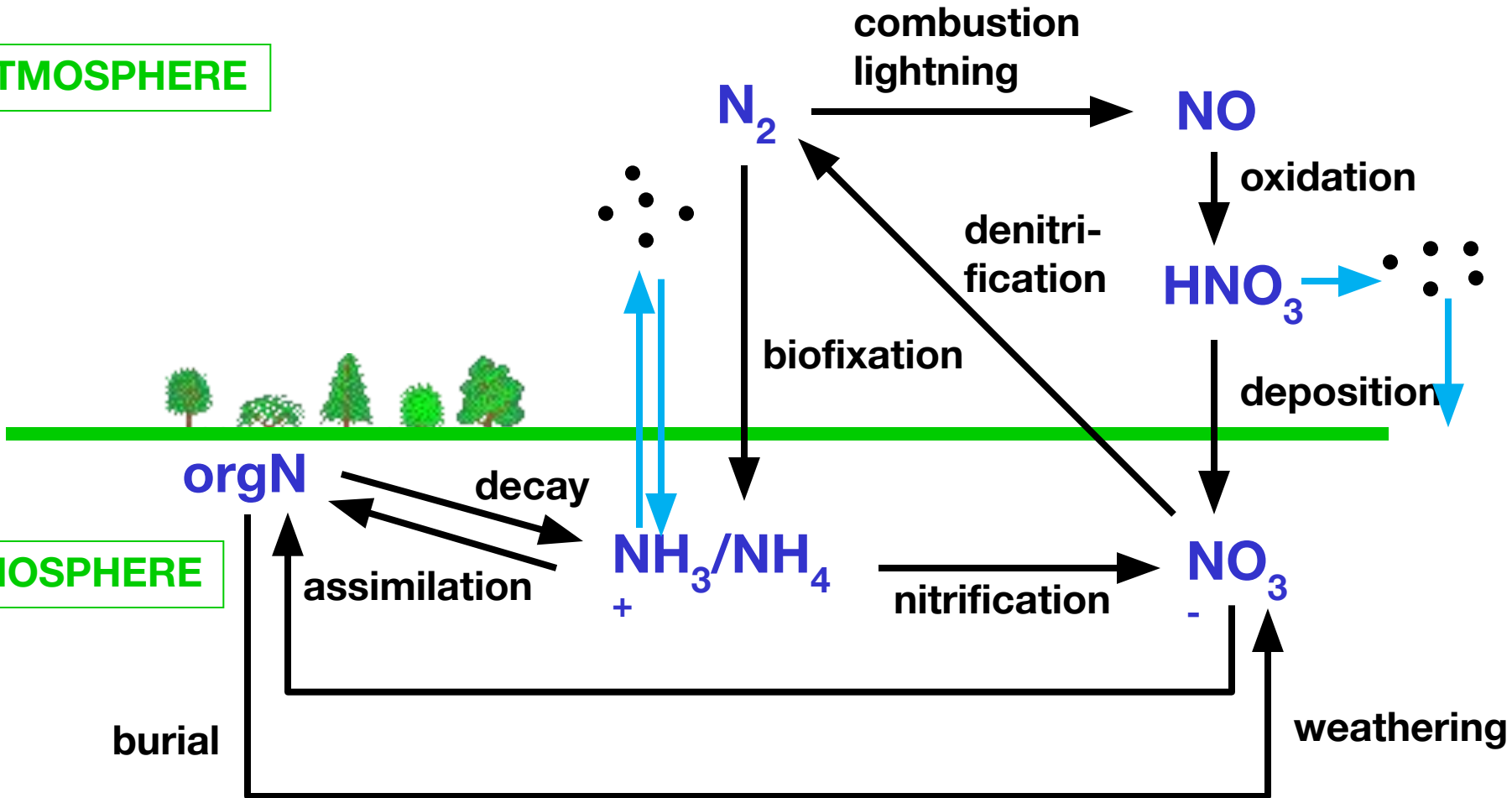
Table 14. Lightning sensitivity to global warming in model computations.

Model	Period	Parameter	LNO _x , Tg a ⁻¹	ΔT, K	Relative change, % K ⁻¹	Reference
GISS Global 2-D model	2×CO ₂ 2 K warming pe- riod	Flash frequency LNO _x	– 5	4.2 2	5–6 10	Price and Rind (1994a) Toumi et al. (1996)
ARPEGE	2×CO ₂	Flash frequency	–	2	5	Michalon et al. (1999)
GISS GCM	~1860–2000	LNO _x	3.6–3.9	1.8	4	Shindell et al. (2001)
E39/C	1992–2015	LNO _x	5.4–5.9	~1	9	Grewé et al. (2002)
GISS II'	1860–2000	LNO _x	6.2–6.5	~0.5	~10	Shindell et al. (2003)
GISS (23 layers, with chem- istry)	2×CO ₂	LNO _x	6.5		22–27	Hopkins (2003)
GISS	2000–2100	LNO _x	4.9–6.9	3.25	12	Grenfell et al. (2003)
ECHAM/CHEM	1960–2105	LNO _x	5.1–5.6	0.7	14	Stenke and Grewé (2004)
GISS1/2	2000–2100	LNO _x	6–13.5	~2	~60	Lamarque et al. (2005)
NCAR (CAM, MOZART)	2000–2100	LNO _x	2.2–2.8	~2	~14	Lamarque et al. (2005)
LMDz/INCA	2000–2100	LNO _x	5–7.5	2.45	22	Hauglustaine et al. (2005)
E39/C	1969–1999	LNO _x	5.2±0.3	0.5–1	–	Dameris et al. (2005)
HadAM3-STOCHEM	1990–2030	LNO _x	7		–	Stevenson et al. (2005)
MOZART 2/NCAR-CSM	2000–2100	LNO _x	3.9–4.5	~2	~15	Murazaki and Hess (2006)
GISS III (G-PUCCINI)	2000–2100	LNO _x	5.2–7.2	~3	~13	Shindell et al. (2006)
GISS III	2000–2030	LNO _x	6.2–6.5	0.68	7	Unger et al. (2006)
MOZART 2 with ECHAM5	2000–2100	LNO _x	~3–4	~2.3	9	Brasseur et al. (2006)

**Models
predict + 4-60
% LNO_x per °K**

THE NITROGEN CYCLE: MAJOR PROCESSES

ATMOSPHERE



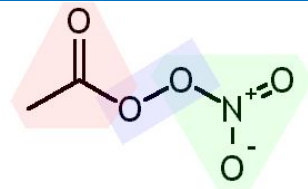
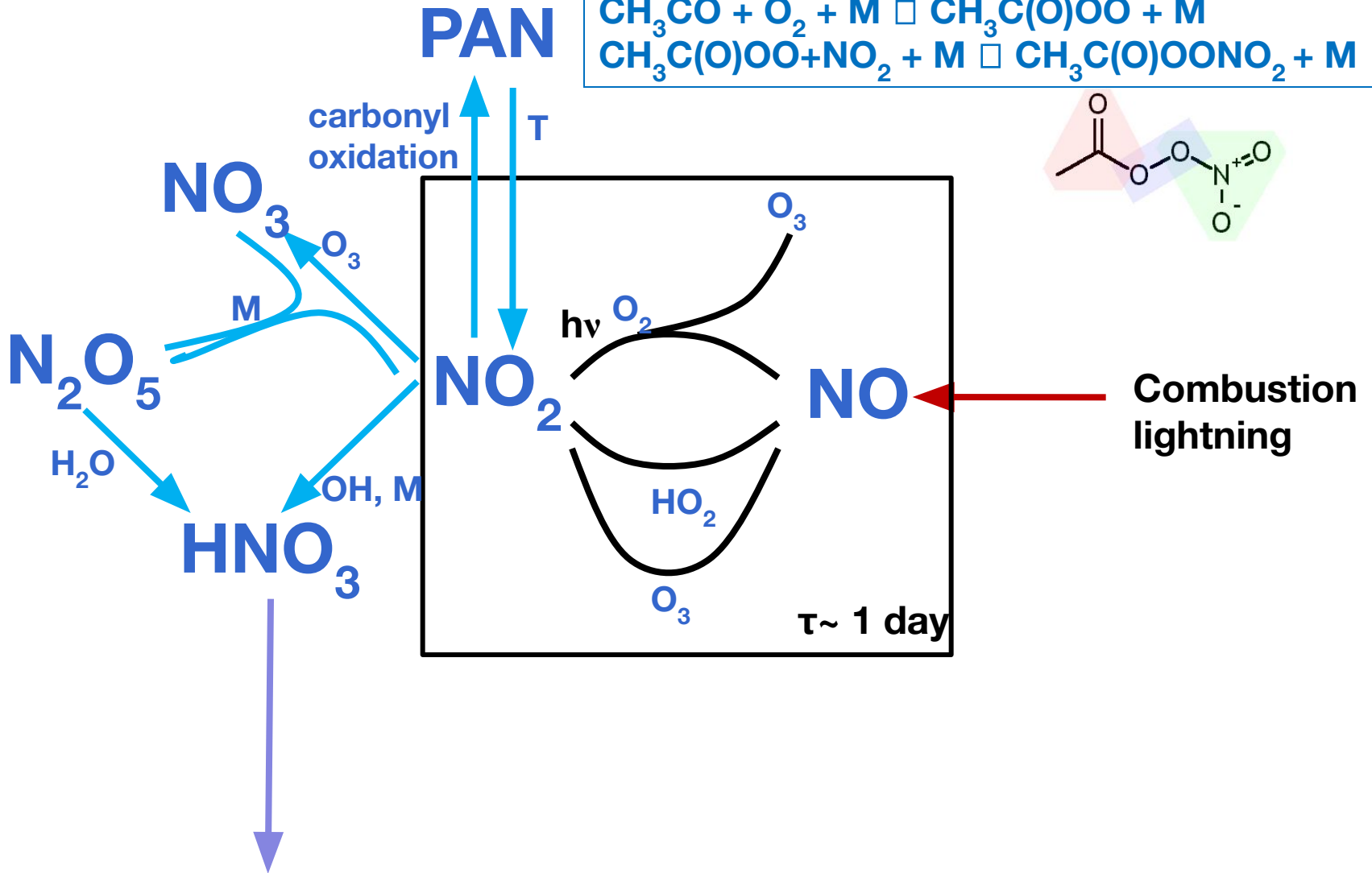
BIOSPHERE

LITHOSPHERE

"fixed" or "odd" N is less stable globally => N_2

NO_y CYCLING

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Combustion lightning