QFL4520 – Química Ambiental II

Parte I – Conceitos sobre o Meio Ambiente

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Parte I - Conceitos sobre o Meio Ambiente

- *A Terra;*
- *Meio Ambiente / Compartimentos Ambientais;*
- *Ciclos Biogeoquímicos;*
- *Compostos de importância ambiental;*
- *Influência Humana sobre o Meio Ambiente (poluição, Química Verde)*

Parte I - Conceitos sobre o Meio Ambiente

Aula 2:

- *Ciclos Biogeoquímicos;*

Ciclos Biogeoquímicos

https://earthobservatory.nasa.gov/Features/CarbonCycle/

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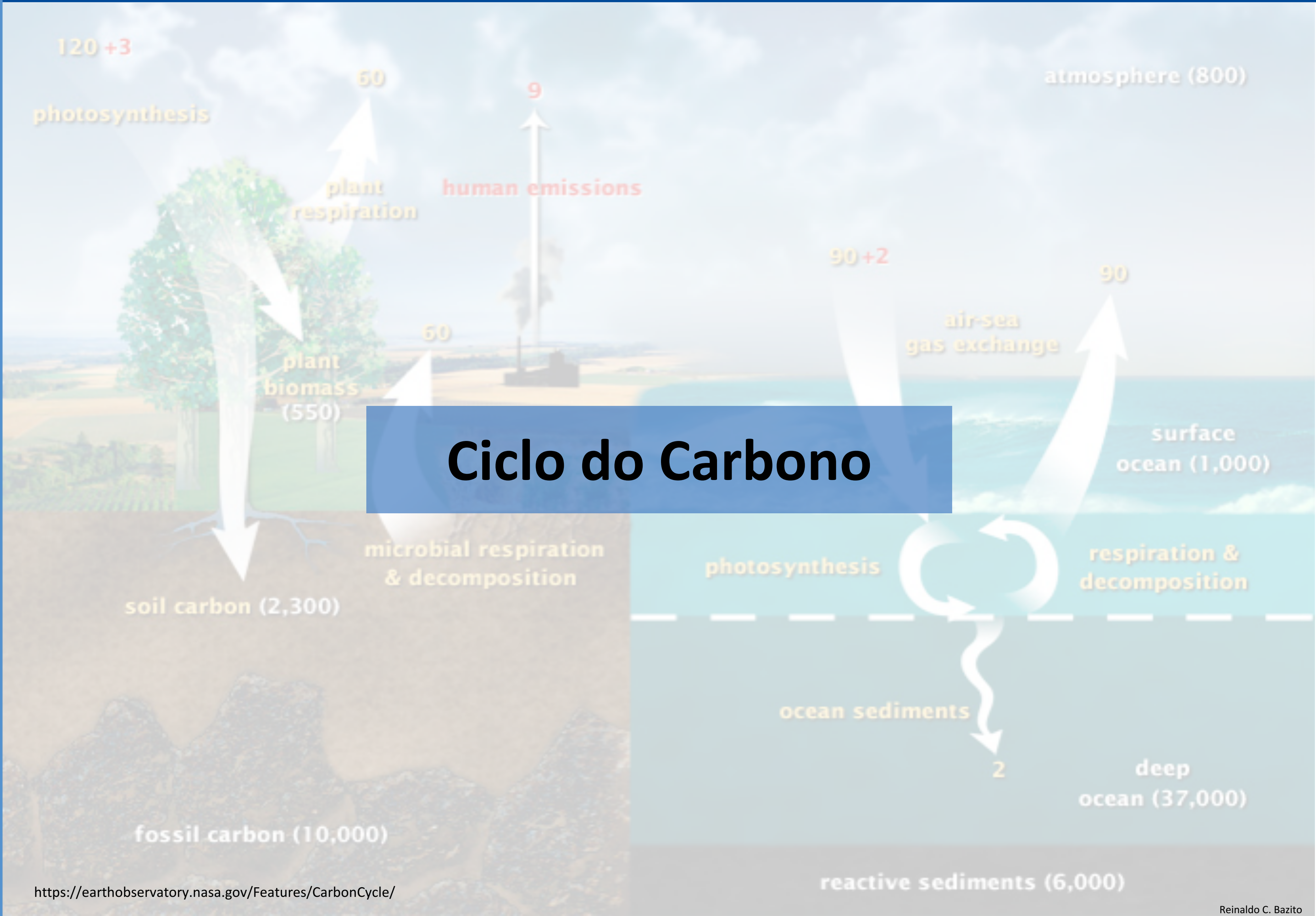
Ciclo do Carbono



https://earthobservatory.nasa.gov/Features/CarbonCycle/

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Ciclo do Carbono

Fluxo e estoques de carbono na Terra

Há dois ”ciclos do carbono”:

- **Ciclo Rápido** – troca ”rápida” entre atmosfera, oceanos, camada superior do solo e
- **Ciclo Lento** – conversão em carbonatos (rochas), eventos geológicos (movimento de placas tectônicas, erupções vulcânicas, etc) – escala de milhares a milhões de anos

Reservatórios de Carbono

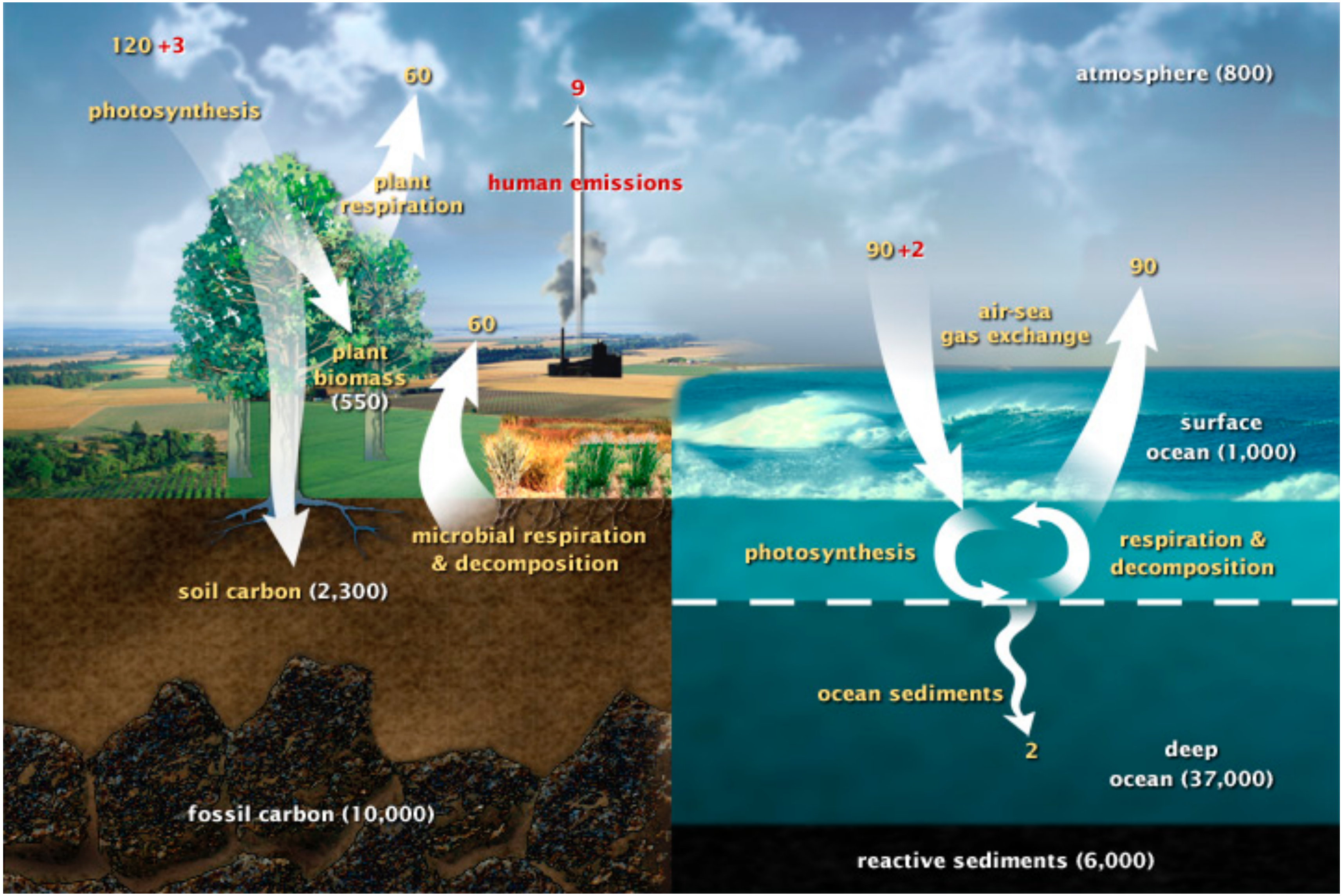
Table 1. Carbon pools in the major reservoirs on Earth.

Pools	Quantity (Gt)
Atmosphere	720
Oceans	38,400
Total inorganic	37,400
Surface layer	670
Deep layer	36,730
Total organic	1,000
Lithosphere	
Sedimentary carbonates	>60,000,000
Kerogens	15,000,000
Terrestrial biosphere (total)	2,000
Living biomass	600–1,000
Dead biomass	1,200
Aquatic biosphere	1–2
Fossil fuels	4,130
Coal	3,510
Oil	230
Gas	140
Other (peat)	250

The Global Carbon Cycle: A Test of Our Knowledge of Earth as a System
BY P. FALKOWSKI, R. J. SCHOLES, E. BOYLE, J. CANADELL, D. CANFIELD, J. ELSER, N. GRUBER, K. HIBBARD, P. HÖGBERG, S. LINDER, F. T. MACKENZIE, B. MOORE III, T. PEDERSEN, Y. ROSENTHAL, S. SEITZINGER, V. SMETACEK, W. STEFFEN
*SCIENCE*13 OCT 2000 : 291-296

http://science.sciencemag.org/content/290/5490/291

Ciclo do Carbono

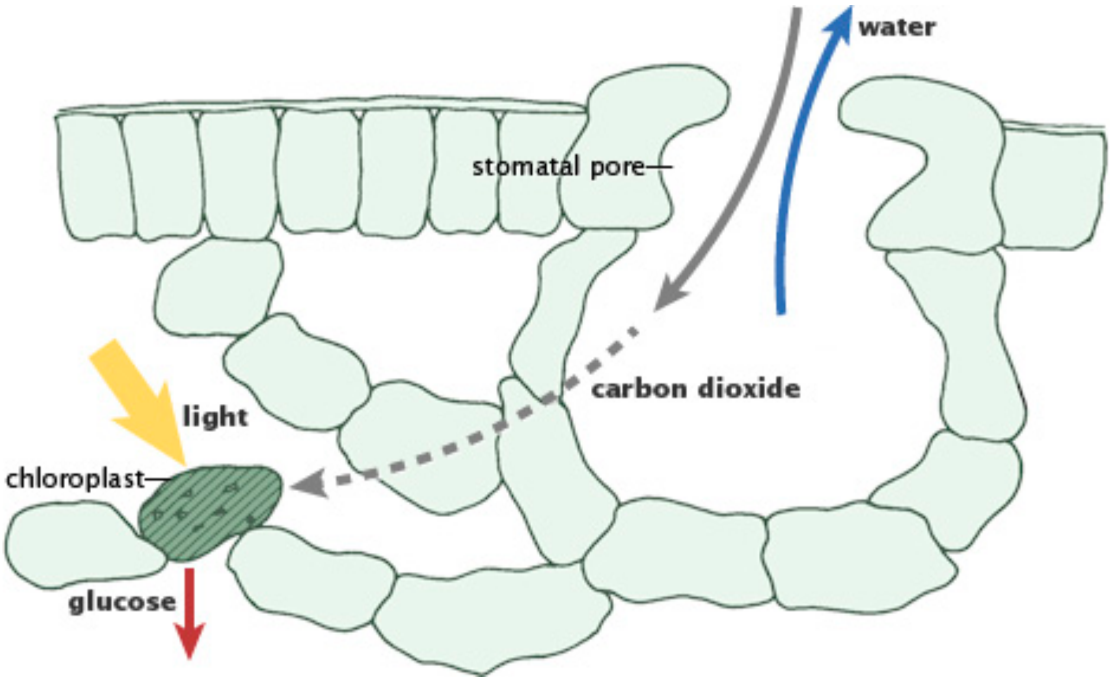


Amarelo = fluxos naturais
Vermelho = Contribuições humanas
Branco = Carbono estocado

Fluxos = GTon C/Ano
Estoques = GTon

https://earthobservatory.nasa.gov/Features/CarbonCycle/

Fotossíntese



https://earthobservatory.nasa.gov/Features/CarbonCycle/

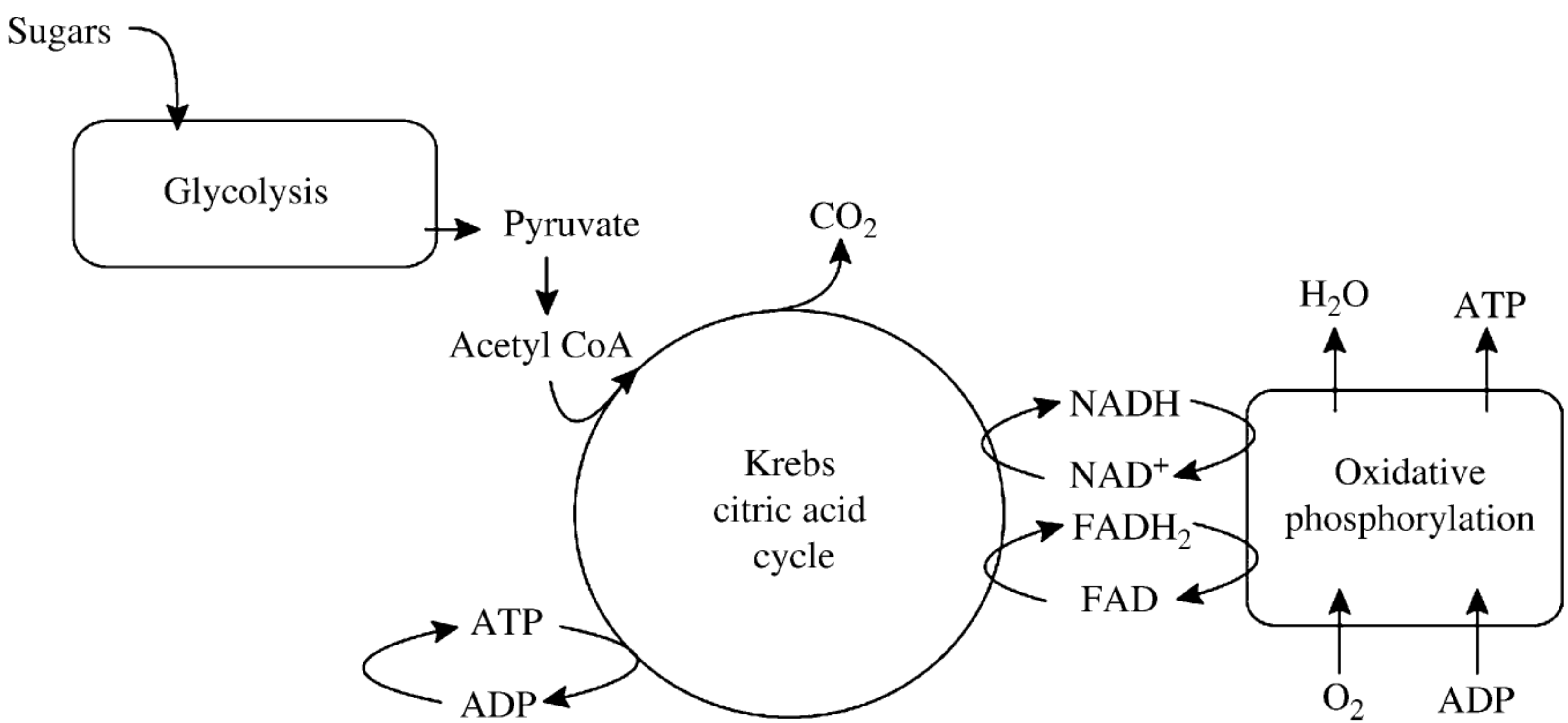
$$CO_2 + H_2O \overset{h\nu}{\rightarrow} \{CH_2O\} + O_2(g)$$

Eficiência ao redor de 3 a 6%

Renewable biological systems for alternative sustainable energy production (FAO Agricultural Services Bulletin - 128)
http://www.fao.org/docrep/w7241e/w7241e05.htm#1.2.1 photosynthetic efficiency

Respiração: **Aeróbica**

$$\{CH_2O\} + O_2(g) \rightarrow CO_2 + H_2O$$



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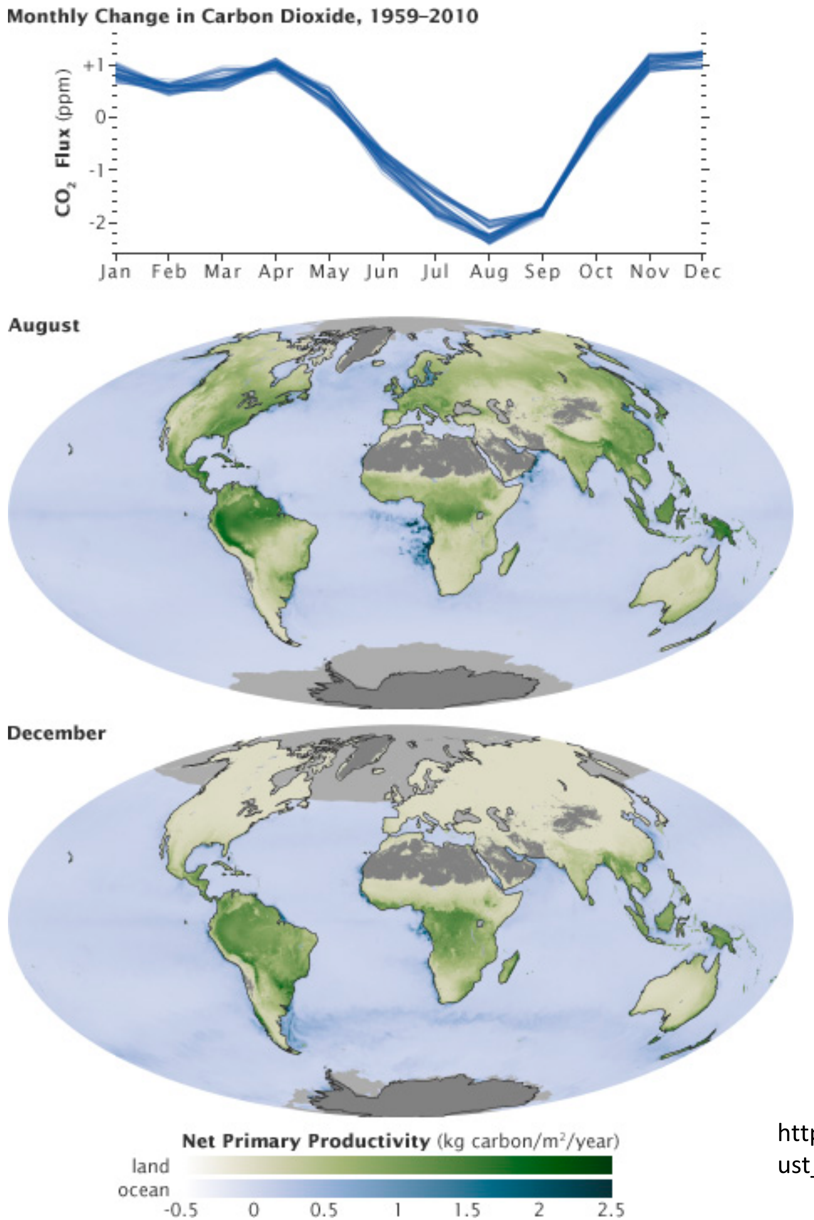
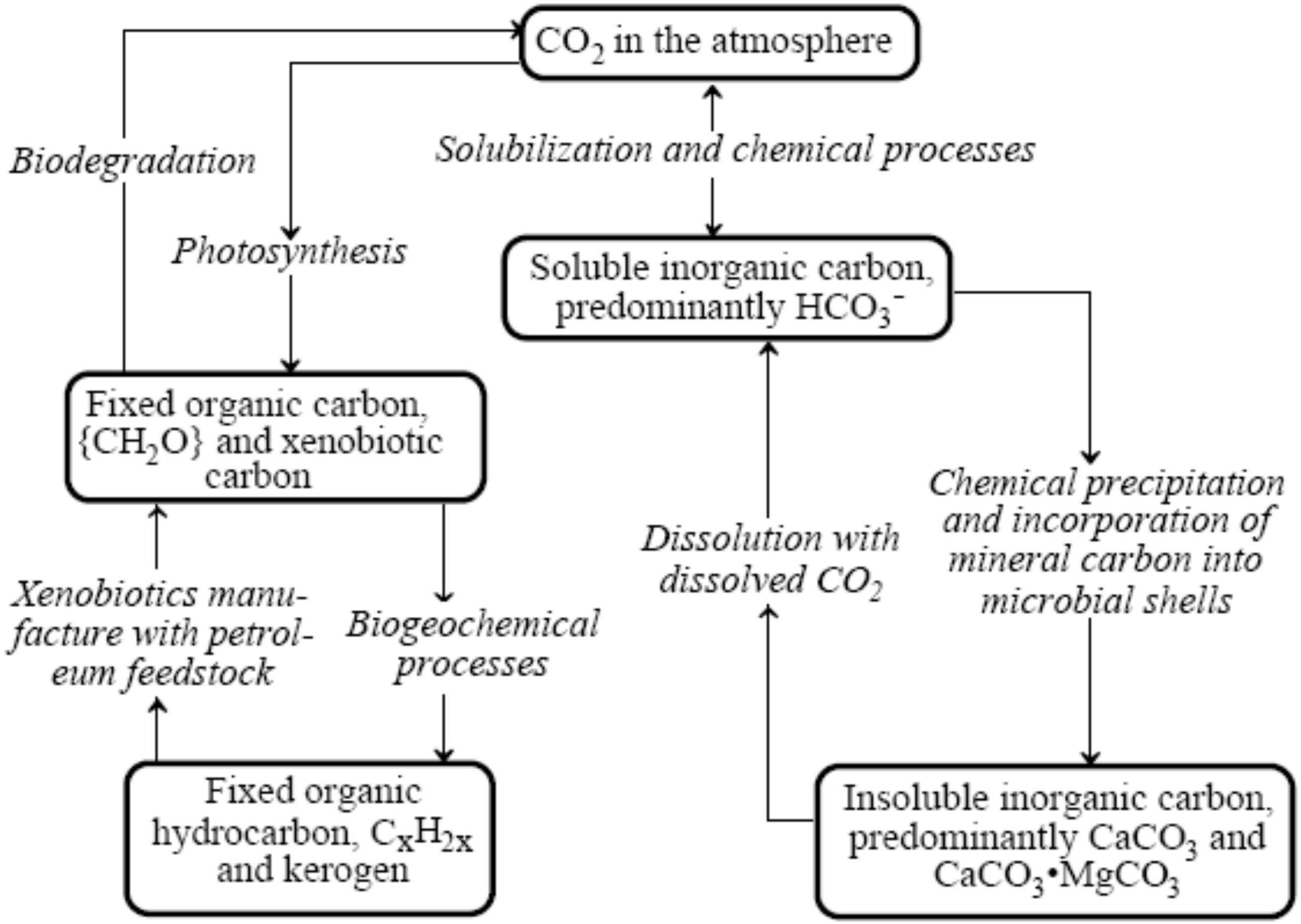
Mudanças Mensais na $[CO_2]$



https://earthobservatory.nasa.gov/Features/CarbonCycle/images/co2_flux_npp_august_december_2010.jpg

Ciclo do Carbono



Manahan, S. E. *Environmental chemistry*; 7th ed.

Ciclo do Carbono

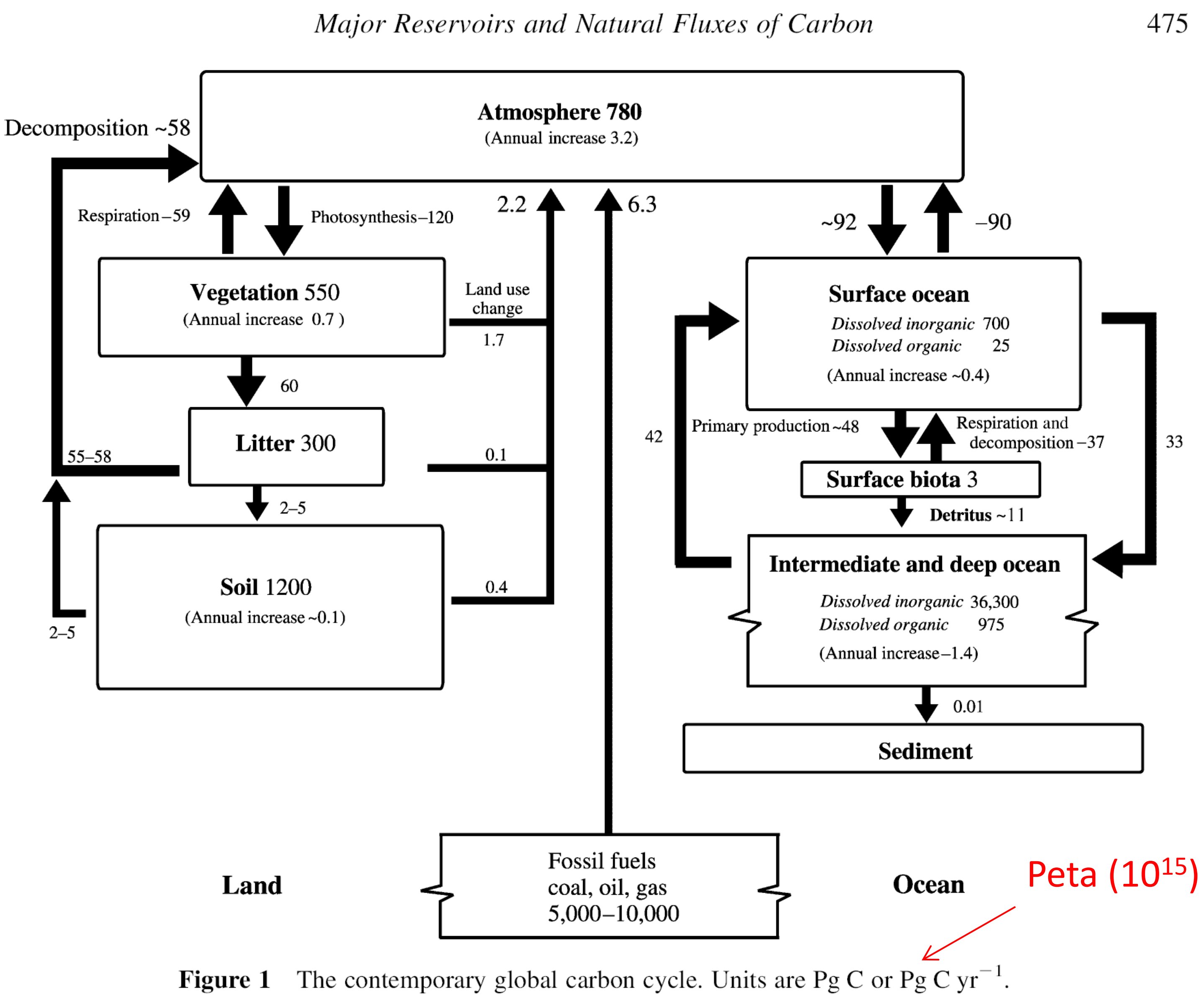


Figure 1 The contemporary global carbon cycle. Units are Pg C or Pg C yr^{-1}.

Holland, H. D.; Turekian, K. K., *Treatise on geochemistry*. 1st ed.; Elsevier/Pergamon: Amsterdam ; Boston, 2004; Vol. 8

Ciclo do Carbono

Table 1 Stocks and flows of carbon.

Carbon stocks (Pg C)	
Atmosphere	780
Land	2,000
Vegetation	500
Soil	1,500
Ocean	39,000
Surface	700
Deep	38,000
Fossil fuel reserves	10,000
Annual flows (Pg C yr^{-1})	
Atmosphere-oceans	90
Atmosphere-land	120
Net annual exchanges (Pg C yr^{-1})	
Fossil fuels	6
Land-use change	2
Atmospheric increase	3
Oceanic uptake	2
Other terrestrial uptake	3

Holland, H. D.; Turekian, K. K., *Treatise on geochemistry*. 1st ed.; Elsevier/Pergamon: Amsterdam ; Boston, 2004; Vol. 8

Ciclo do Carbono

Table 2 Area, carbon in living biomass, and net primary productivity of major terrestrial biomes.

Biome	*Area* (10^9 ha)		*Global carbon stocks* (Pg C)						*Carbon stocks* (Mg C ha^{-1})				*NPP* (Pg C yr^{-1})	
	WBGU	*MRS*	*WGBU*			*MRS IGBP*			*WBGU*		*MRS IGPB*		*Ajtay*	*MRS*
			Plants	*Soil*	*Total*	*Plants*	*Soil*	*Total*	*Plants*	*Soil*	*Plants*	*Soil*		
Tropical forests	17.6	17.5	212	216	428	340	214	553	120	123	194	122	13.7	21.9
Temperate forests	1.04	1.04	59	100	159	139	153	292	57	96	134	147	6.5	8.1
Boreal forests	1.37	1.37	88	471	559	57	338	395	64	344	42	247	3.2	2.6
Tropical savannas and grasslands	2.25	2.76	66	264	330	79	247	326	29	117	29	90	17.7	14.9
Temperate grasslands and shrublands	1.25	1.78	9	295	304	23	176	199	7	236	13	99	5.3	7.0
Deserts and semi-deserts	4.55	2.77	8	191	199	10	159	169	2	42	4	57	1.4	3.5
Tundra	0.95	0.56	6	121	127	2	115	117	6	127	4	206	1.0	0.5
Croplands	1.60	1.35	3	128	131	4	165	169	2	80	3	122	6.8	4.1
Wetlands	0.35		15	225	240				43	643			4.3	
Total	15.12	14.93	466	2,011	2,477	654	1,567	2,221					59.9	62.6

Source: Prentice *et al*. (2001).

Holland, H. D.; Turekian, K. K., *Treatise on geochemistry*. 1st ed.; Elsevier/Pergamon: Amsterdam ; Boston, 2004; Vol. 8

Ciclo do Carbono

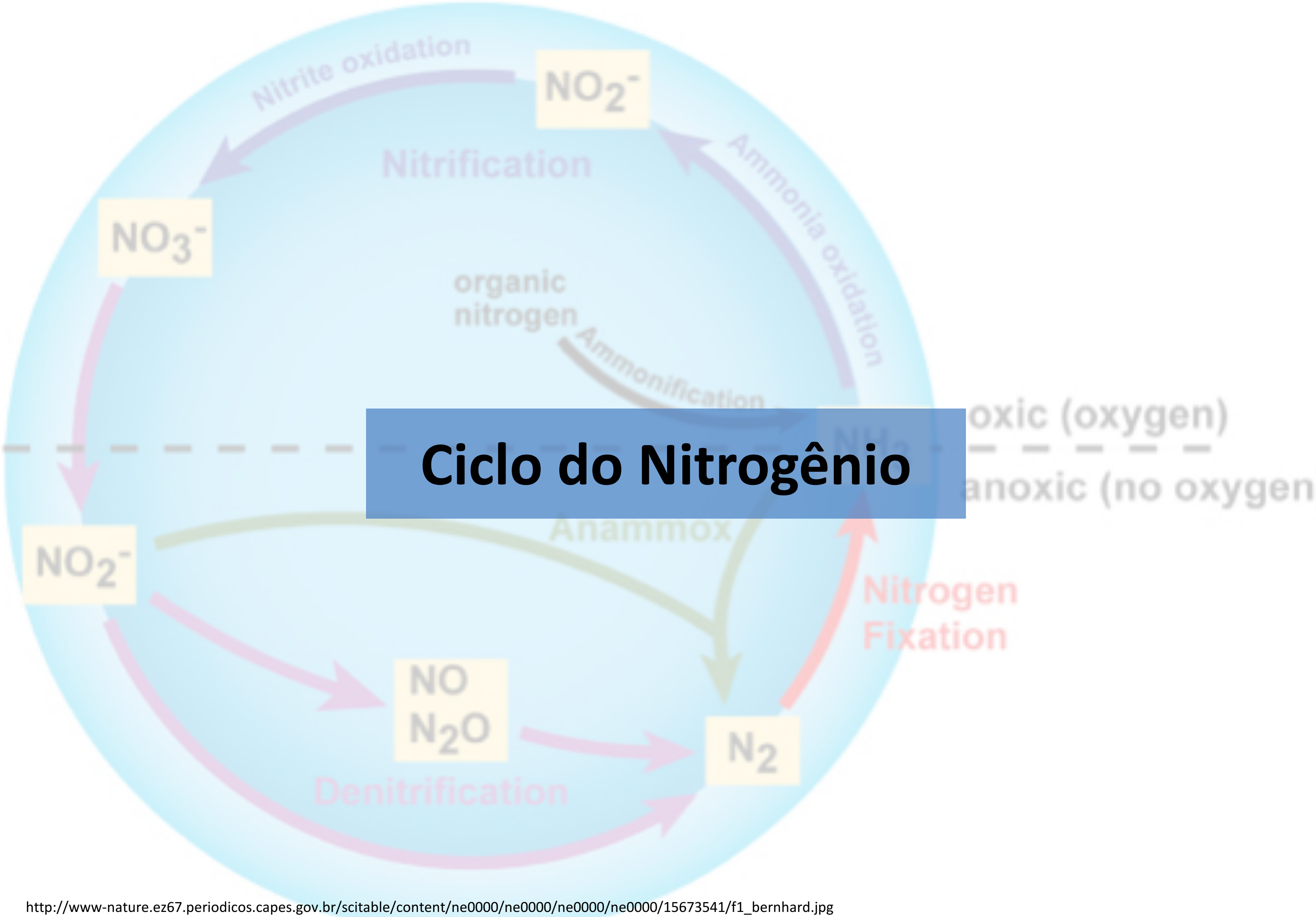
Table 3 The distribution of 1,000 CO_2 molecules in the atmosphere–ocean.

Atmosphere	15
Ocean	985
CO_2	5
HCO_3^-	875
CO_3^{2-}	105
Total	1,000

Source: Sarmiento (1993).

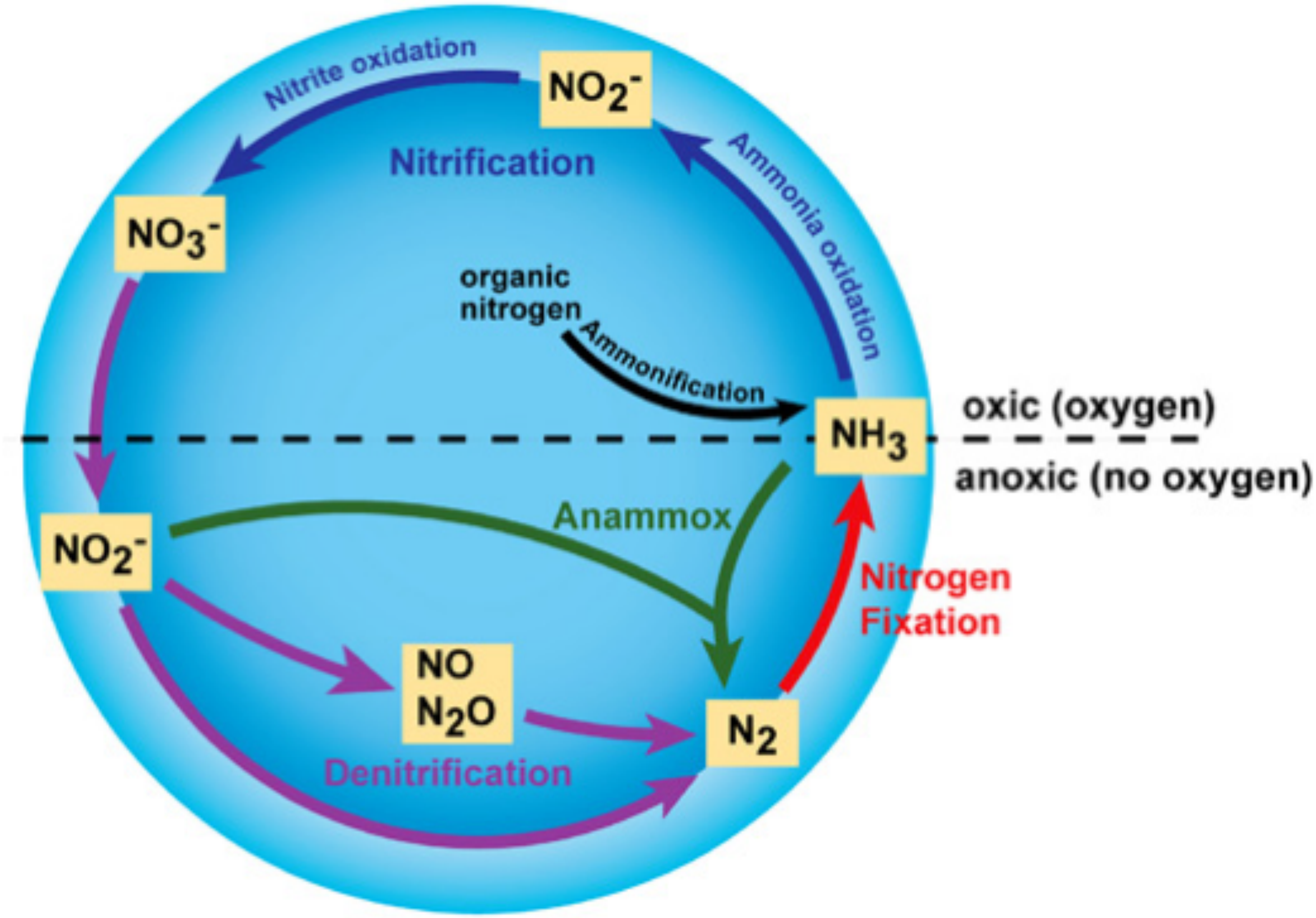
Holland, H. D.; Turekian, K. K., *Treatise on geochemistry*. 1st ed.; Elsevier/Pergamon: Amsterdam ; Boston, 2004; Vol. 8

Ciclo do Nitrogênio



http://www-nature.ez67.periodicos.capes.gov.br/scitable/content/ne0000/ne0000/ne0000/ne0000/15673541/f1_bernhard.jpg

Ciclo do Nitrogênio



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Ciclo do Nitrogênio

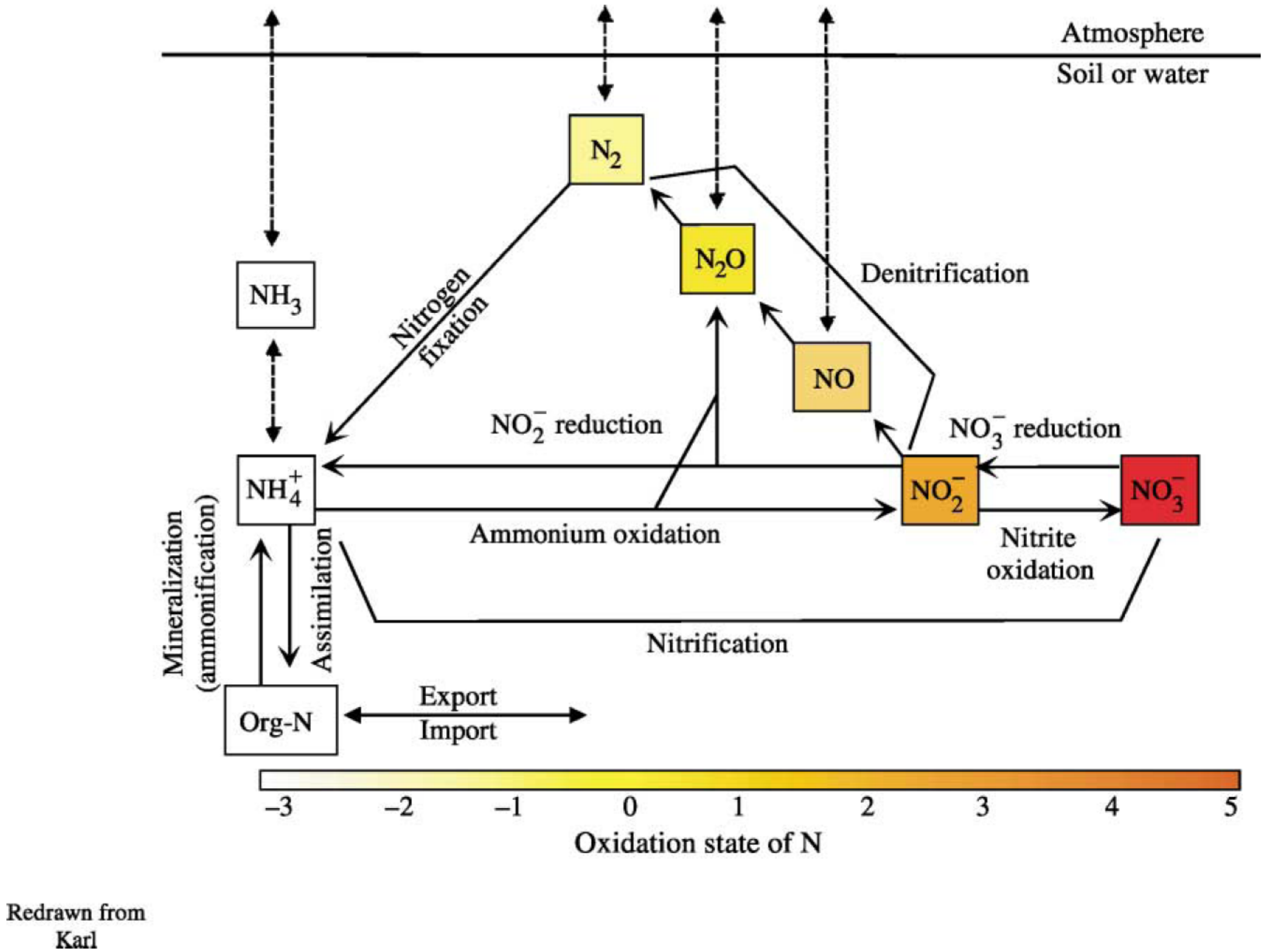


Figure 1 The processes of nitrogen fixation, assimilation, nitrification, decomposition, ammonification, and denitrification (after Karl, 2002).

Holland, H. D.; Turekian, K. K., *Treatise on geochemistry*. 1st ed.; Elsevier/Pergamon: Amsterdam ; Boston, 2004; Vol. 8

Ciclo do Nitrogênio

Fixação de Nitrogênio:

$$N_2 + 8\,H^+ + 8\,e^- \longrightarrow 2\,NH_3 + H_2$$

Genus	Phylogenetic Affiliation	Lifestyle
Nostoc, Anabaena	Bacteria (Cyanobacteria)	free-living,aerobic, phototrophic
Pseudomonas, Azotobacter, Methylomonas	Bacteria	free-living, aerobic, chemoorganotrophic
Alcaligenes, Thiobacillus	Bacteria	free-living, aerobic, chemolithotrophic
Methanosarcina, Methanococcus	Archaea	free-living, anaerobic, chemolithotrophic
Chromatium, Chlorobium	Bacteria	free-living, anaerobic, phototrophic
Desulfovibrio, Clostridium	Bacteria	free-living, anaerobic, chemoorganotrophic
Rhizobium, Frankia	Bacteria	symbiotic, aerobic, chemoorganotrophic

http://www-nature.ez67.periodicos.capes.gov.br/scitable/knowledge/library/the-nitrogen-cycle-processes-players-and-human-15644632

Nitrificação *(oxidação aeróbia da amônia por bactérias gerando nitrito e nitrato)*

1) $NH_3 + O_2 + 2\,e^- \longrightarrow NH_2OH + H_2O$ Enzima amônia mono-oxigenase

2) $NH_2OH + H_2O \longrightarrow NO_2^- + 5\,H^+ + 4\,e^-$ Enzima hidroxilamina oxidoredutase

Bactérias dos gêneros Nitrosomonas, Nitrosospira, e Nitrosococcus

$$NO_2^- + \frac{1}{2}O_2 \longrightarrow NO_3^-$$

Bactérias dos gêneros Nitrospira, Nitrobacter, Nitrococcus, and Nitrospina

http://www-nature.ez67.periodicos.capes.gov.br/scitable/knowledge/library/the-nitrogen-cycle-processes-players-and-human-15644632

Ciclo do Nitrogênio

Anamox *(oxidação anaeróbia da amônia)*

"perda" de nitrogênio em ambientes aquáticos

$$NH_4^+ + NO_2^- \longrightarrow N_2 + 2\,H_2O$$

Bactérias do filo Planctomycetes

http://www-nature.ez67.periodicos.capes.gov.br/scitable/knowledge/library/the-nitrogen-cycle-processes-players-and-human-15644632

Ciclo do Nitrogênio

<u>Desnitrificação</u> *(nitrato é convertido em nitrogênio gasoso, passando por intermediários) – processo anaeróbio*

1) $NO_3^- \longrightarrow NO_2^- \longrightarrow NO + N_2O \longrightarrow N_2$

2) $2\ NO_3^- + 10\ e^- + 12\ H^+ \longrightarrow N_2 + 6\ H_2O$

Bactérias dos gêneros Bacillus, Paracoccus, and Pseudomonas
Necessitam de C orgânico também!

http://www-nature.ez67.periodicos.capes.gov.br/scitable/knowledge/library/the-nitrogen-cycle-processes-players-and-human-15644632

Ciclo do Nitrogênio

Amonificação *(nitrogênio orgânico é convertido em amônia)*

http://www-nature.ez67.periodicos.capes.gov.br/scitable/knowledge/library/the-nitrogen-cycle-processes-players-and-human-15644632

Ciclo do Nitrogênio

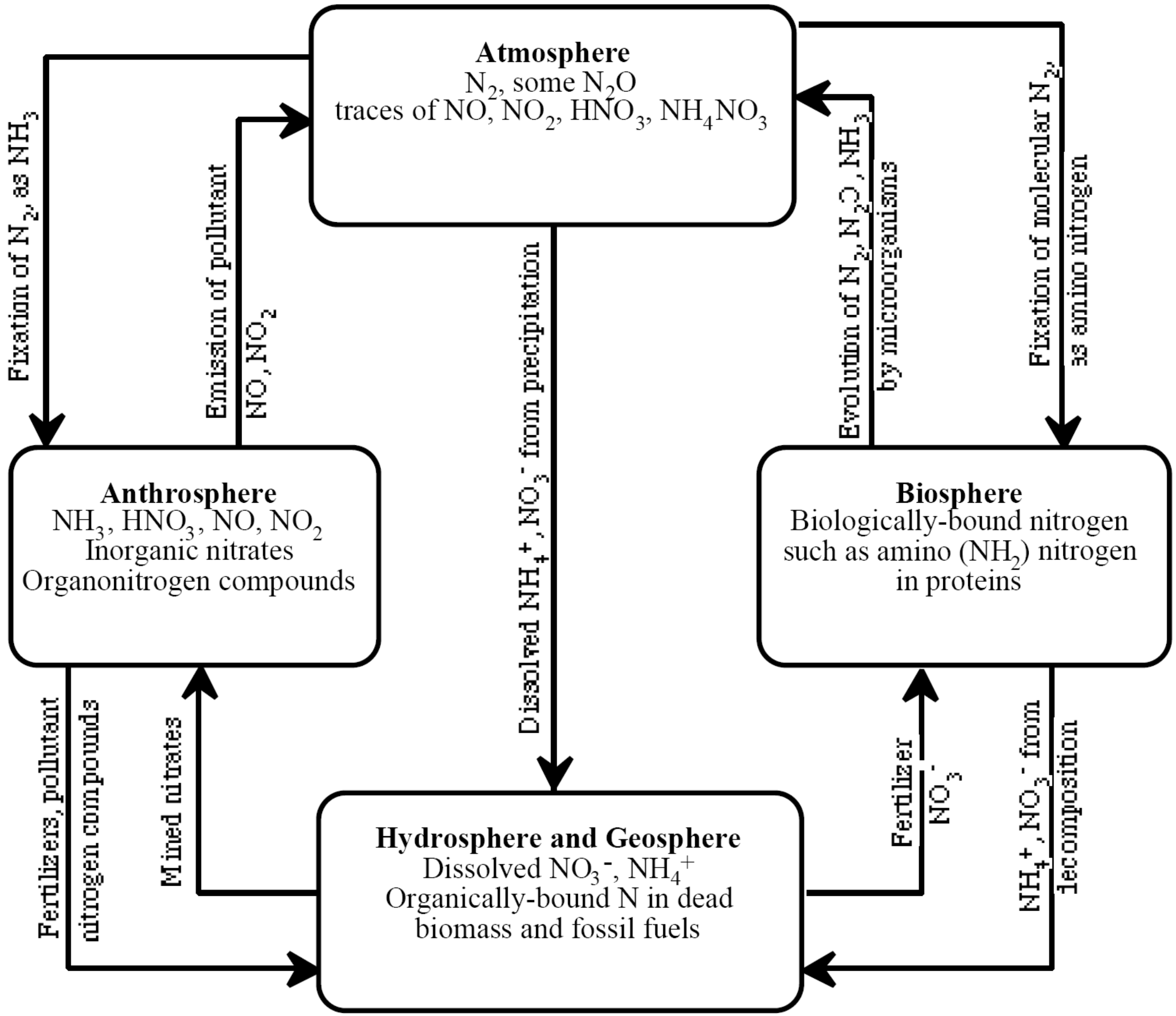


Figure 1.6. The nitrogen cycle.

Holland, H. D.; Turekian, K. K., *Treatise on geochemistry*. 1st ed.; Elsevier/Pergamon: Amsterdam ; Boston, 2004; Vol. 8

Ciclo do Nitrogênio

Tera (10^{12})

Table 2 N amounts in global reservoirs ($Tg\,N\,yr^{-1}$).

Reservoirs	*Amount*	*Percentage of total*
Atmosphere, N_2	3,950,000,000	79.5
Sedimentary rocks	999,600,000	20.1
Ocean		
N_2	20,000,000	0.4
NO_3^-	570,000	0.0
Soil organics	190,000	0.0
Land biota	10,000	0.0
Marine biota	500	0.0

Source: Mackenzie (1998) except ocean, N_2 from Schlesigner (1997).

Holland, H. D.; Turekian, K. K., *Treatise on geochemistry*. 1st ed.; Elsevier/Pergamon: Amsterdam ; Boston, 2004; Vol. 8

Ciclo do Nitrogênio

Table 4 Global creation and distribution rates of Nr ($Tg\,N\,yr^{-1}$).

Reactive nitrogen

Biological nitrogen fixation

	~1970 (Delwiche, 1970)	1970 (Svensson and Söderlund, 1976)	~1980 (Rosswall, 1983[a])	1990 (Galloway et al., 1995)	1990s (Schlesinger, 1997)
Natural Nr creation					
Terrestrial BNF	30	140	44–200	90–130	100
Marine BNF	10	30–130	1–130	40–200	15
Total lightning	7.6	?	0.5–30	3	5
Anthropogenic Nr creation					
Haber–Bosch	30	36	60	78	80
BNF, cultivation	14	89		43	40
Fossil-fuel combustion		19	10–20	21	24
Total terrestrial	74	194		255	249
Total global	174	274		375	264
Atmospheric emission					
NO_x, fossil-fuel combustion		19	10–20	21	24
NO_x, other		21–89	0–90	14.5	24
Terrestrial NH_3		113–244	36–250	53	62
Marine NH_3		0		13	13
Total emissions		253		102	123
Atmospheric deposition					
Terrestrial NO_y		32–83	110–240	26.5	30
Marine NO_y		11–33		12.3	14[b]
Terrestrial NH_x		91–186	40–116	52	40
Marine NH_x		19–50		17	16[b]
Organic N			10–100		
Total deposition		253	173–496	110	100
Riverine flux to coast	30	13–24	13–40	76[c]	36[d]
Denitrification[e]					
Continental N_2O		16–69	16–69	9.1	11.7
Marine N_2O		20–80	9–90	2	4
Continental N_2	43	91–92	43–390	130–290	13–233
Marine N_2	40	5–99	0–330	150–180	110
Total denitrification	83	236		386	249

[a] Deposition values for land plus ocean; NH_3 emissions include marine. [b] Wet. [c] Total. [d] Dissolved. [e] N_2O emissions are included with the realization that N_2O is also produced during nitrification.

Holland, H. D.; Turekian, K. K., *Treatise on geochemistry*. 1st ed.; Elsevier/Pergamon: Amsterdam ; Boston, 2004; Vol. 8

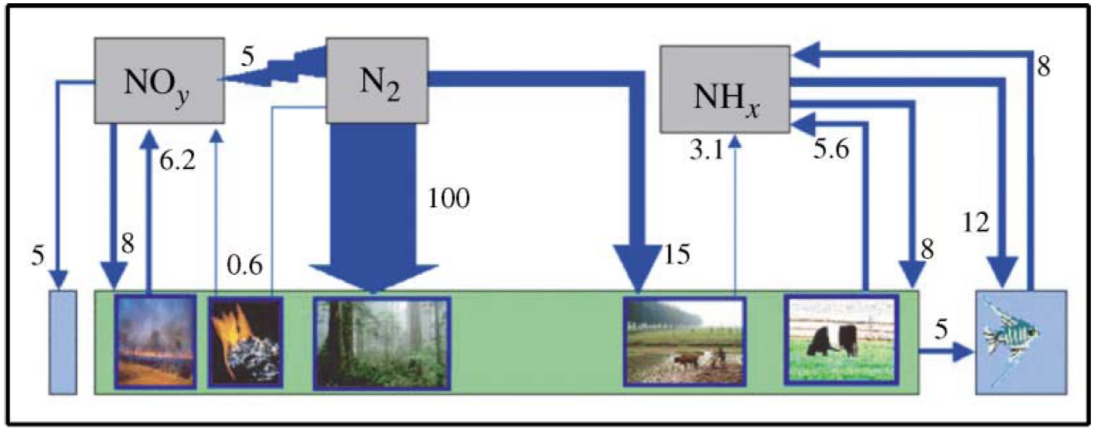
Ciclo do Nitrogênio

Table 5 Global Nr creation and distribution in 1890 and 1990 (Tg N yr^{-1}).

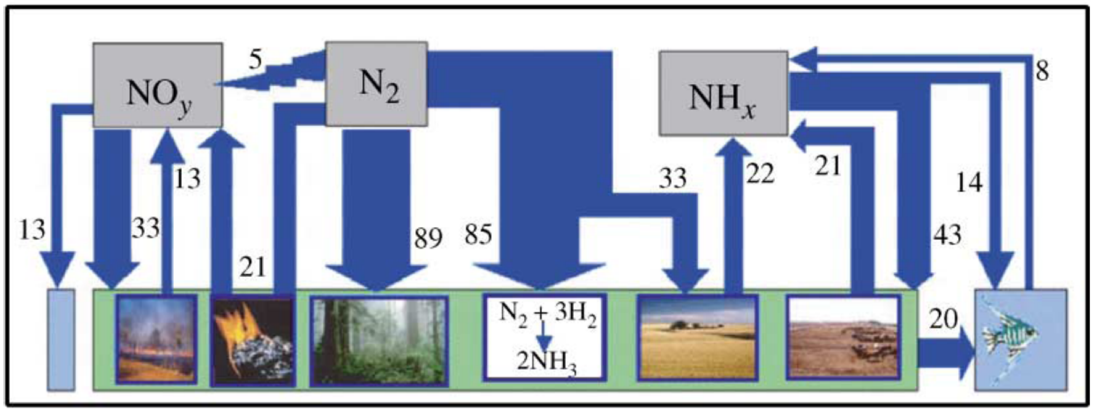
	1890	*1990*
Natural Nr creation		
BNF, terrestrial	100	89
BNF, marine	120	120
Total lightning	5	5
Anthropogenic Nr creation		
Haber–Bosch	0	85
BNF, cultivation	15	33
Fossil-fuel combustion	0.6	21
Nr creation		
Total terrestrial	121	233
Total global	241	353
Atmospheric emission		
NO_x, fossil-fuel combustion	0.6	21
NO_x, other	6.2	13.0
NH_3, terrestrial	8.7	43.0
NH_3, marine	8	8
Total emissions	24	85
Atmospheric deposition		
NO_y, terrestrial	8	33
NO_y, marine	5	13
NH_x, terrestrial	8	43
NH_x, marine	12	14
Total deposition	33	103
Riverine flux to coast (DIN)	5	20

Source: Galloway and Cowling (2002). N_2O emissions are included here with the realization that N_2O is also produced during nitrification; deposition values are for land plus ocean.

Ciclo do Nitrogênio



(a)



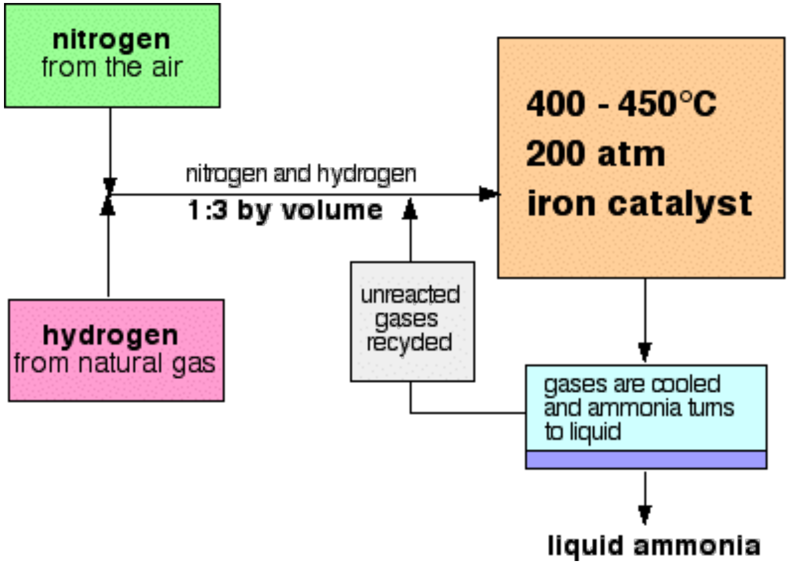
(b)

Figure 3 Global nitrogen budgets for: (a) 1890 and (b) 1990, Tg N yr^{-1}. Emissions to the (left) NO_y box from (first

Processo Haber-Bosch

Fritz Haber

Carl Bosch



$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)} \quad \Delta H = -92\ kJ\ mol^{-1}$$

http://www.chemguide.co.uk/physical/equilibria/haber.html

https://www.britannica.com/biography/Fritz-Haber

https://www.britannica.com/biography/Carl-Bosch

Óxidos de Nitrogênio na Combustão

NO_x (NO e NO_2 – maiores contribuições) **e** N_2O (menor contribuição)

Formação de NO_x em processos de combustão:

1) N_2 do ar (***NO_x térmico*** e ***NO_x "imediato"*** - prompt NO_x)

2) Compostos com N presentes no combustível (NO_x de combustível)

Óxidos de Nitrogênio na Combustão

NO_x térmico (mecanismo de Zeld'ovich):

$N_2 + O \rightarrow NO + N$
$N + O_2 \rightarrow NO + O$
$N + OH \rightarrow NO + H$

NO_x prompt (mecanismo de Fenimore):

$CH + N_2 \rightarrow HCN + N$
$HCN + O \rightarrow NCO + H$
$NCO + H \rightarrow NH + CO$
$NH + H \rightarrow N + H_2$

Óxidos de Nitrogênio na Combustão

NO_x de combustível

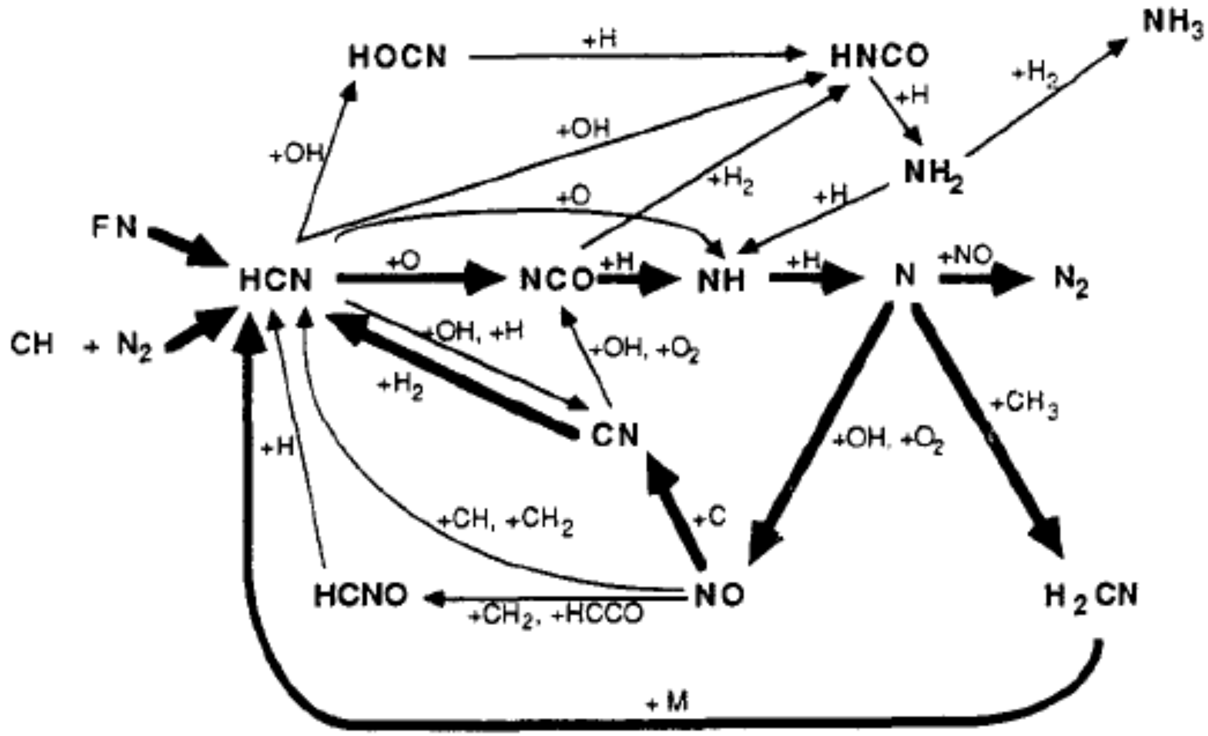
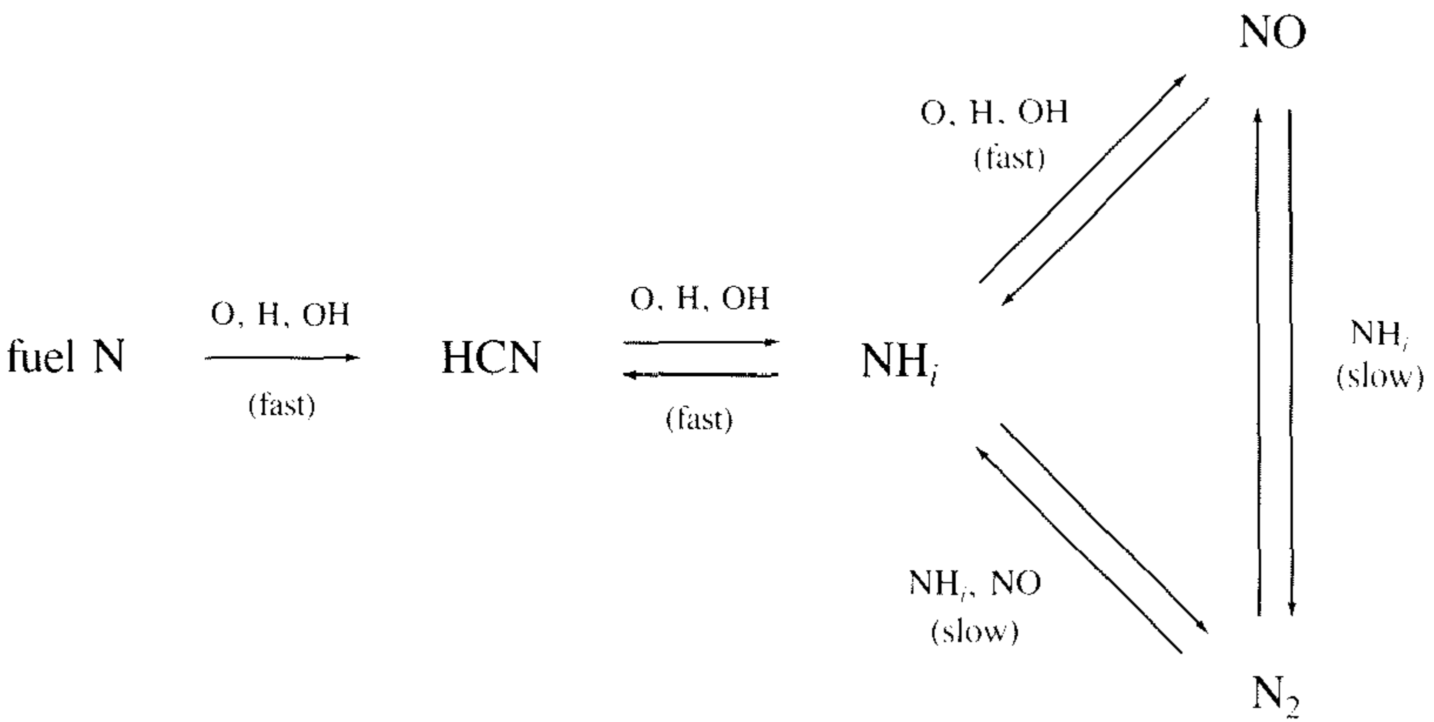


FIG. 11. Reaction path diagram illustrating the major steps in prompt NO formation and conversion of fuel nitrogen (FN) to NO. The bold lines represent the most important reaction paths.

http://www-sciencedirect-com.ez67.periodicos.capes.gov.br/science/article/pii/0360128589900178

NO_x de combustível

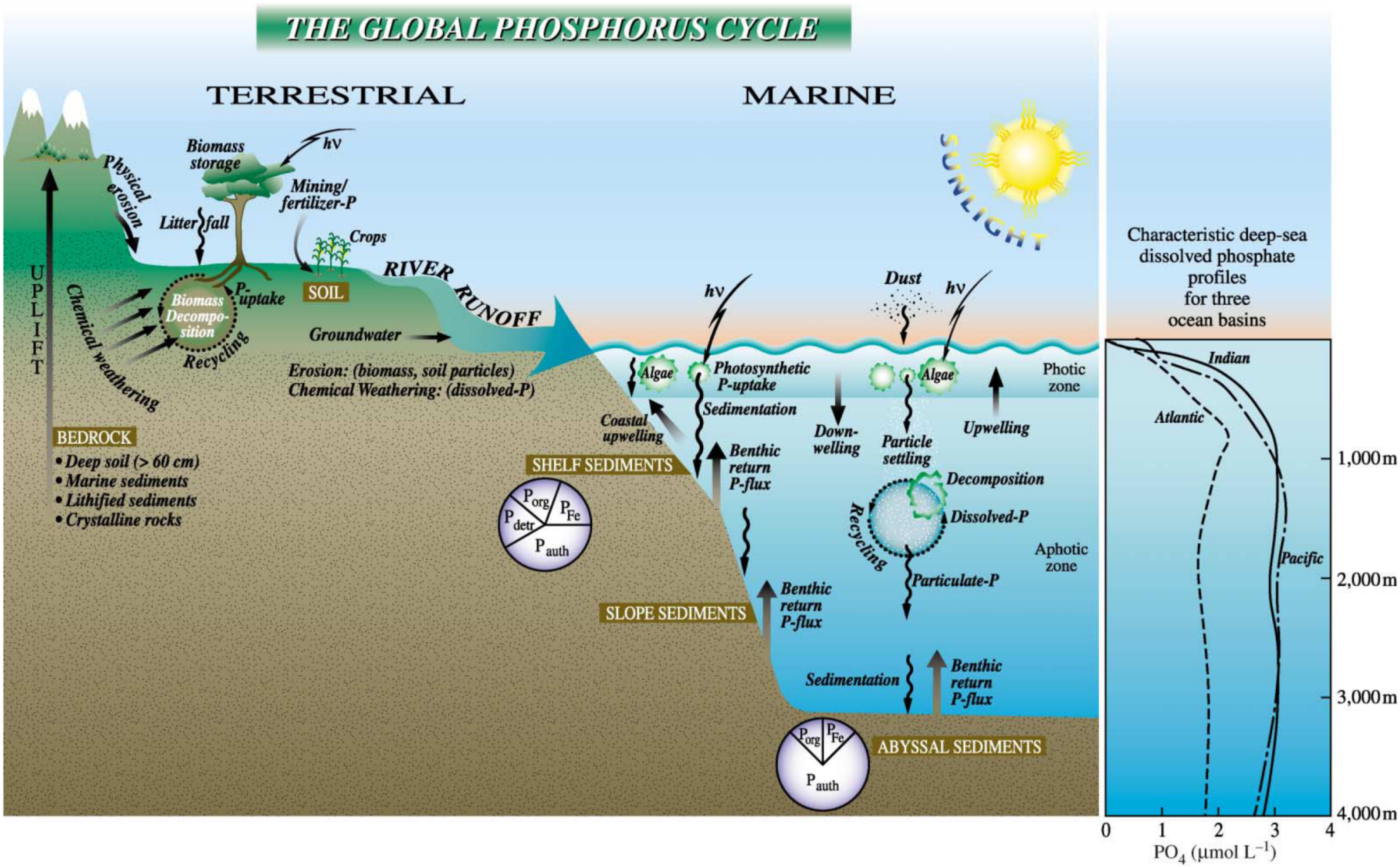


http://authors.library.caltech.edu/25069/5/AirPollution88-Ch3.pdf

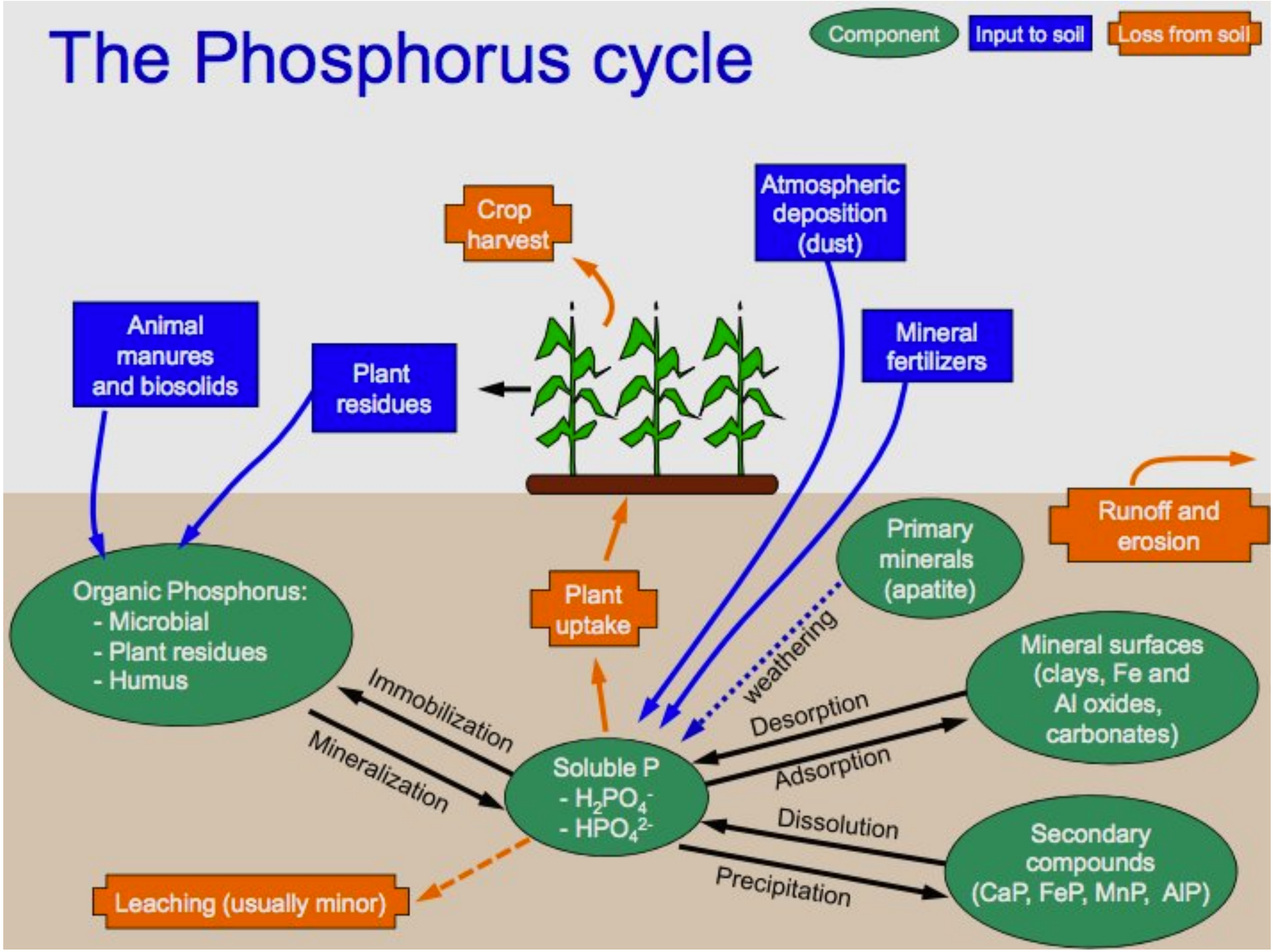
Ciclo do Fósforo

https://upload.wikimedia.org/wikipedia/commons/9/91/Phosphorus_Cycle_copy.jpg

Ciclo do Fósforo

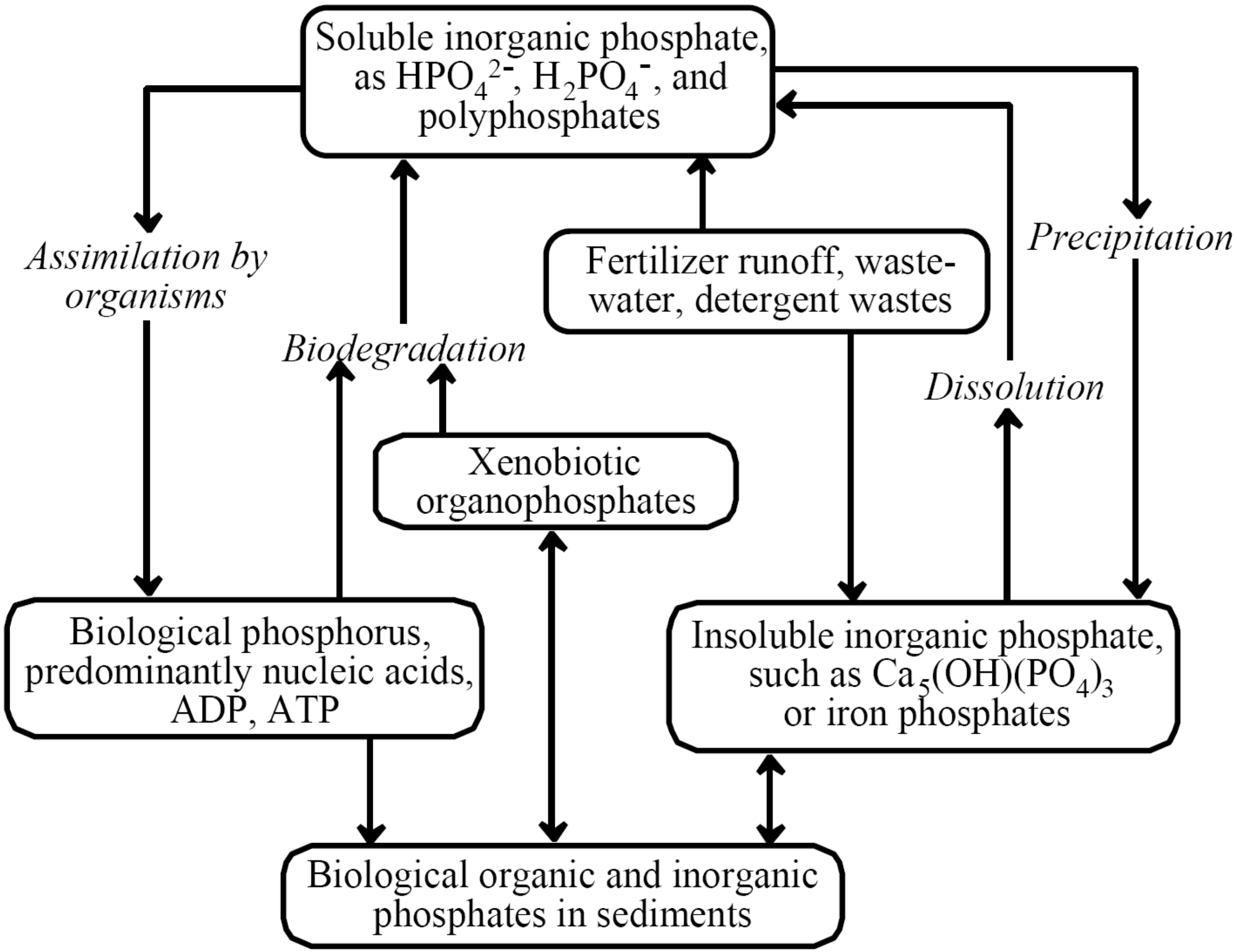


Ciclo do Fósforo



https://upload.wikimedia.org/wikipedia/commons/9/91/Phosphorus_Cycle_copy.jpg

Ciclo do Fósforo



ıre 1.7. The phosphorus cycle.

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Ciclo do Enxofre

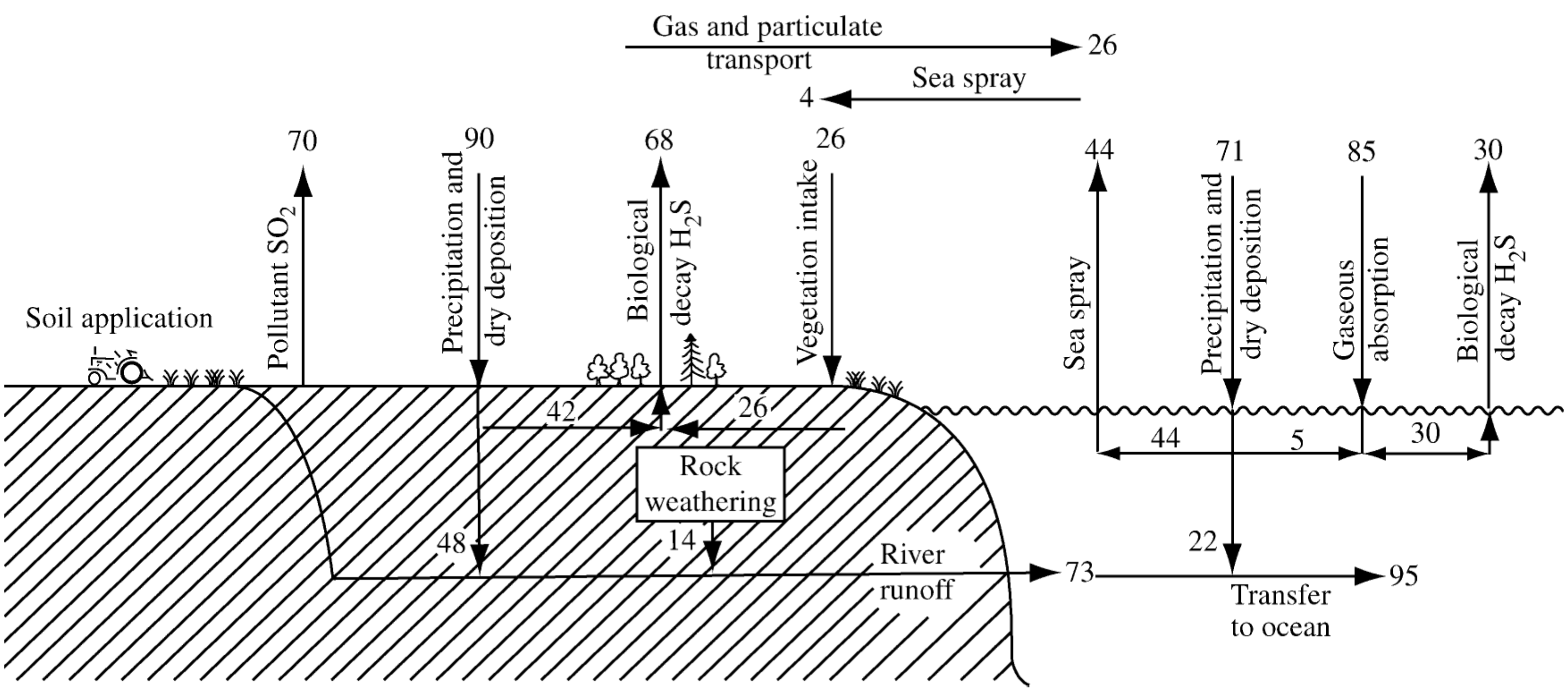


Figure 1 A generalized geochemical cycle for sulfur of the early 1970s. Note the large emissions of hydrogen sulfide from the land and oceans and that volcanic sulfur emissions are neglected (units: Tg (s) a^{-1}).

Ciclo do Enxofre

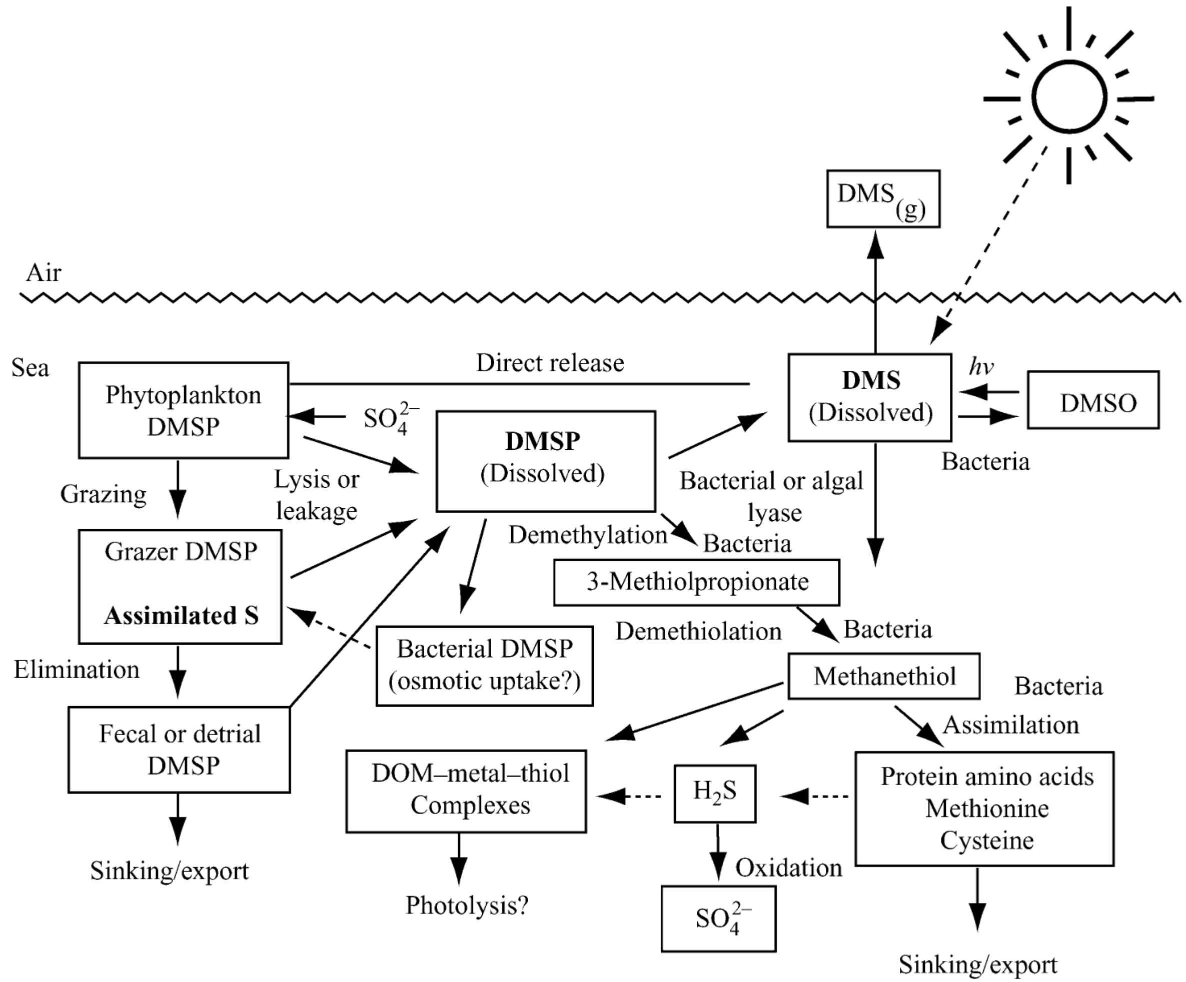


Figure 11 The biogeochemical cycles of DMSP and DMS in surface waters of the oceans (source Kiene *et al.*, 2000).

Ciclo do Enxofre

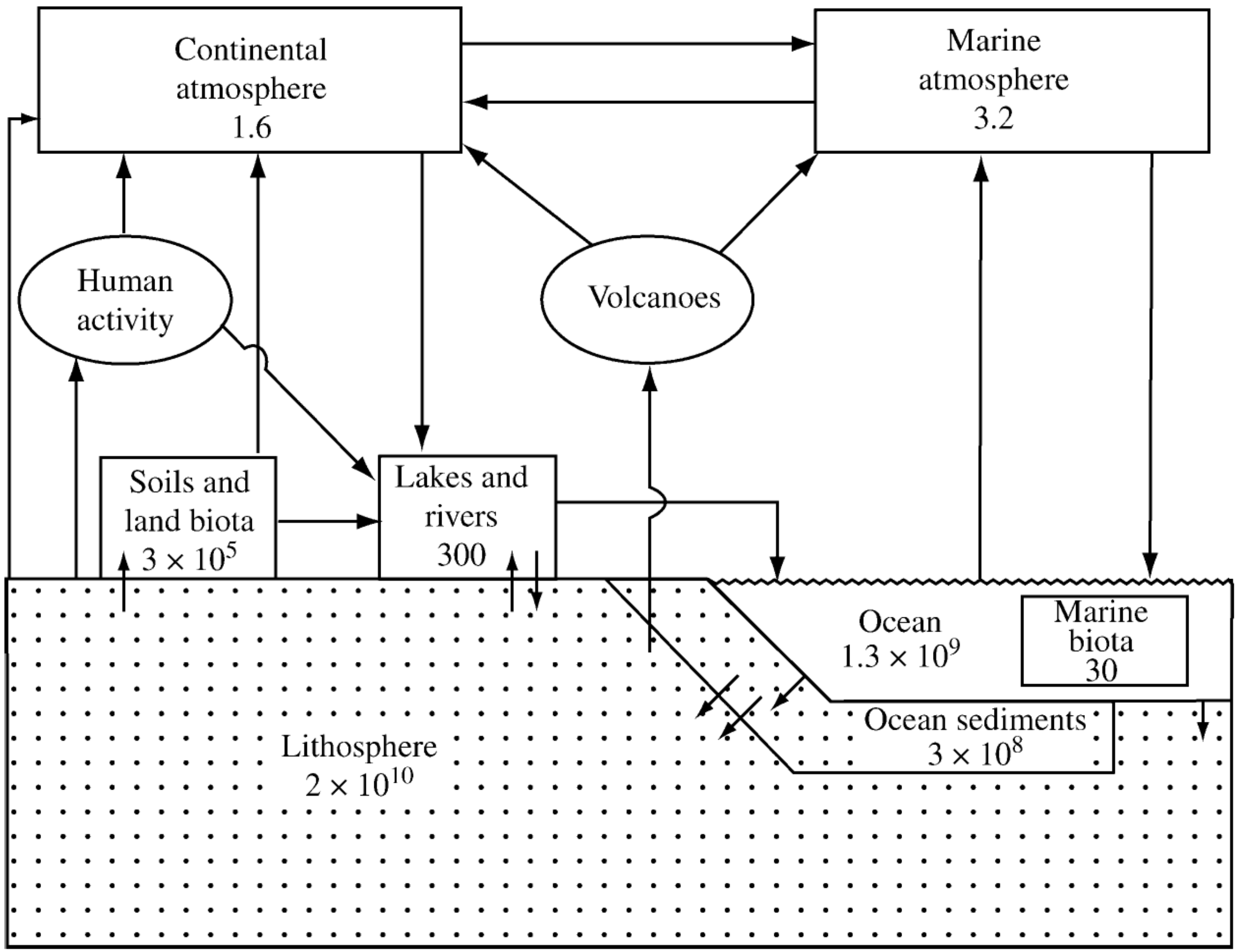


Figure 15 Major reservoirs and burdens of sulfur as Tg(S) (source Charlson *et al.*, 1992).

Ciclo do Enxofre

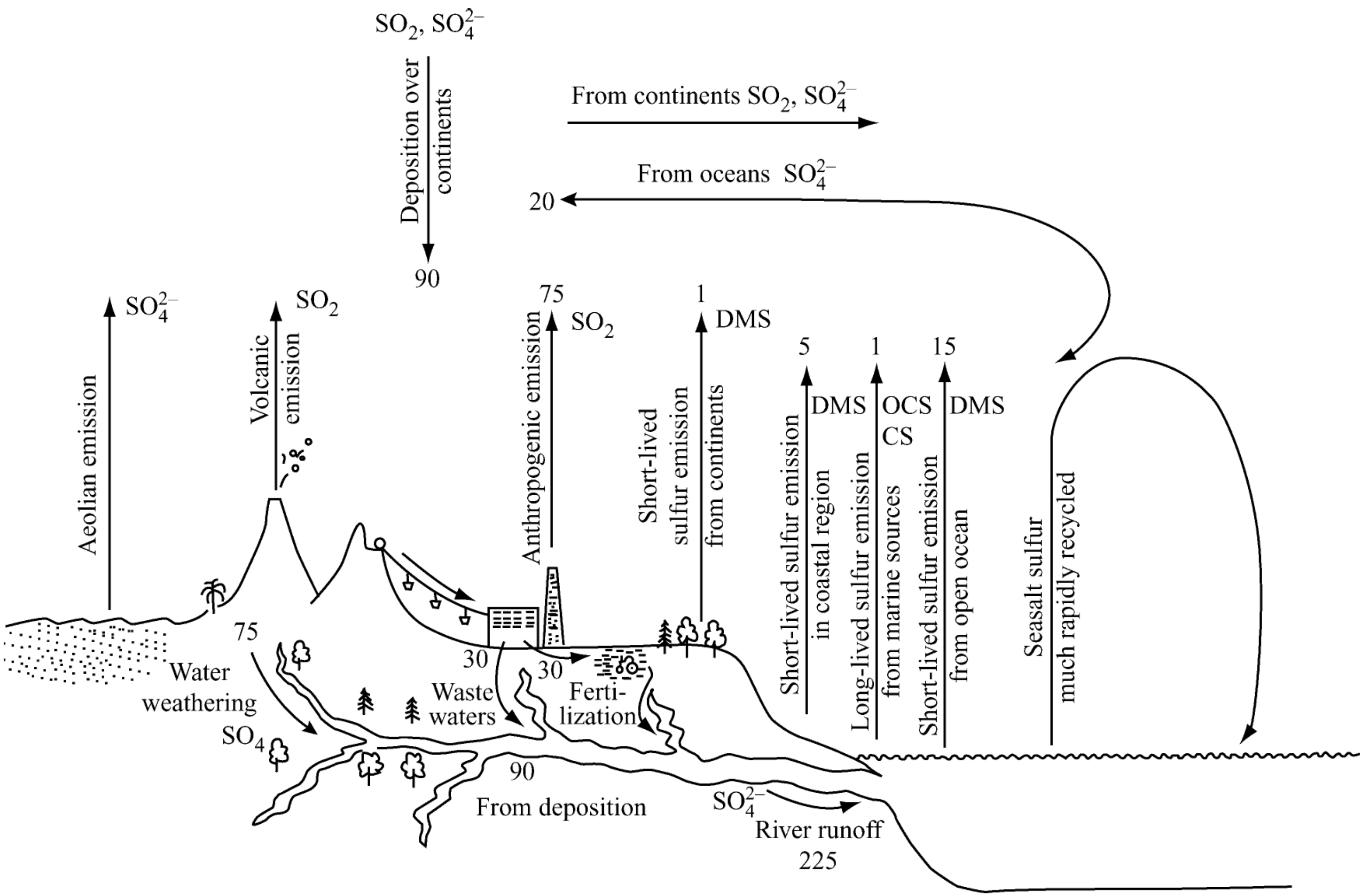
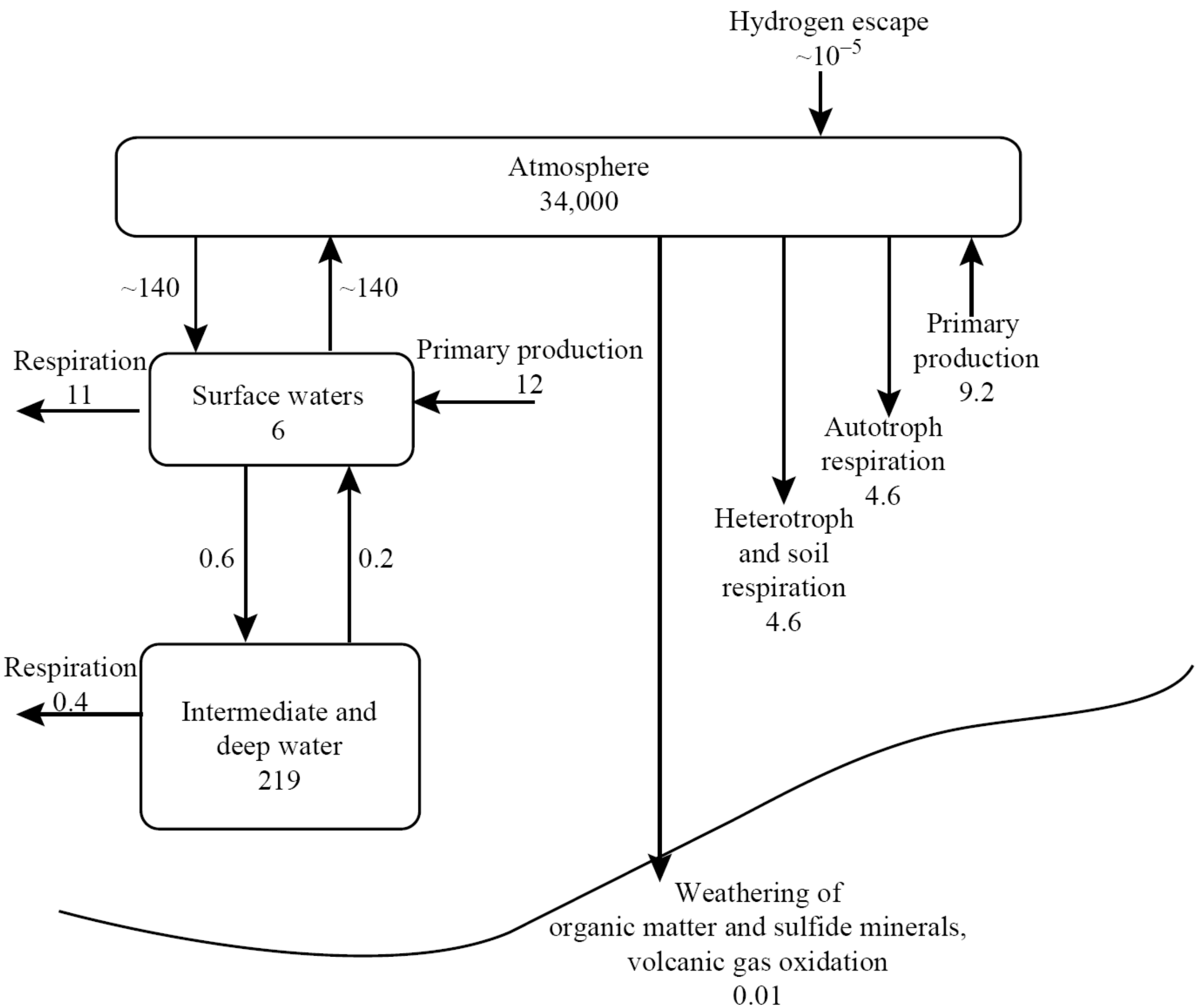


Figure 22 Global cycle showing key fluxes at Tg(S) yr^{-1}. The formula for the most significant components are marked against each flux.

Ciclo do Oxigênio

Atmospheric O_2 throughout Earth's History 527



igure 7 Global budget for molecular oxygen, including gas and dissolved O_2 reservoirs (sources Keeling *et al.*, 1993; Bender *et al.*, 1994a,b).

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Bibliografia Específica

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