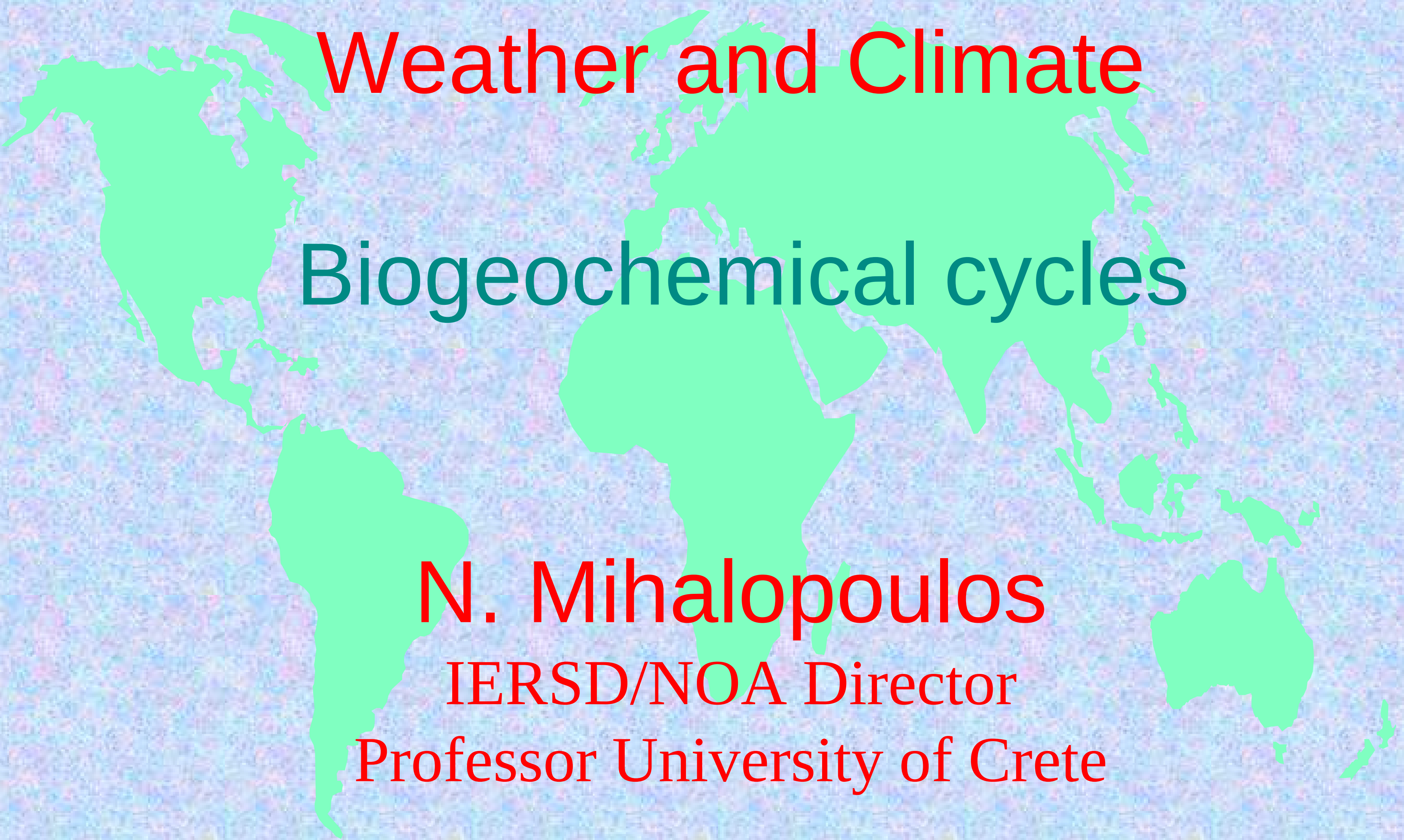


EARTH SYSTEM SCIENCE:
Weather and Climate

Biogeochemical cycles

N. Mihalopoulos
IERSD/NOA Director
Professor University of Crete

N cycle:
Galloway IGAC conference, Crete 2002;
Galloway et al., *Biogeochemistry*, 2004;

Fe cycle:
Jickells et al., *Science* 2005.

Reactive N vs *Unreactive N*

- Unreactive N is N_2 (78% of earth's atmosphere)
- Reactive N (Nr) includes all biologically, chemically and physically active N compounds in the atmosphere and biosphere of the Earth
  - e.g., ammonia, organic N, nitric oxides, nitrous oxide, nitrates
- Nitrogen controls productivity of most natural ecosystems
- N_2 is converted to Nr by nature primarily via:
  - Biological Nitrogen Fixation (N_2--> organic N)
- N_2 is converted to Nr by humans via:
  - Fossil fuel combustion (N_2 ----> NO_x)
  - Haber Bosch process (N_2 ----> NH_3)
  - Legume cultivation (N_2 ----> organic N; BNF)

Nitrogen Cycle

- ***Forms of Nr in the atmosphere:***

Inorganic: *(NO, NO_2, N_2O, HNO_3, NO_3^-, NO_3, N_2O_5)*

NOx = NO + NO_2

Organic N:

Amines, Aminoacids, Hydrazines, Nitramines, (R-N Type)

Alkyl nitrites (RONO), alkyl nitrates (RONO2), Alkylperoxynitrates (ROONO2), Peroxyacylnitrates (RC(O)OONO$_2$=PAN).

***NOy*= HNO_3 + NO_3^- + PAN + NO_3 + N_2O_5 +……**

From 1860 to 1995

Grain Production

Protein sources

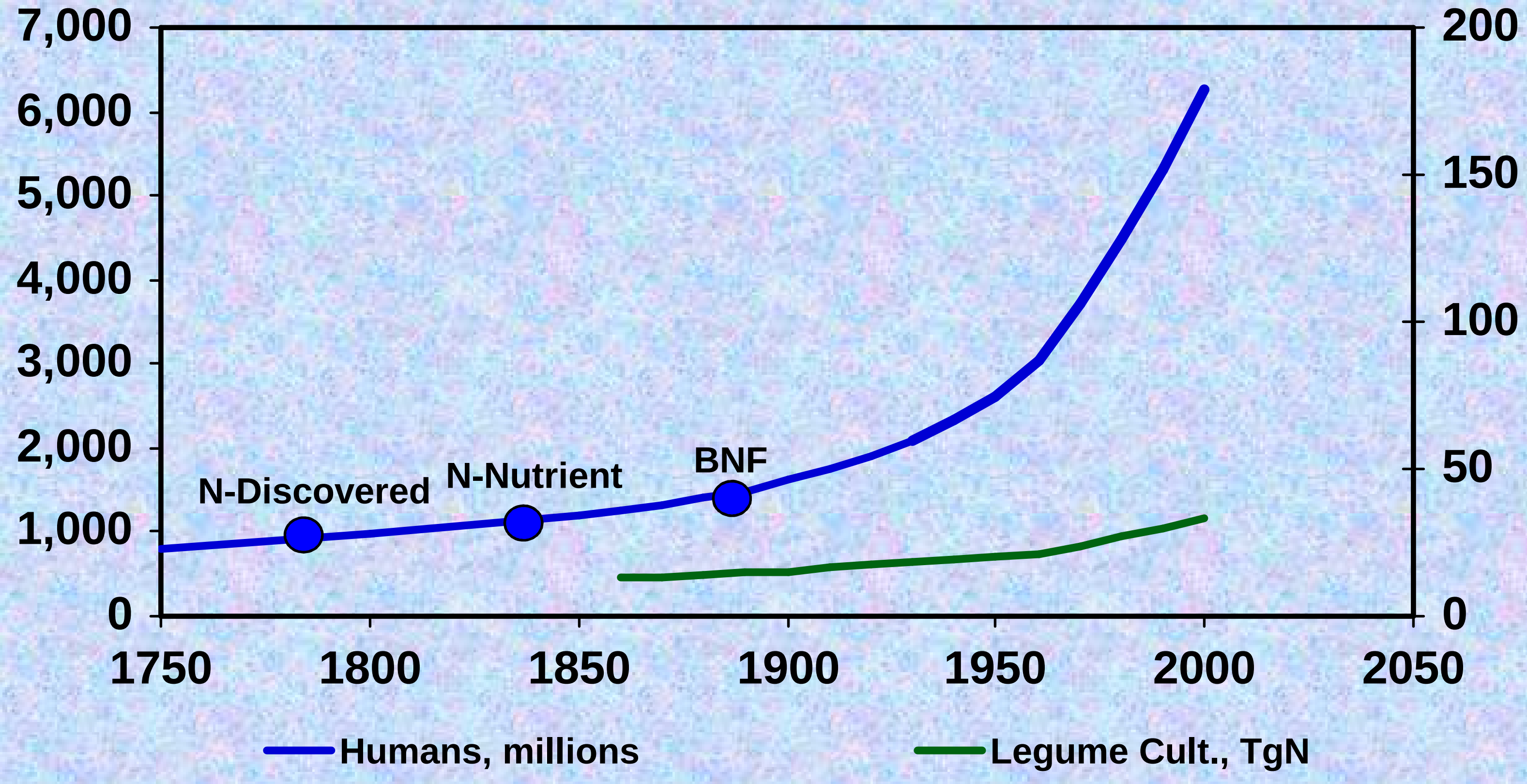
Meat Production

N_r is a byproduct

Energy Production

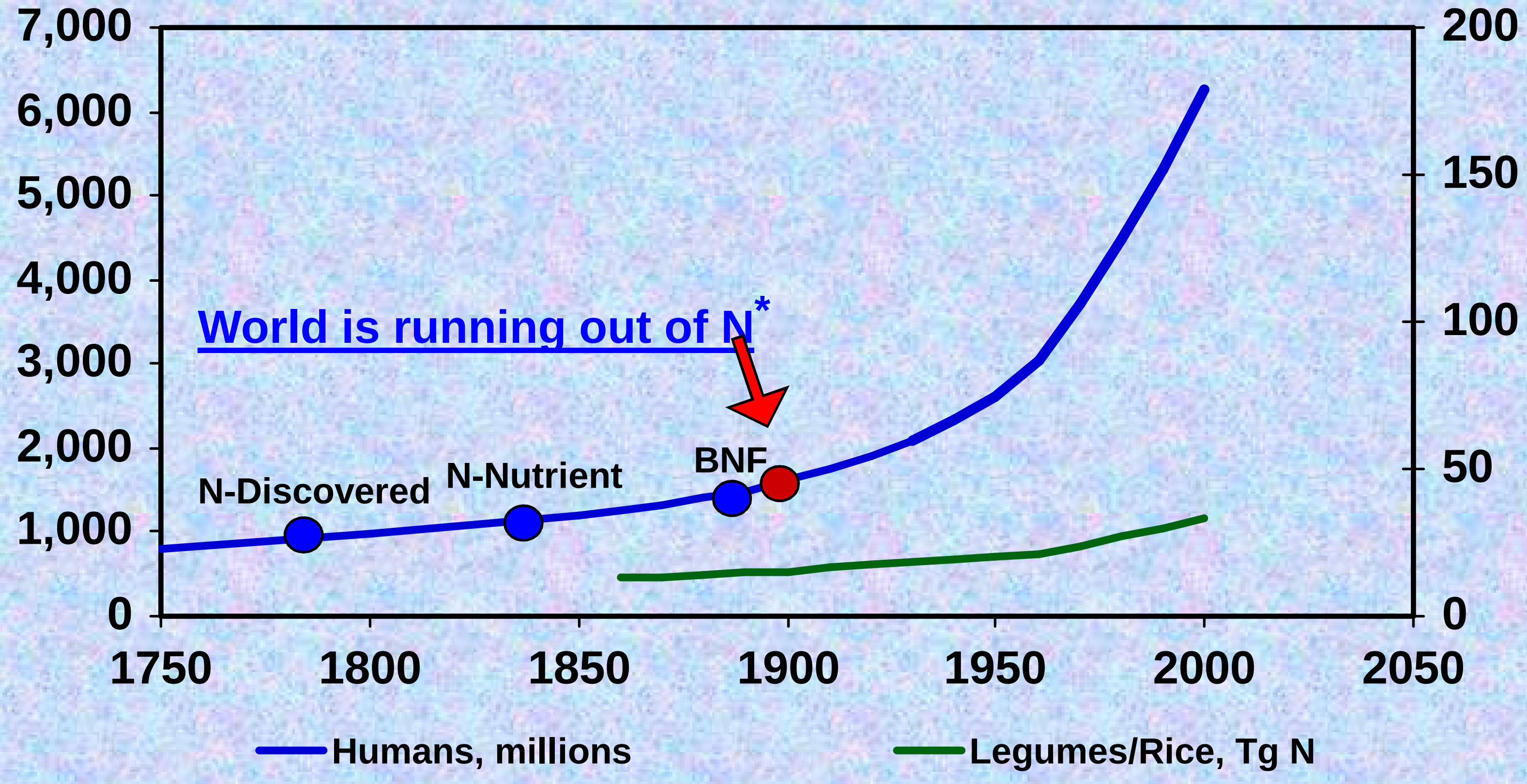
The History of Nitrogen

--Nr Creation: Legumes--



The History of Nitrogen

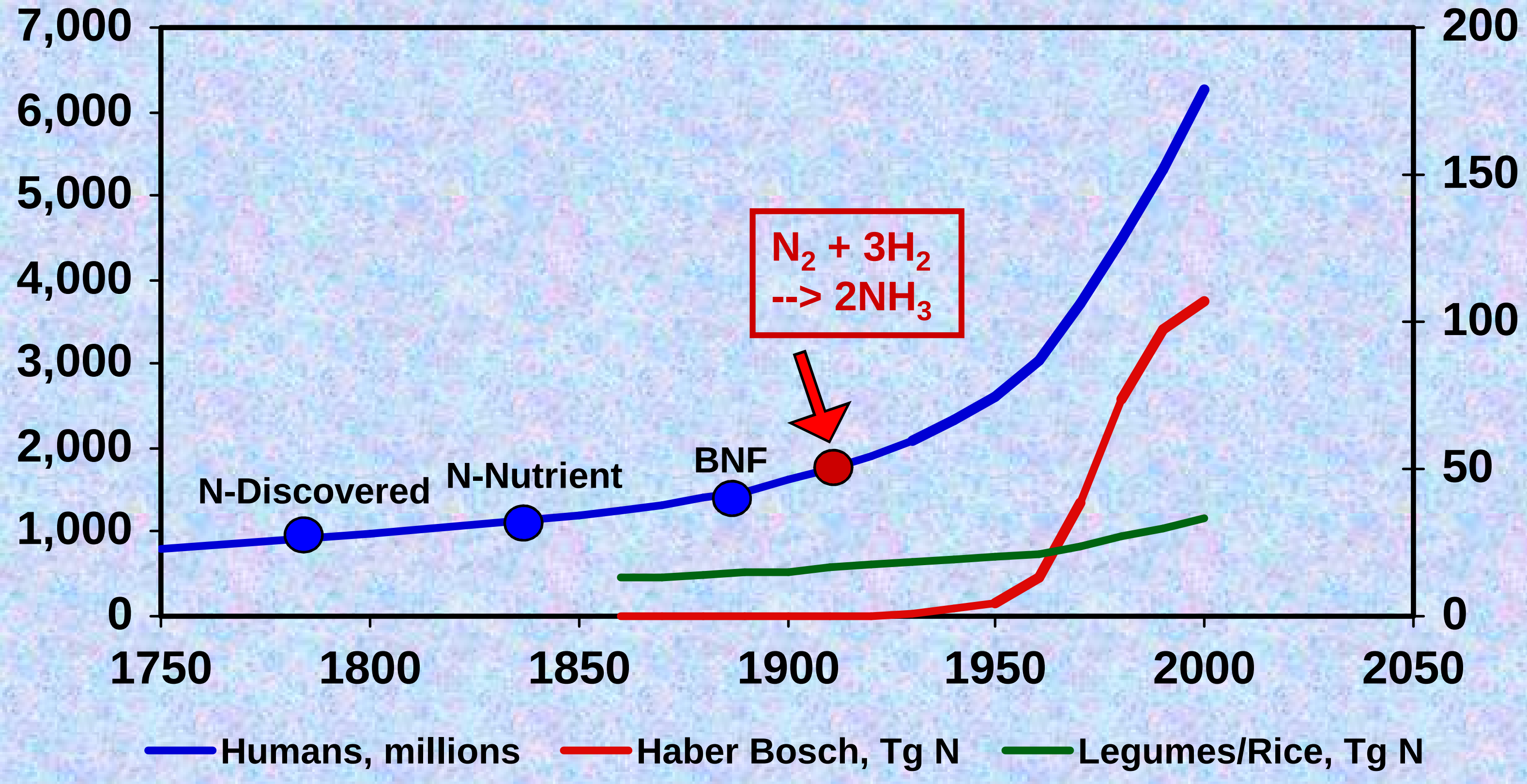
--N_r Shortages--



*1898, Sir William Crookes, president of the British Association for the Advancement of Science

The History of Nitrogen

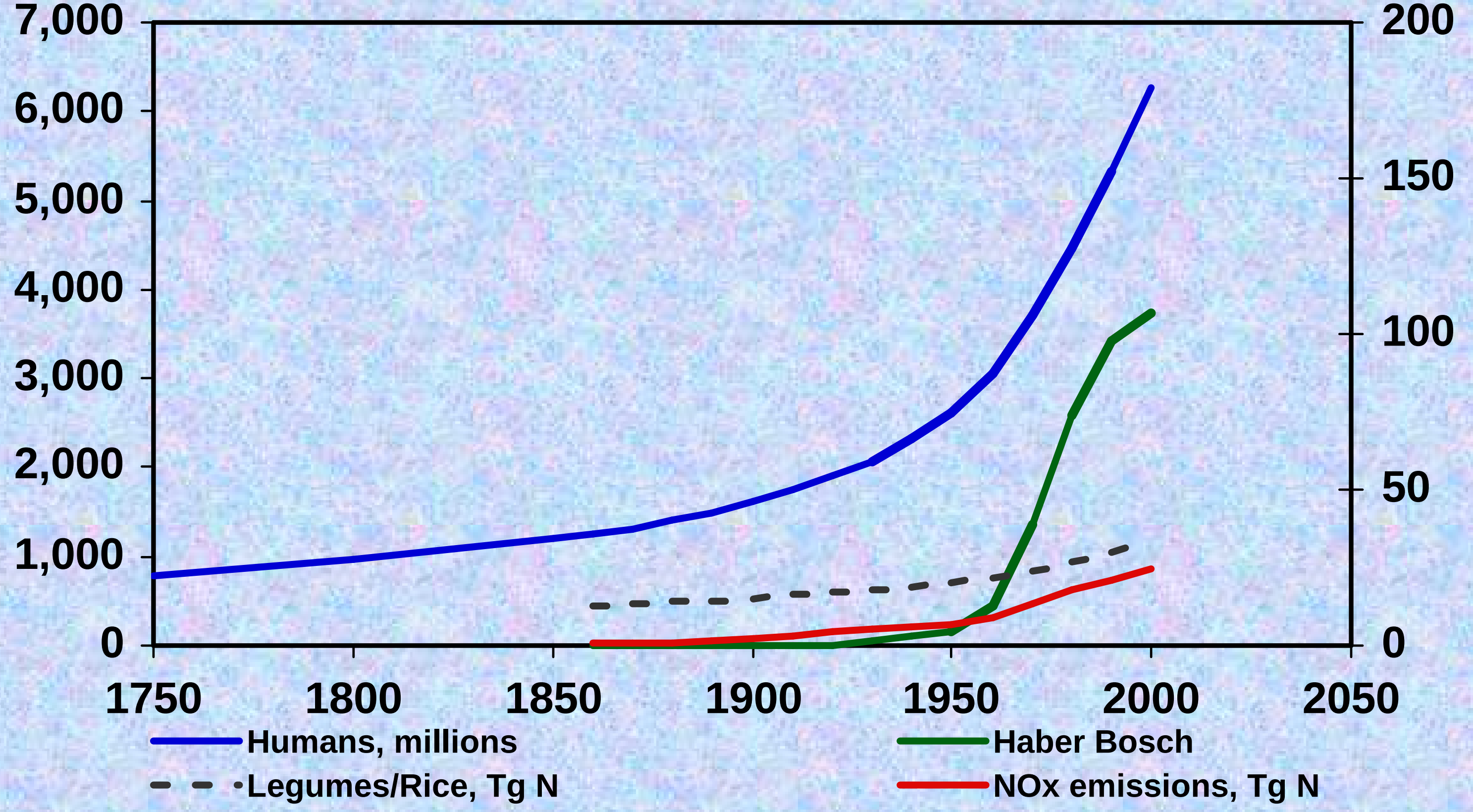
--N_r Creation, Haber Bosch!--



15 Tg N does not equal 130 Tg N

The History of Nitrogen

--N_r Creation, Fossil Fuel Combustion--



BNF sources (today)	**Source estimate**
Seed legumes	10 (8–12 Tg Nyr^{-1})
Leguminous cover crops (forages and green manures such as clover, alfalfa, vetches)	12 (10–14 Tg Nyr^{-1})
Wet rice and sugar cane fields	5–9 Tg Nyr^{-1})
Non-Rhizobium N-species	4 (2–6 Tg Nyr^{-1})
Total **BNF in 1860**	**30-34** **15**

•The conversion of N_2 to Nr requires energy to break the N:N triple bond.

•In the natural world, physical (lightning) and biological (BNF) processes provide this energy.

•Nr creation by lightning is highest in tropical terrestrial
regions where convective activity is the largest.
BNF rates in terrestrial systems are also generally highest in tropical regions.

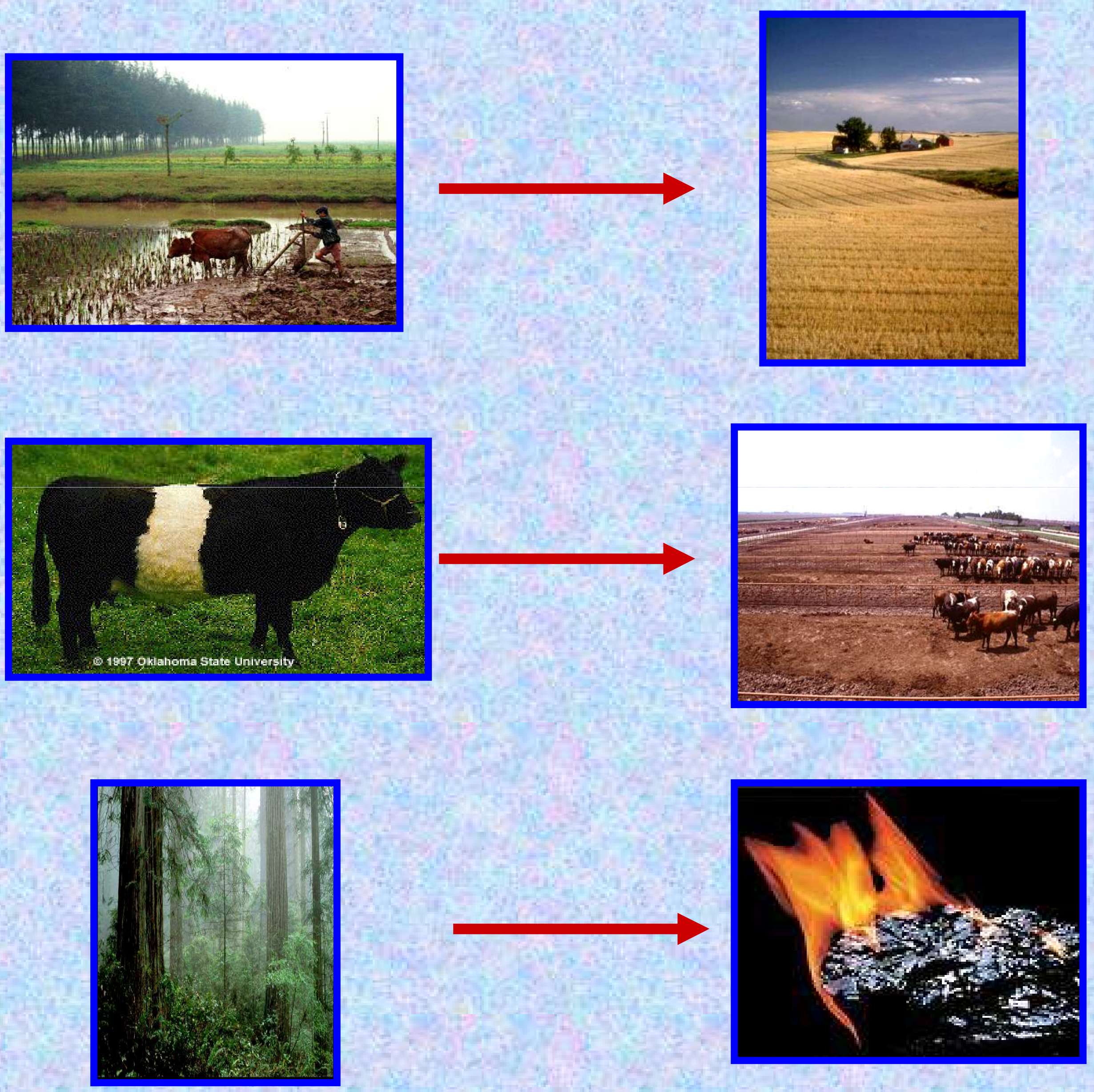
- Relative to cultivation-induced BNF, about three times as much Nr was created with the Haber-Bosch process.
- In 1995, 100 Tg N of NH3 was created. Of this amount, about 86% was used to make fertilizers and the rest was dispersed to the environment during processing or used in the manufacture of refrigerants, explosives, plastics, rocket fuels etc.
- The increase in energy production by fossil fuels resulted in increased NOx emissions from 0.3 Tg N in 1860 to 24.5 Tg Nin the early 1990s.

•Summary

In the early 1990s, Nr creation by anthropogenic activities was 156 Tg N, a factor of 10 increase over 1860, contrasted to only a factor of 4.5 increase in global population.

Food production accounted for 77%, energy production accounted for 16%, and production for industrial uses accounted for 9%.

From 1860 to 1995



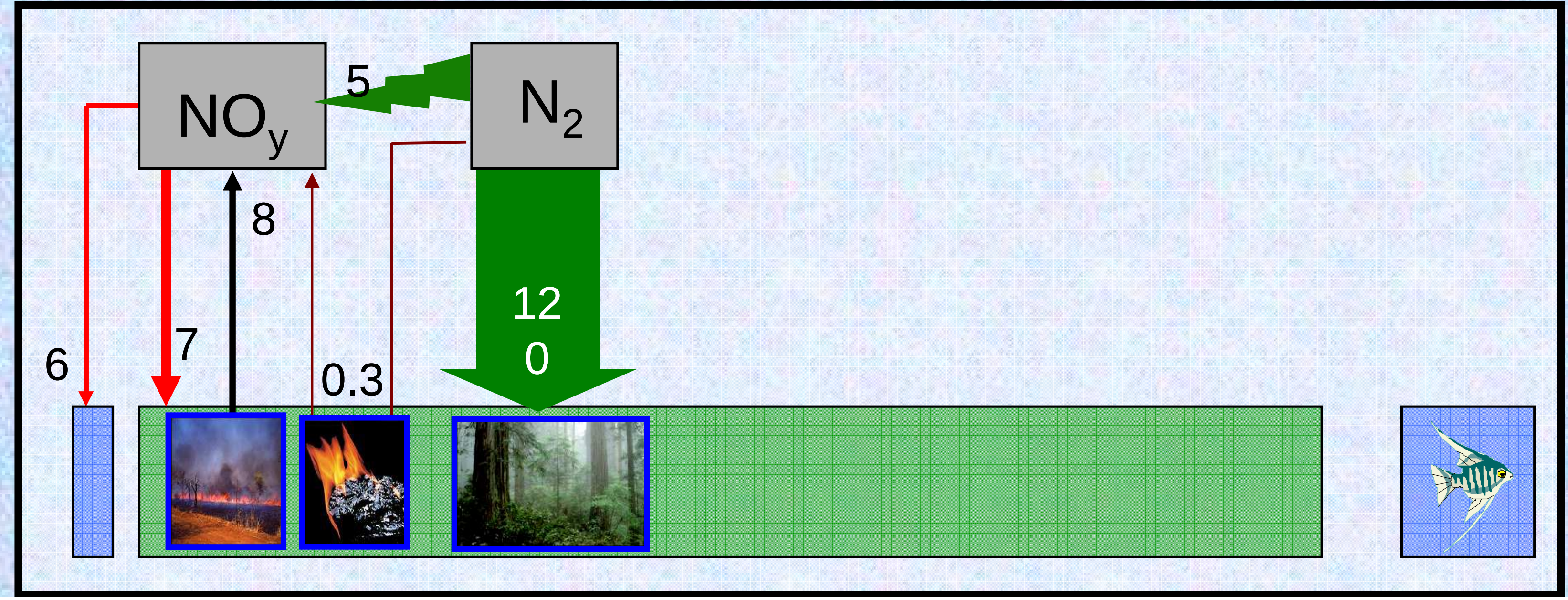
Grain Production

Meat Production

Energy Production

The Global Nitrogen Budget in 1860 and mid-1990s, TgN/yr

1860



The Global Nitrogen Budget in 1860 and mid-1990s, TgN/yr

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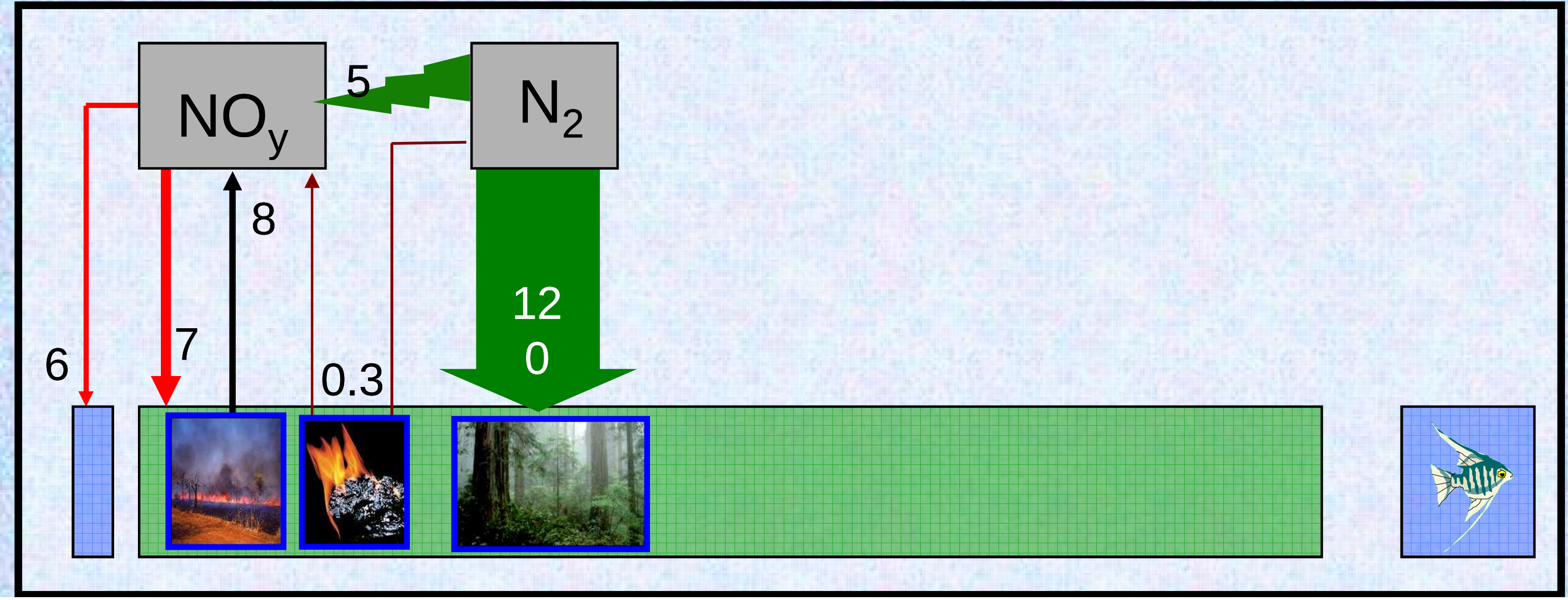
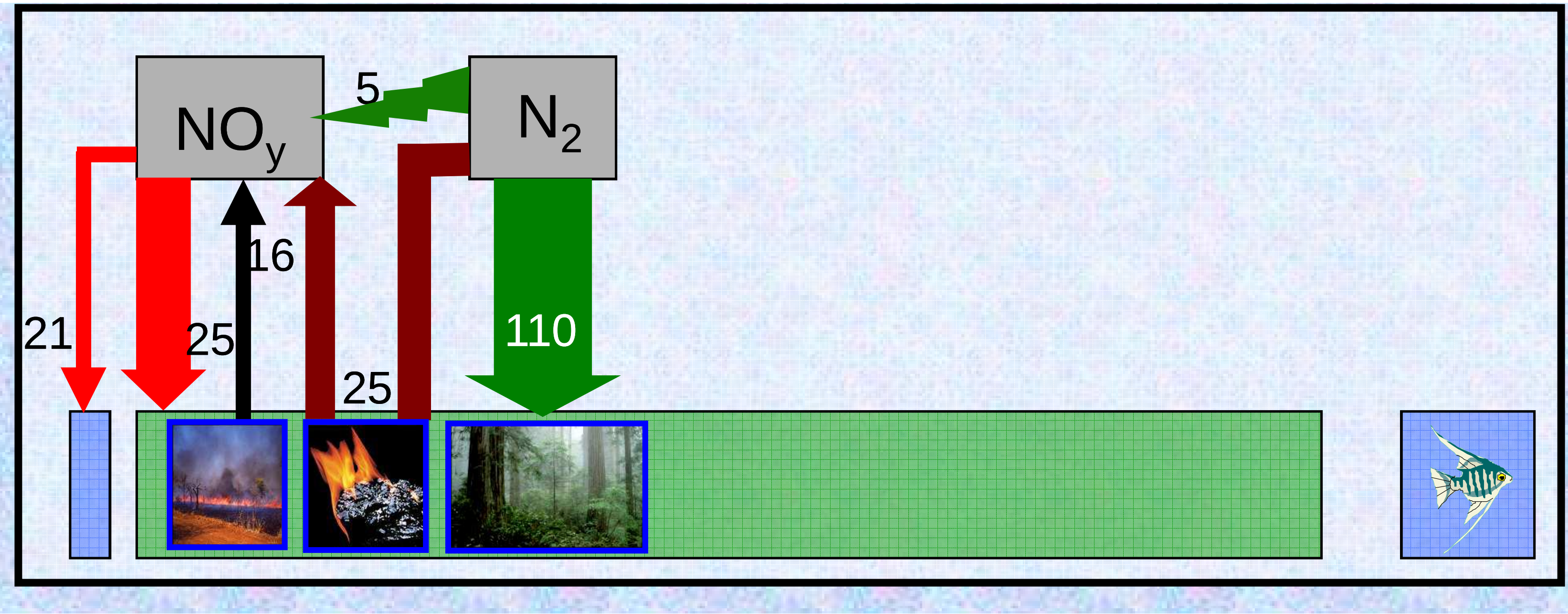
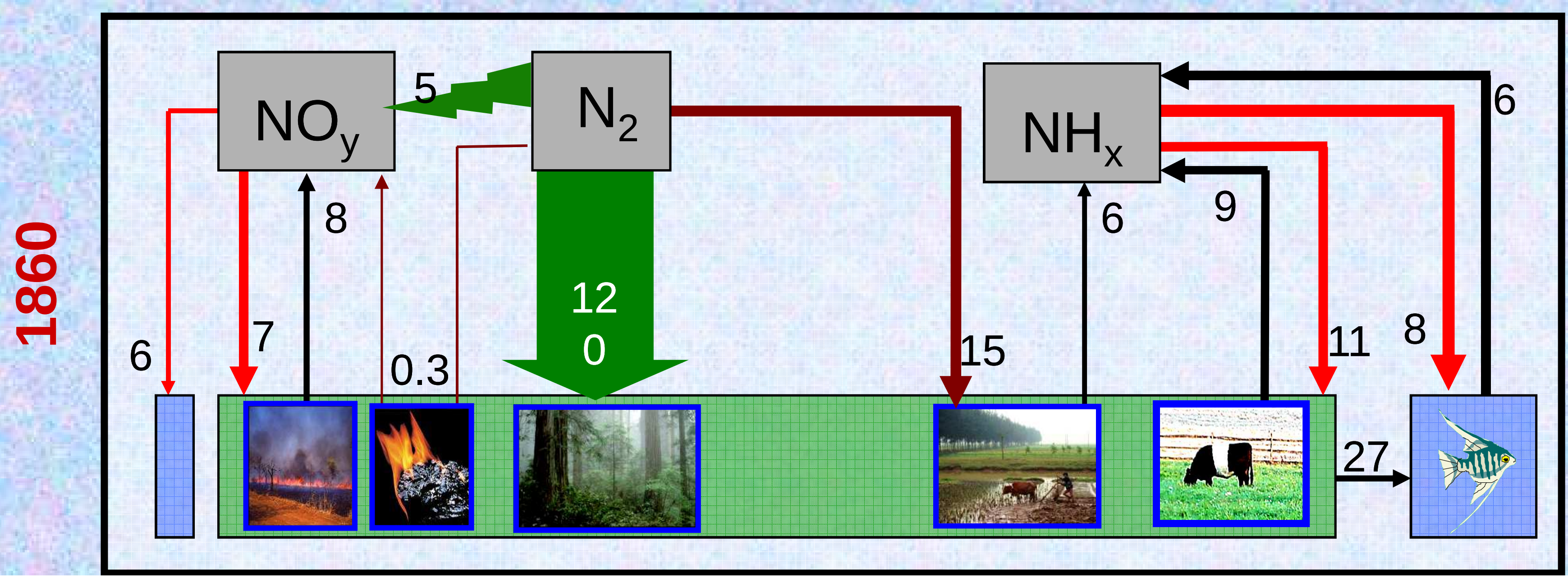
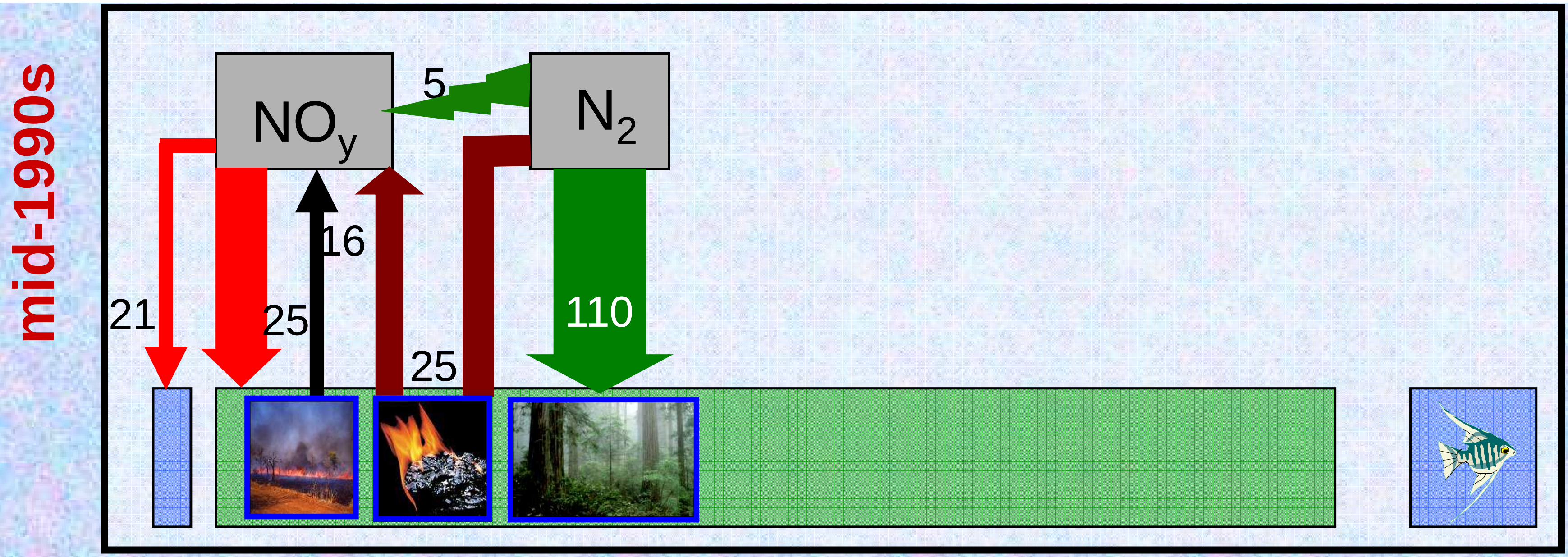


mid-1990s



The Global Nitrogen Budget in 1860 and mid-1990s, TgN/yr





The Global Nitrogen Budget in 1860 and mid-1990s, TgN/yr

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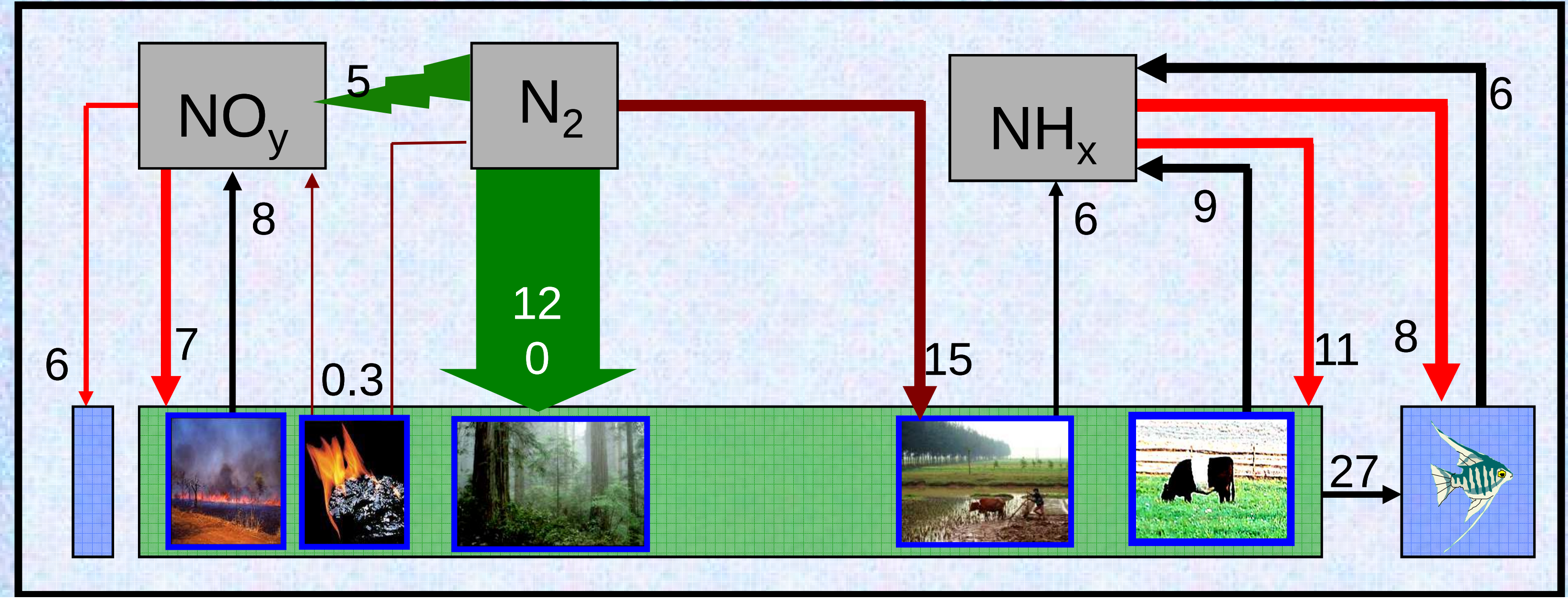
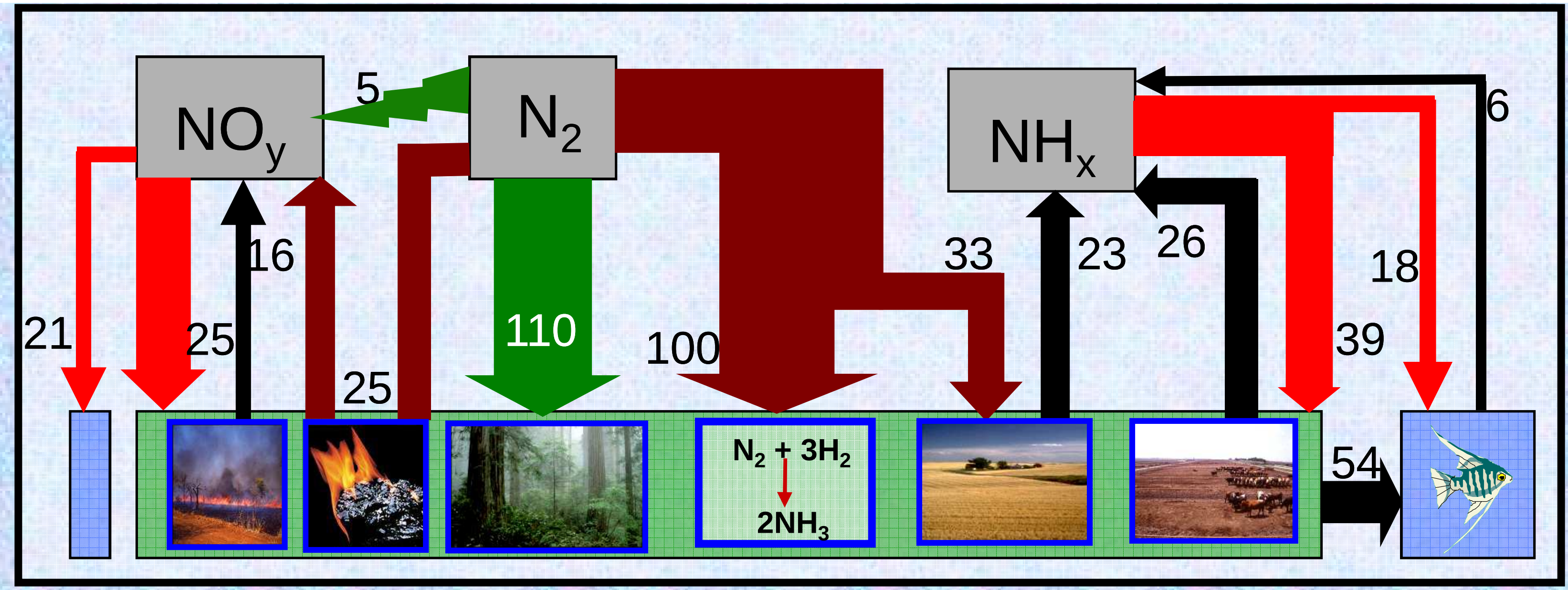
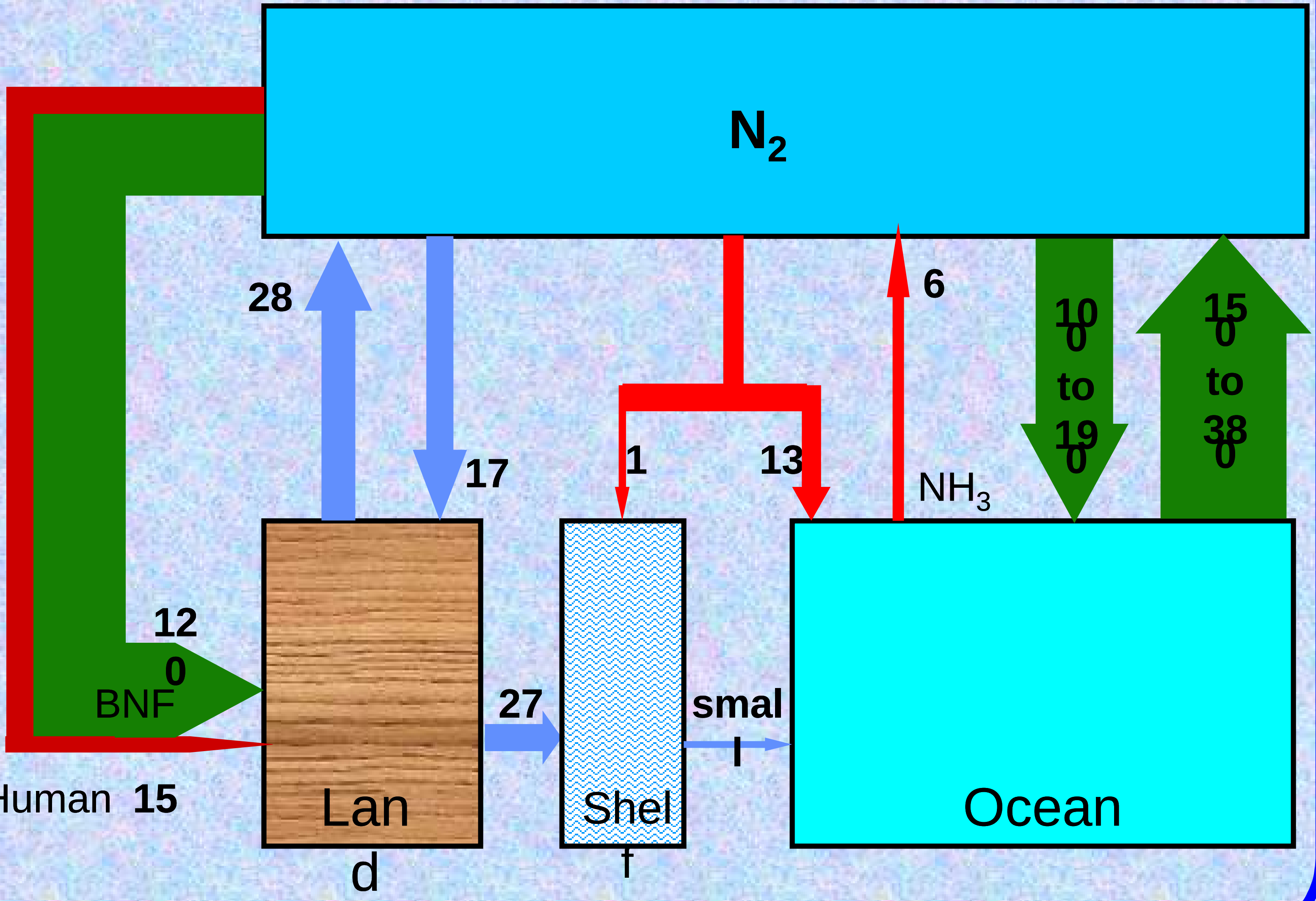


mid-1990s



1860: Land-Atmosphere-Ocean Connections, Tg N/yr



N_2

28

17

1

13

6

NH_3

100 to 190

150 to 380

120

BNF

Human 15

27

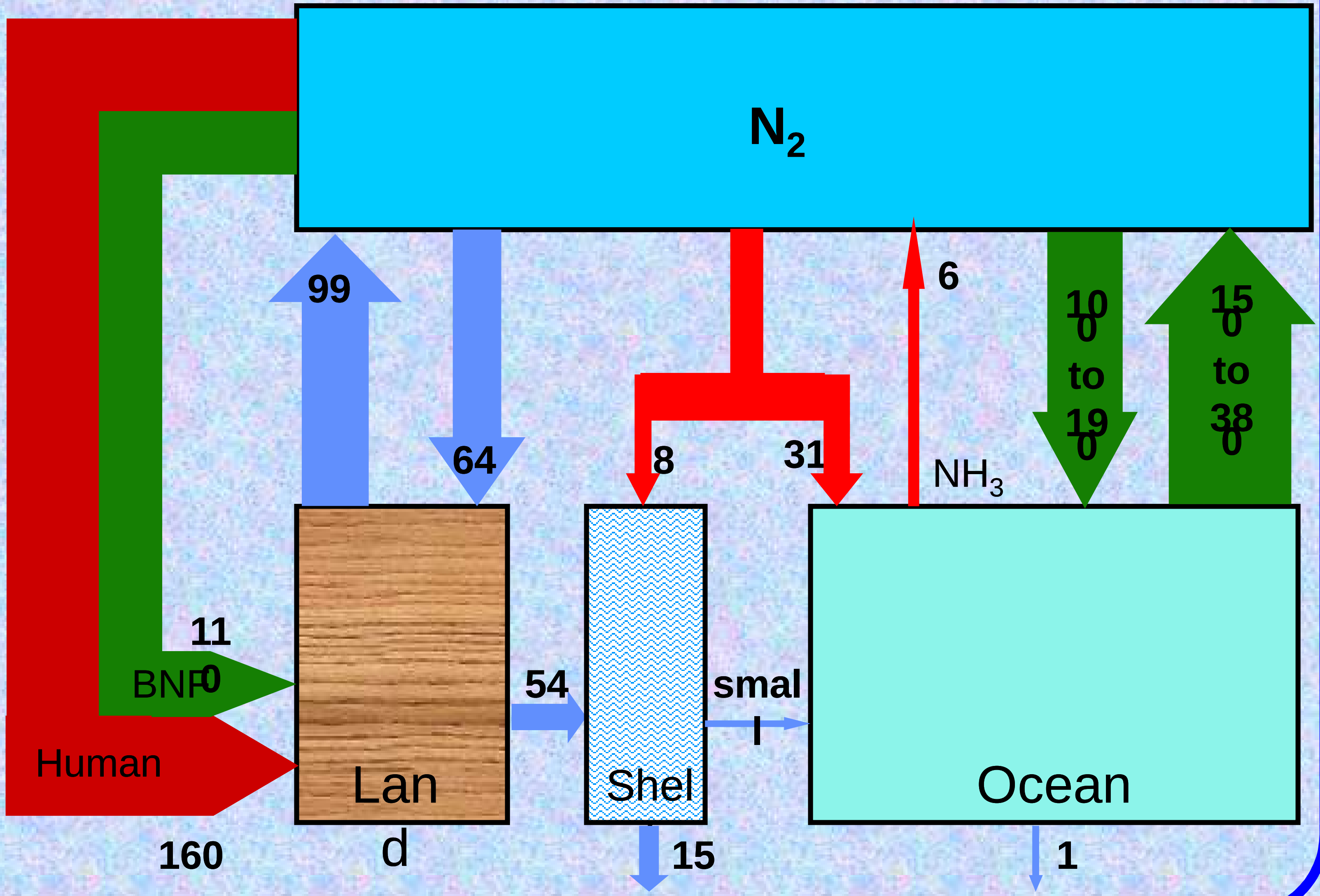
small

Land

Shelf

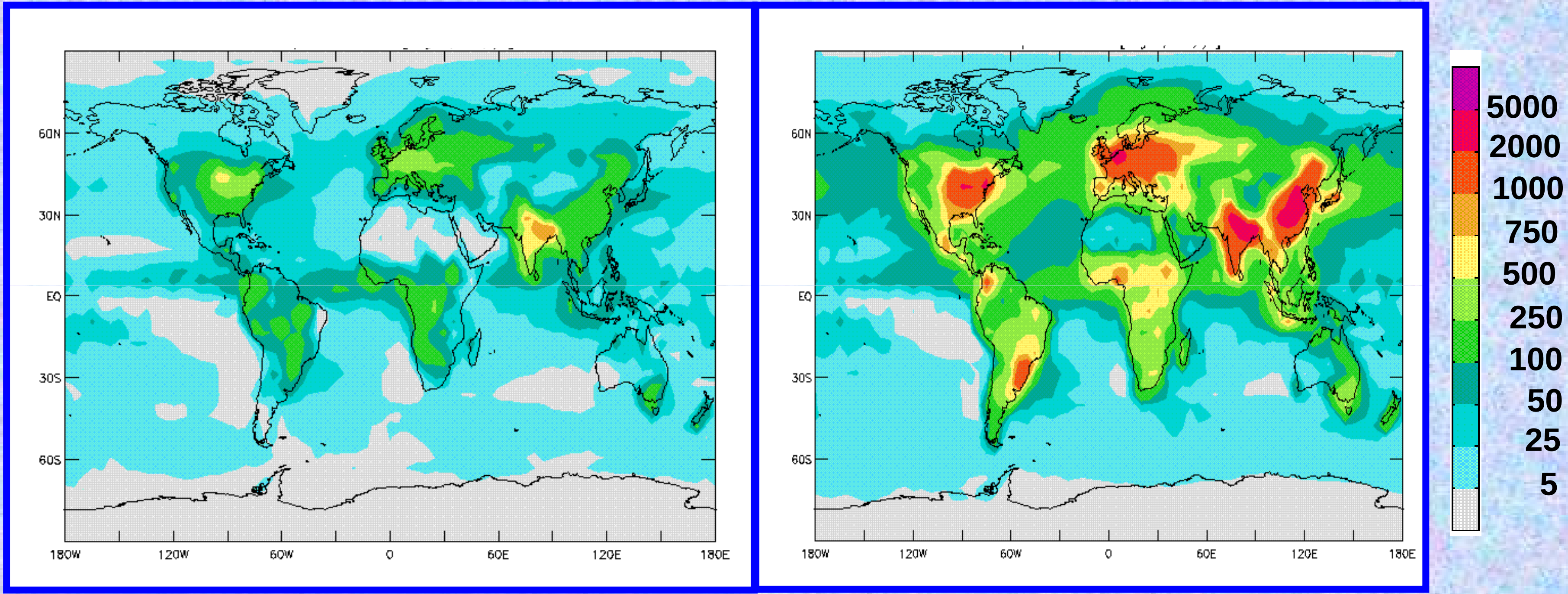
Ocean

1993: Land-Atmosphere-Ocean Connections, Tg N/yr



Nitrogen Deposition
Past and Present

mg N/m^2/yr



1860

1993

Frank Dentener, 2002

Nr and Agricultural Ecosystems

- Haber-Bosch has facilitated agricultural intensification
- 40% of world's population is alive because of it
- An additional 3 billion people by 2050 will be sustained by it
- But, all N that enters agroecosystem is released to the environment.

Nr and the Atmosphere

- NO_x emissions contribute to O_3 and OH, which define the oxidizing capacity of the atmosphere
- NO_x emissions are responsible for tens of thousands of excess-deaths per year in the United States
- O_3 and N_2O contribute to atmospheric warming
- N_2O emissions contribute to stratospheric O_3 depletion

Nr and Terrestrial Ecosystems

- N is the limiting nutrient in most temperate and polar ecosystems
- Nr deposition increases and then decreases forest and grassland productivity
- Nr additions probably decrease biodiversity across the entire range of deposition (e.g. Aber et al., 1995).

Nr and Freshwater Ecosystems

- Surface water acidification
  - Tens of thousands of lakes and streams
  - Biodiversity losses

- As reductions in SO_2 emissions continue, Nr deposition becomes more important.

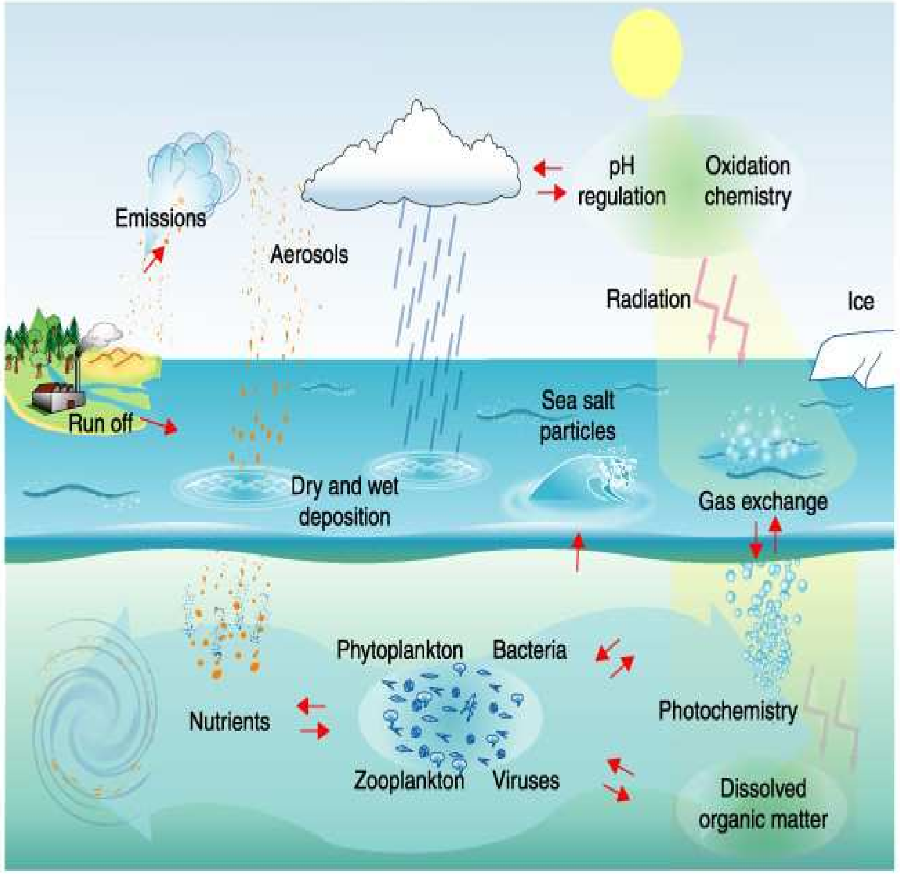
Nr and Coastal Ecosystems

Contributions of N deposition to "new" N inputs in estuarine and coastal waters (Paerl, 2000)

Coastal Dinoflagellate blooms resulting from nitrogen over-enrichment

Pamlico Sound, NC	**~30%**	**Paerl and Fogel 1994**
North Sea	**~30%**	**GESAMP 1989**
Waquoit Bay, MA	**29%**	**Valiela et al. 1996**
Narragansett Bay	**12%**	**Nixon 1995**
Long Island Sound	**20%**	**L. I. Sound Study 1996**
New York Bight	**38%**	**Valigura et al. 1996**
Barnegat Bay, NJ	**40%**	**Moser et al. 1999**
Rhode River, MD	**40%**	**Correll and Ford 1982**
Sarasota/Tampa Bay, FL	**30%**	**Sarasota Bay NEP 1996**

Nr and Open Ocean Ecosystems



◆ Atmospheric deposition is a more important Nr source than riverine injection.

◆ Atmospheric Nr inputs to open ocean have increased 3-fold since 1860, and will double by 2050 (Galloway et al. 2002).

◆ Episodic Nr deposition to mid-ocean gyres has the potential to have significant effect on primary production (SOLAS, 2002; Jickells, 2002).

THE BIG PICTURE

- Food and energy production results in creation of ~160 Tg N/yr of new Nr, most of which is released to the environment.
- We know where some of it goes and we generally know what it does when it gets there.

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  - ***How to feed and fuel the global population without releasing excess N to environmental reservoirs.***

THE BIG PICTURE

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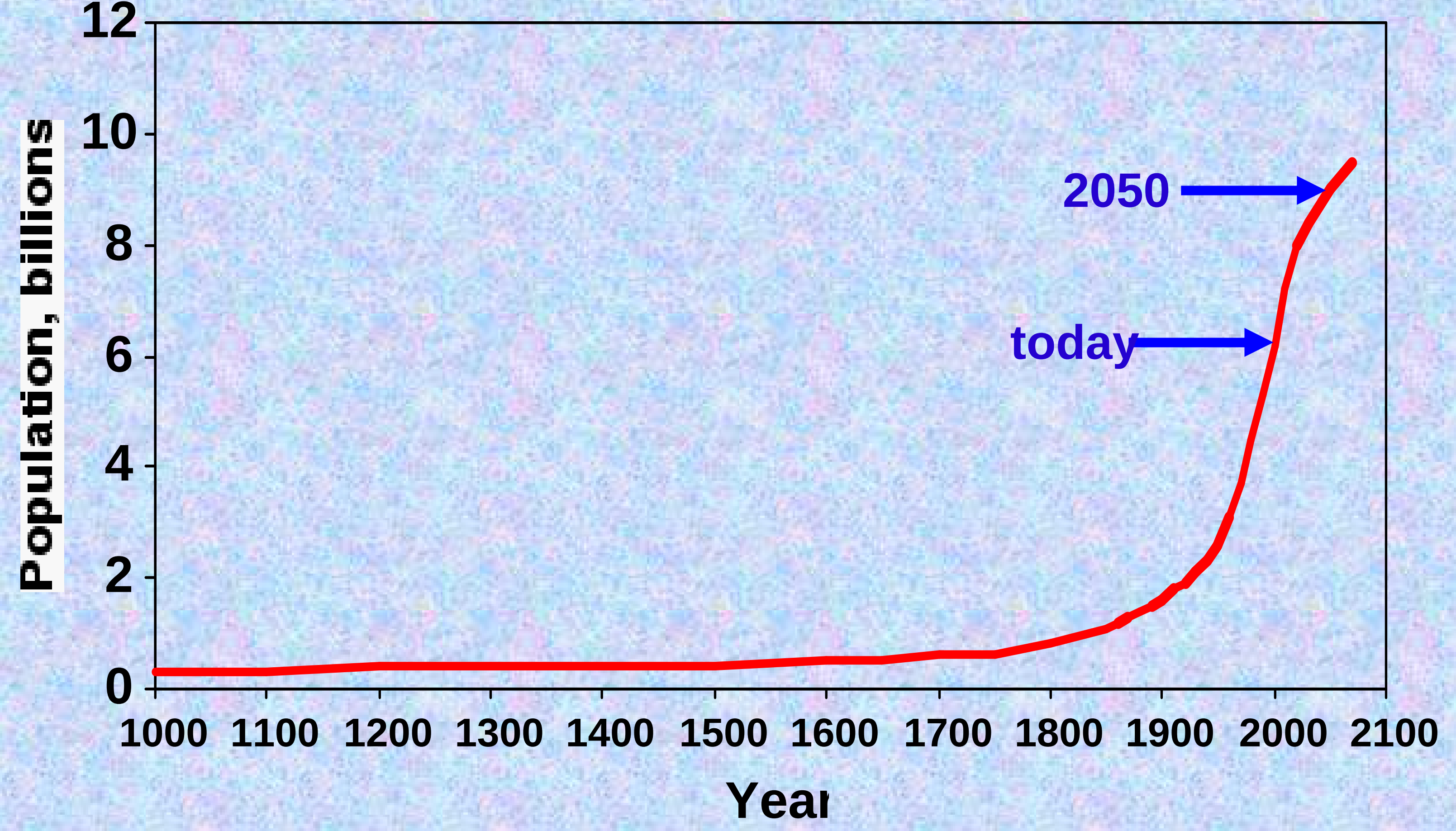
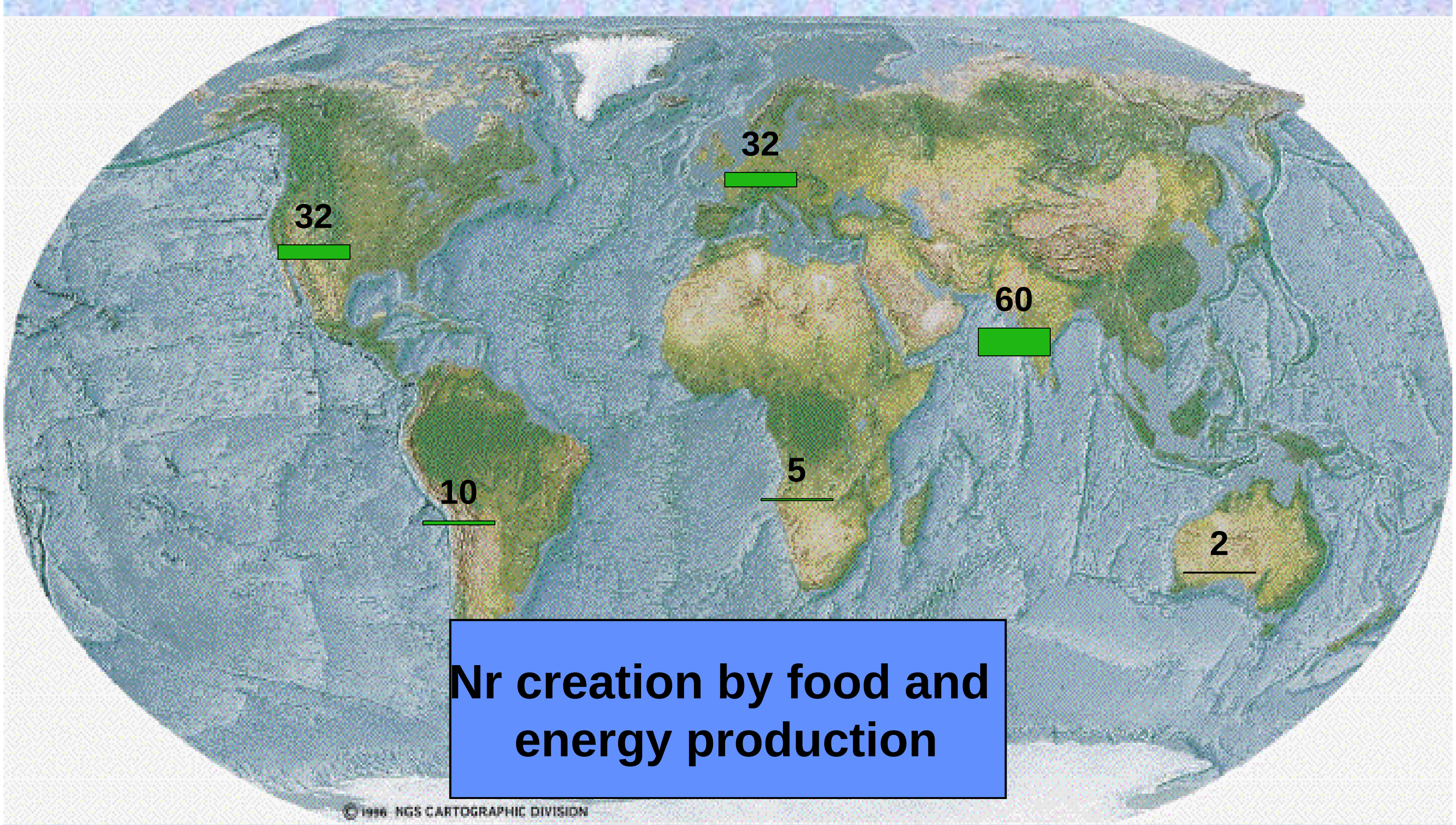
- We know where some of it goes and we generally know what it does when it gets there.
- We do not know:
  - *How much is stored in ecosystems vs. how much is denitrified to* N_2*.*
  - *How to feed and fuel the global population without releasing excess N to environmental reservoirs.*
- **We know another thing--Nr creation will increase in the future, as will Nr accumulation and an intensification of the N Cascade.**

Nr Creation Rates by Food and Energy Production in 2050



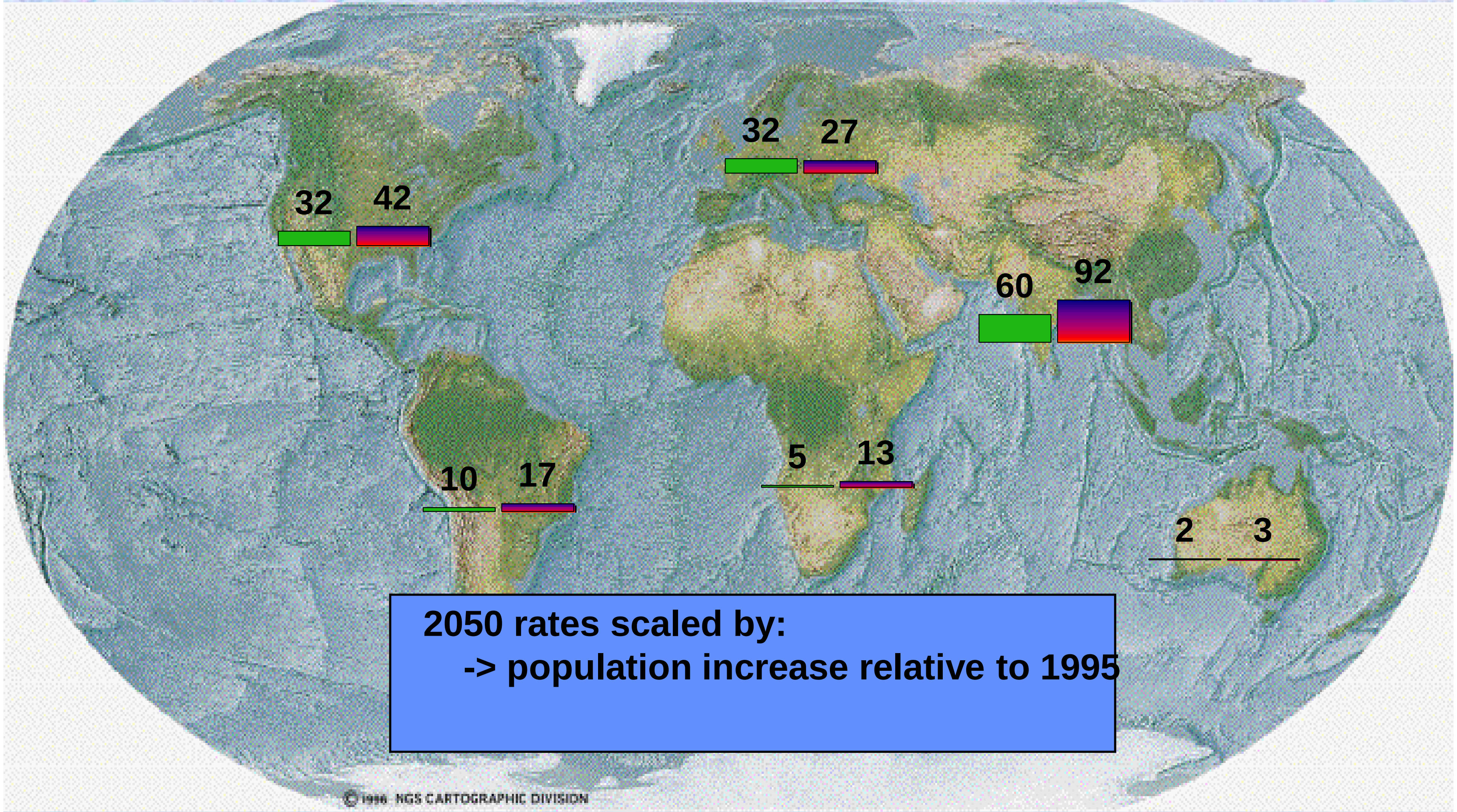
Nr Creation Rates
1995
TgN/yr



Nr creation by food and energy production

Nr Creation Rates
1995 (left) and 2050 (right)

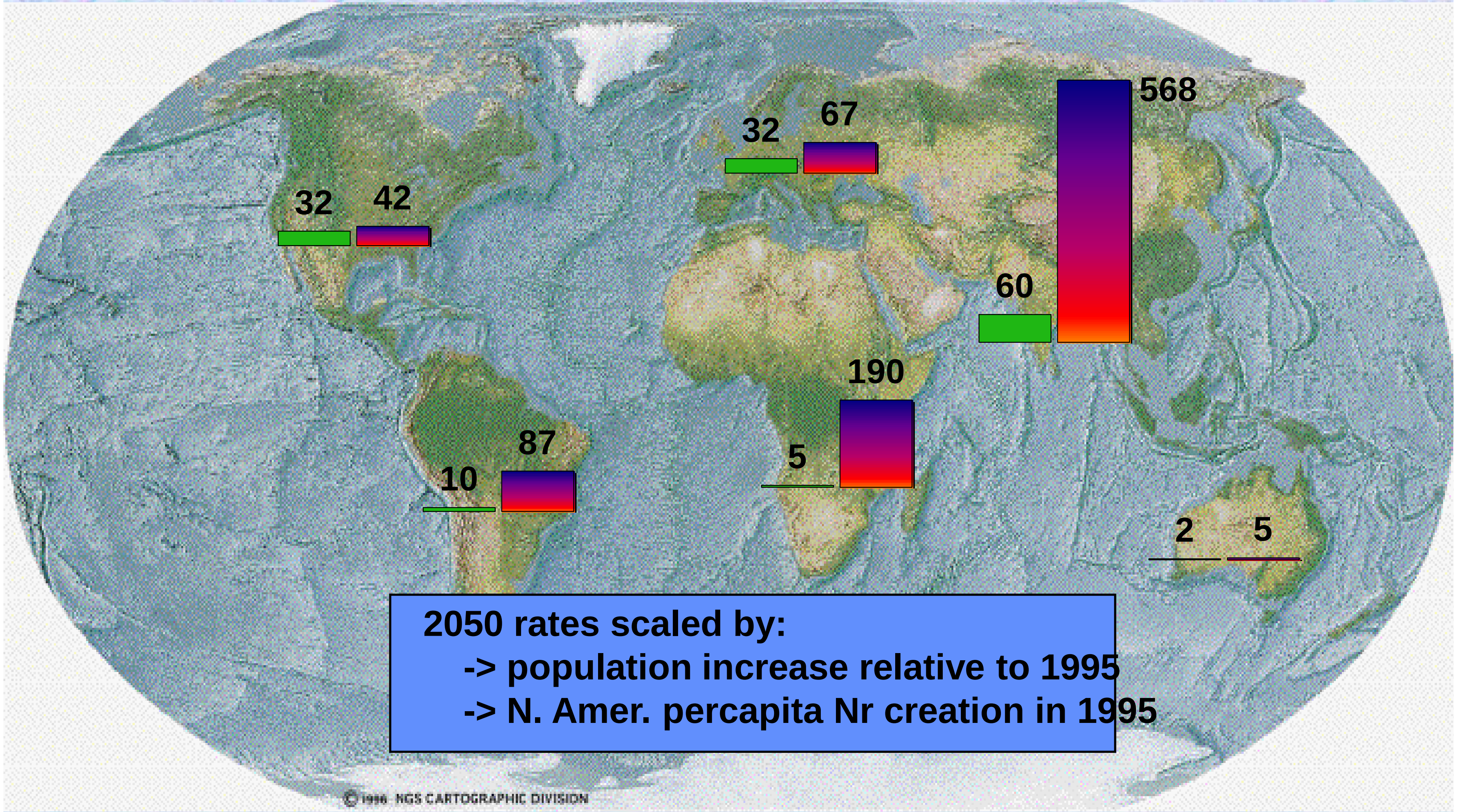
TgN/yr



2050 rates scaled by:
-> population increase relative to 1995

Nr Creation Rates
1995 (left) and 2050 (right)

TgN/yr

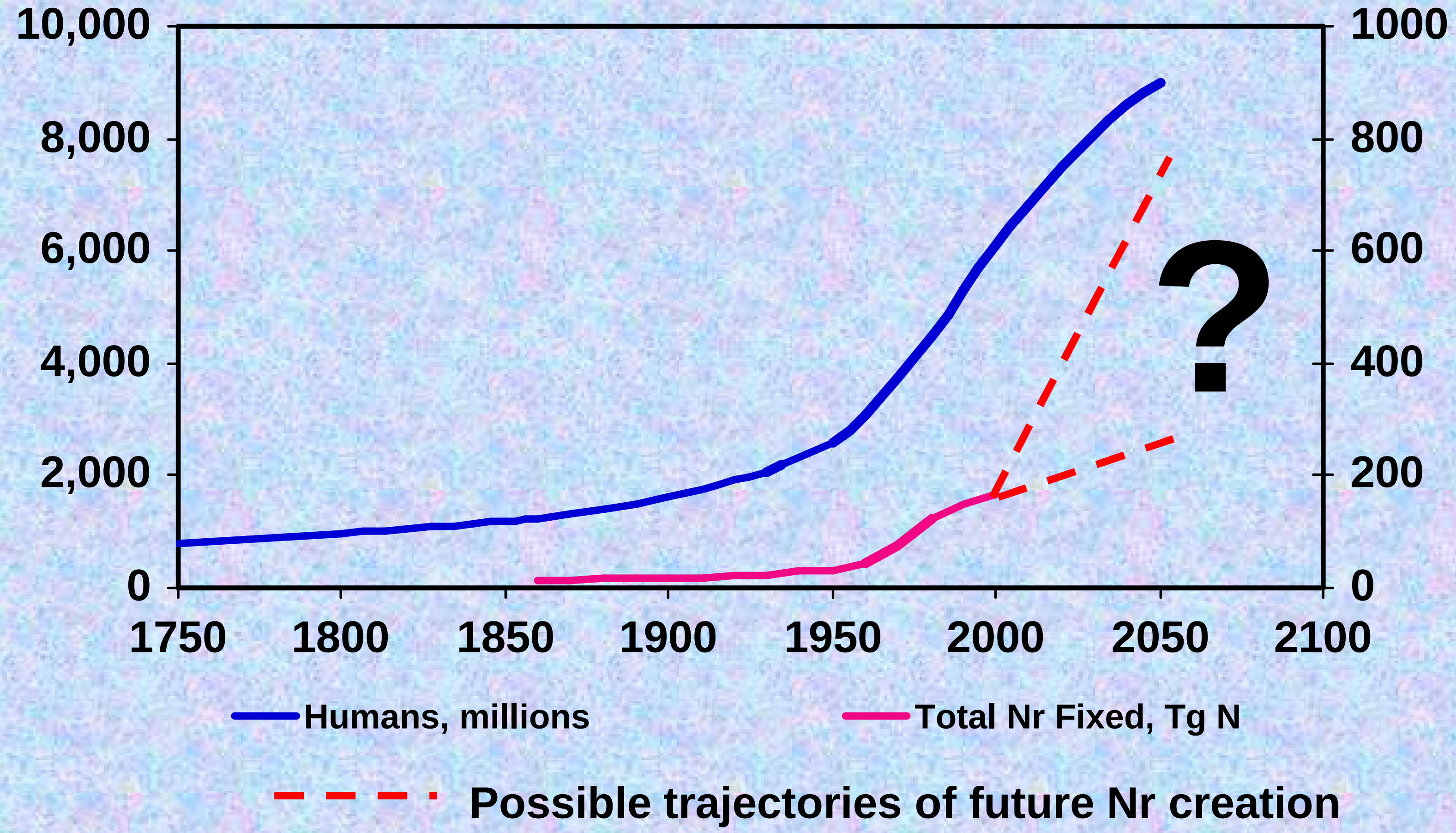


2050 rates scaled by:

- **-> population increase relative to 1995**
- **-> N. Amer. percapita Nr creation in 1995**

The Future of Nitrogen

--N_r Creation, Total--



The Challenge to all Parties

Maximize food and energy production while maintaining environmental and human health!

Fe origin ?

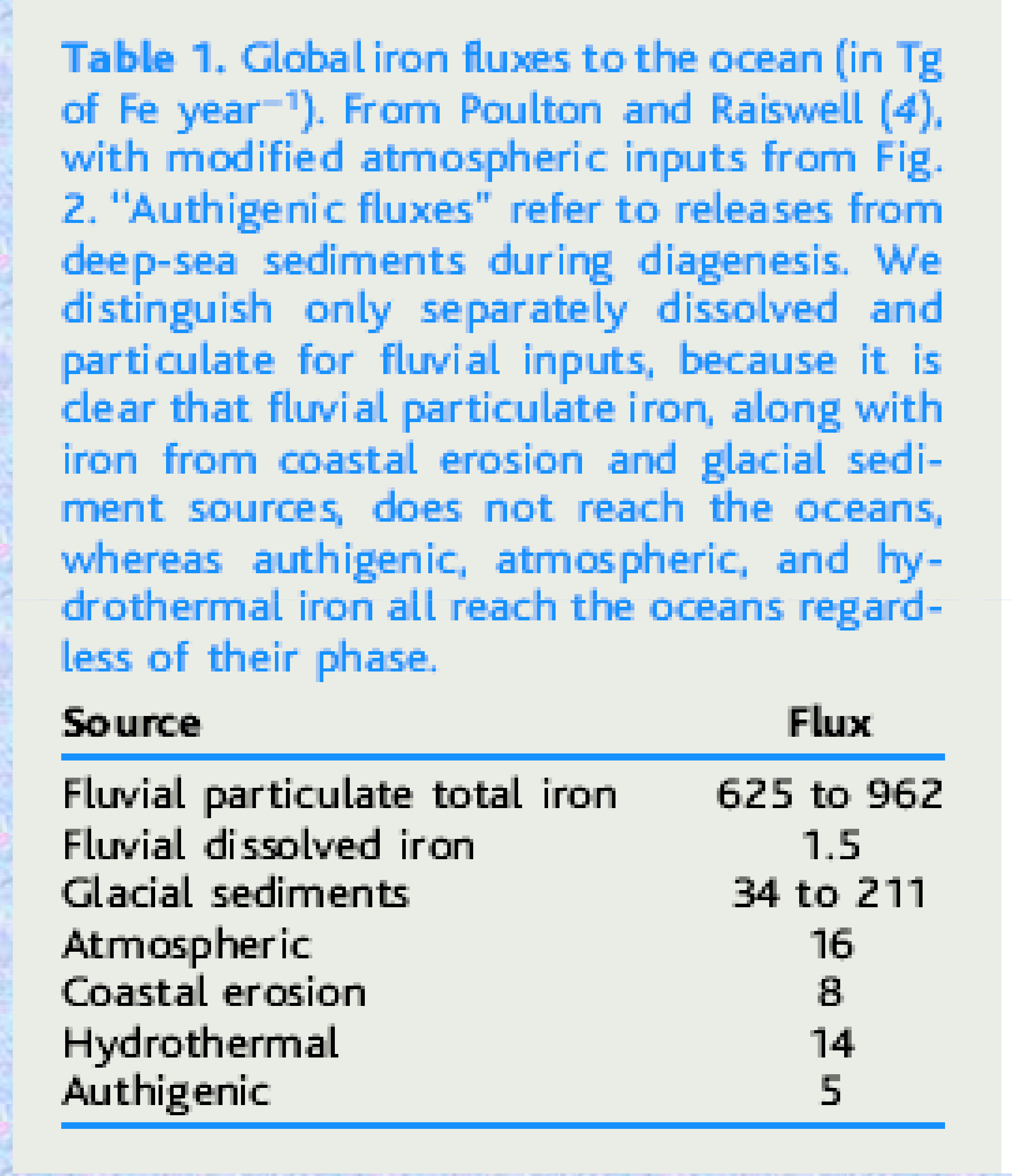


Table 1. Global iron fluxes to the ocean (in Tg of Fe $year^{-1}$). From Poulton and Raiswell (4), with modified atmospheric inputs from Fig. 2. "Authigenic fluxes" refer to releases from deep-sea sediments during diagenesis. We distinguish only separately dissolved and particulate for fluvial inputs, because it is clear that fluvial particulate iron, along with iron from coastal erosion and glacial sediment sources, does not reach the oceans, whereas authigenic, atmospheric, and hydrothermal iron all reach the oceans regardless of their phase.

Source	Flux
Fluvial particulate total iron	625 to 962
Fluvial dissolved iron	1.5
Glacial sediments	34 to 211
Atmospheric	16
Coastal erosion	8
Hydrothermal	14
Authigenic	5

From Jickells et al., 2005

Iron is an essential nutrient for all organisms.

Iron is very insoluble under oxidizing conditions above pH 4.

The main source of iron is rivers. However, fluvial and glacial particulate iron is efficiently trapped in near-coastal areas.

Hence, the dominant external input of iron to the surface of the open ocean is aeolian dust transport, mainly from the great deserts of the world.

In large areas of the world ocean where the concentrations of nutrients are high, chlorophyll is low (HNLC waters; equatorial Pacific and much of the southern oceans).

Martin [1990] hypothesized that primary productivity in HNLC regions was limited by the availability of iron.

Additionally, certain nitrogen fixing organisms
such as trichodesmium have higher iron requirements.

Increased supplies of iron may impact the production of the macronutrient fixed nitrogen and influence productivity in oligotrophic tropical waters.

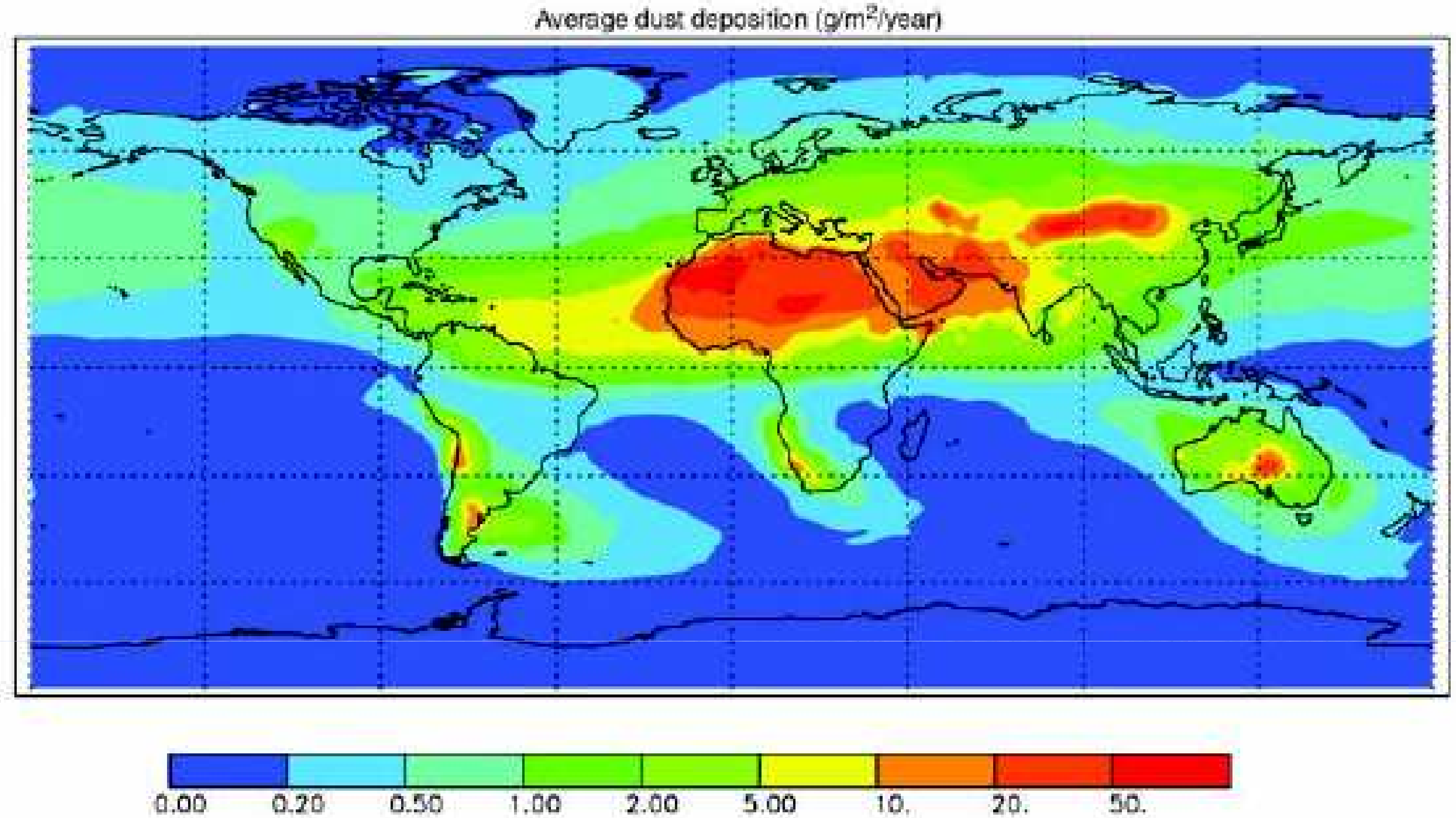


Fig. 2. Dust fluxes to the world oceans based on a composite of three published modeling studies that match satellite optical depth, in situ concentration, and deposition observations (*11*, *14*, *15*). The models have been extensively compared to observations, and although individual models show strengths and weaknesses, this composite appears to match observations well. Total atmospheric dust inputs to the oceans = 450 Tg year^{-1}. Percentage inputs to ocean basins based on this figure are as follows: North Atlantic, 43%; South Atlantic, 4%; North Pacific, 15%; South Pacific, 6%; Indian, 25%; and Southern Ocean, 6%.

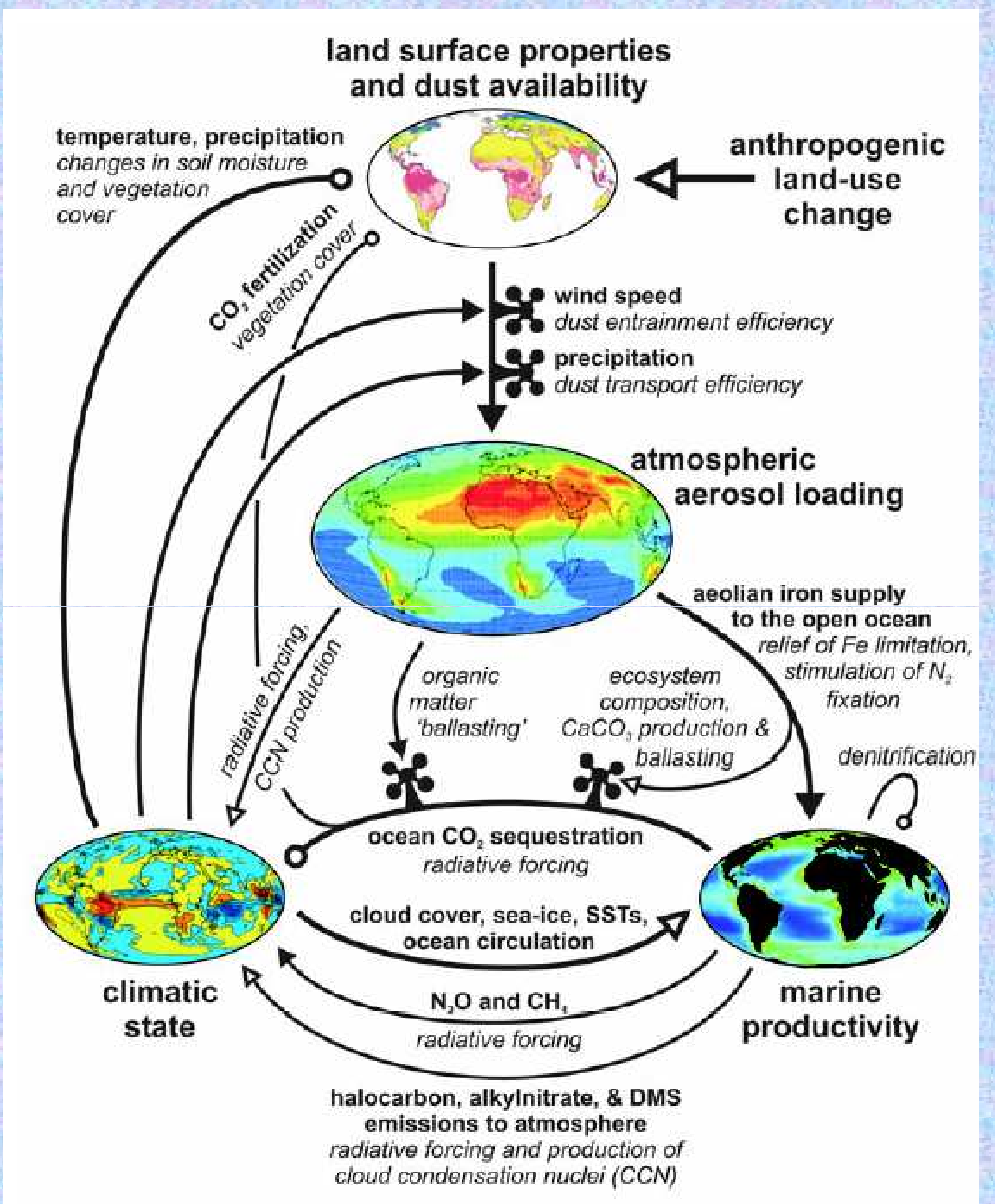
Dust has important but uncertain direct impacts on climate and radiative budgets and possibly rainfall patterns.

The iron content of soil dust is on average, 3.5%. At a seawater pH of 8, soluble ferric iron rapidly reprecipitates, setting up a competition between adsorption to water column particulates, active biological uptake, and organic complexation.

- An average enrichment factor of 1.3 has been reported for iron implying additional noncrustal sources.

- If other iron sources are significant, it means that in addition to perturbing the iron cycle by changing dust source production, we may be influencing it by human activity producing modest amounts of rather soluble iron.

- More data is required to address the importance of alternative sources of iron.



Jickells et al., Science, 2005

Table 2. Effects of dust/iron (Fe) on ocean biogeochemistry. (In addition, there are dust effects on the climate system via albedo and the hydrological cycle; see text.)

Interaction	**Mechanism**	**Area***	**Reference**
Primary productivity	Reduction in Fe limitation allows more efficient use of macronutrients and hence CO_2 uptake.	HNLC and other Fe-limited areas	(*36*, *42*)
N_2 fixation	Reduction in Fe limitation on nitrogen fixation increases primary production and hence CO_2 uptake.	Subtropical gyres	(*1*, *43*)
Changes in species composition	Species-selective relief of iron stress.	Global	(*42*)
Ballast effect	Increases sinking rate of organic matter, reducing organic matter regeneration within seasonal mixed layer; promotes CO_2 uptake.	Probably only significant in areas of high dust deposition	(*52*)
DMS	Increased productivity leads to increased DMS emissions and increased aerosol formation.	HNLC and other Fe-limited areas	(*54*)
N_2O and NO_3^-	Increased fluxes of organic matter to deep waters lower oxygen concentrations and promote denitrification, release N_2O, and lower oceanic nitrate inventory.	Upwelling systems	(*53*)
N_2O and CH_4	Increased productivity leads to changes in euphotic zone methane and N_2O concentrations.	HNLC and other Fe-limited areas	(*54*, *57*)
H_2S	Increased fluxes of organic matter to deep waters lower oxygen concentrations and promote sulfate reduction; sulphide production lowers iron inventory.	Upwelling systems	
Halocarbons and alkyl nitrates	Biogenic gases linked to primary productivity. These are greenhouse gases, linked to aerosol formation and to the ozone cycle.	As for DMS	(*54*)
Isoprene and CO	Biogenic trace gases linked to primary productivity. These gases influence atmospheric oxidizing capacity.	As for DMS	(*54*, *57*)

*Most impacts have effects throughout the oceans, but where appropriate, we identify here areas that are most sensitive to changes in dust/iron flux.

- The previous figures demonstrates the complexity of the global iron cycle.

- Low Fe solubility leads to limitation of marine productivity, with potentially large-scale feedbacks (either positive or negative) within the global climate system.

- There are however considerable uncertainties in our understanding of these interactions, requiring research that integrates across the whole Earth system such as on
  - (i) dust deposition processes,
  - (ii) aerosol iron bioavailability, and
  - (iii) the impact of iron on marine nitrogen fixation and trace gas emissions.