THE NITROGEN CYCLE

TOPICS FOR TODAY

1. **The Nitrogen Cycle**
2. Fixed Nitrogen in the Atmosphere
3. Sources of NOx
4. What about N_2O?
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

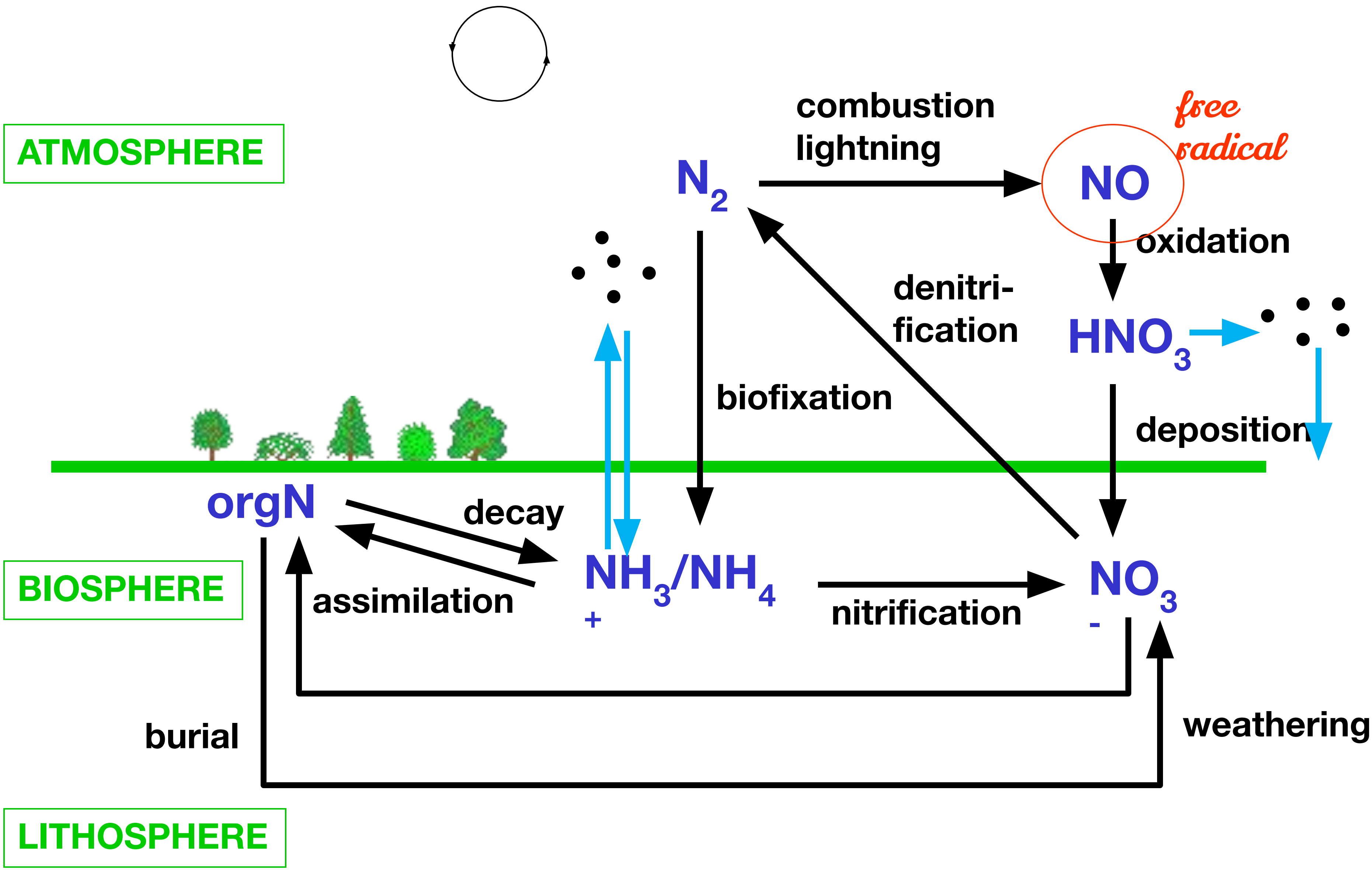
N has 5 electrons in valence shell □9 oxidation states from –3 to +5

Increasing oxidation number (oxidation reactions)

-3	0	+1	+2	+3	+4	+5
NH_3 **Ammonia** NH_4^+ **Ammonium** $R_1N(R_2)R_3$ **Organic N**	N_2	N_2O **Nitrous oxide**	NO **Nitric oxide** *free radical*	HONO **Nitrous acid** NO_2^- **Nitrite**	NO_2 **Nitrogen dioxide** *free radical*	HNO_3 **Nitric acid** NO_3^- **Nitrate** N_2O_5 **Nitrogen pentoxide**

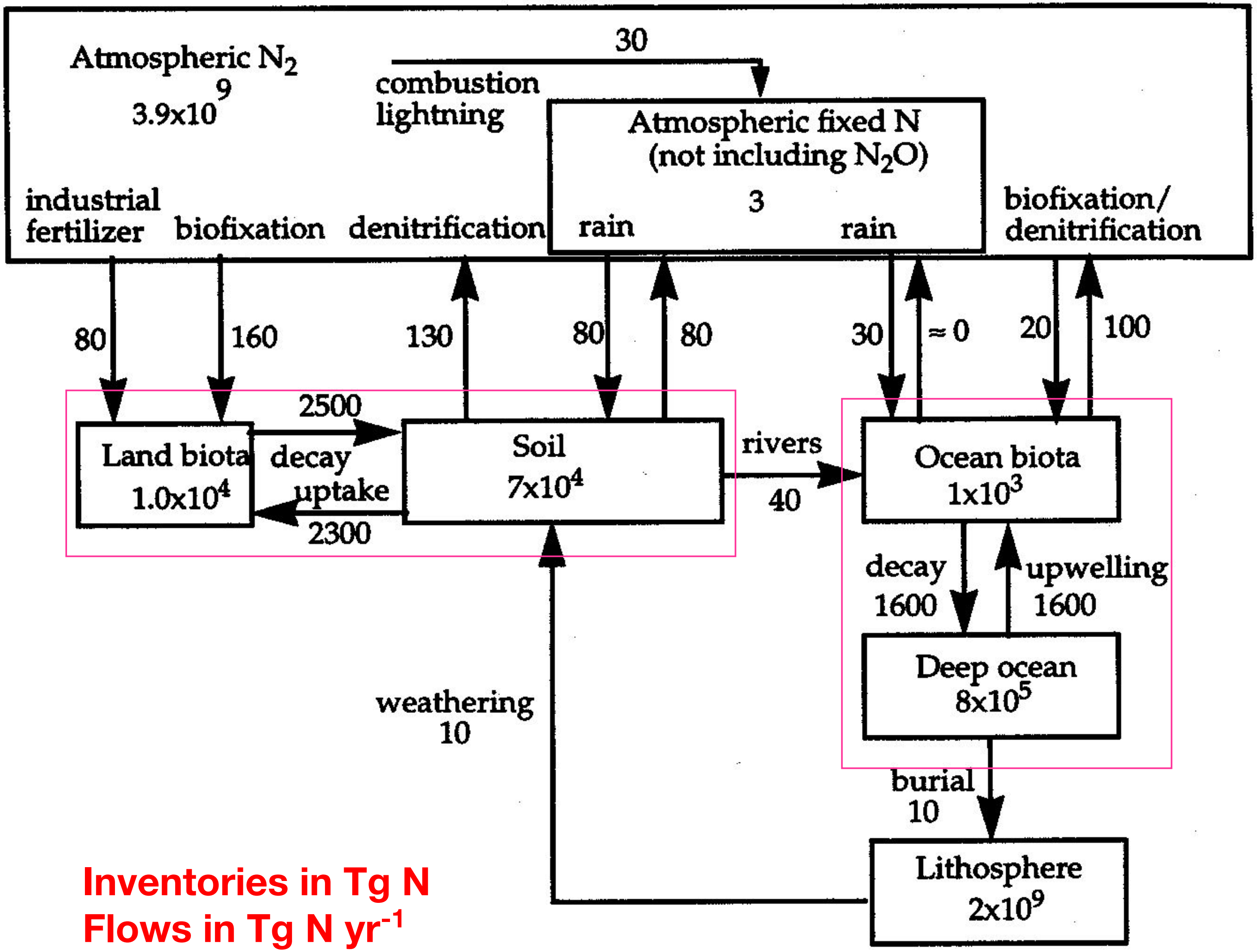
Decreasing oxidation number (reduction reactions)

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}

[Jacob, 1999]

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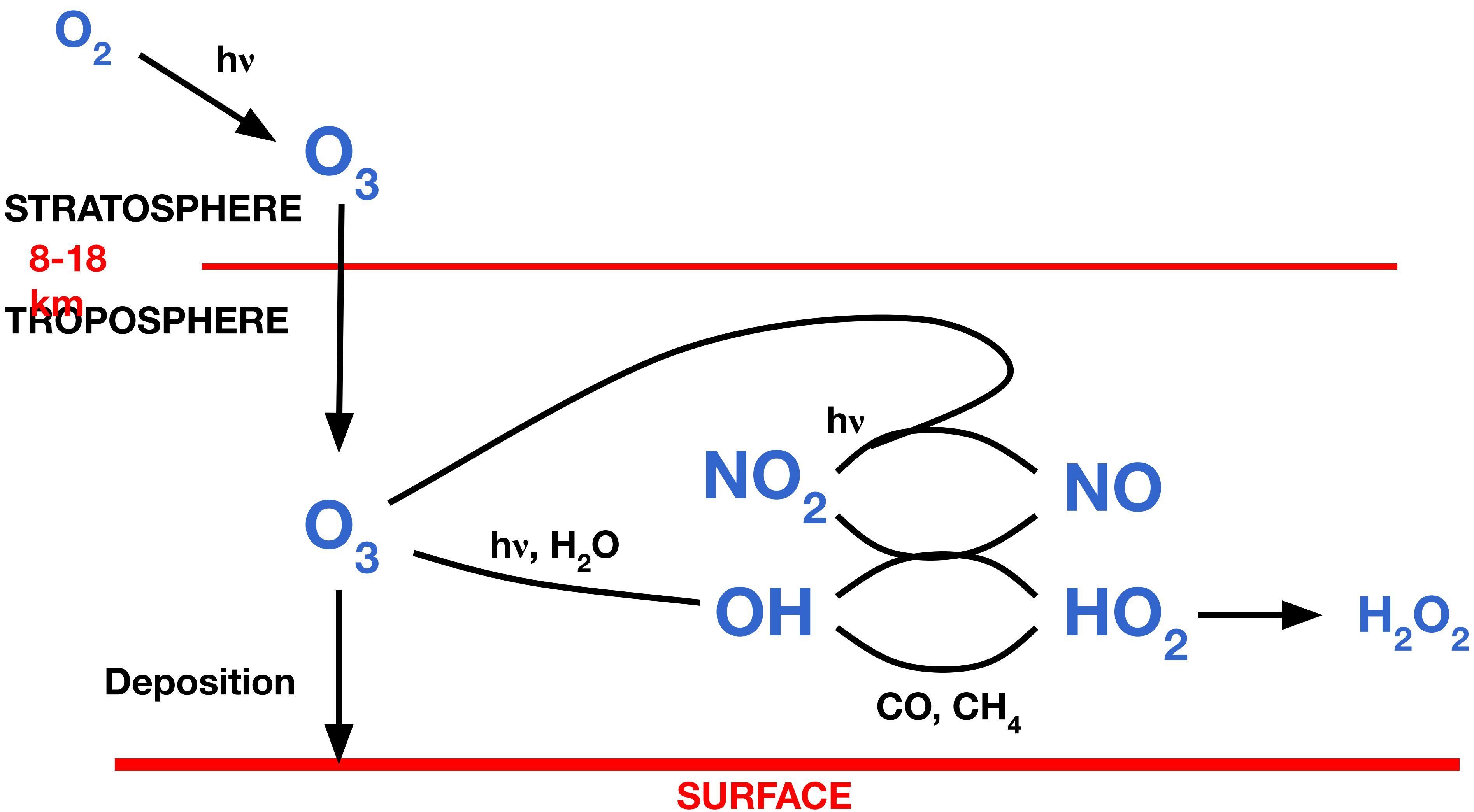
NOx: KEY TO MAINTAINING THE OXIDIZING POWER OF THE TROPOSPHERE

- ALSO key player in stratospheric O_3 loss



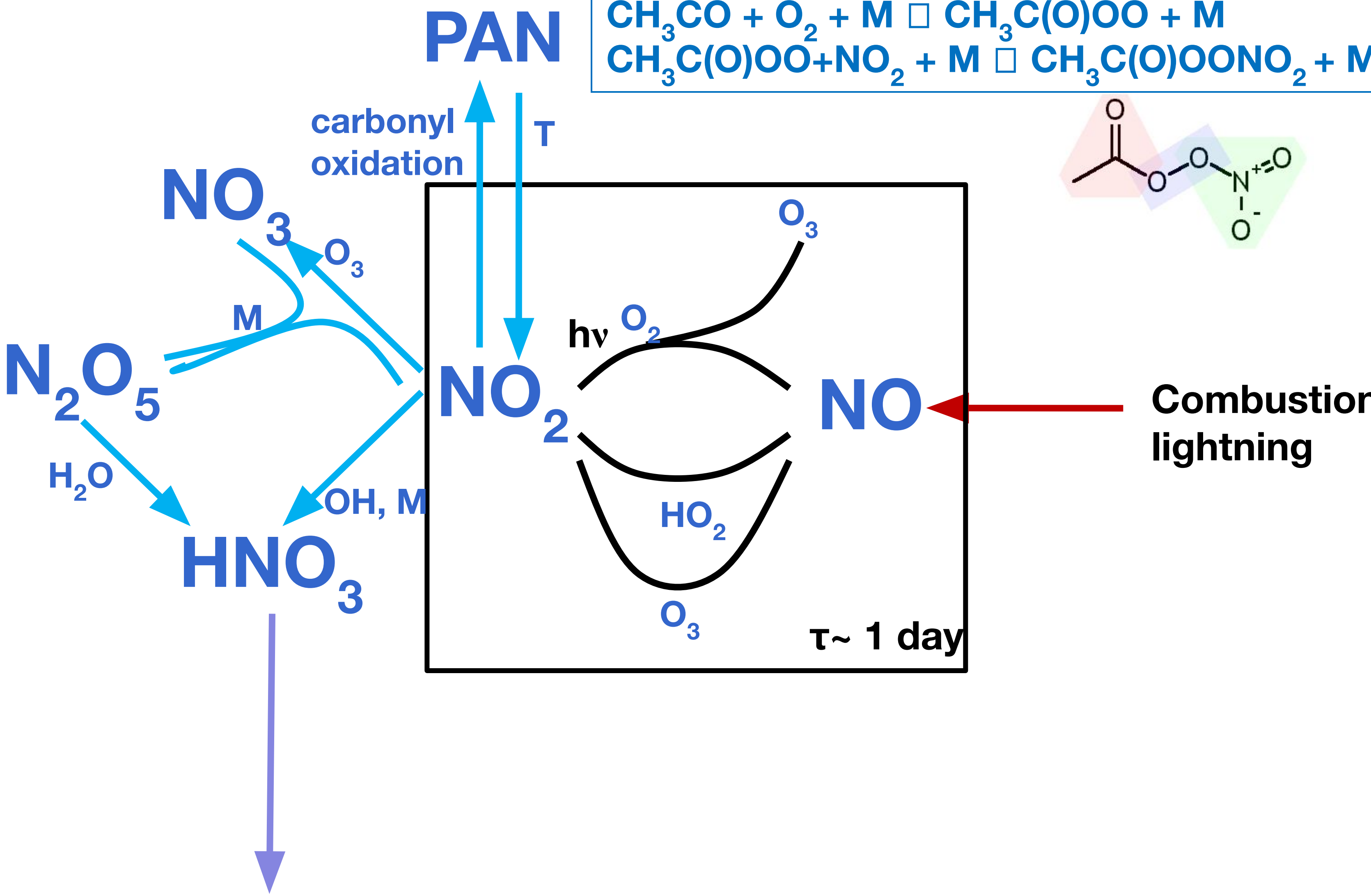
NO_y CYCLING

Example of PAN formation from acetaldehyde:

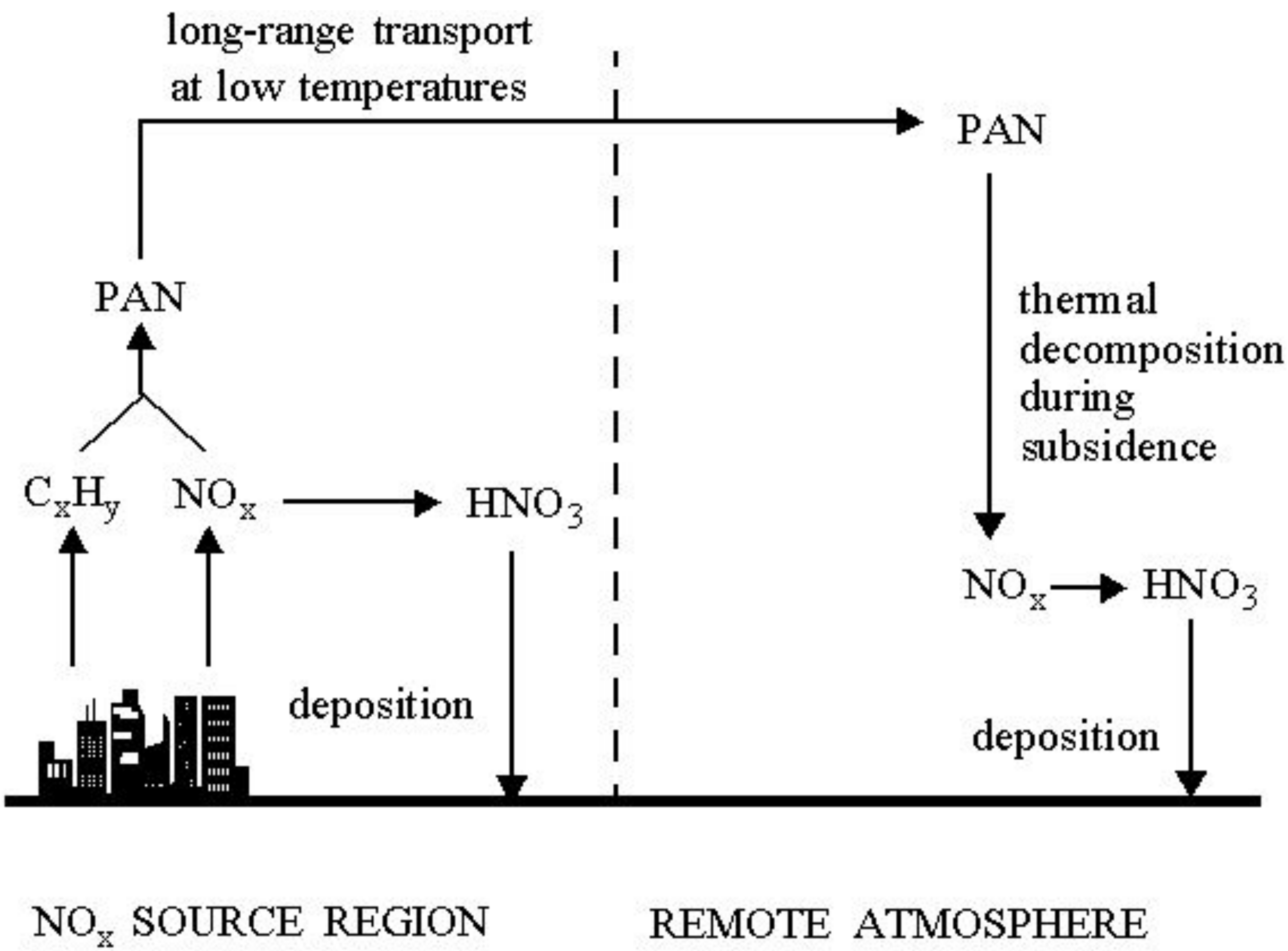
$CH_3CHO + OH$ □ $CH_3CO + H_2O$

$CH_3CO + O_2 + M$ □ $CH_3C(O)OO + M$

$CH_3C(O)OO + NO_2 + M$ □ $CH_3C(O)OONO_2 + M$



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



[Jacob, 1999]

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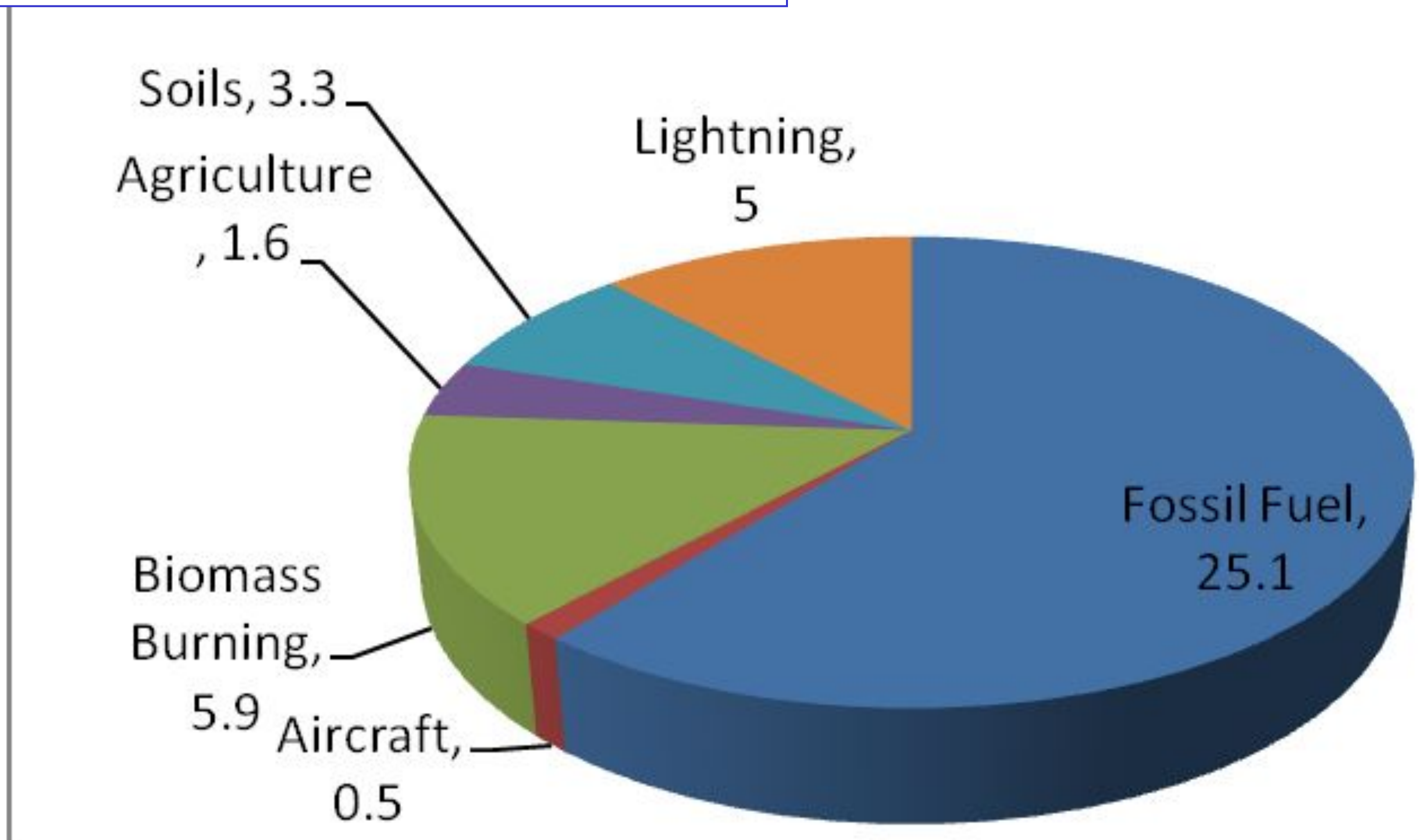
NO_x EMISSIONS (Tg N yr^{-1}) TO TROPOSPHERE

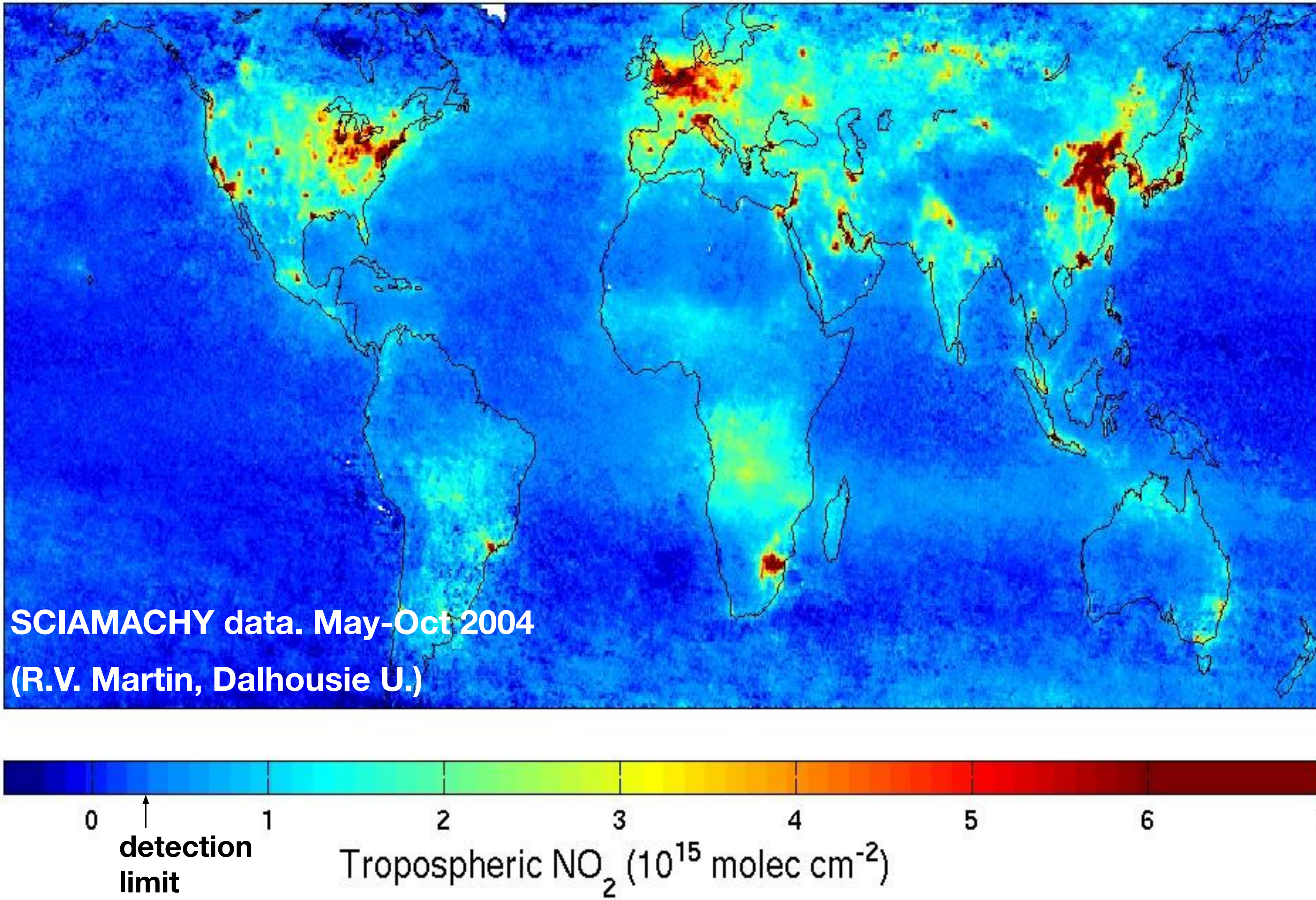
Zeldovich Mechanism: combustion and lightning
At high T (~2000K) oxygen thermolyzes:

O_2 □□ $O + O$
$O + N_2$ □□ $NO + N$
$N + O_2$ □□ $NO + O$

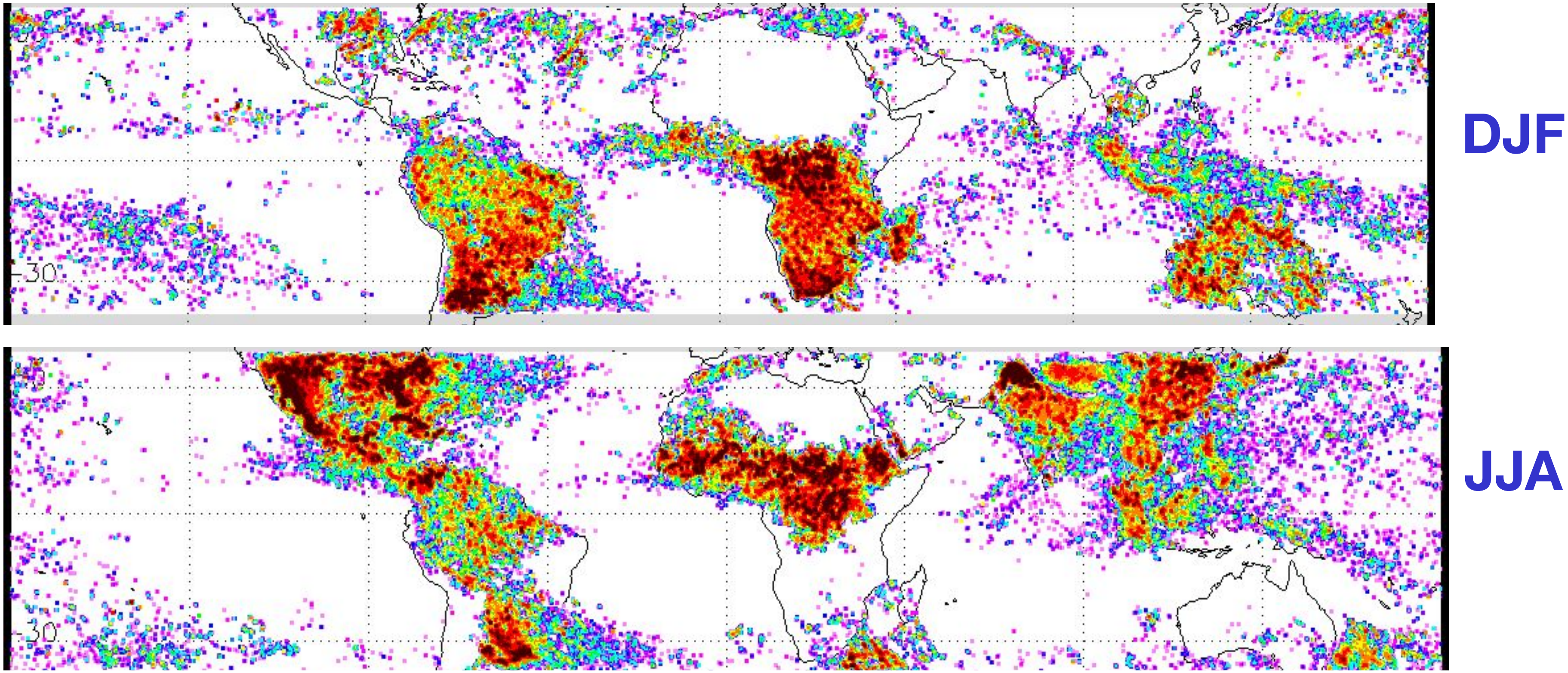


[IPCC, 2007]

USING SATELLITE OBSERVATIONS OF NO_2 TO MONITOR NO_x EMISSIONS



LIGHTNING FLASHES SEEN FROM SPACE (2000)



Bottom-up Emission Estimate:

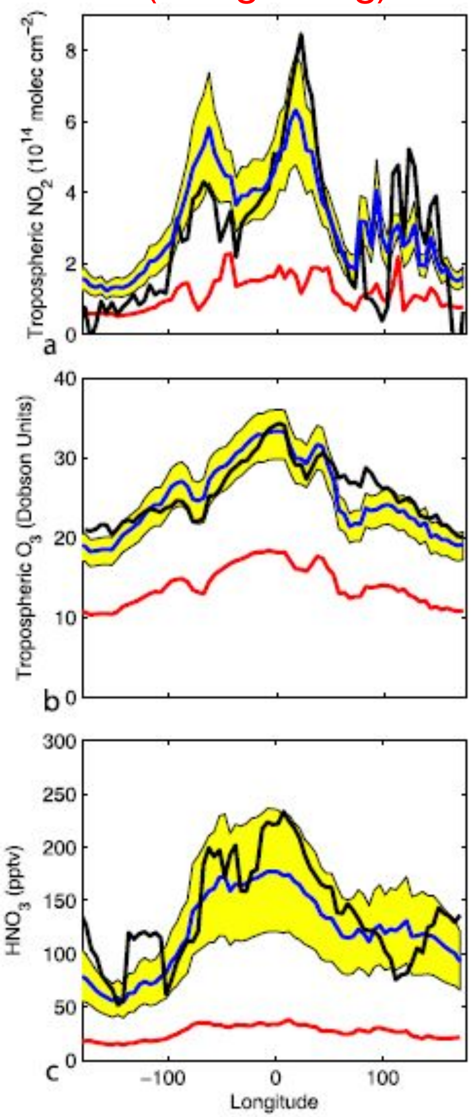
Emission = (# flashes) x (NO_x molecules /flash)

IC or CG flash?
Length of flash?

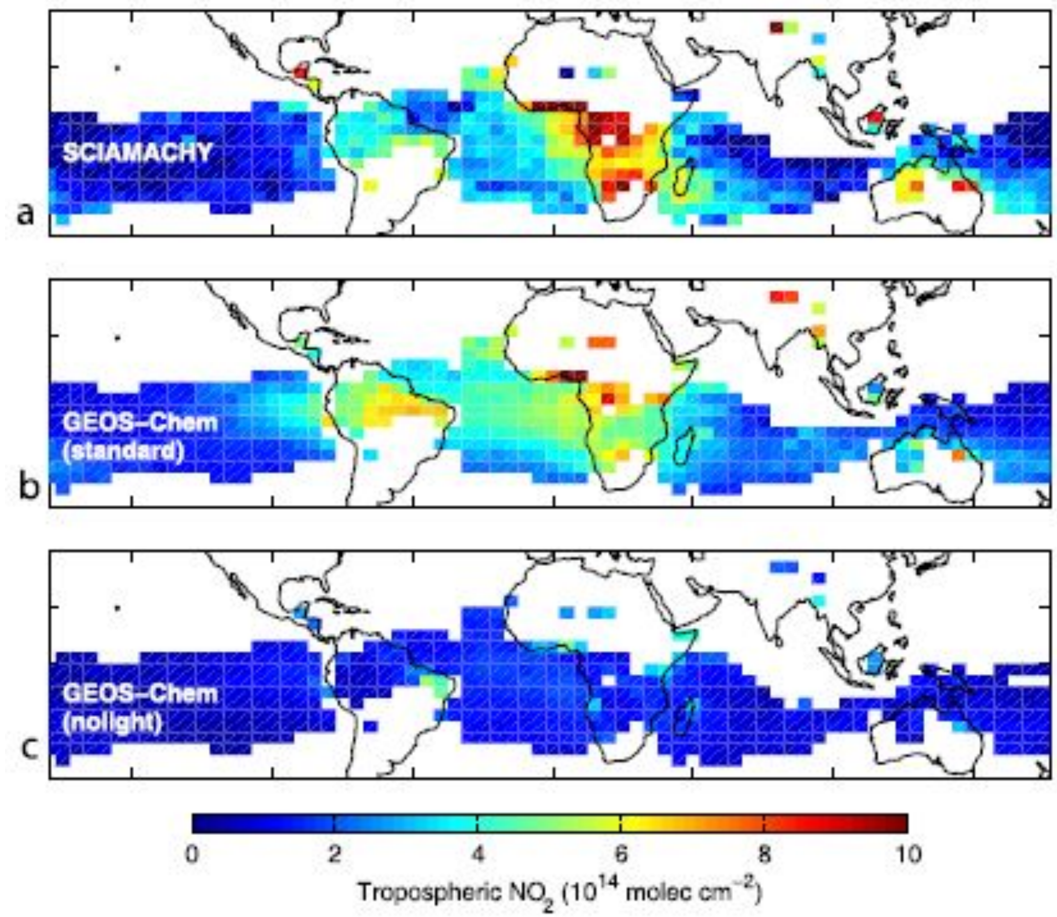
HIGHLY UNCERTAIN

TOP-DOWN ESTIMATES OF GLOBAL LIGHTNING NOx EMISSIONS

Obs (satellite)
Model (6 TgN/yr)
Model (4-8 TgN/yr)
Model (no lightning)



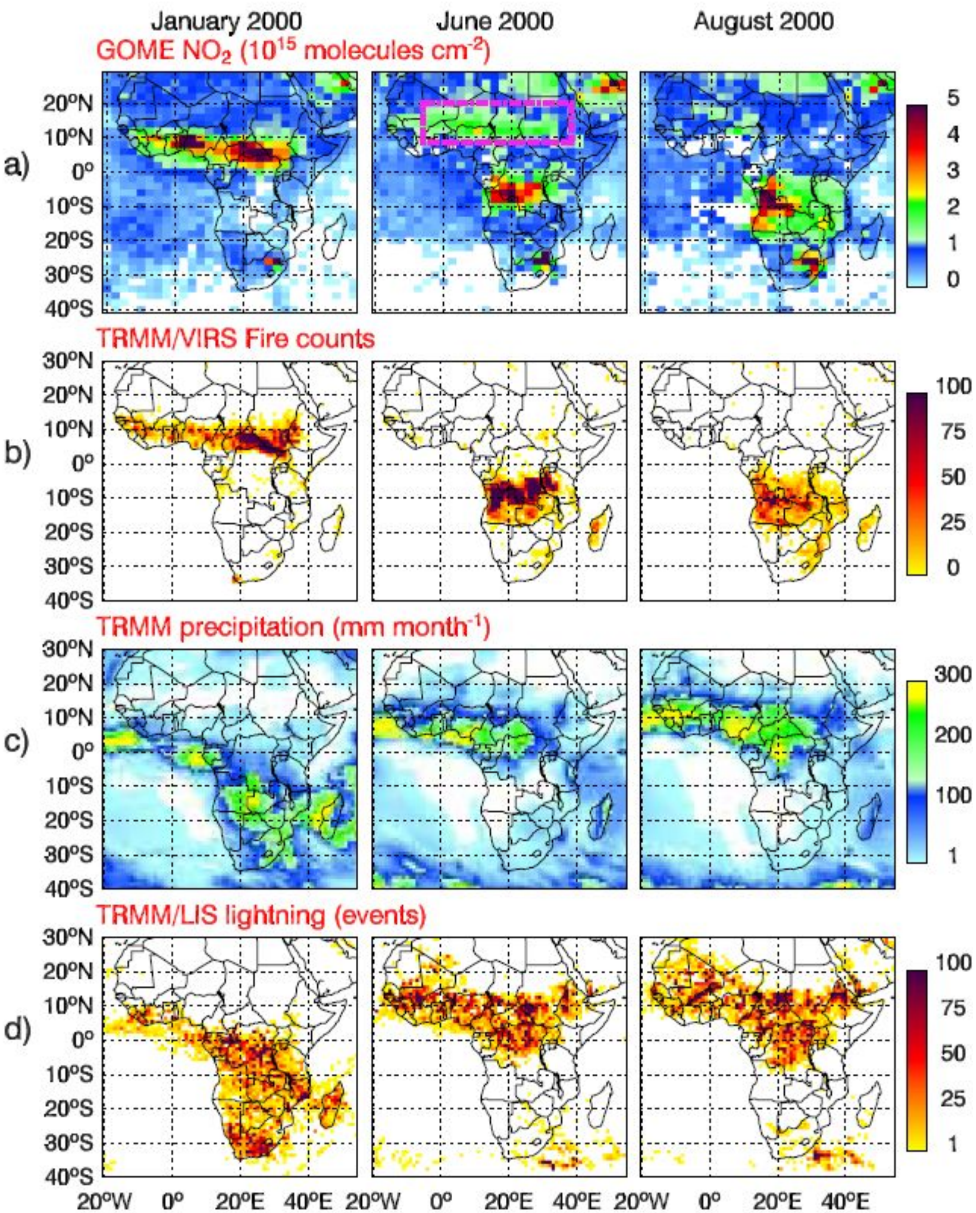
Using SCIAMACHY (NO_2), OMI (O_3), ACE-FTS (HNO_3): Target locations/times where NO_2 column is dominated by lightning source



Global source of 6 ± 2 TgN/yr from lightning

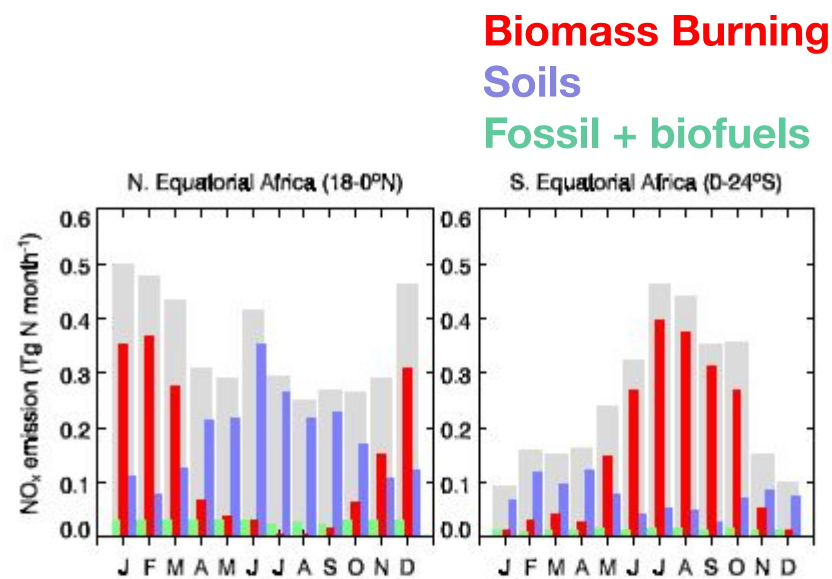
[Martin et al., 2007]

USING SATELLITE OBSERVATIONS TO ESTIMATE SOIL NOx EMISSIONS



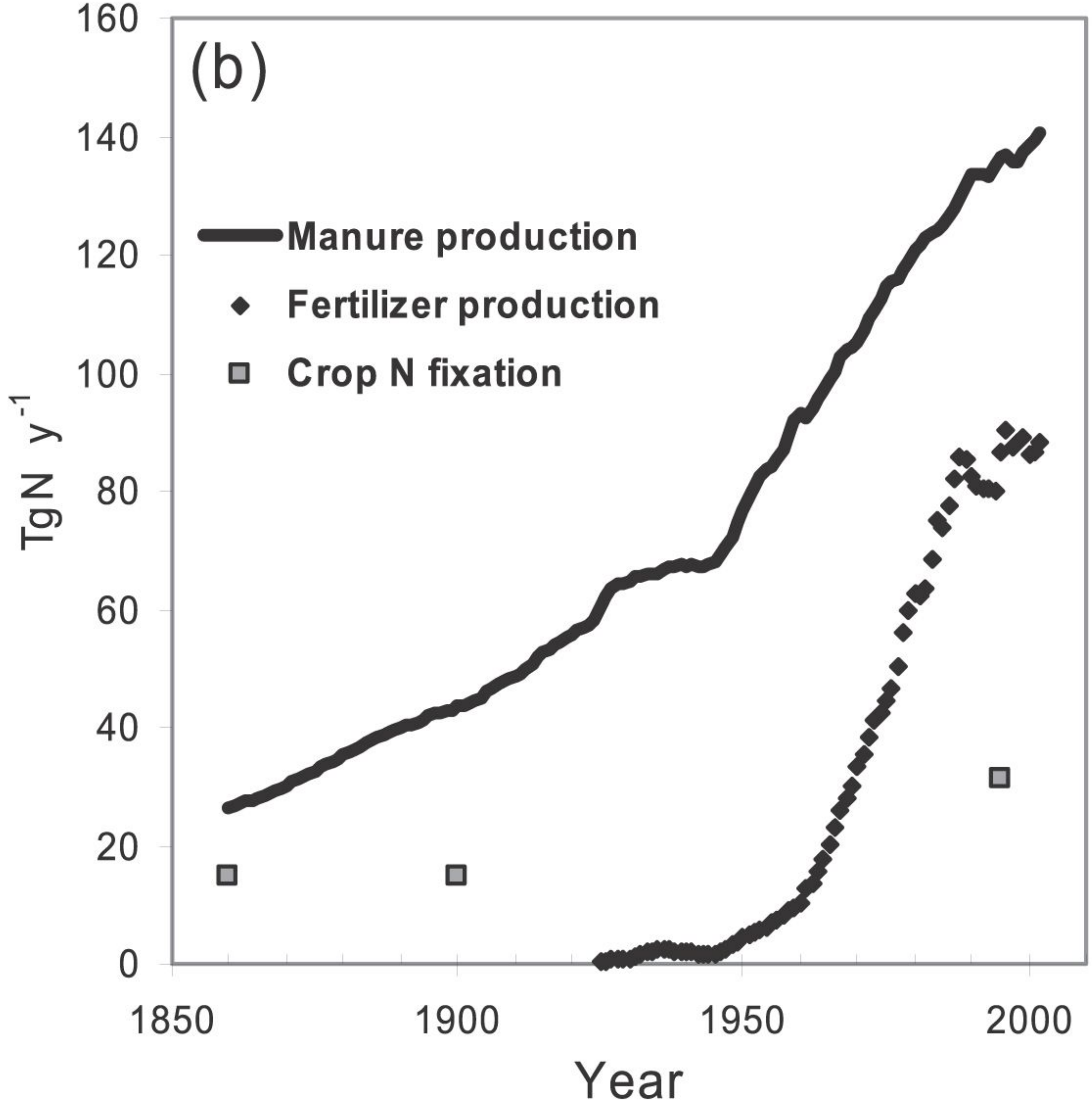
Use GOME observations over Africa:
Soils: 3.3 TgN/year
Biomass Burning: 3.8 TgN/year
40% of surface NOx emissions!

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



[Jaeglé et al., 2004]

GROWING CONTRIBUTION OF AGRICULTURE TO N CYCLE



[IPCC, 2007]

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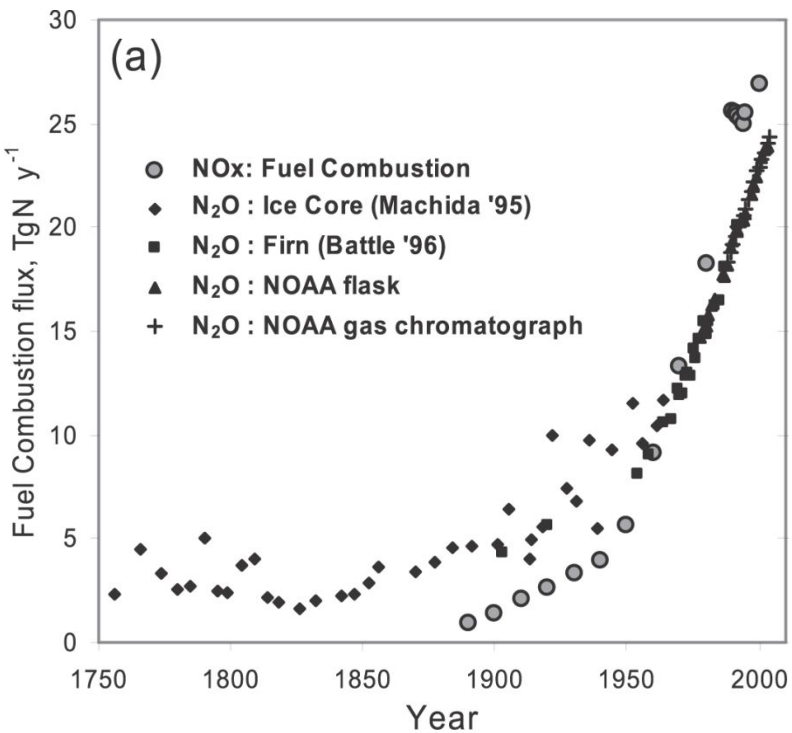
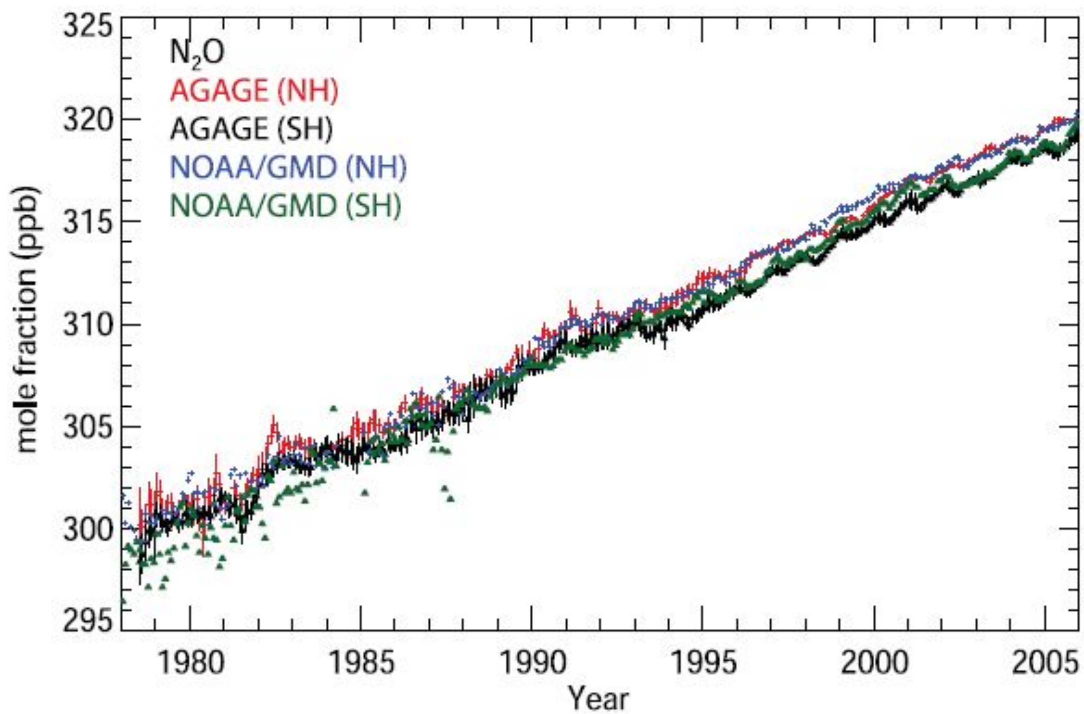
N_2O: LOW-YIELD PRODUCT OF BACTERIAL NITRIFICATION AND DENITRIFICATION

Important as

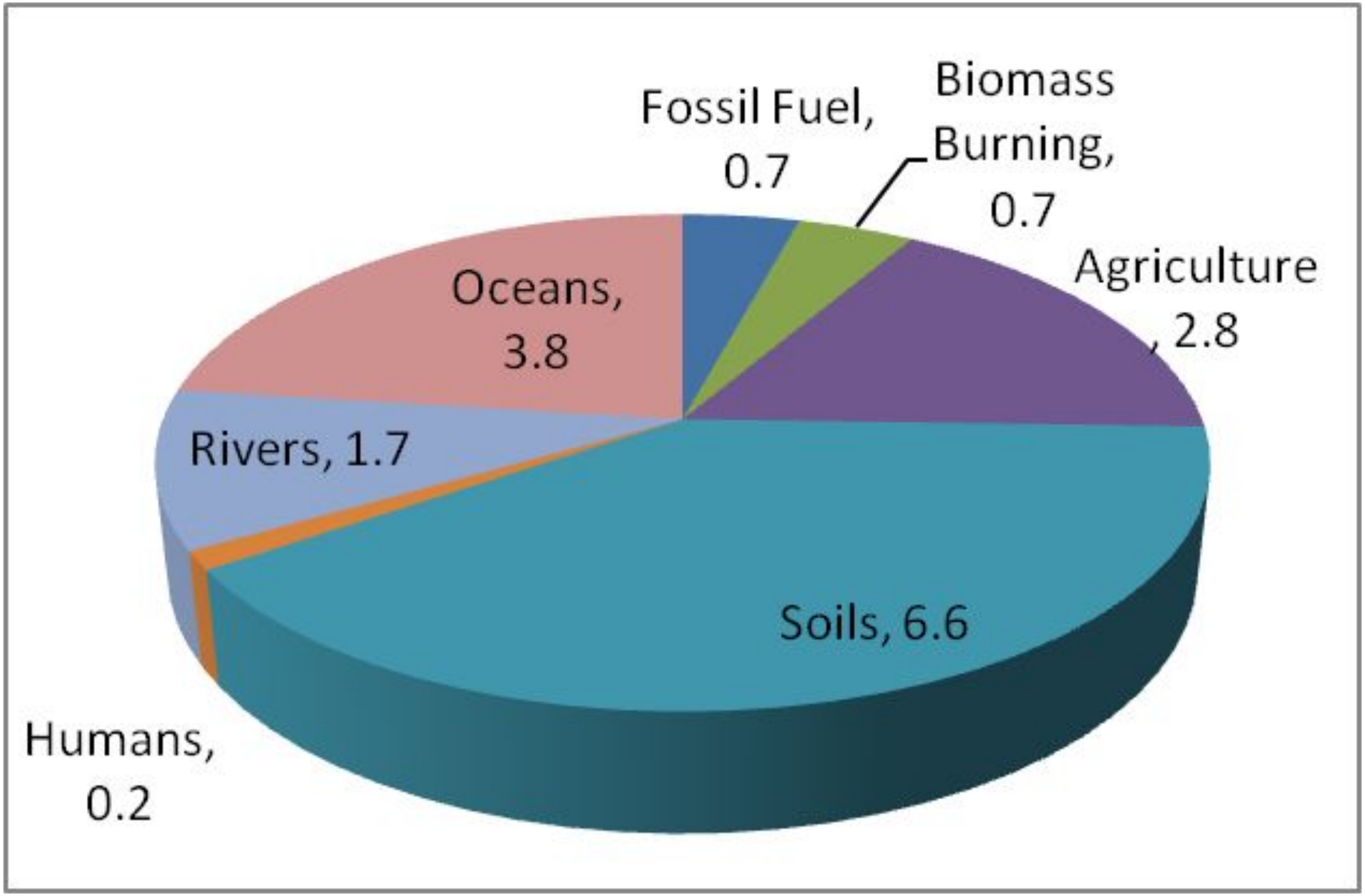
- **source of NO_x radicals in stratosphere**
- **greenhouse gas**





[IPCC, 2007]

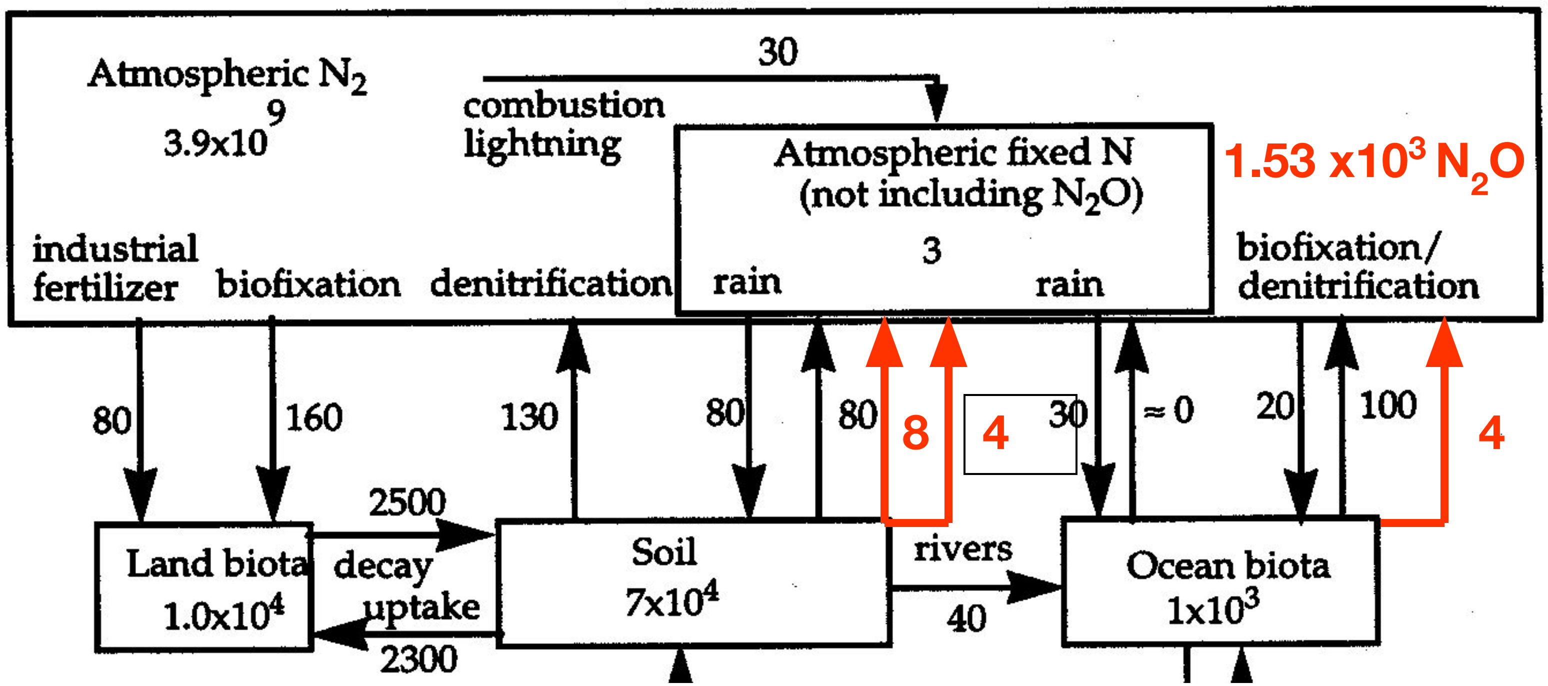
N_2O EMISSIONS (Tg N yr^{-1}) TO TROPOSPHERE



Source is MOSTLY (~75%) natural

[IPCC, 2007]

ADDING N_2O 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!
(N_2O atm mass = $5.13\ 10^{18}$ kg x $3.1\ 10^{-7}$ x28/29 = 1535 Tg)

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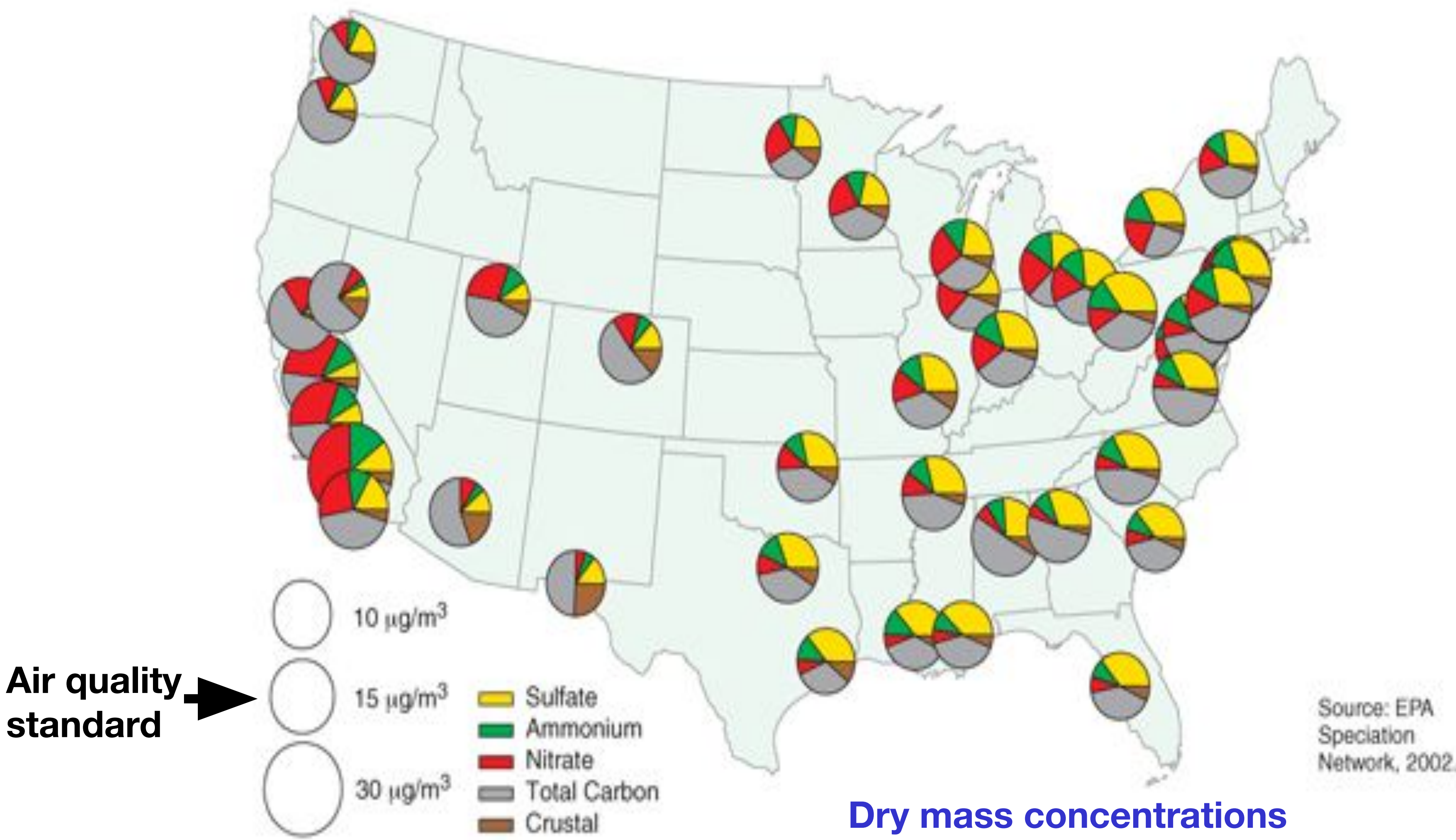
ANNUAL MEAN $PM_{2.5}$ CONCENTRATIONS AT U.S. SITES

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



Dry mass concentrations

FORMATION OF SULFATE-NITRATE-AMMONIUM AEROSOLS

Thermodynamic rules:

$$H_2SO_4(g) \xrightarrow{H_2O} SO_4^{2-} + 2H^+$$

Sulfate always forms an aqueous aerosol

$$NH_3(g) \xrightarrow{H_2O} NH_4^+ + OH^-$$

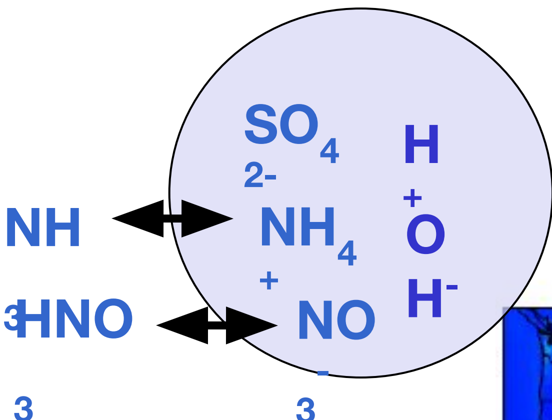
Ammonia dissolves in the sulfate aerosol totally or until titration of acidity, whichever happens first

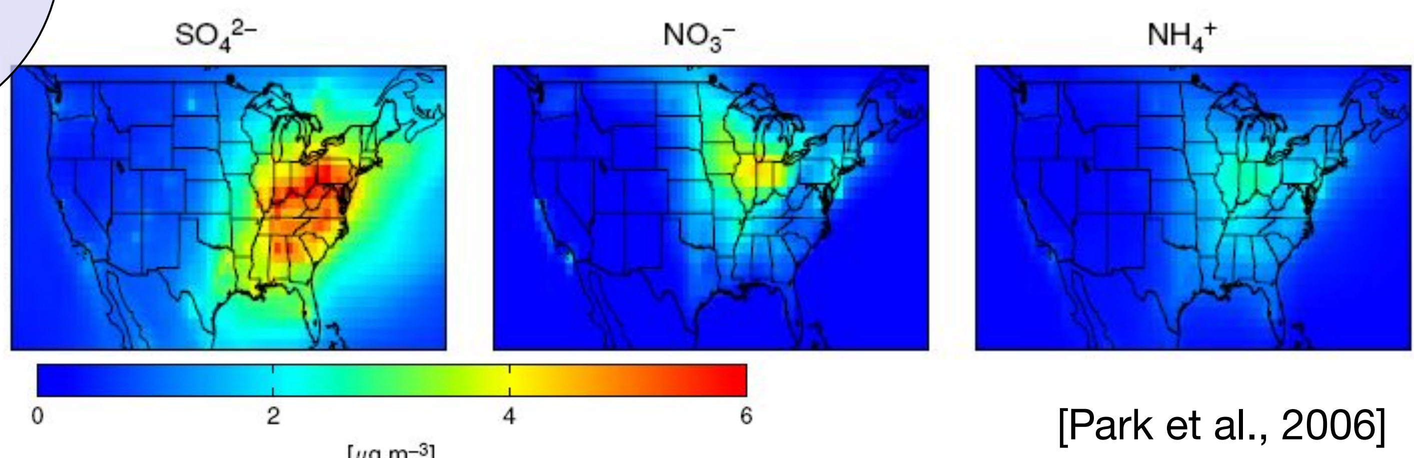
$$HNO_3(g) \xrightarrow{H_2O} NO_3^- + H^+$$

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

$$NH_3(g) + HNO_3(g) \rightleftharpoons NH_4NO_3(aerosol)$$

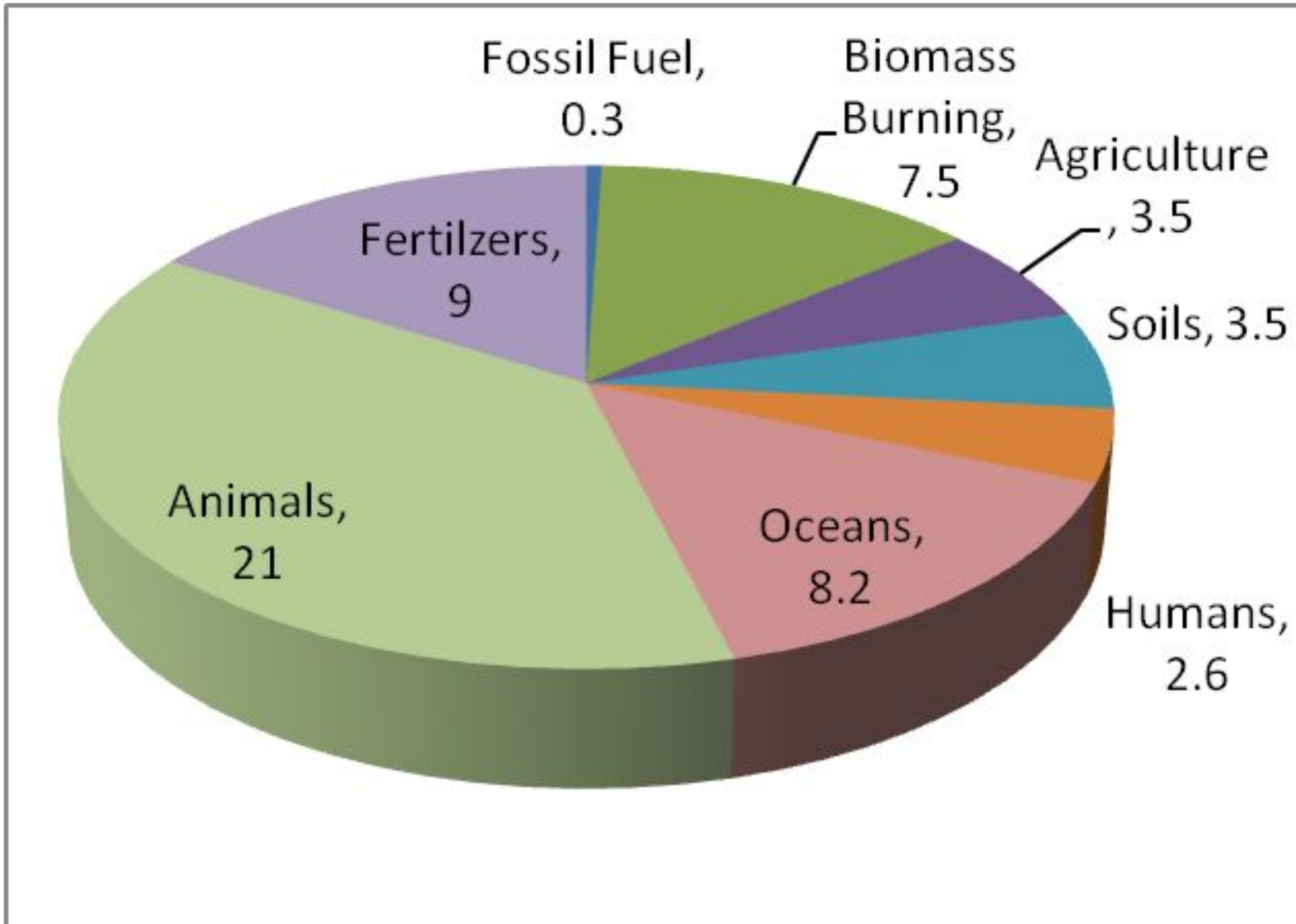
HNO_3 and excess NH_3 can also form a solid aerosol if RH is low





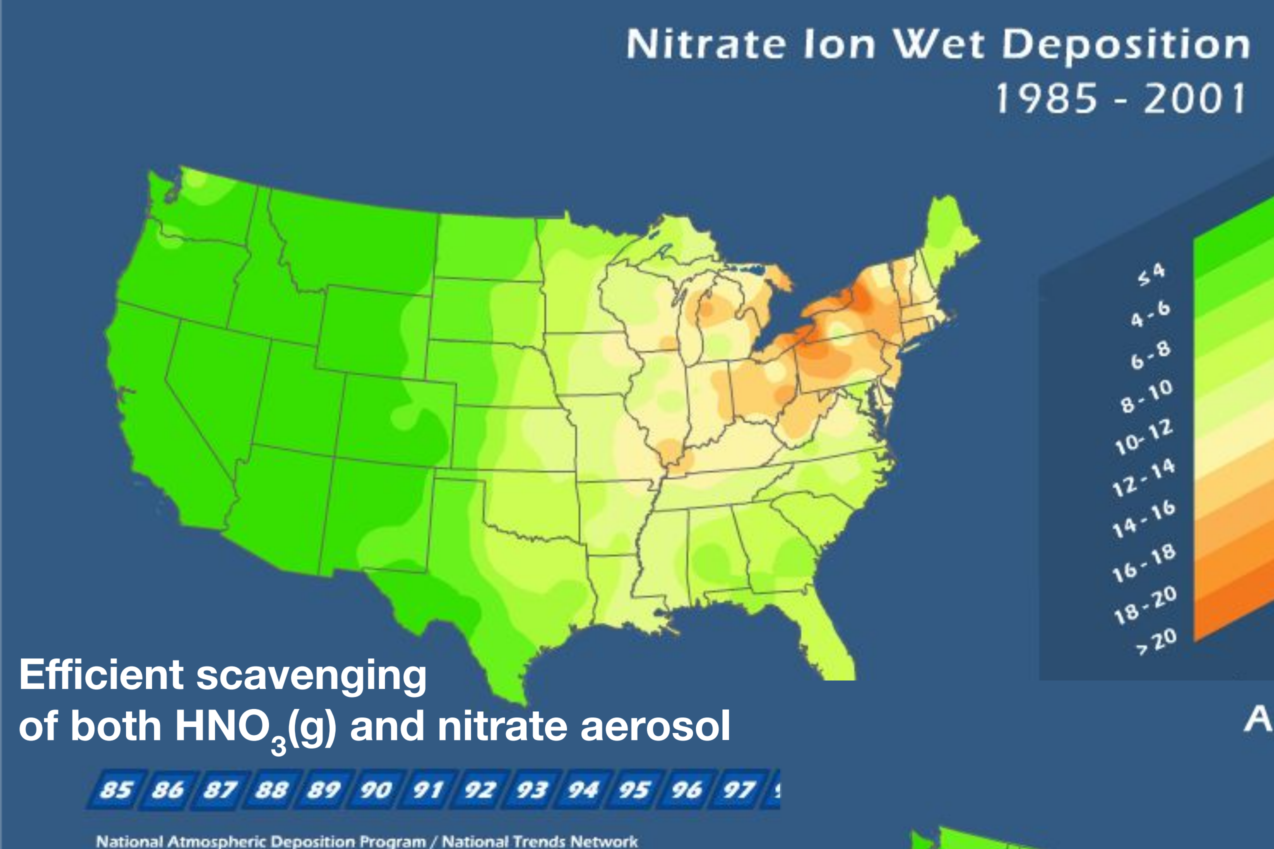
[Park et al., 2006]

GLOBAL SOURCES OF AMMONIA

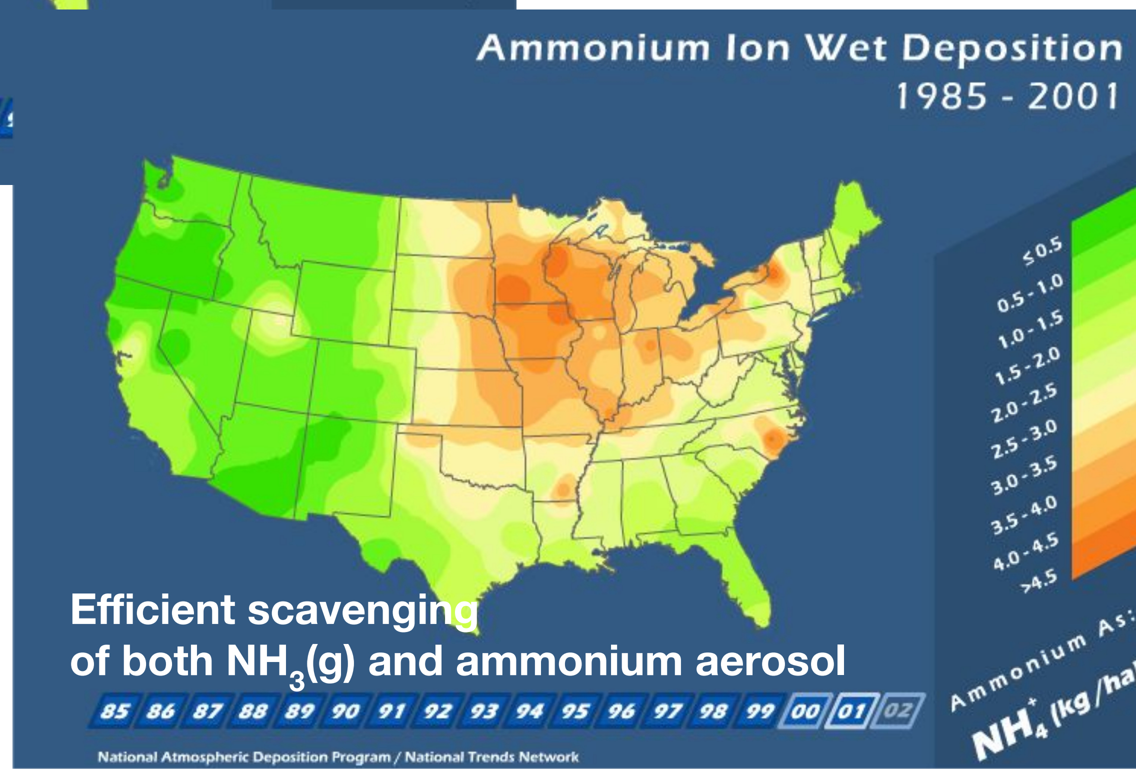


VERY UNCERTAIN!
Measurements are tough, so hard to verify regional estimates.

[Park et al., 2004]



Efficient scavenging of both HNO_3(g) and nitrate aerosol



Efficient scavenging of both NH_3(g) and ammonium aerosol

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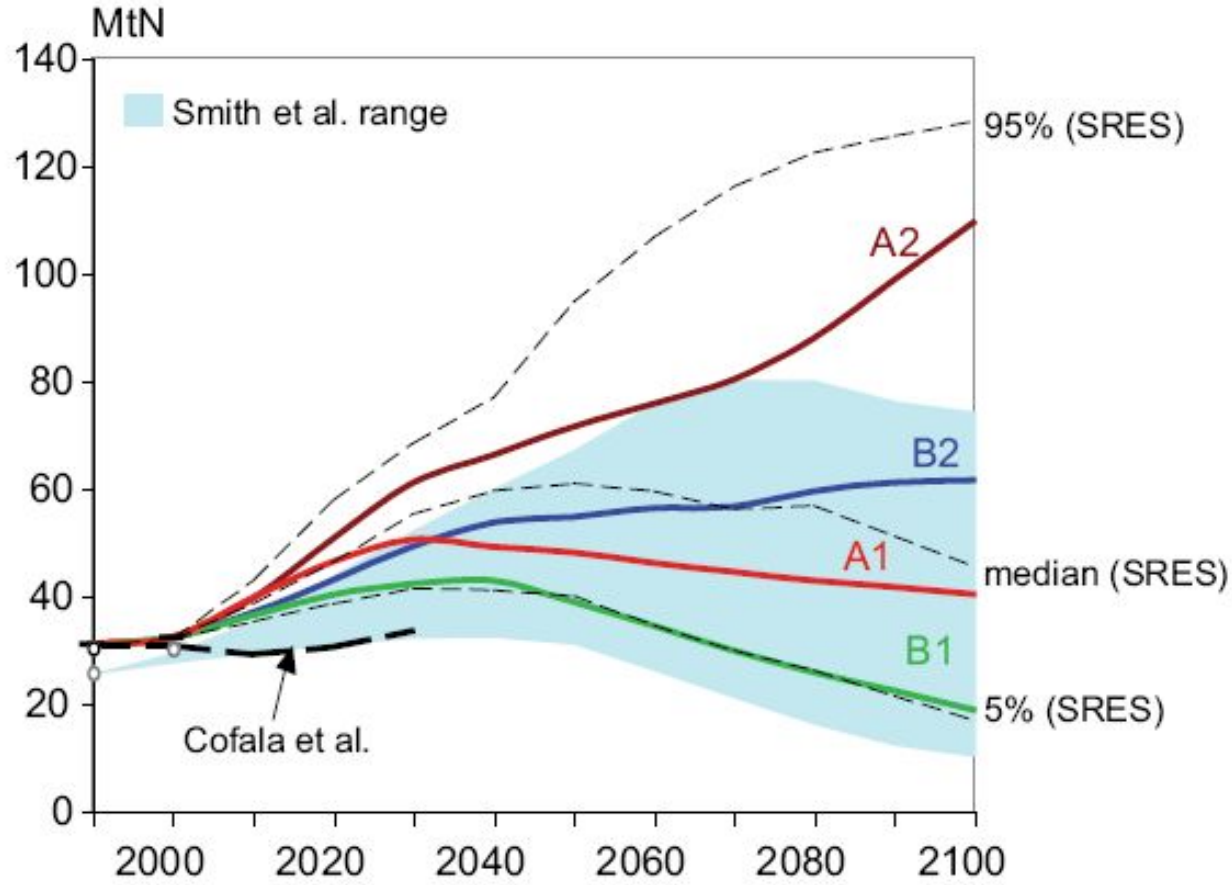
PREDICTED CHANGES IN ANTHROPOGENIC NO_x EMISSIONS



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 NOx 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 CH_4 (negative forcing)

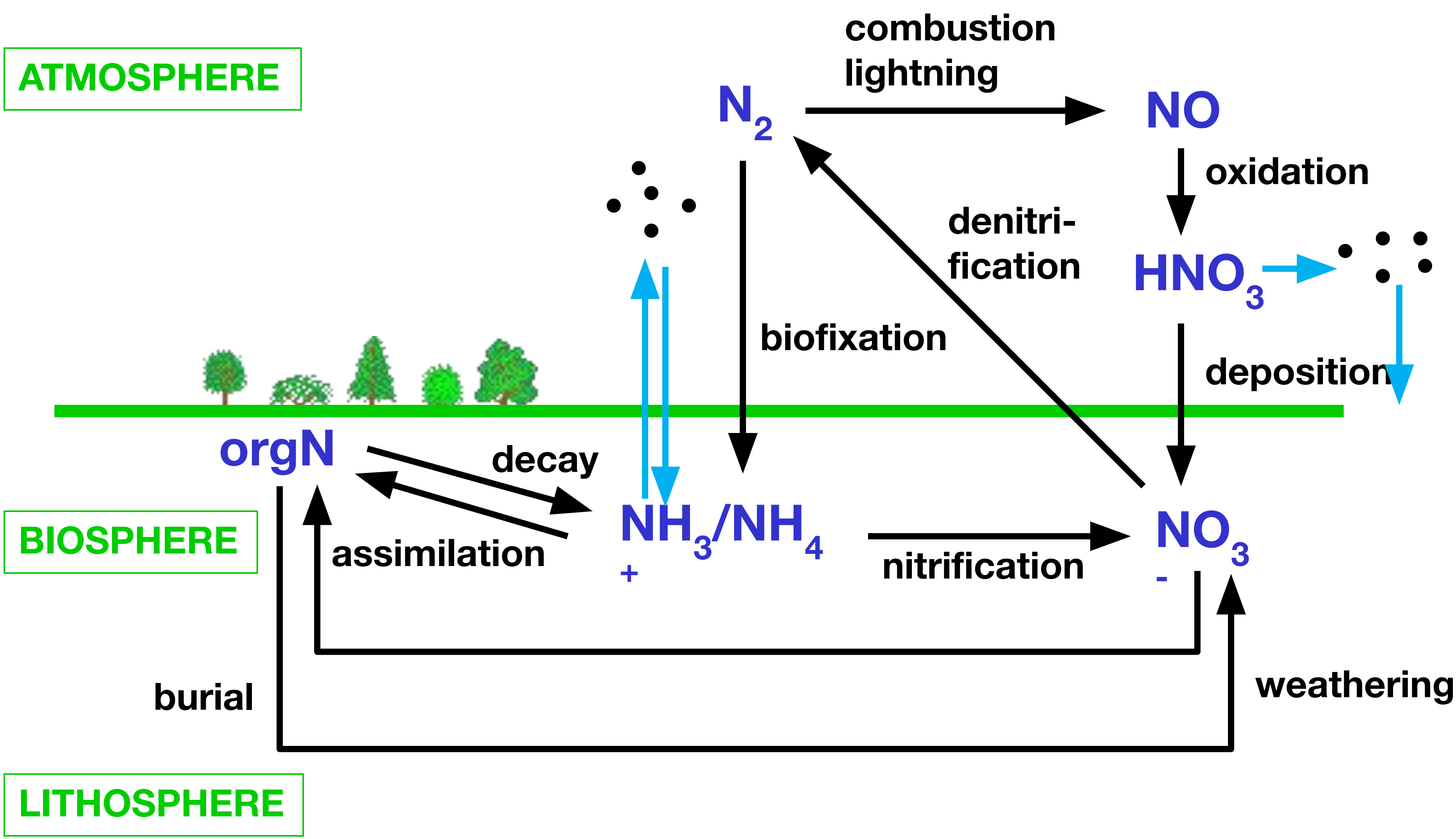
U. Schumann and H. Huntrieser: The global lightning-induced nitrogen oxides source 3861

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	$2\times CO_2$	Flash frequency	–	4.2	5–6	Price and Rind (1994a)
Global 2-D model	2 K warming period	LNO_x	5	2	10	Toumi et al. (1996)
ARPEGE	$2\times CO_2$	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	Grewe et al. (2002)
GISS II′	1860–2000	LNO_x	6.2–6.5	~0.5	~10	Shindell et al. (2003)
GISS (23 layers, with chemistry)	$2\times CO_2$	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 Grewe (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



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

NO_y CYCLING

Example of PAN formation from acetaldehyde:

$CH_3CHO + OH$ □ $CH_3CO + H_2O$

$CH_3CO + O_2 + M$ □ $CH_3C(O)OO + M$

$CH_3C(O)OO{+}NO_2 + M$ □ $CH_3C(O)OONO_2 + M$