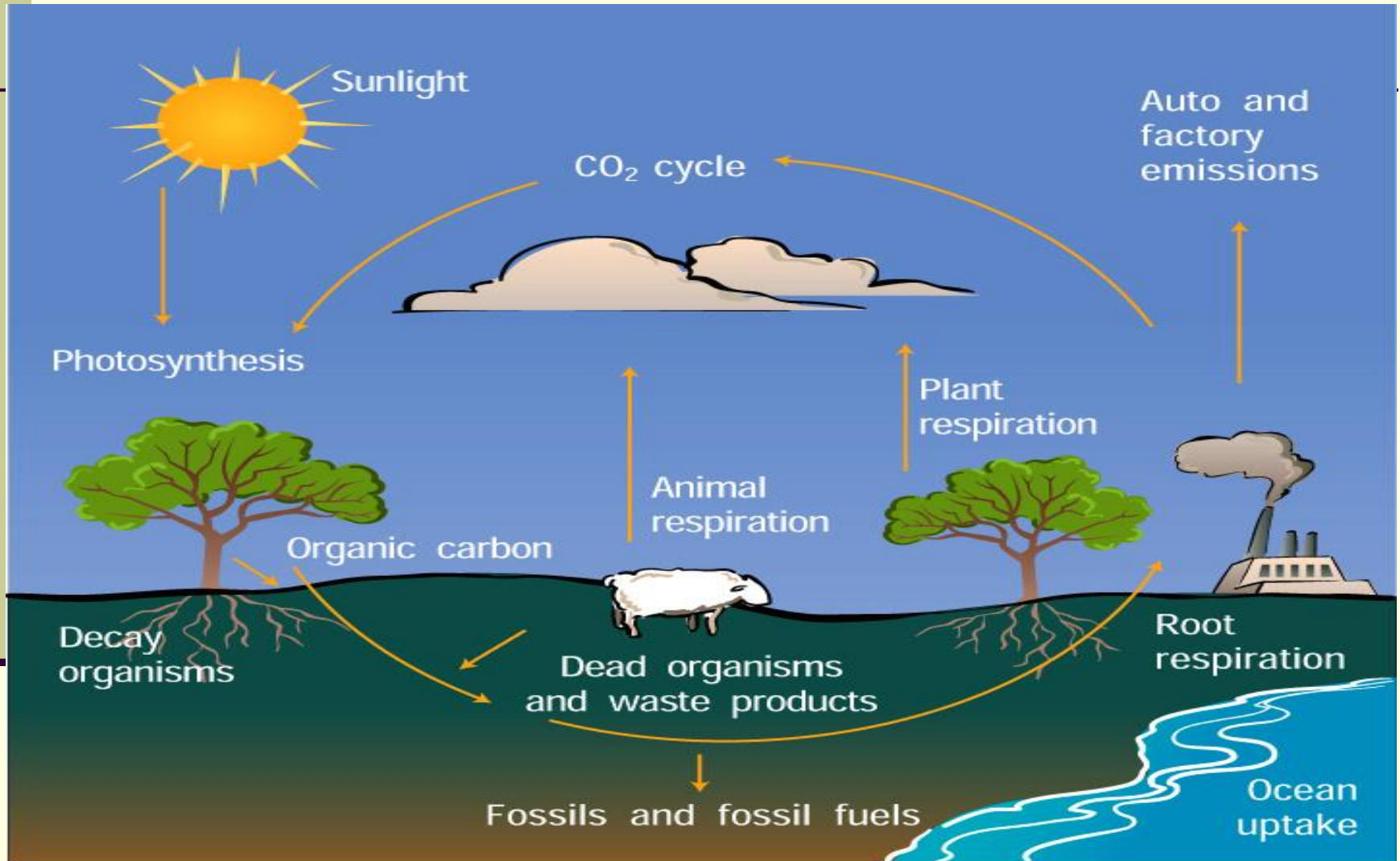


CICLOS BIOGEOQUÍMICOS

Life and biogeochemical cycles

<http://nca2014.globalchange.gov/report/sectors/biogeochemical-cycles>

CICLO DO CARBONO



National Center for Atmospheric Research

Fast and slow processes in the carbon cycle

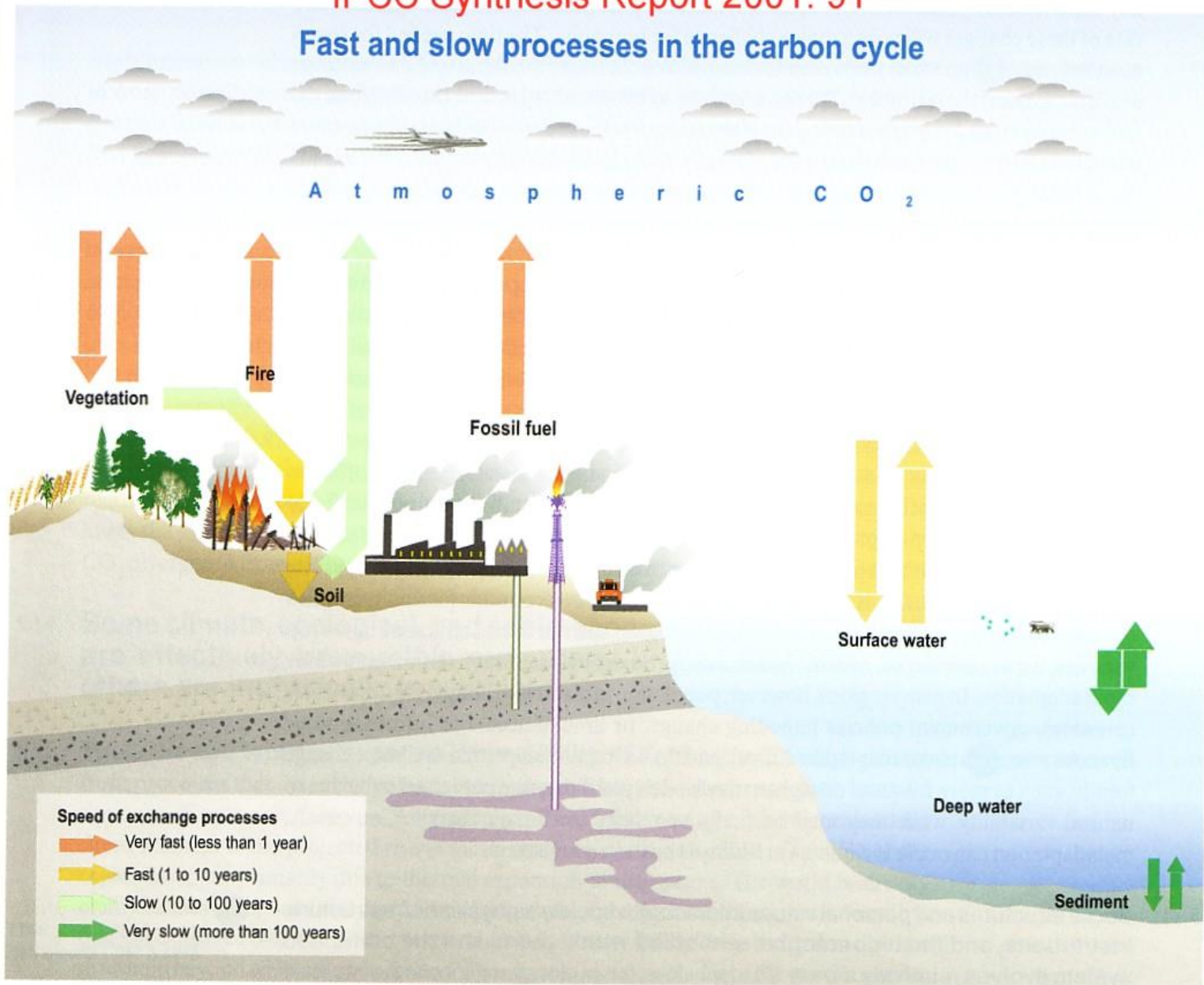


Figure 5-4: The range of time scales of major processes within the global carbon cycle leads to a range of response times for perturbations of CO₂ in the atmosphere, and contributes to the development of transient sinks, as when the atmospheric CO₂ concentration rose above its pre-1750 equilibrium level.

Ciclo do carbono

■ Principais compartimentos:

- Atmosfera ~800 Pg como CO₂ ~ 400 ppmv
- Biota, 75% em florestas ~400-600 Pg C
- Solo (1 m): 1500-2000 Pg C em várias formas orgânicas. 1/3 ocorre em florestas
- Oceano ~39.000 Pg C

■ Principais influências antrópicas

- Mudanças no uso da terra
- Queima de combustível fóssil

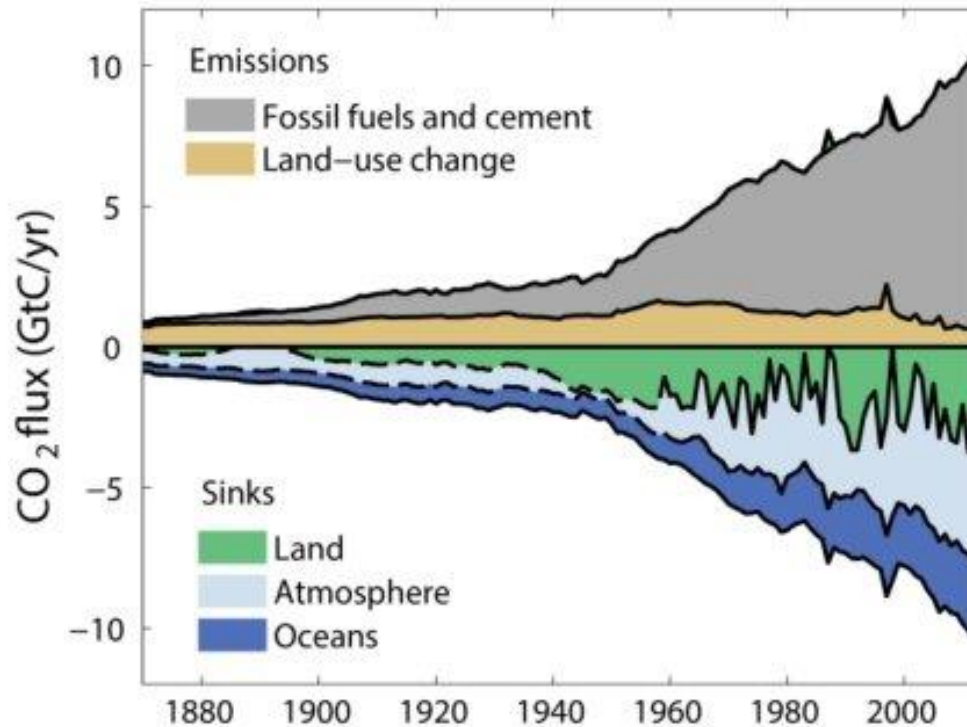
1Pg= 1 bilhão de toneladas métricas= 10^{15} g de C

Global Carbon Budget

Emissions to the atmosphere are balanced by the sinks

Average sinks since 1870: 41% atmosphere, 31% land, 28% ocean

Average sinks since 1959: 45% atmosphere, 28% land, 27% ocean

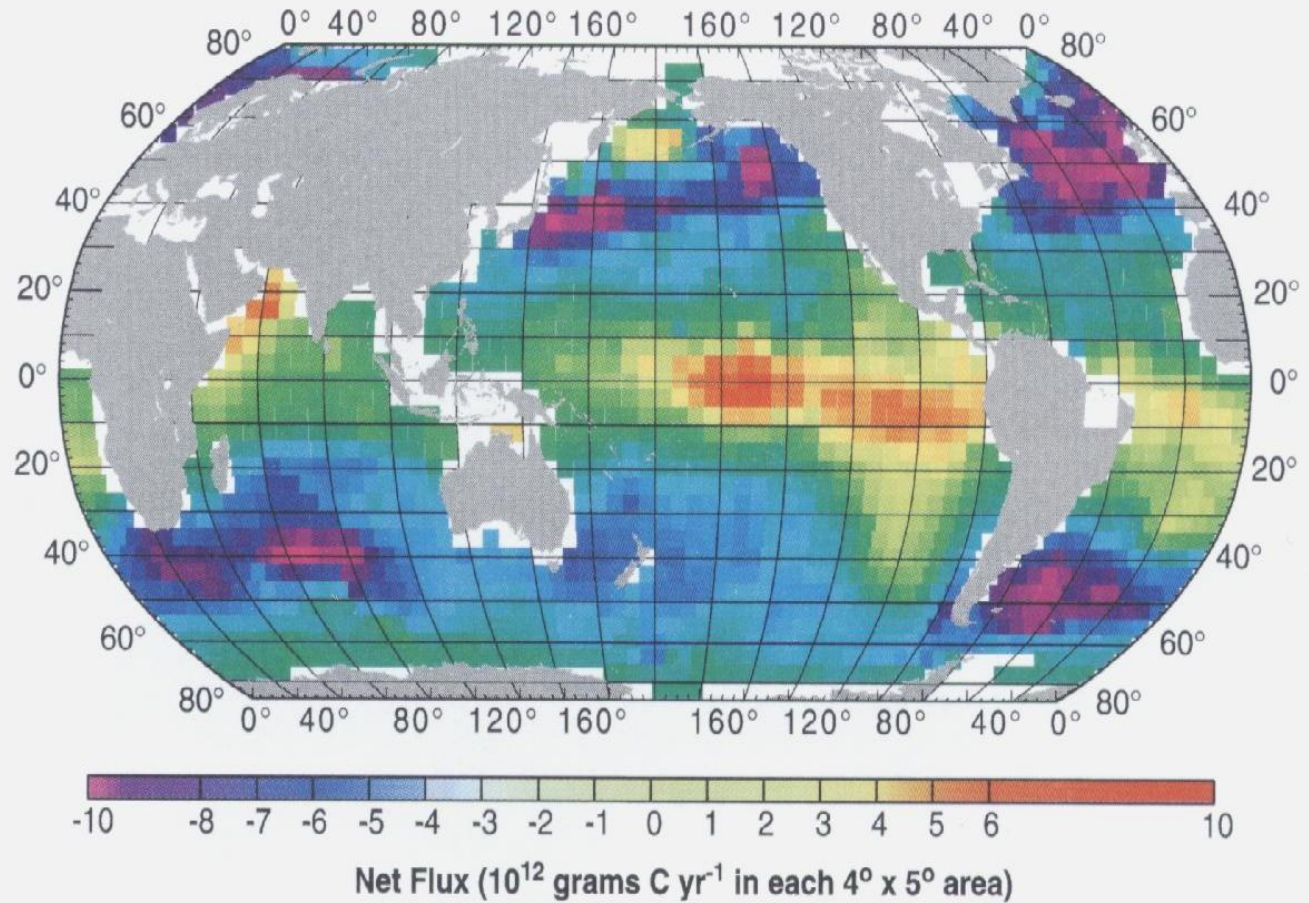


Source: [CDIAC Data](#); Houghton & Hackler (in review); [NOAA/ESRL Data](#); [Joos et al 2013](#); [Khatiwala et al 2013](#);

[Le Quéré et al 2013](#); [Global Carbon Project 2013](#)

Cores azul e violeta= o oceano retira CO₂ da atmosfera

Fig. 2.30.
Mean annual exchange of CO₂ across the sea surface (Takahashi et al. 1997). *Blue and purple colours* denote regions in which the ocean takes up large amounts of CO₂ while *orange and yellow colours* denote areas where significant outgassing of CO₂ occurs



IGBP series

Fig. 2.31.

Cores amarelo e laranja = oceano emite CO₂ para a atmosfera

-
- Os ciclos não devem ser vistos separadamente. A disponibilidade de um elemento pode interagir com a biosfera terrestre de tal modo que pode mudar a disponibilidade dos outros nutrientes.
 - Exemplo: os ecossistemas terrestres são limitados pelo N, a taxa de mineralização do N determina a Produtividade Primária Líquida (PPL) total de um sistema. Por outro lado, isso controla a retirada de carbono da atmosfera e a assimilação de fósforo e enxofre.

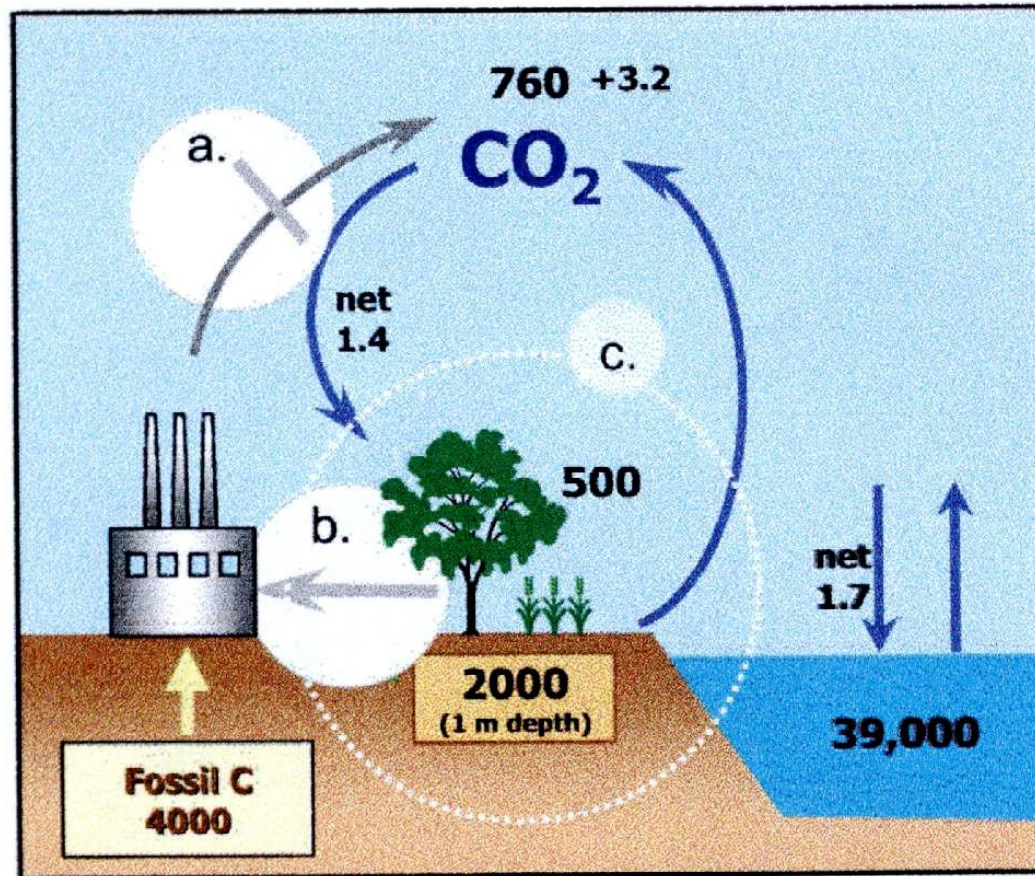
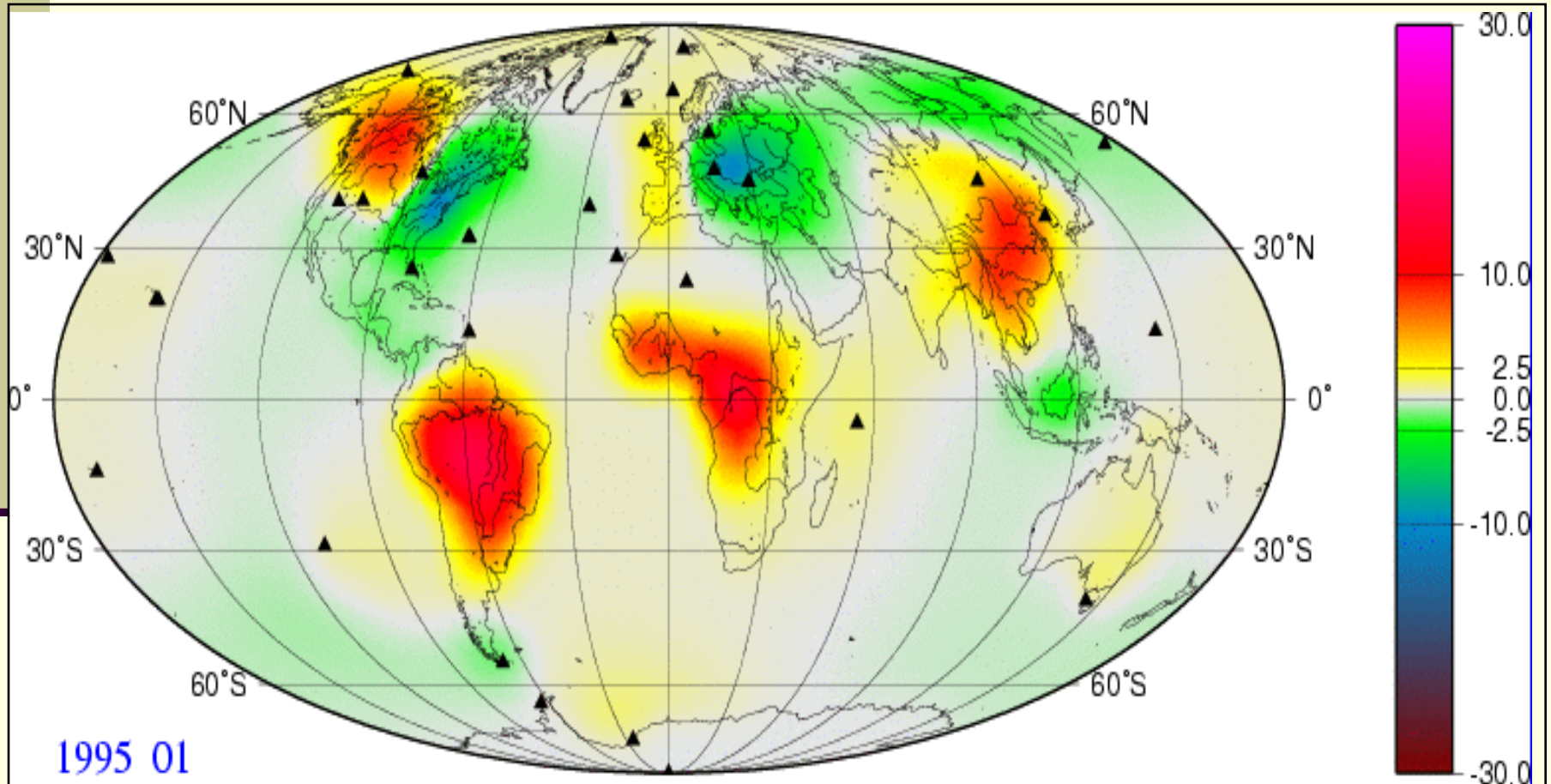


Fig. 9. The accumulation of atmospheric CO₂ can be suppressed in one of three ways, by: (a) reducing emissions from fossil fuels; (b) using recently photosynthesized C as a fuel (bio-fuel); or (c) increasing the amounts of C stored in soils and phytomass.

Trocas de Carbono



Troca de C

- CO_2 entra na biomassa \rightarrow fotossíntese (120 Pg C ano⁻¹). 60 Pg C ano⁻¹ sai \rightarrow respiração
- Ao mesmo tempo a respiração heterotrófica (microorganismos) e queimadas devolve esse C para a atmosfera \rightarrow fechando o ciclo.
- Atmosfera \leftrightarrow oceano 90 Pg C ano⁻¹.

Biological Terrestrial C Sink Mechanisms

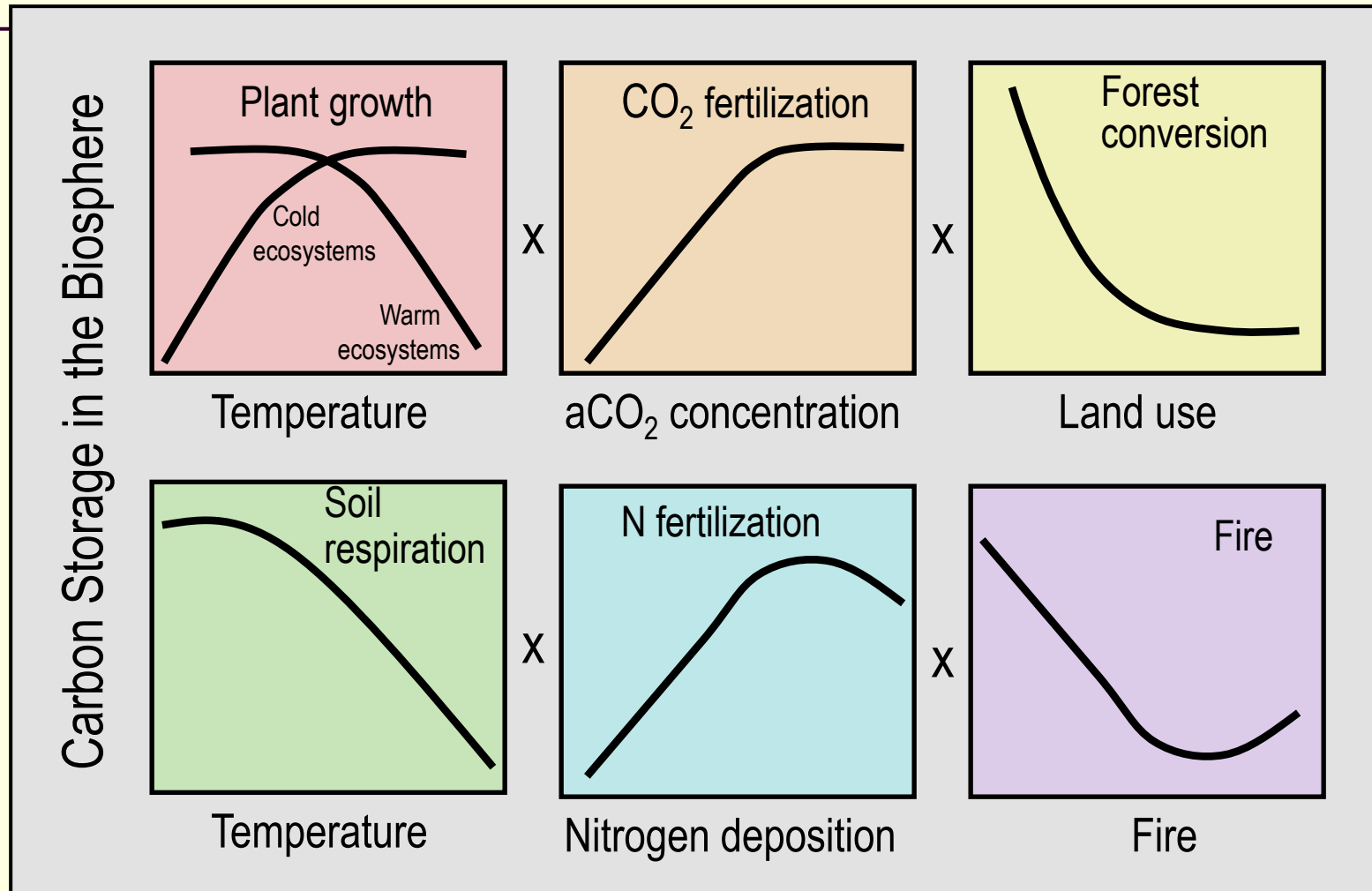
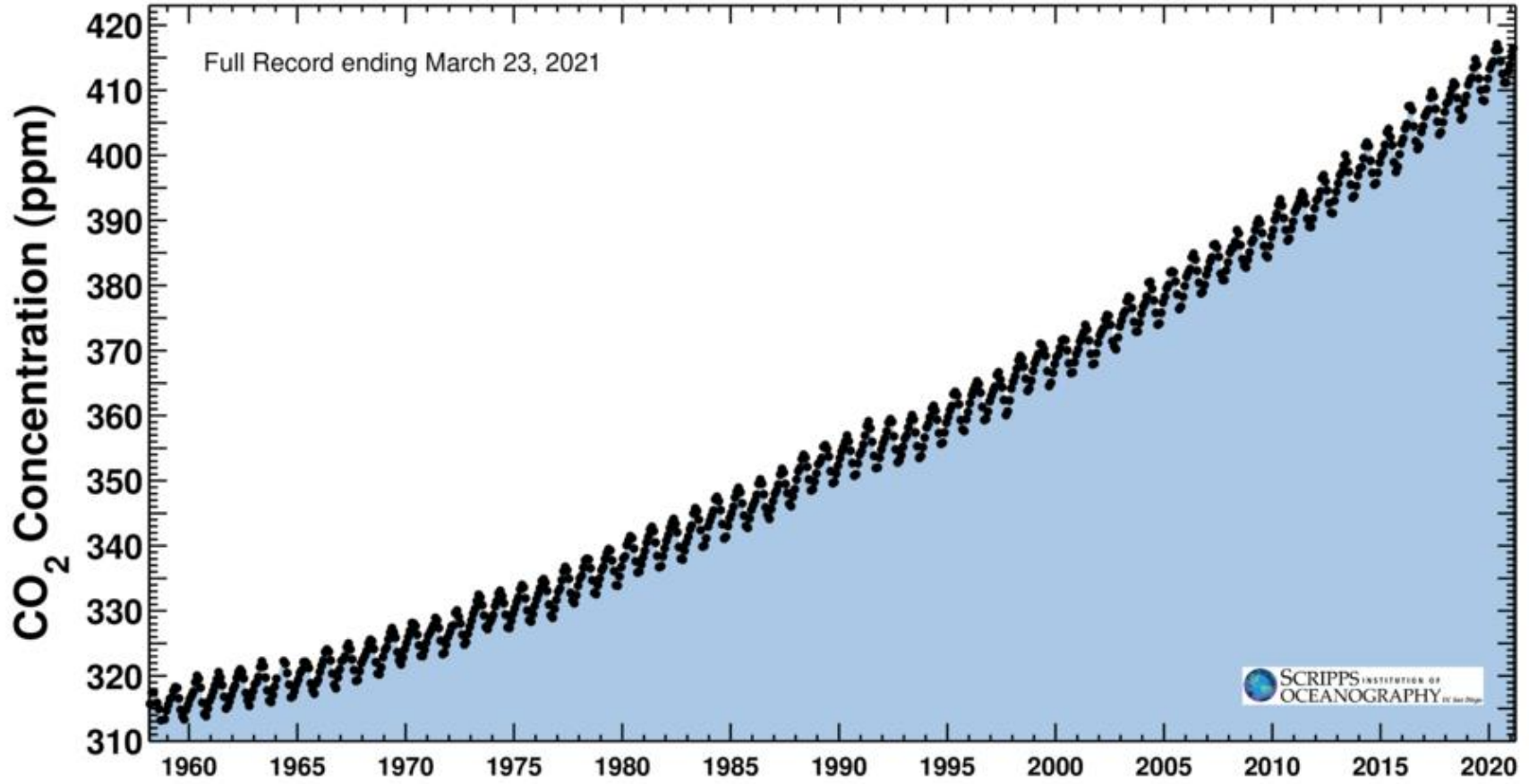


Gráfico de Keeling

March 22, 2021

Carbon dioxide concentration at Mauna Loa Observatory



First Detection of Systematic Atmospheric CO₂ Variations

The Concentration and Isotopic Abundances of Carbon Dioxide in the Atmosphere

By CHARLES D. KEELING, Scripps Institution of Oceanography, University of California, La Jolla, California

(Manuscript received March 25, 1960)

Abstract

A systematic variation with season and latitude in the concentration and isotopic abundance of atmospheric carbon dioxide has been found in the northern hemisphere. In Antarctica, however, a small but persistent increase in concentration has been found. Possible causes for these variations are discussed.

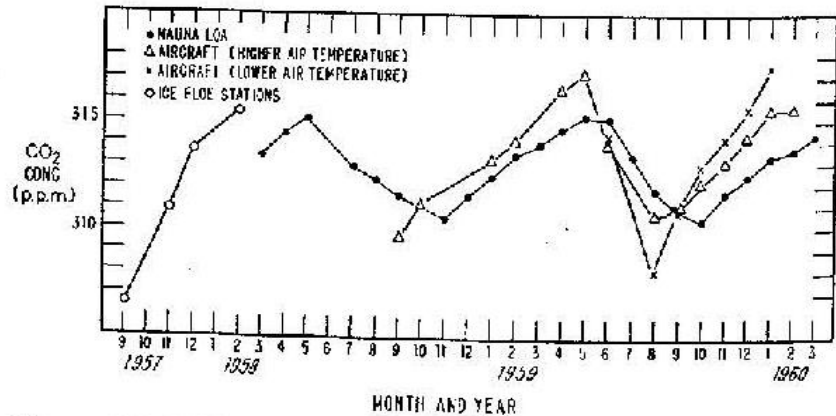
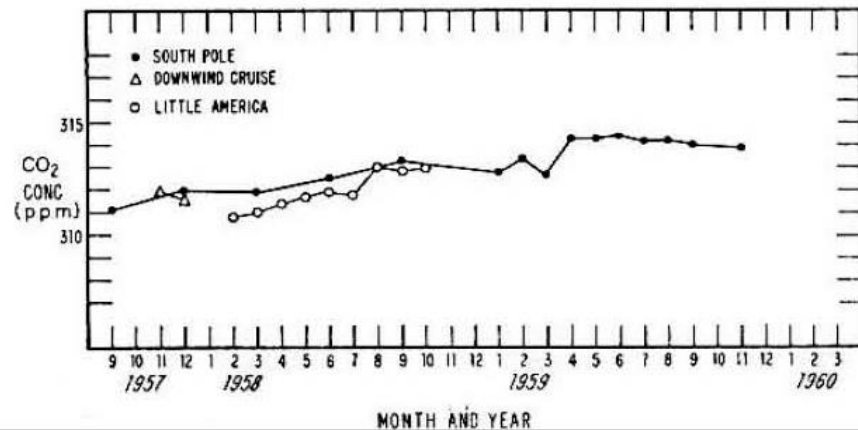


Fig. 1. Variation in concentration of atmospheric carbon dioxide in the Northern Hemisphere.

Tellus XII (1960), 2

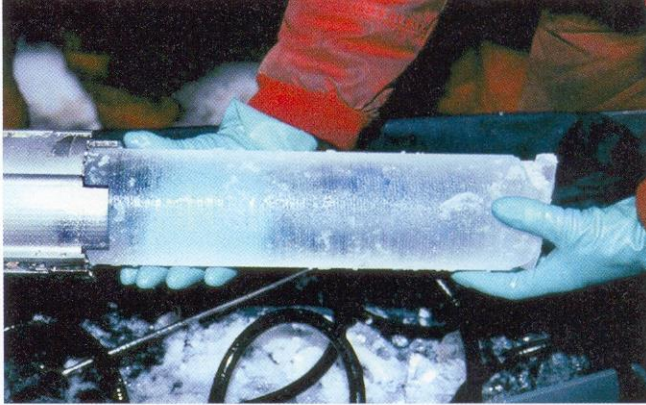


Charles David Keeling
(1928-2005)

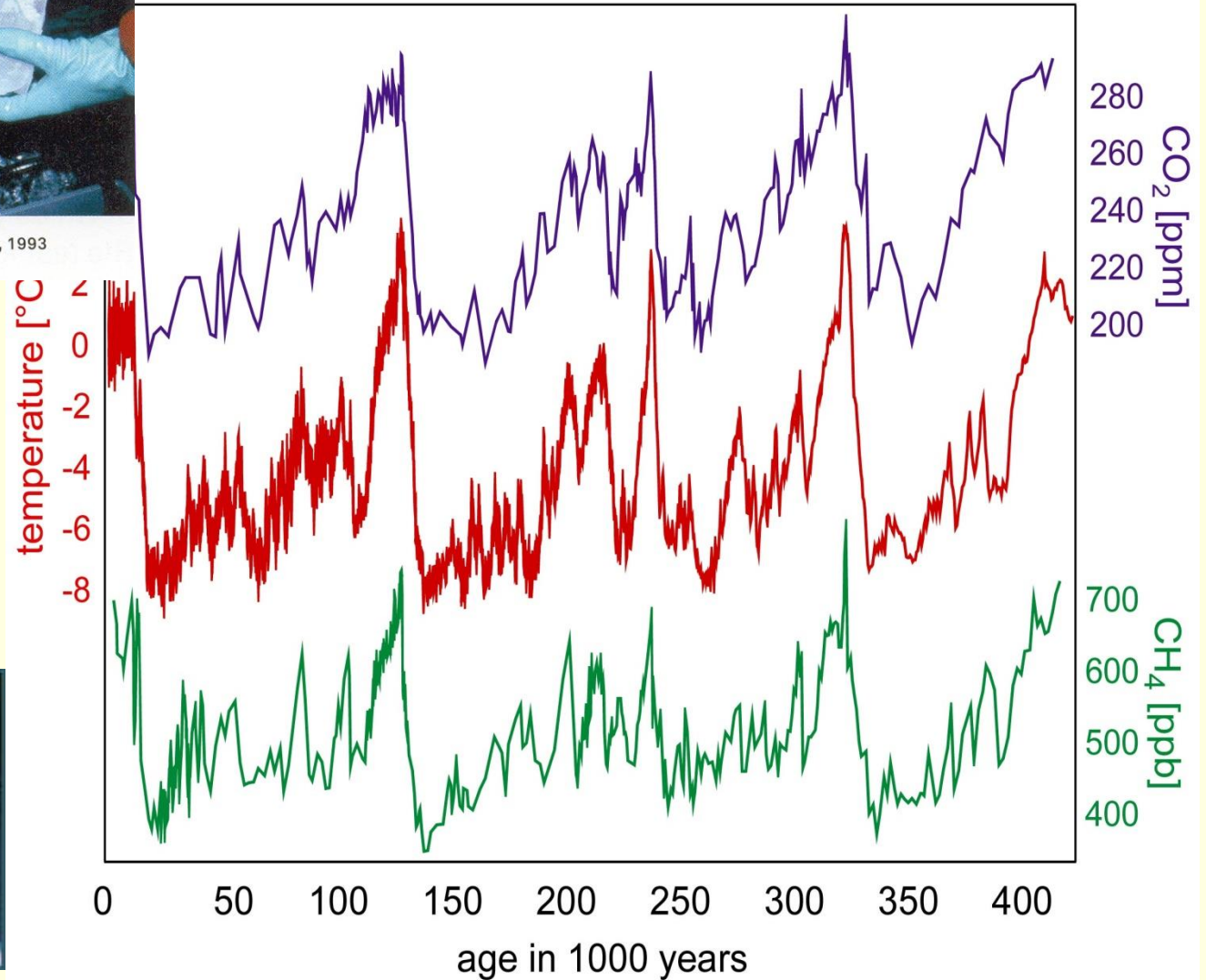


C. D. Keeling, Tellus, v12, 200, 1960

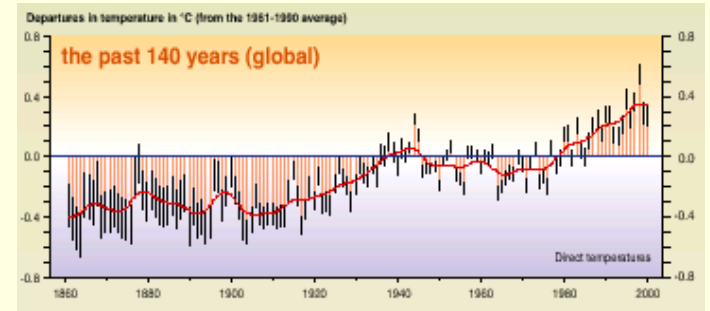
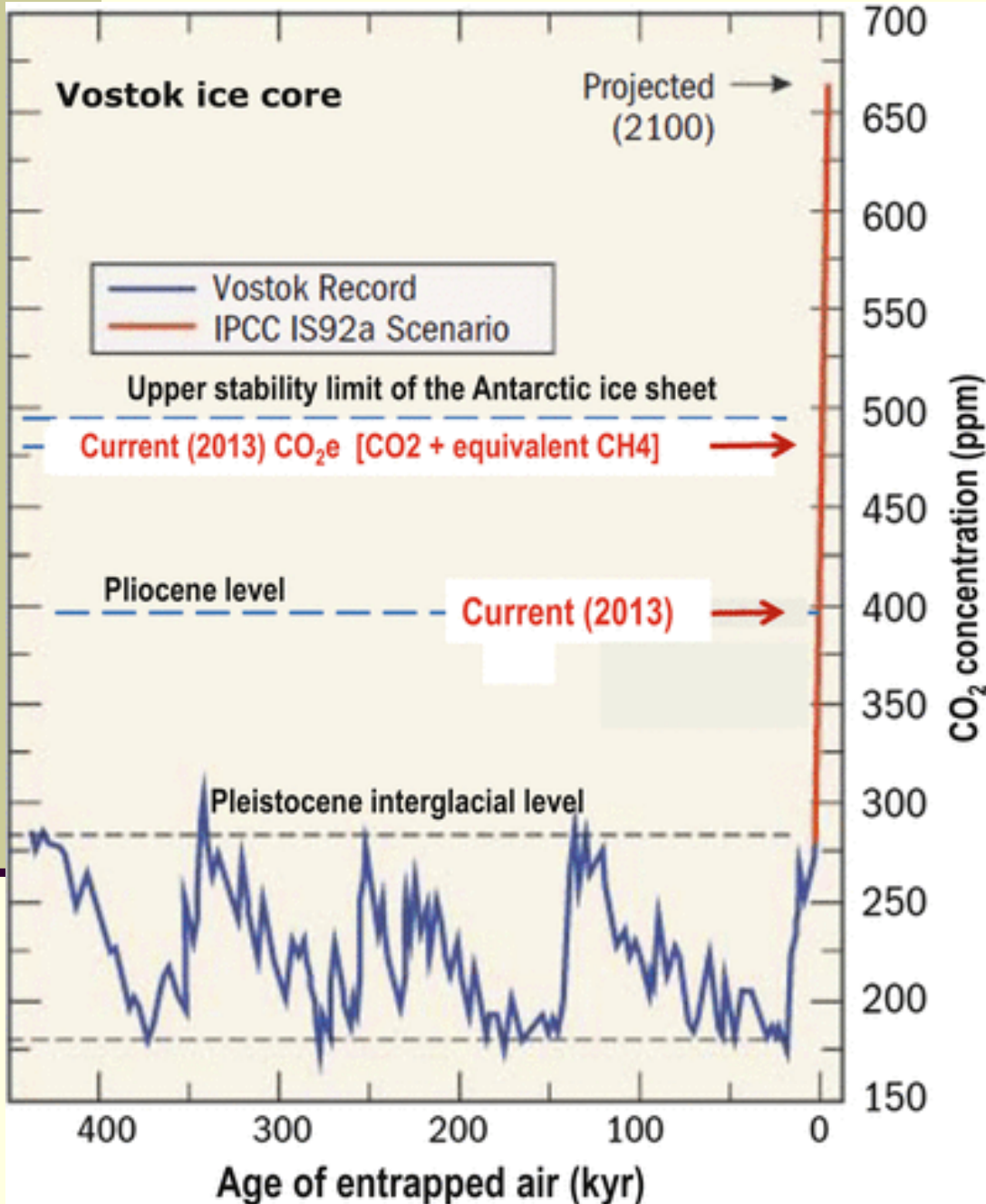
Vostok (Antarctica): 4 glacial cycles



GLACIOLOGIST REMOVING AN ICE CORE, ANTARCTICA, 1993



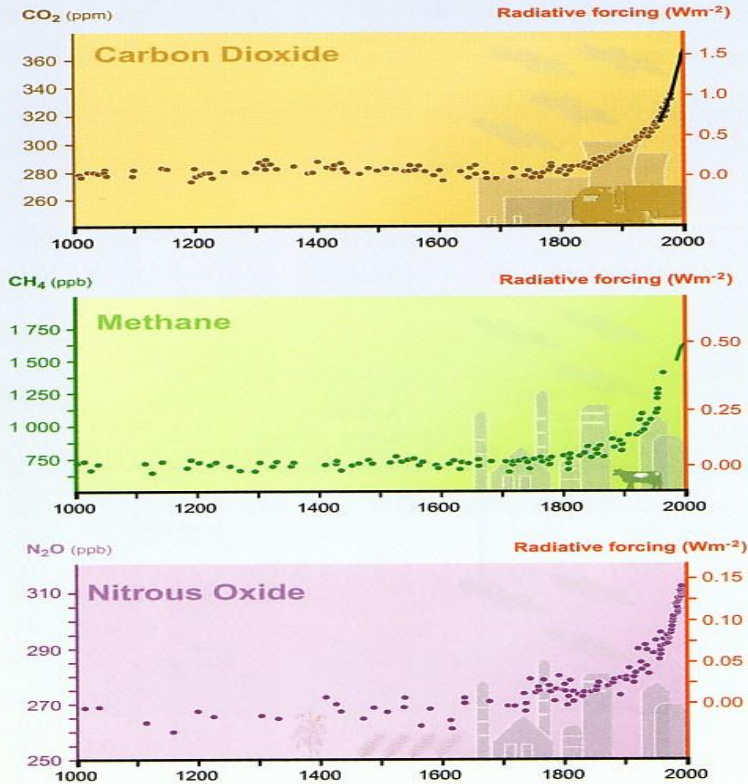
Mudança do clima passado e futuro



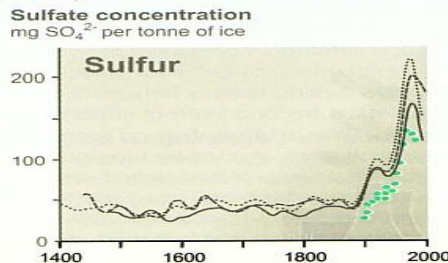
← 280 ppm

Indicators of the human influence on the atmosphere during the industrial era

Global atmospheric concentrations of three well-mixed greenhouse gases



Sulfate aerosols deposited in Greenland ice



SO_2 emissions from United States and Europe ($Mt S yr^{-1}$)

A concentração atmosférica dos gases estufa (CO_2 , CH_4 , N_2O) está aumentando em resposta às atividades humanas

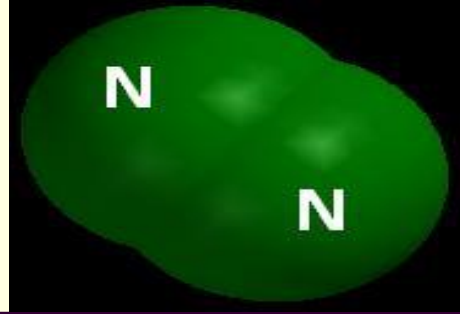
WGI TAR Figures SPM-2, 3-2b, 4-1a, 4-1b, 4-2, & 5-4a

Figure 2-1: Records of past changes in atmospheric composition over the last millennium demonstrate the rapid rise in greenhouse gases and sulfate aerosols that is attributable primarily to industrial growth since 1750. The top three panels show increasing atmospheric concentrations of carbon dioxide (CO_2), methane (CH_4), and nitrous oxide (N_2O) over the past 1,000 years. Early sporadic data taken from air trapped in ice (symbols) matches up with continuous atmospheric observations from recent decades (solid lines). These gases are well mixed in the atmosphere, and their concentrations reflect emissions from sources throughout the globe. The estimated positive radiative forcing from these gases is indicated on the righthand scale. The lowest panel shows the concentration of sulfate in ice cores from Greenland (shown by lines for three different cores) from which the episodic effects of volcanic eruptions have been removed. Sulfate aerosols form from sulfur dioxide (SO_2) emissions, deposit readily at the surface, and are not well mixed in the atmosphere. Specifically, the increase in sulfate deposited at Greenland is attributed to SO_2 emissions from the U.S. and Europe (shown as symbols), and both show a decline in recent decades. Sulfate aerosols produce negative radiative forcing.

Ciclo do Nitrogênio

- Contrariamente ao ciclo do C → quase todo o N relevante à biogeoquímica está na atmosfera
- menores quantidades → oceano, rochas e sedimentos
- Nitrogênio orgânico → solos, vegetação e atmosfera
- tripla ligação: quebra apenas por altas temperaturas e por microorganismos.

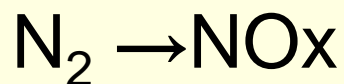
Fixação do Nitrogênio



- Processo → formas ativas quimicamente.
- Microorganismos aeróbicos e anaeróbicos (algumas bactérias e algumas algas)
- Exemplos: fixação biológica pela redução catalisada por enzimas (nitrogenase): N_2 para NH_3 ou NH_4^+
- Combustão, relâmpagos, produção industrial de amônia, fertilizantes, etc.
- Uma vez fixado, o nitrogênio é assimilado na biomassa (plantas, microrganismos)
- *Nitrificação*: oxidação para NO_2^- e NO_3^-
- *Desnitrificação*: redução de NO_3^- para N_2 , N_2O , NO

Atividades antrópicas

1. Cultivo de leguminosas e arroz
2. Processo Haber-Bosch ($\text{N}_2 \rightarrow \text{NH}_3$)
3. Queima de combustível fóssil:



Em 100 anos (1890/1990)

População: de 1,5 bilhão para 5,3 bilhões

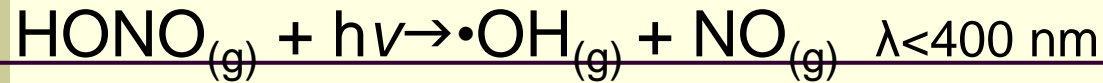
Prod. Alimento: cresceu 7 vezes

Prod. Energia: cresceu 90 vezes

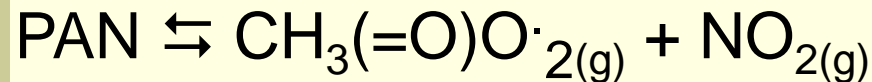
Compostos de N

- **NO+NO₂**: equilíbrio químico e fotolítico na atmosfera.
- **·NO₃**: radical nitrato, formado na reação $\text{NO}_2 + \text{O}_3$, é prontamente fotolizado → importante na química noturna
- **N₂O₅**: relacionado ao equilíbrio $\text{NO}_3 + \text{NO}_2$. Se hidrolisa nos aerossóis para formar ácido nítrico-química noturna
- **HNO₃**: produto de oxidação do NO_x, é adsorvido prontamente nos aerossóis.

- **HONO**: ácido nitroso, fonte de radicais $\cdot\text{OH}$



- **PAN**: importante no transporte e reciclagem de NO_x

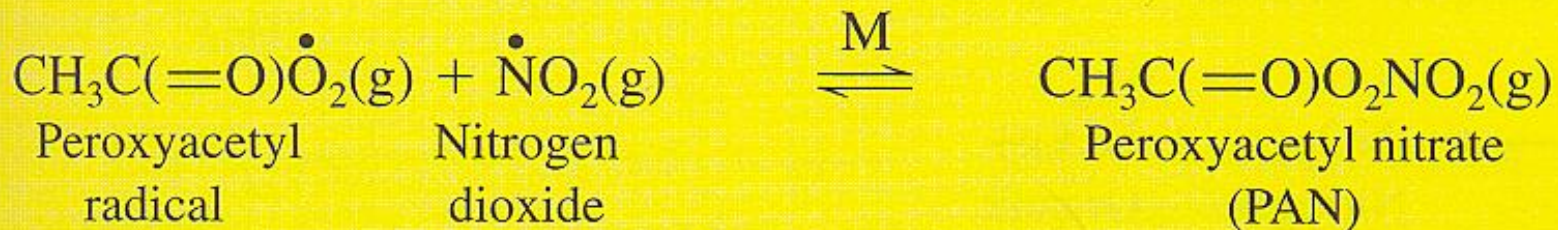
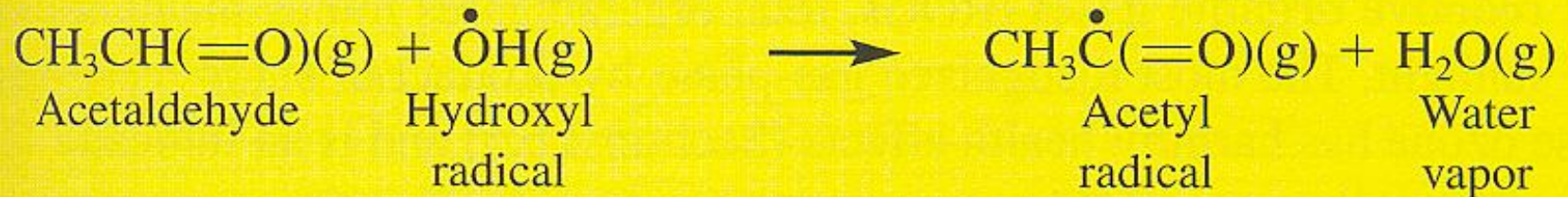


- **RONO₂**: nitratos orgânicos, formados durante a oxidação de hidrocarbonetos pelos radicais $\cdot\text{OH}$ ou NO_3 .

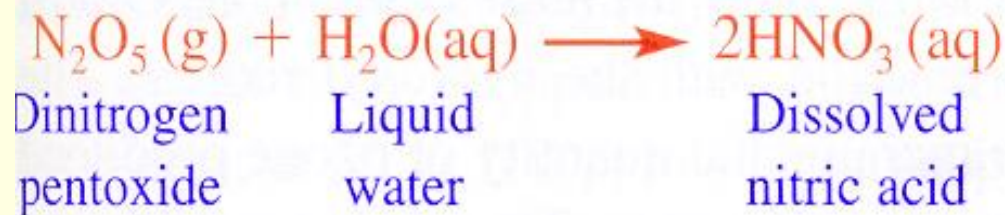
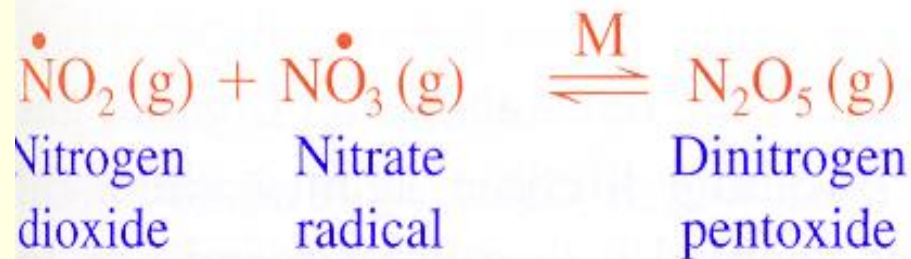
- **NO_y**: NO_x , HNO_3 , HONO , HO_2NO_2 , NO_3^- , radical NO_3 , PAN , N_2O_2 , nitratos orgânicos.

Nitratos orgânicos

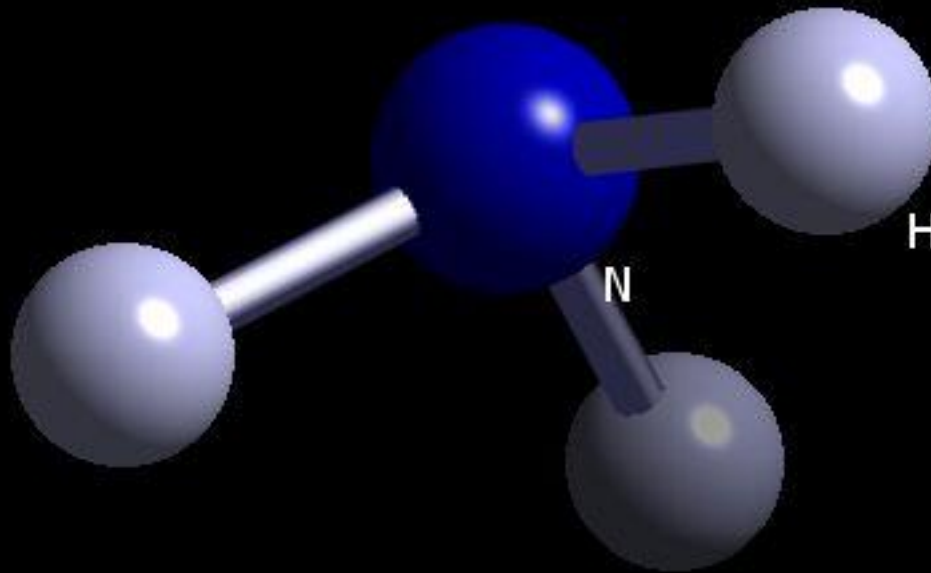
- Produtos finais oxidados das reações dos HCNM com NO_x em atmosfera poluída.



Química noturna



hydrogen (I) nitride (ammonia)



-principal agente que neutraliza da atmosfera: água de chuva, aerossóis, água de nuvens.

-tempo de residência = 1 a 2 semanas

-gera aerossóis: $2\text{NH}_3 + \text{H}_2\text{SO}_4 \rightarrow (\text{NH}_4)_2\text{SO}_4$

Table 5.12
Global Budget of Ammonia

<i>Ammonia</i>	TgN yr ⁻¹
<i>Sources</i> ¹	
Domestic animals	21.3 (20-40)
Human excrement	2.6 (2.6-4)
Soil emissions	6 (6-45)
Biomass burning	5.7 (1-9)
Wild animals	0.1 (0.1-6)
Industry	0.2
Fertilizer losses	9 (5-10)
Fossil fuel combustion	0.1 (0.1-2.2)
Ocean	8.2 (5-15)
<i>Sinks</i> ²	
Wet precipitation (land)	11 (11-80)
Wet precipitation (ocean)	10 (6-26)
Dry deposition (land)	11 (10-150)
Dry deposition (ocean)	5
Reaction with OH	3 (1-9)

¹ The best estimates are from Bouwman *et al.* 1997, and the ranges adapted from Warneck, 1988; Quinn *et al.*, 1990; Schlesinger and Hartley, 1992; and Dentener and Crutzen, 1994.

² The best estimates are from MOGUNTIA simulations (Dentener and Crutzen, 1994) and the ranges adapted from Warneck, 1988, and Duce *et al.*, 1991.

☐ ÓXIDO NITROSO

☐ Gás incolor e inodoro

☐ gás estufa ~6%
(200 vezes mais efetivo que o CO_2)

☐ Destruição da camada de O_3

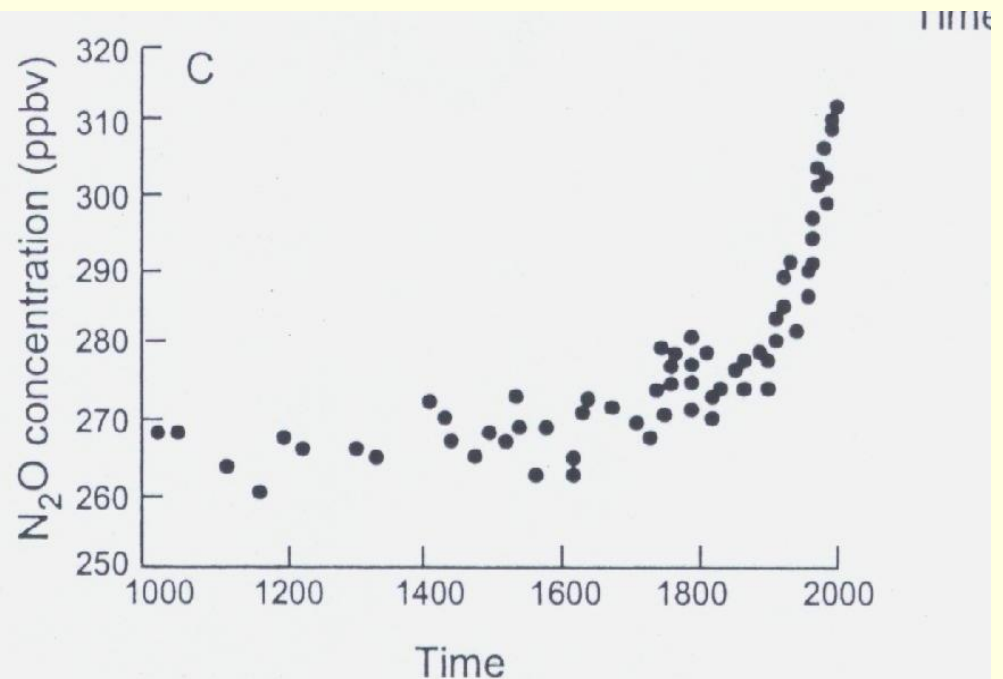
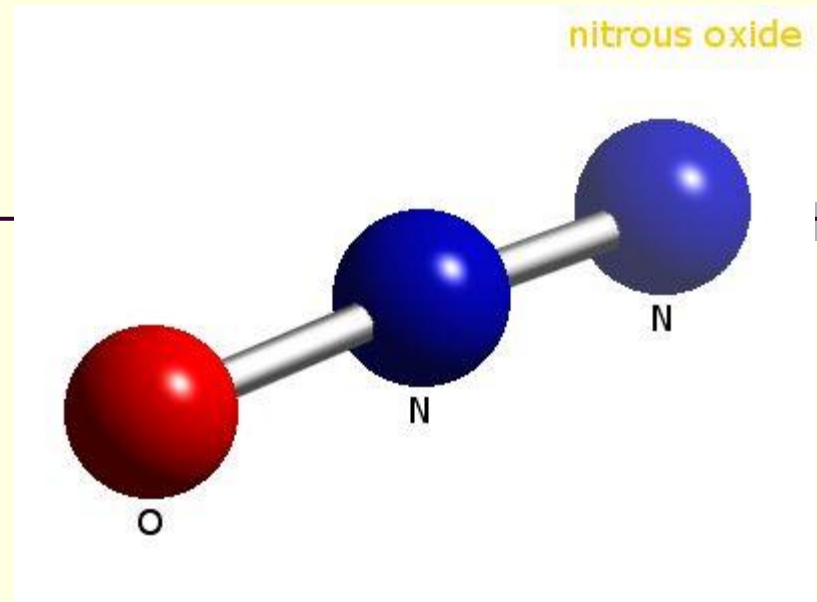
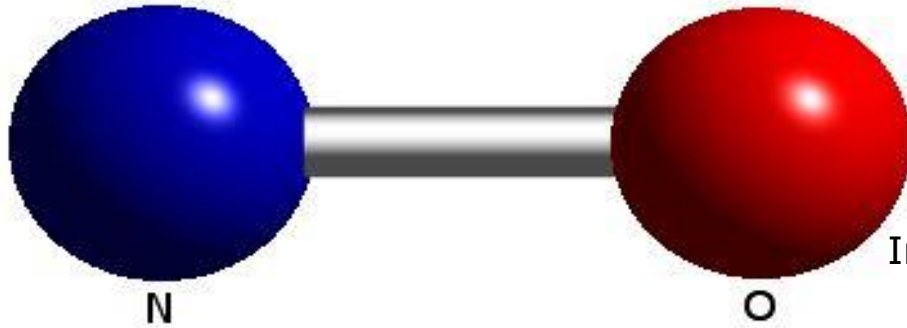


Table 5.13
Estimated Sources and Sinks
of N₂O, TgN yr⁻¹

<i>Sources</i>	
<i>Natural</i>	
Oceans	3.0 (1-5)
Tropical soils	
Wet forests	3.0 (2.2-3.7)
Dry savannas	1.0 (0.5-2.0)
Temperate soils	
Forests	1.0 (0.5-2.3)
Grasslands	1.0
Total natural sources	9.0
<i>Anthropogenic</i>	
Cultivated soils	3.5 (1.8-5.3)
Biomass burning	0.5 (0.2-1.0)
Industrial sources	1.3 (0.7-1.8)
Cattle and feed lots	0.4 (0.2-0.5)
Total anthropogenic sources	5.7
<i>Total sources</i>	14.7 (10-17)
<i>Sinks</i>	
Stratospheric photochemistry	12.3 (9-16)
Removal by soils	?
<i>Total sinks</i>	12.3 (9-16)
<i>Atmospheric increase</i>	3.9 (3.1-4.7)

Adapted from IPCC, 1994.

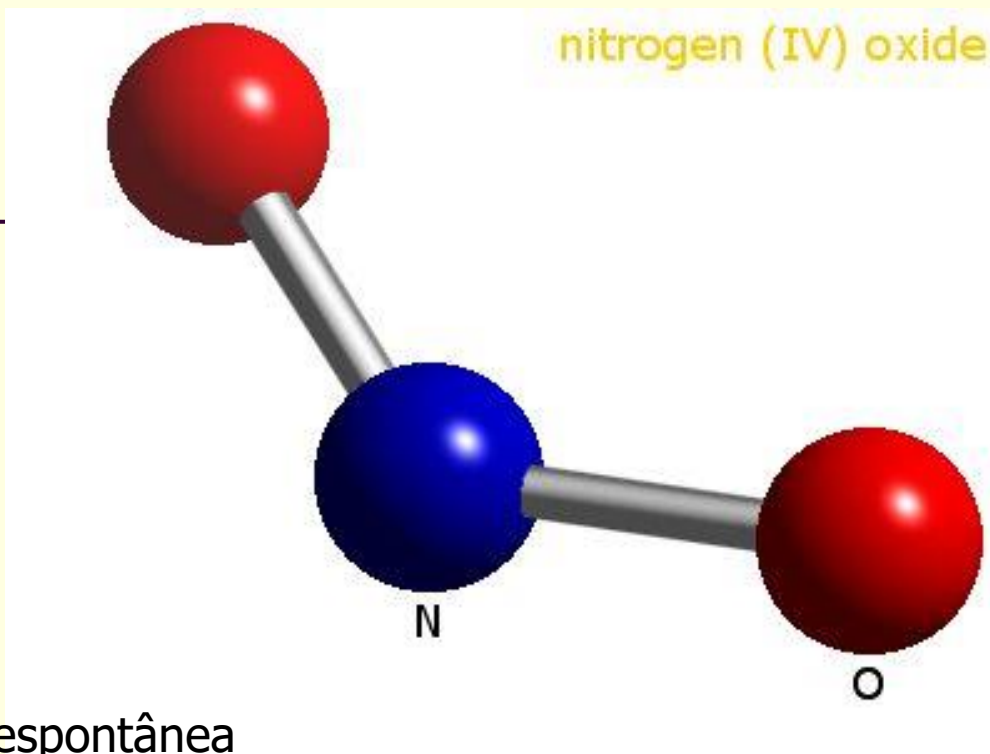
nitric oxide



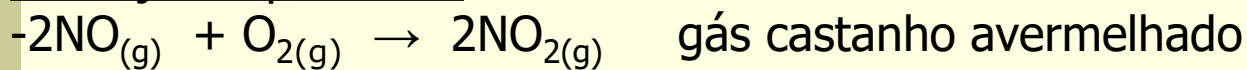
In: Atmospheric Pollution, M. Jacobson

Gás incolor

- Fonte principal natural: nitrificação
- queimadas
- relâmpagos
- chuva ácida
- reativo (precursor do O_3 trop.)



Oxidação espontânea



-formação do smog fotoquímico

-Produção de ácidos e vários compostos de N → PAN, chuva ácida e compostos orgânicos nitrados

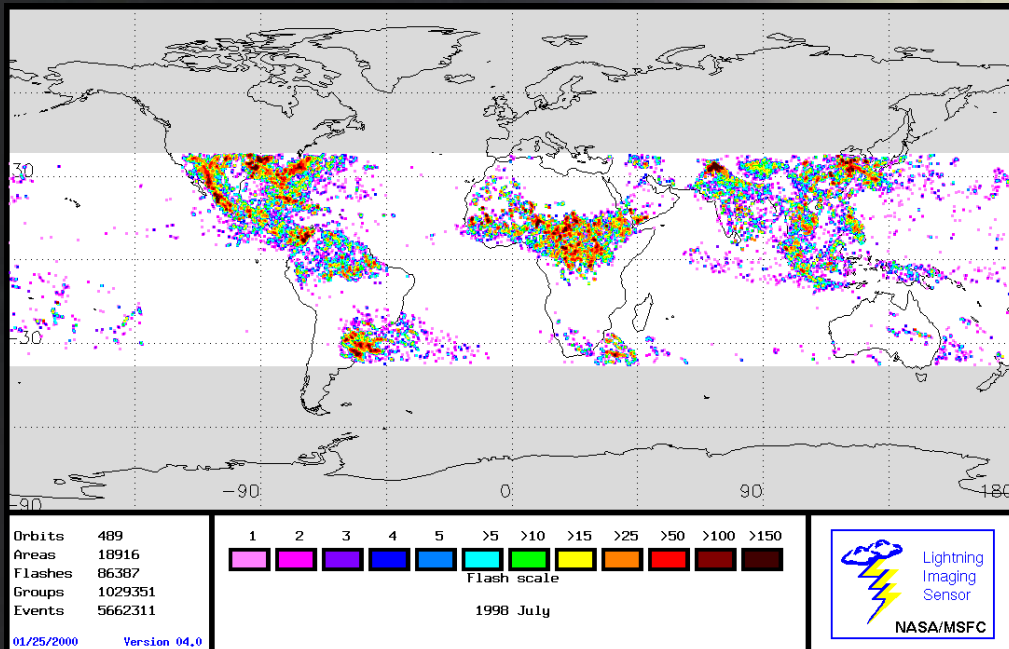
- produção de O_3

Table 5.14
Global Budget of NO_x in the Troposphere

	TgN yr ⁻¹
<i>Sources</i>	
Fossil fuel combustion	19.9 (14-28)
Biomass burning	12.0 (4-24)
Release from soils	20.2 (4-40)
Lightning discharges	8.0 (2-20)
NH ₃ oxidation	3 (0-10)
Ocean surface	<1
Aircraft	0.5
Injection from the stratosphere	0.1 (0.6 total NO _y)
<i>Total sources</i>	64 (25-112)
<i>Sinks</i>	
Wet deposition of NO ₃ ⁻ (land)	19 (8-30)
Wet deposition of NO ₃ ⁻ (ocean)	8 (4-12)
Dry deposition of NO _x	16 (12-22)
<i>Total sinks</i>	43 (24-64)

Based on Logan, 1983; IPCC, 1994; and Davidson, 1991.

Produção de NOx pelos relâmpagos

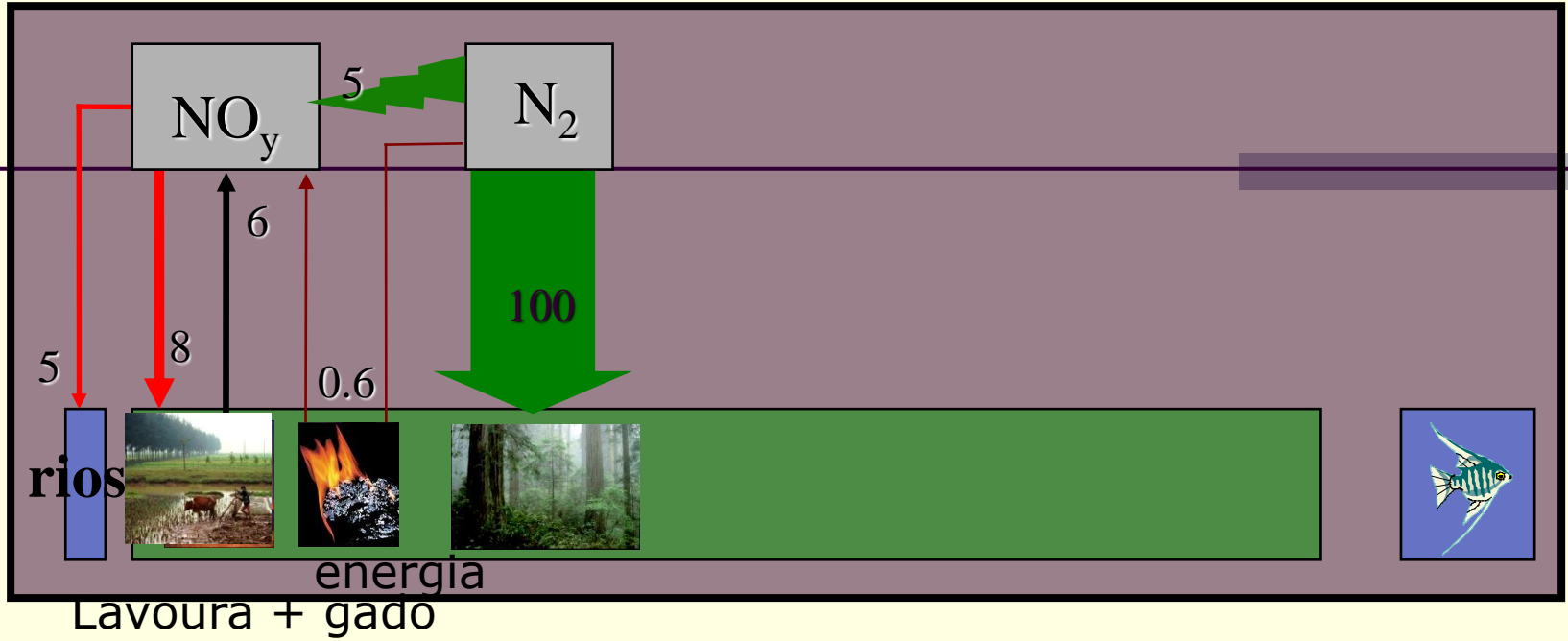


Global flash frequency:
40-100 flashes/s

Global NOx production:
2-20 TgN/yr

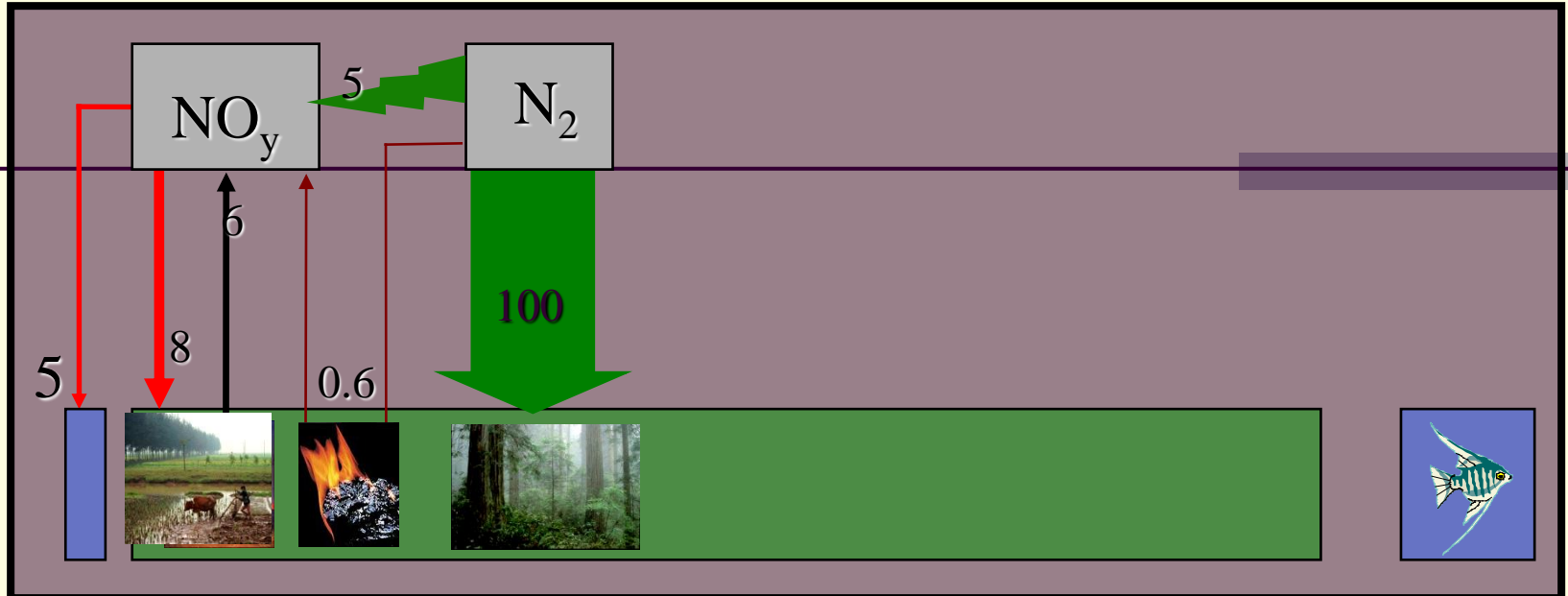
Balço de N em 1890 e em 1990, TgN ano⁻¹

1890

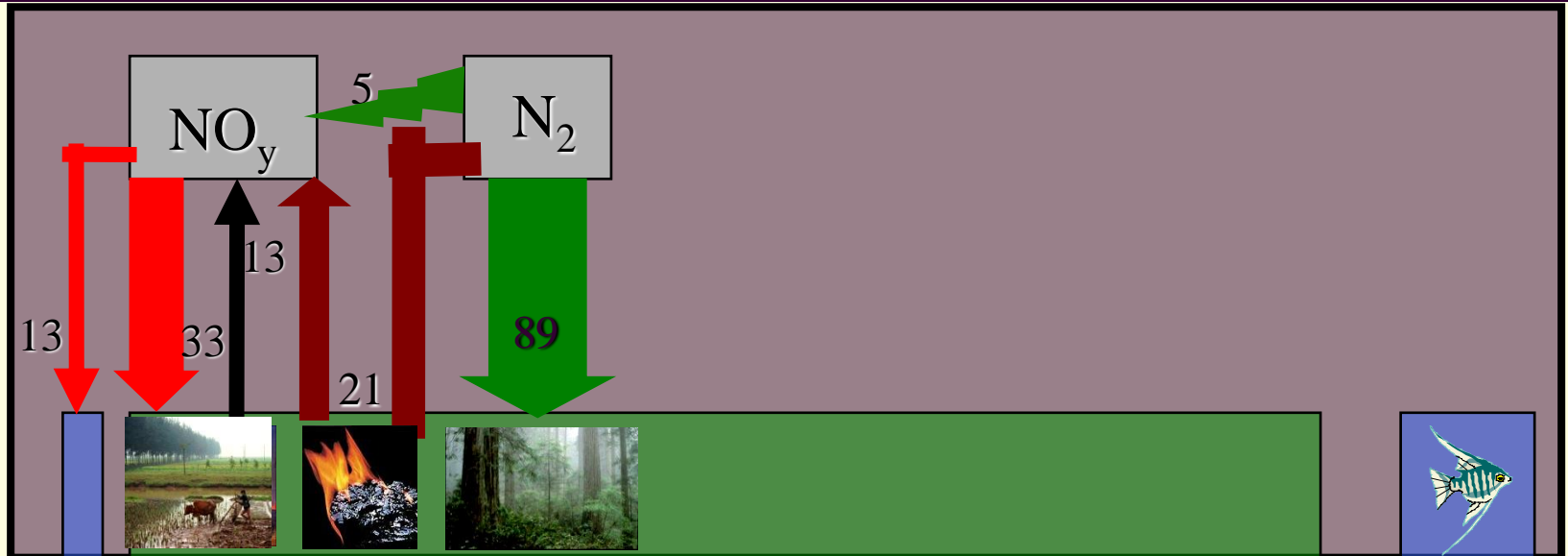


Balço de N Global em 1890 e em 1990 Tg N/ano

1890

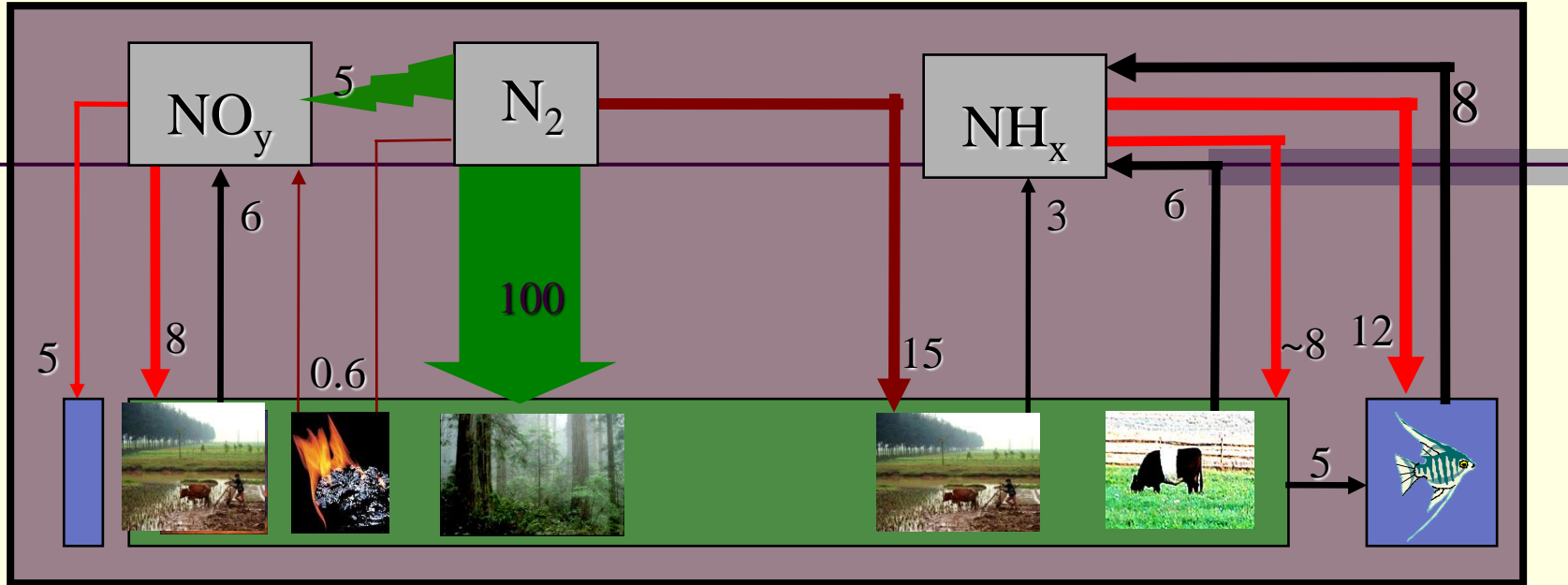


mid-1990s

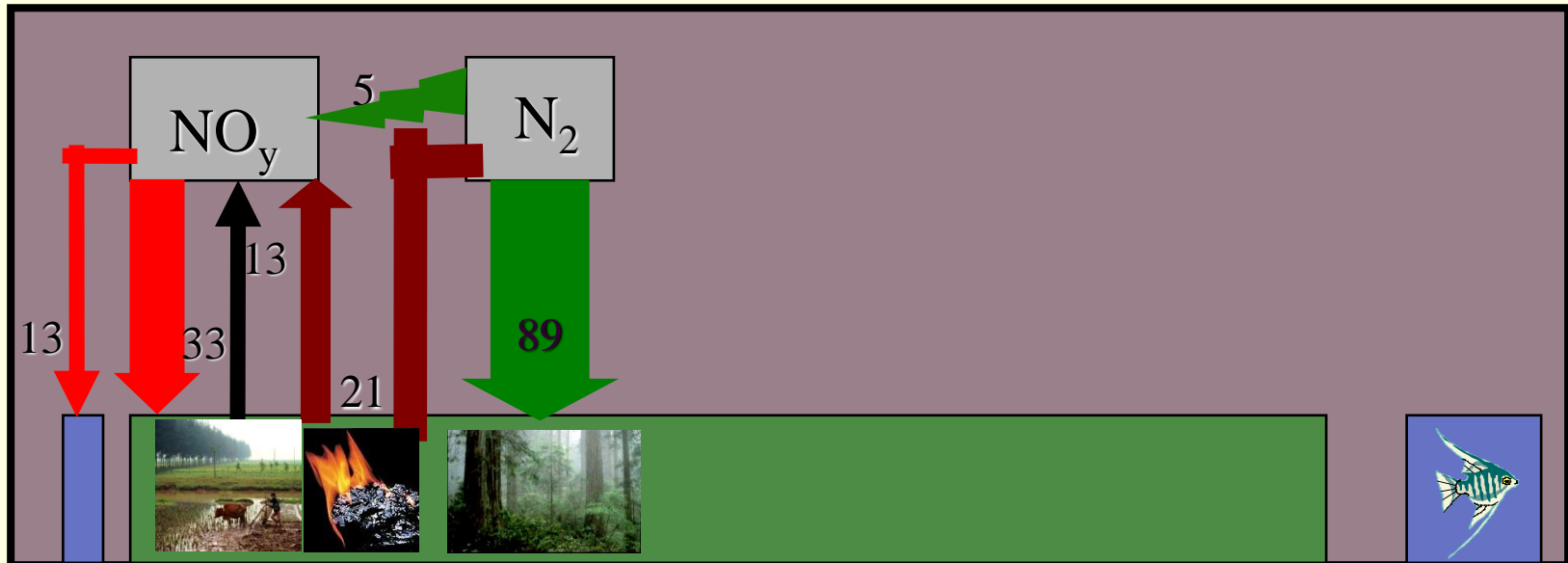


Balço de N em 1890 e em 1990, TgN/yr

1890

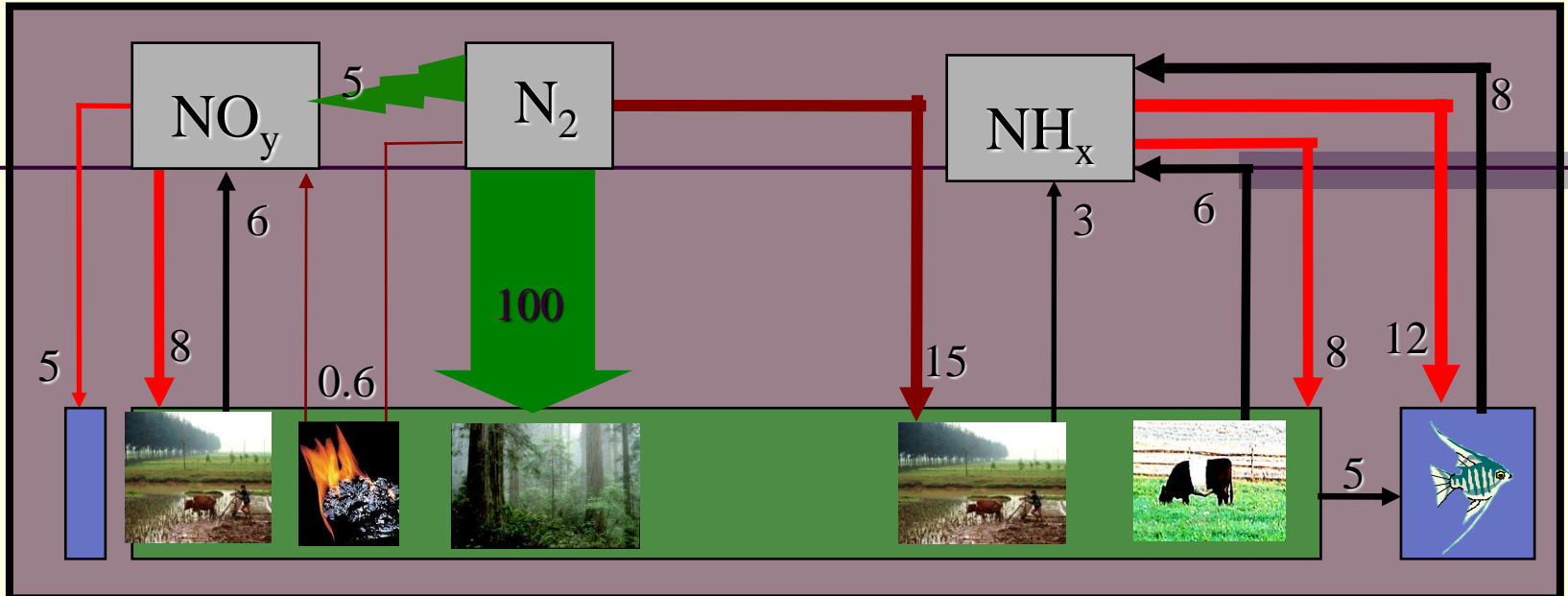


mid-1990s

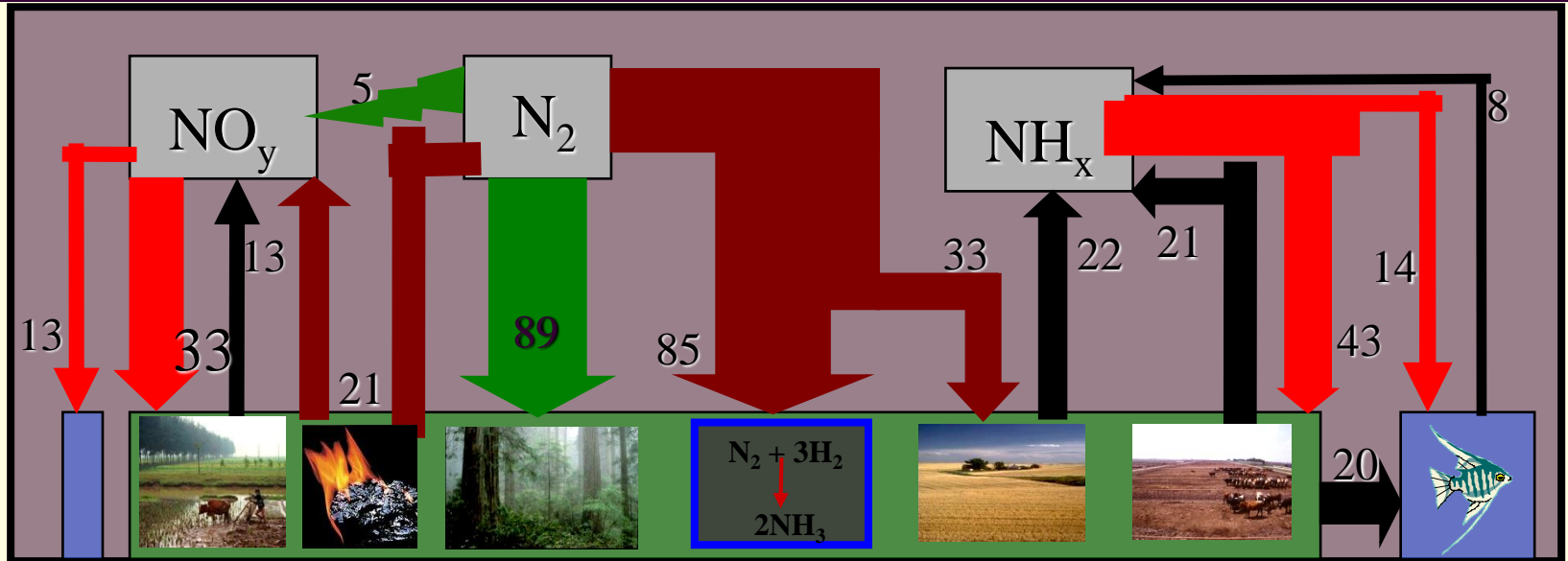


Balço de N em 1890 e em 1990, TgN/yr

1890

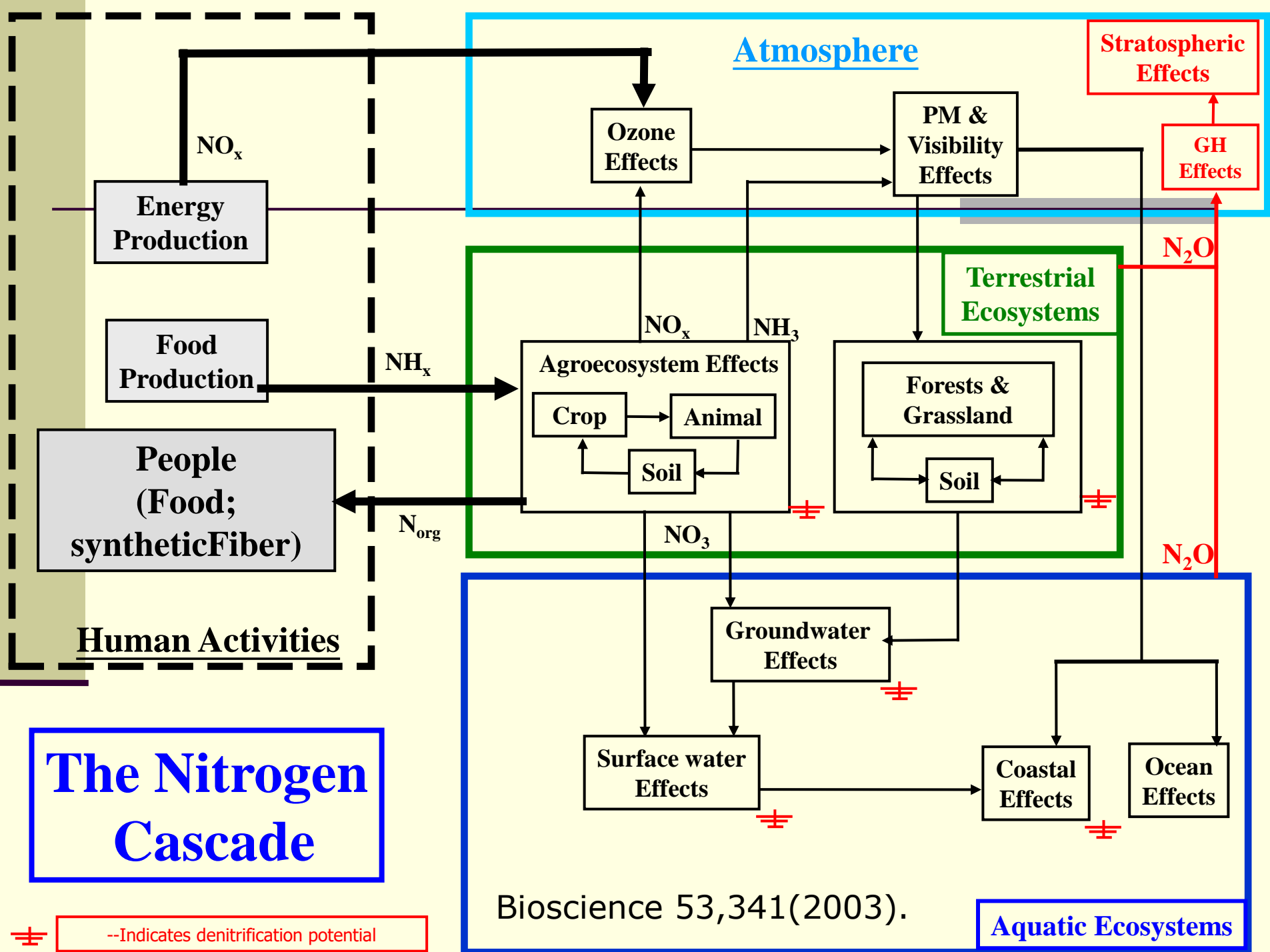


mid-1990s



Cascata do Nitrogênio

- Sequência de transferências, transformações e efeitos ambientais.
- Um átomo de N reativo criado (como NH_x ou NO_x) pode alterar os processos biogeoquímicos e as trocas entre reservatórios ambientais.
- Saturação de nitrogênio → morte de florestas temperadas (diminuição da resistência por fungos e baixa temperatura).



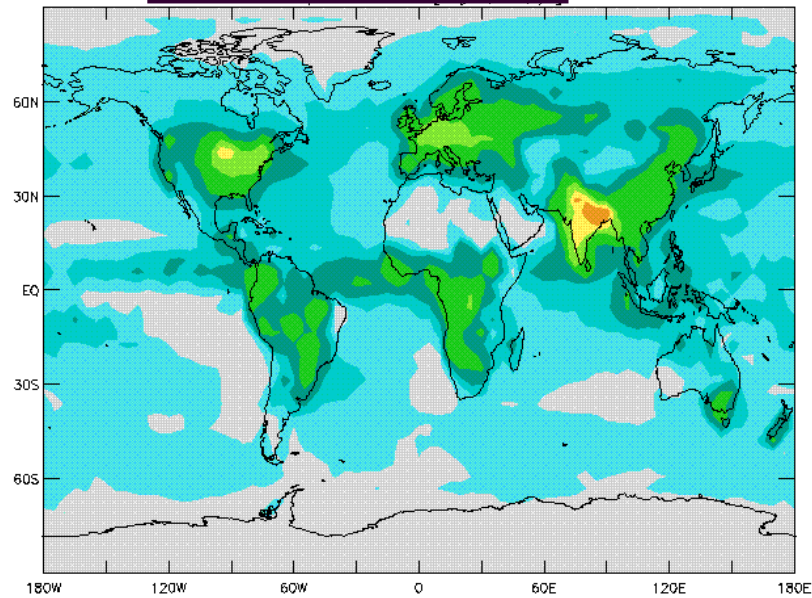
1 molécula de NO emitida durante a queima de combustíveis fósseis pode:

- **Aumentar a conc. de O₃ troposférico**
- **Diminuir a visibilidade = aumenta as conc. de partículas MP_{2,5}**
- **Aumentar a acidez da chuva**
- **Aumentar a acidez do solo**
- **Aumentar o efeito estufa**
- **Diminuir o O₃ estratosférico**

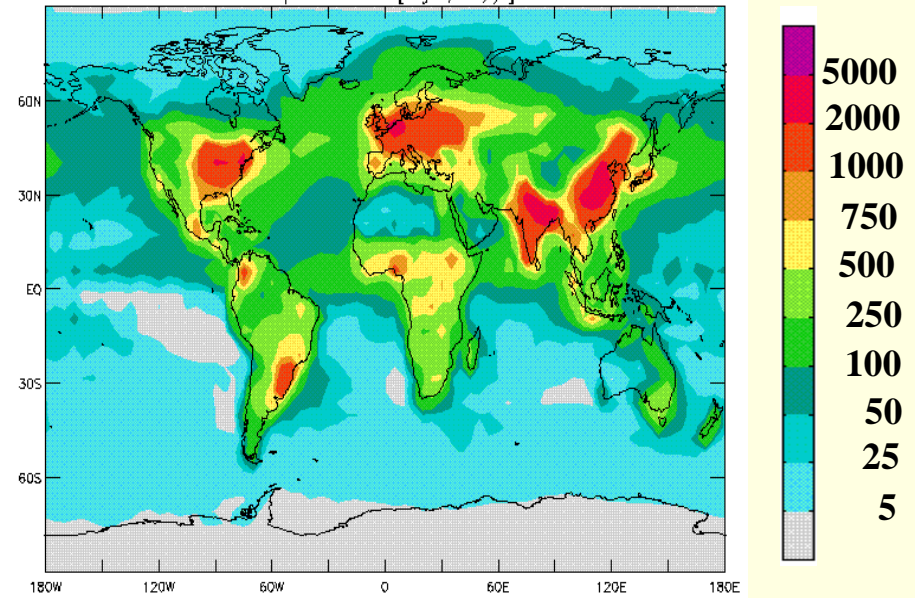
Nitrogen Deposition

Past and Present

mg N/m²/yr



1860



1993

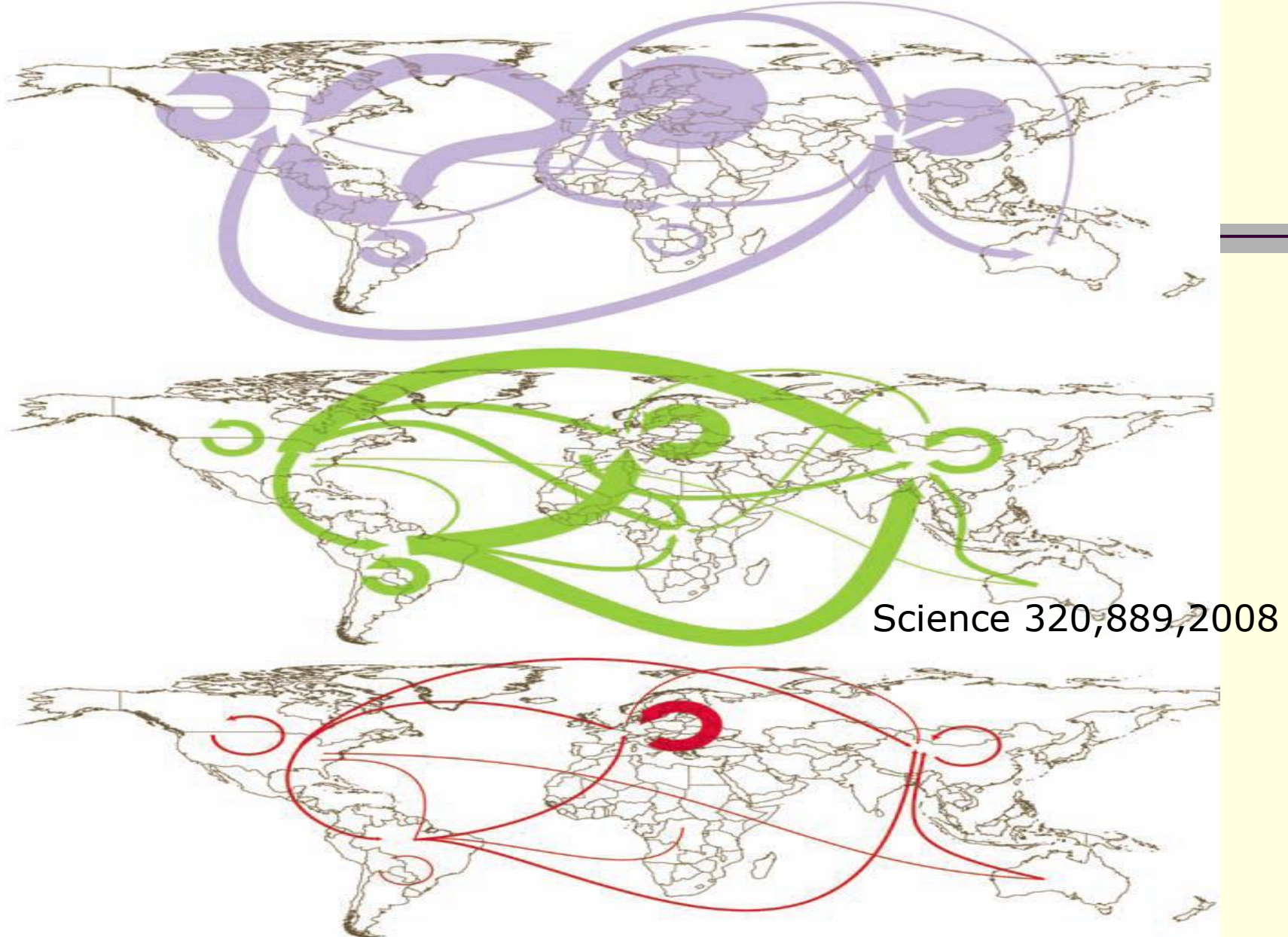


Fig. 1. N contained in internationally traded (A) fertilizer (31 Tg N), (B) grain (12 Tg N), and (C) meat (0.8 Tg N). Data are for 2004 and are in units of thousand of tons. Minimum requirements for drawing a line are 50,000 tons N, 20,000 tons N, and 10,000 tons N for fertilizer, grain, and meat, respectively (42).

Ciclo do Enxofre

- ❖ S é um elemento essencial para vida no planeta
- ❖ S reduzido é nutriente-chave para manutenção da vida (ex.: integridade estrutural de proteínas)
- ❖ S no estado oxidado (SO_4^{2-}) é o 2o. ânion mais abundante nos rios e oceanos
- ❖ Principal agente causador de acidez em água de chuva
- ❖ Forma substâncias insolúveis com metais (FeS_2) em solos, sedimentos e minerais

Reservatórios de Enxofre



Atmosfera: 512×10^{12} g S
(0,000004%)



Água do mar: 1280×10^{18} g S
(~11%)

Rochas: 7800×10^{18} g S (68%)

Sedimentos: 2375×10^{18} g S (~21%)

S nos Compartimentos

Table 13-3 Major sulfur reservoirs (Tg S)

Reservoir	Major form(s)	Burden
Continental atmosphere ^a	OCS, SO ₄ ²⁻ , SO ₂ , DMS, H ₂ S	1.6
Marine atmosphere ^a	OCS, SO ₄ ²⁻ , SO ₂ , H ₂ S, DMS	3.2
Soils and land biota ^a	Reduced	3 × 10 ⁵
Lakes and rivers ^d	SO ₄ ²⁻	300
Marine biota ^e	Reduced	30
Seawater ^{a,b}	SO ₄ ²⁻	1.3 × 10 ⁹
Ocean sediments ^{a,c}	Gypsum (CaSO ₄), pyrite (FeS ₂)	3 × 10 ⁸
Rest of lithosphere ^{a,c}	Pyrite (FeS ₂), gypsum (CaSO ₄)	2.4 × 10 ¹⁰

^a Freney *et al.* (1983); ^b Volkov and Rozanov (1983); ^c Migdisov *et al.* (1983).

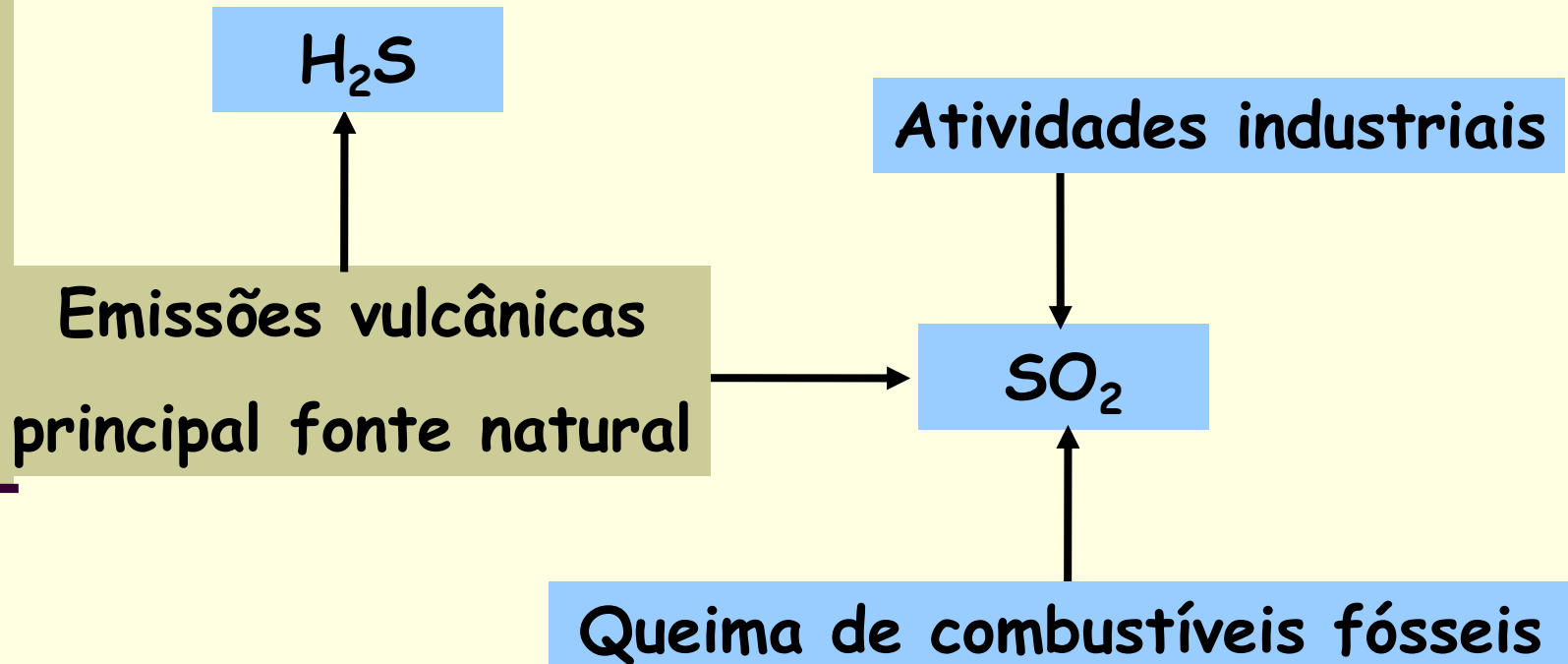
^d Calculated from mass of surface freshwater (1.3×10^{20} g H₂O) and average sulfate concentration (2.5×10^{-6} g S/g H₂O).

^e Calculated from carbon in ocean biota (3000 Tg) and approximate mass ratio for sulfur to carbon of 1 : 100.

Compostos de enxofre

⇒ Os mais importantes presentes na atmosfera são:
 $(\text{CH}_3)_2\text{S}$, H_2S , SO_2 , SO_3 e SO_4^{2-}

⇒ principal forma de entrada na atmosfera são as atividades humanas



Carvão 3% do peso em enxofre

petróleo 0,05% de enxofre em sua composição

Dióxido de enxofre (SO_2)

Impacto toxicológico

⇒ agrava as doenças respiratórias preexistentes e contribui para seu desenvolvimento

⇒ irritante do sistema respiratório

⇒ provoca tosse, sensação de falta de ar, diminuição da resistência às infecções.

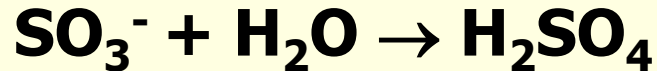
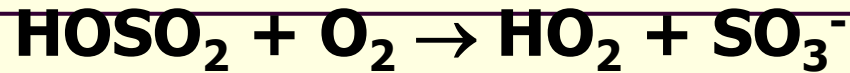
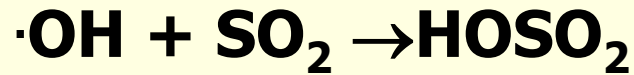
⇒ dose letal em humanos: 500 ppm

Londres 1952: "névoa negra" SO_2 + MP (poeira)

Impacto ambiental

⇒ Chuva ácida

CHUVA ÁCIDA



- Prejuízos ecológicos e econômicos - danos
- às florestas
- à fauna e flora aquáticas
- aos materiais de construção
- pH da água de chuva: 4,5-5,6
- Aerossol de sulfato → degradação da visibilidade – dispersão da luz.
- Queima de carvão e emissões de vulcão: SO_2 e HCl

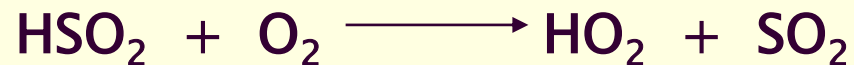
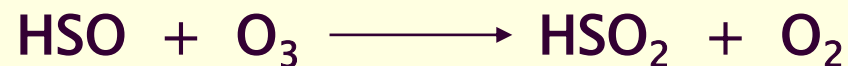
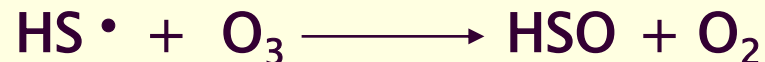
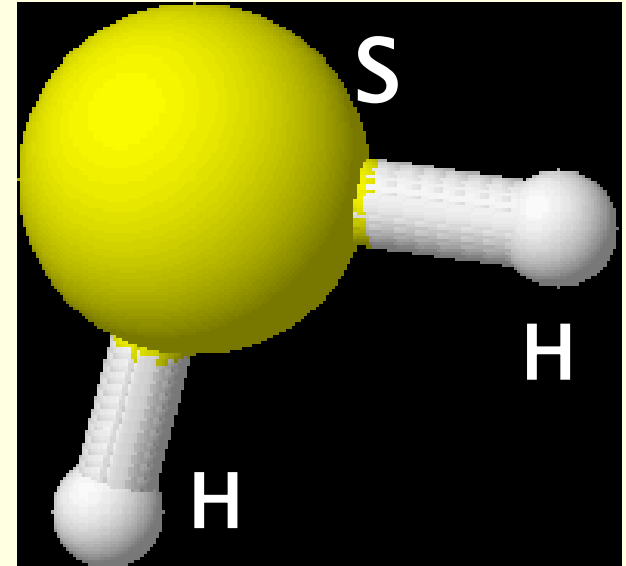
Estados de Oxidação do S

Table 13-1 Some naturally occurring sulfur compounds

Oxidation state	Gas	Aerosol	Aqueous	Soil	Mineral	Biological
-II	H ₂ S, RSH RSR OCS CS ₂	—	H ₂ S, HS ⁻ , S ²⁻ RS ⁻	S ²⁻ , HS ⁻ MS	S ²⁻ HgS CuS ₂ , etc.	Methionine CH ₃ S(CH ₂) ₂ CHNH ₂ Cysteine HSCH ₂ CHNH ₂ COOH D cysteine
-I	RSSR	—	RSSR	SS ²⁻	FeS ₂	—
0	CH ₃ SOCH ₃ ⁺	—	—	S ₈	—	—
II			S ₂ O ₃ ²⁻	—		
IV	SO ₂	SO ₂ · H ₂ O HSO ₃ ⁻	SO ₂ · H ₂ O HSO ₃ ⁻ SO ₃ ²⁻ HCHO · SO ₂	SO ₃ ²⁻	—	—
VI	SO ₃	H ₂ SO ₄ , HSO ₄ ⁻ SO ₄ ²⁻ (NH ₄) ₂ SO ₄ , etc. Na ₂ SO ₄ CH ₃ SO ₃ H	SO ₄ ²⁻ HSO ₄ ⁻ , SO ₄ ²⁻ CH ₃ SO ₃ ⁻	CaSO ₄	CaSO ₄ · H ₂ O MgSO ₄	

Sulfeto de hidrogênio (H₂S)

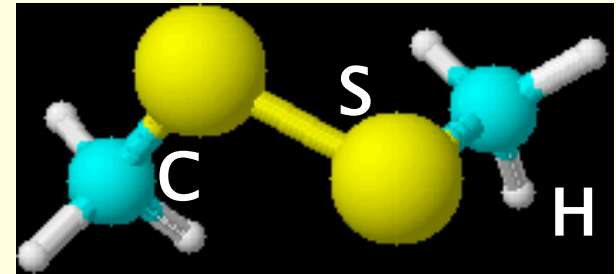
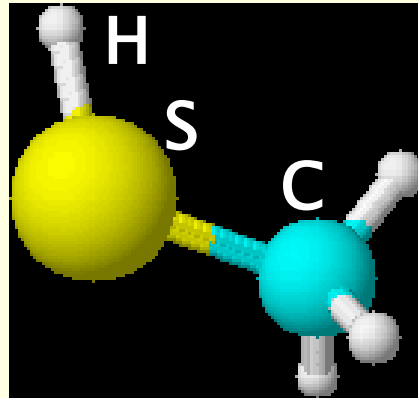
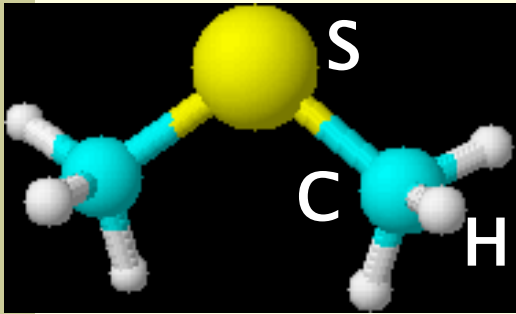
- ❖ É o principal gás reduzido de enxofre liberado de ecossistemas terrestres
- ❖ Fontes incluem vulcões, vegetais e solos, queima de biomassa, oceanos e atividades industriais
- ❖ Representa 1% (0,1 Tg S ano⁻¹) do total do S emitido por vulcões



Dimetil sulfeto DMS (CH_3SCH_3)

Metano tiol (CH_3SH)

Dimetil dissulfeto (CH_3SSCH_3)



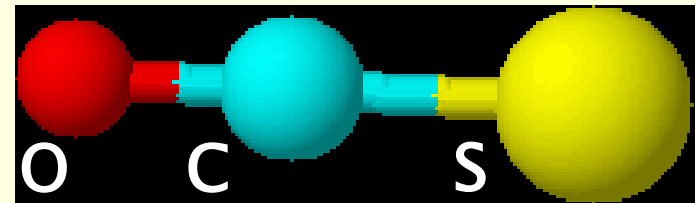
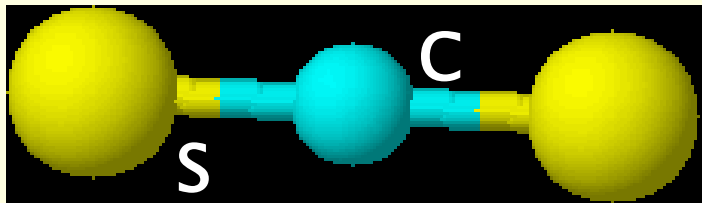
❖ Gases reduzidos de enxofre

❖ DMS é emitido por algas marinhas e fotossíntese de fitoplâncton e constitui a maior emissão de enxofre na forma reduzida

❖ Fluxo de DMS estimado em 16 Tg S ano^{-1}

Dissulfeto de Carbono (CS_2)

Sulfeto de Carbonila (OCS)

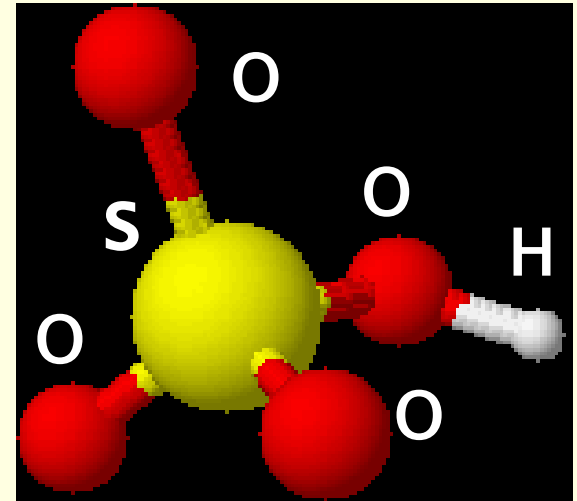
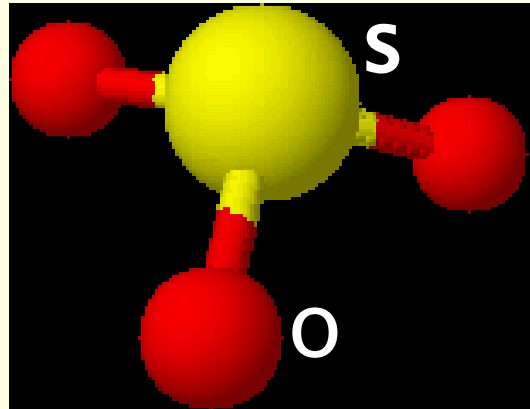
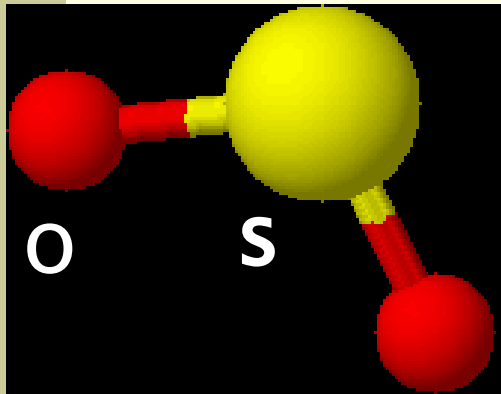


- ❖ CS_2 é um gás reduzido de enxofre emitido tanto por fontes biogênicas quanto antropogênicas
- ❖ OCS é o gás de S mais abundante na atmosfera e é emitido e absorvido pela vegetação e é também produzido pela oxidação do CS_2

Dióxido de Enxofre (SO_2)

Trióxido de Enxofre (SO_3^-)

Ácido Sulfúrico (H_2SO_4)



- ❖ $\text{SO}_2 + \text{SO}_3^- = \text{SO}_x$ são liberados principalmente na queima de combustíveis fósseis
- ❖ SO_2 produto de oxidação de gases reduzidos de S
- ❖ SO_3^- intermediário na oxidação do SO_2 e precursor do H_2SO_4