The nitrogen cycle

Eutrophication and the nitrogen cascade

Why are biogeochemical cycles interesting?

- The details underlying biogeochemical cycles may be rather technical.
- Conservation of ecosystems may focus on the “bio” rather than the “geochemical”
- However, chronic changes in ecosystems that lead to notable changes in the “bio” component often can be traced back to the “geochemical” elements.
- For example, Wareham forest is a mosaic of ecosystems that depend on the complex geochemistry of podzol like soils
- Carbon to nitrogen ratios are very important.

Why are biogeochemical cycles important?

- Processes taking place in the soil (terrestrial) or water (aquatic) ecosystems have visible effects on the biota.
- Net primary productivity (the underlying driver of all ecosystems) depends on biogeochemical cycles.
- Biogeochemical processes also may be of global concern, particularly when they affect the atmosphere.
- At a local level a key process is eutrophication. This may change an ecosystem from one (temporally) stable state into another.

What is eutrophication?

- Eutrophication comes from Greek *eu trophos*, i.e. well nourished
- The process by which an ecosystem, or parts of it, becomes progressively enriched with nutrients.
- Terms often used for lakes and other water bodies
  - Eutrophic
  - Mesotrophic
  - Oligotrophic
- When taken to extremes a system may become "dystrophic" or "hypertrophic"
- Two key nutrients typically implicated
  - Nitrogen
  - Phosphorous
- Both are added to ecosystems naturally, and through human activity

Impacts of phosphates and nitrates

- It was once assumed that phosphorous was the key **limiting** nutrient in lakes, while nitrogen was a key **limit** for terrestrial ecosystems (remember Leibnitz and modelling)
- More recent research shows a more complex picture
- Phosphate enrichment is a very important element of freshwater eutrophication.
- However, nitrogen derived compounds can play a particularly important role in the eutrophication of coastal ecosystems

Where do inputs of P and N come from?

- Both P and N are used as fertilizers
- N is more mobile than P and moves through run off and ground water
- P tends to bind to sediments
- Sewage and manure contain both at high concentrations
- Phosphates are also present in detergents

Algal mat (Poole harbour)

Direct impact of eutrophication

- Algal mats or blooms can have the most visible and damaging impact
- When an algal mat (or algal bloom) decays, oxygen is depleted
- Can lead to fish kills

Toxic blooms

- Tends to be associated with intensified agriculture (blooms common in countries with high inputs)

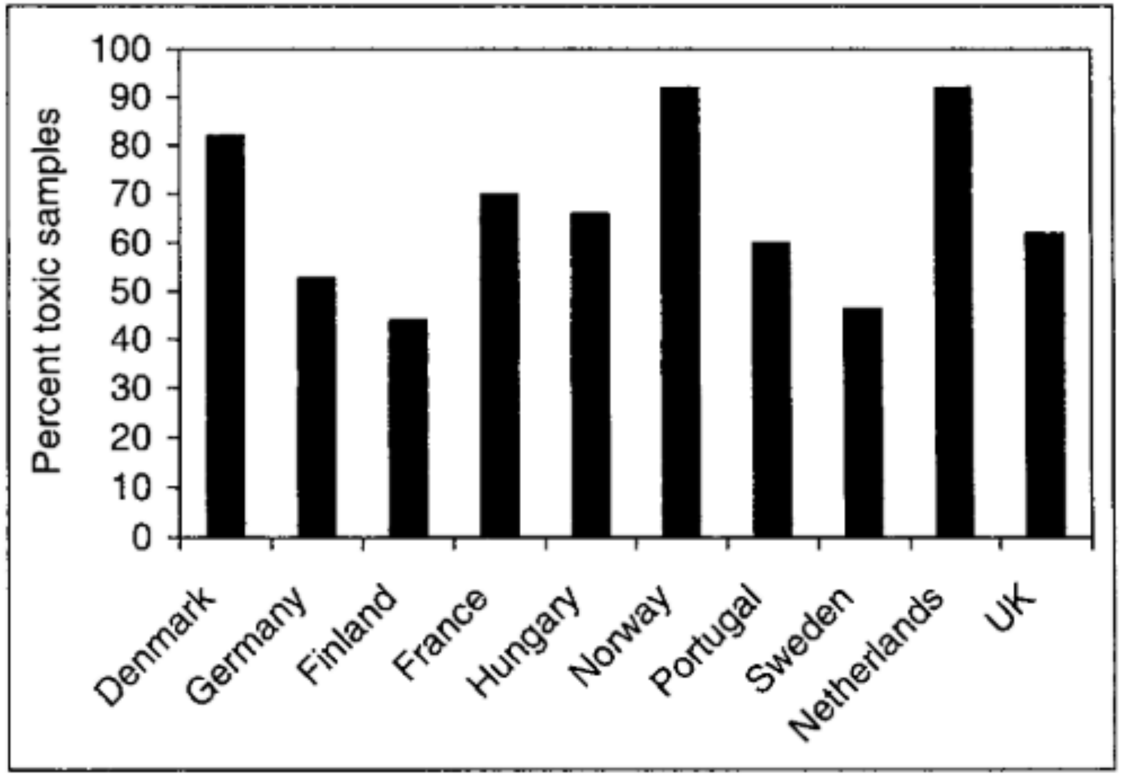
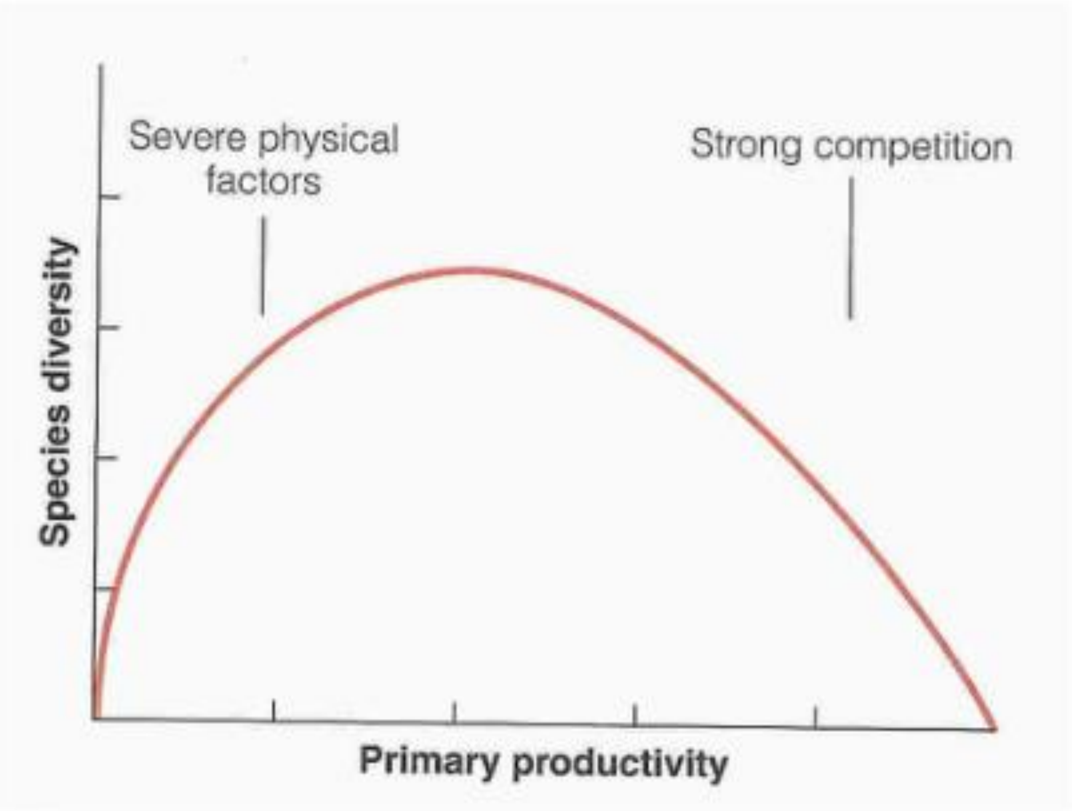


Fig. 1: Frequencies of toxic cyanobacterial blooms in 11 European coun-

Effects on salt marshes

Intermediate productivity hypothesis

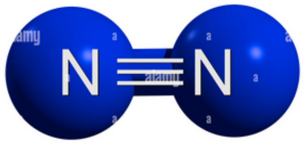
- There can be a “hump backed” relationship between productivity and species richness.



“Improved” grassland

Why focus on nitrogen?

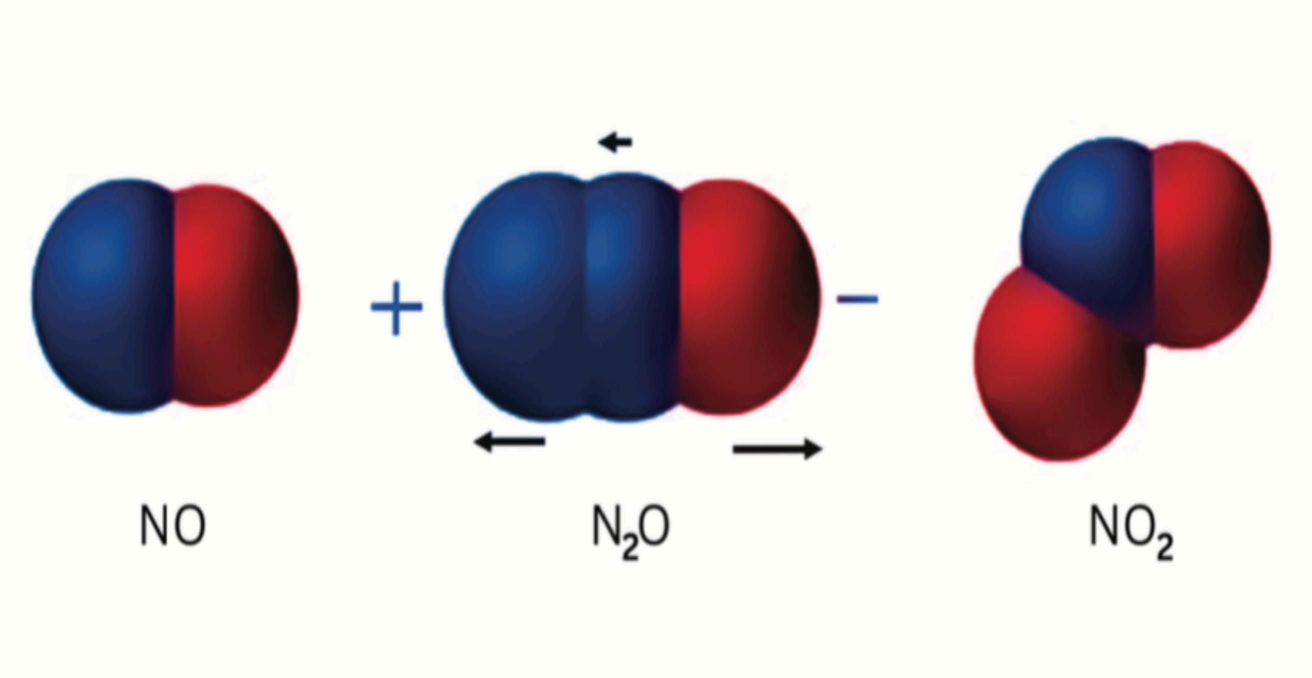
- The elements nitrogen (N), carbon (C), phosphorus (P), oxygen (O), and sulphur (S) are all necessary for life, and so are present in all ecosystems
- Total amount of N in the atmosphere, soils, and waters of Earth is approximately 4×10^{21} grams (g)
- More than the total mass of C + P + O + S !
- But … > 99% of N unavailable for use
- N_2 held together by triple bond



Nitrous oxides

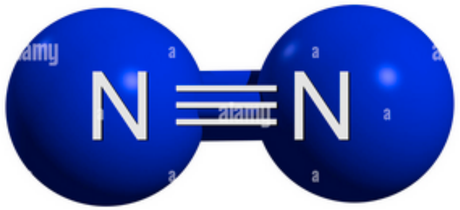
- The atmosphere also contains nitrous oxides as trace gases
- Three oxides of nitrogen
- Commonest is N_20 at around 0.34 ppm (compare with CO_2 at around 460 ppm)
- Released through burning of fossil fuels.
- Dissolves in water to form nitric acid
- Contributes to “acid rain”
- Harmful to human health at high concentrations

Nitrous oxides



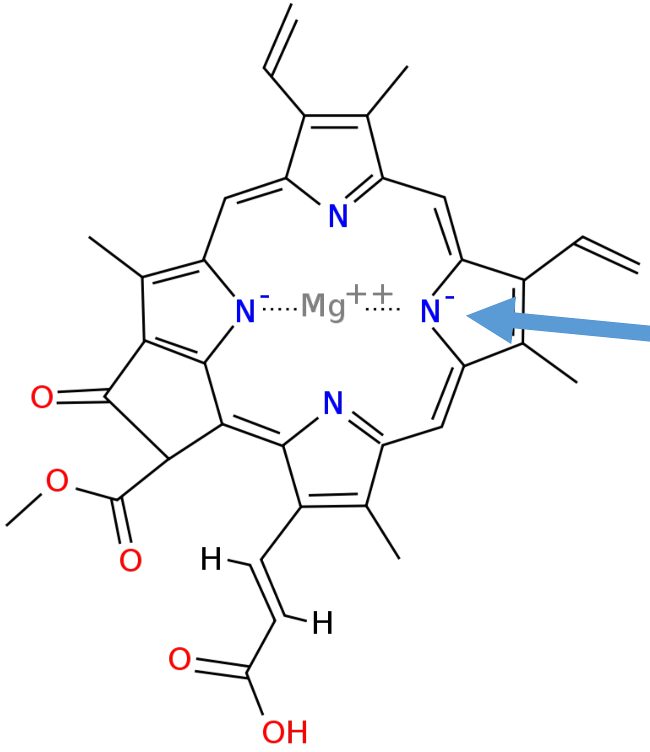
Breaking the triple bond

- In order to play a role in ecosystems the nitrogen triple bond has to be broken.
- Nitrogen is a component of chlorophyll, amino acids and ATP

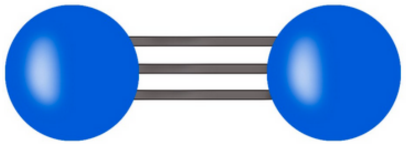


Chlorophyll

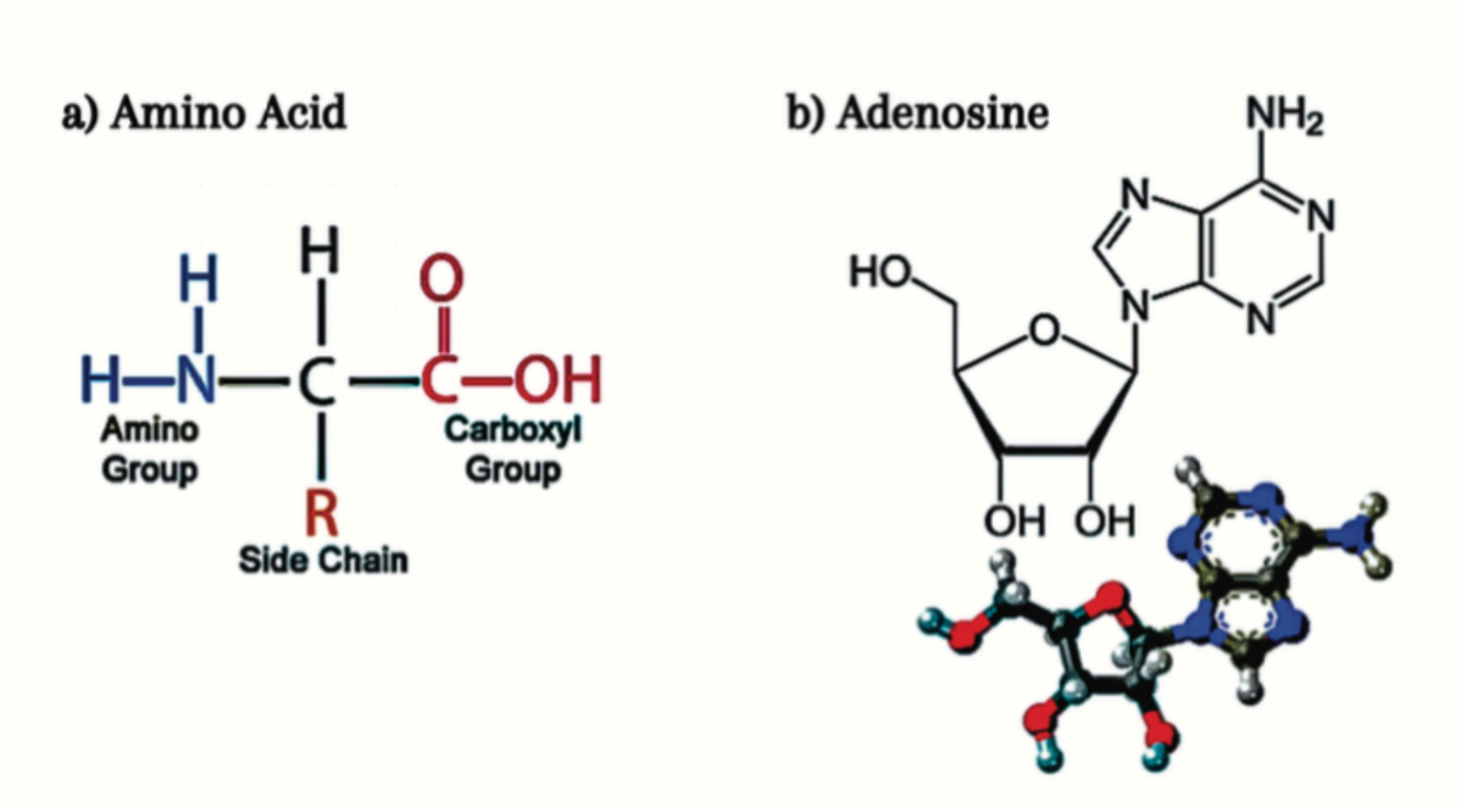
$C_{55}H_{72}O_5N_4Mg$



How does it go from this to that?



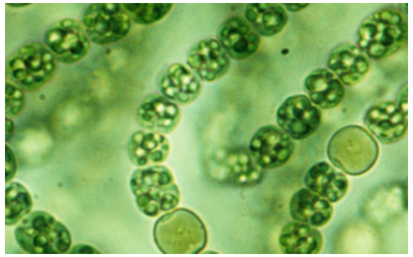
Amino acids and ATP



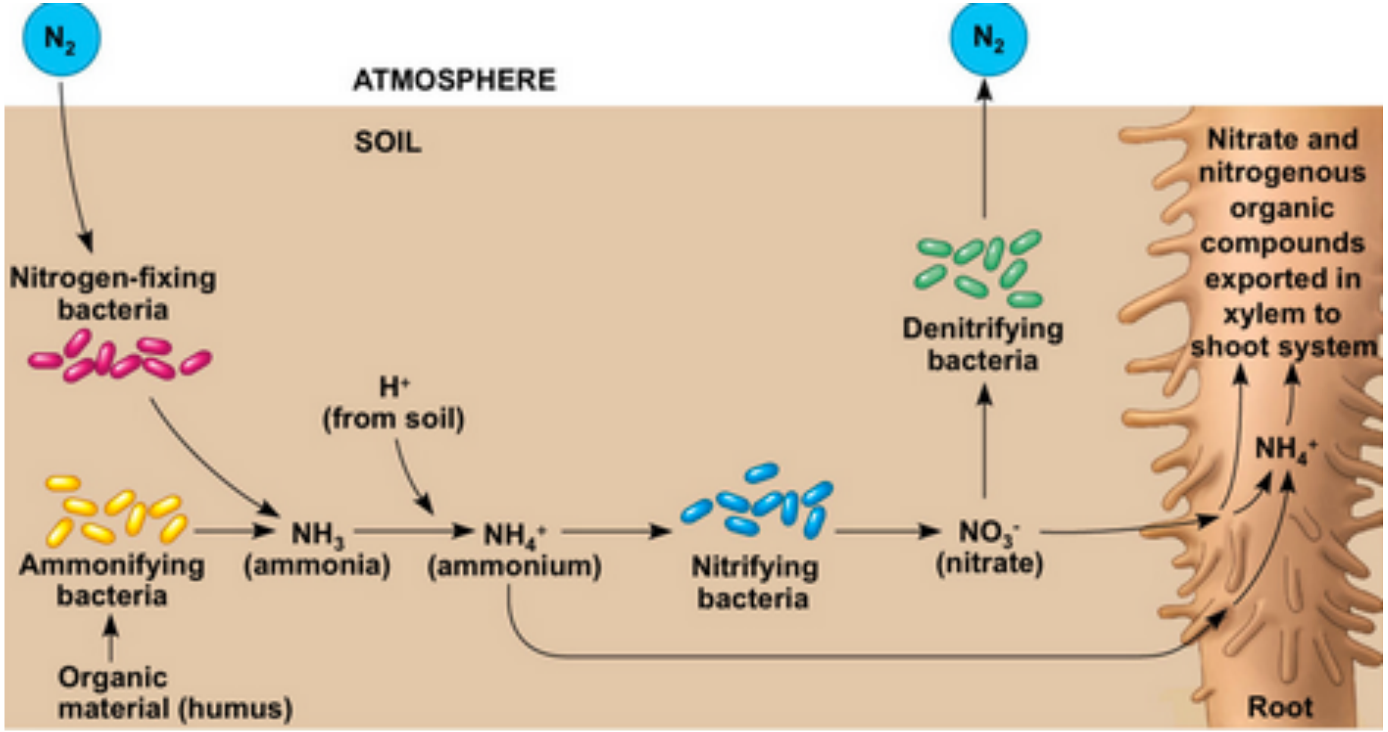
Biological nitrogen fixation

- Nitrogen fixation occurs naturally in soils through a range of microbes known as diazatrophs.
  - Bacteria,e.g. Azobacter
  - Archea (“blue green algae”)
- Symbiotic relationships with some plants, particularly legumes.
- Looser relationship with other plants, e.g. rice

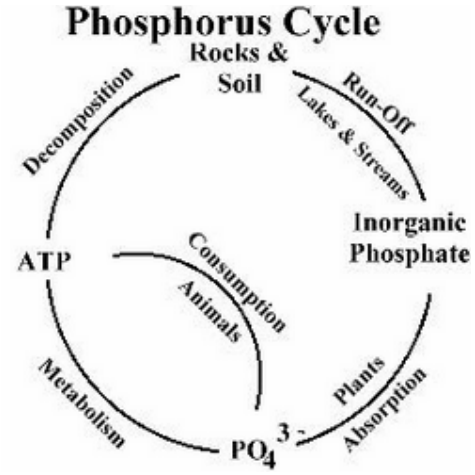
Biological nitrogen fixation

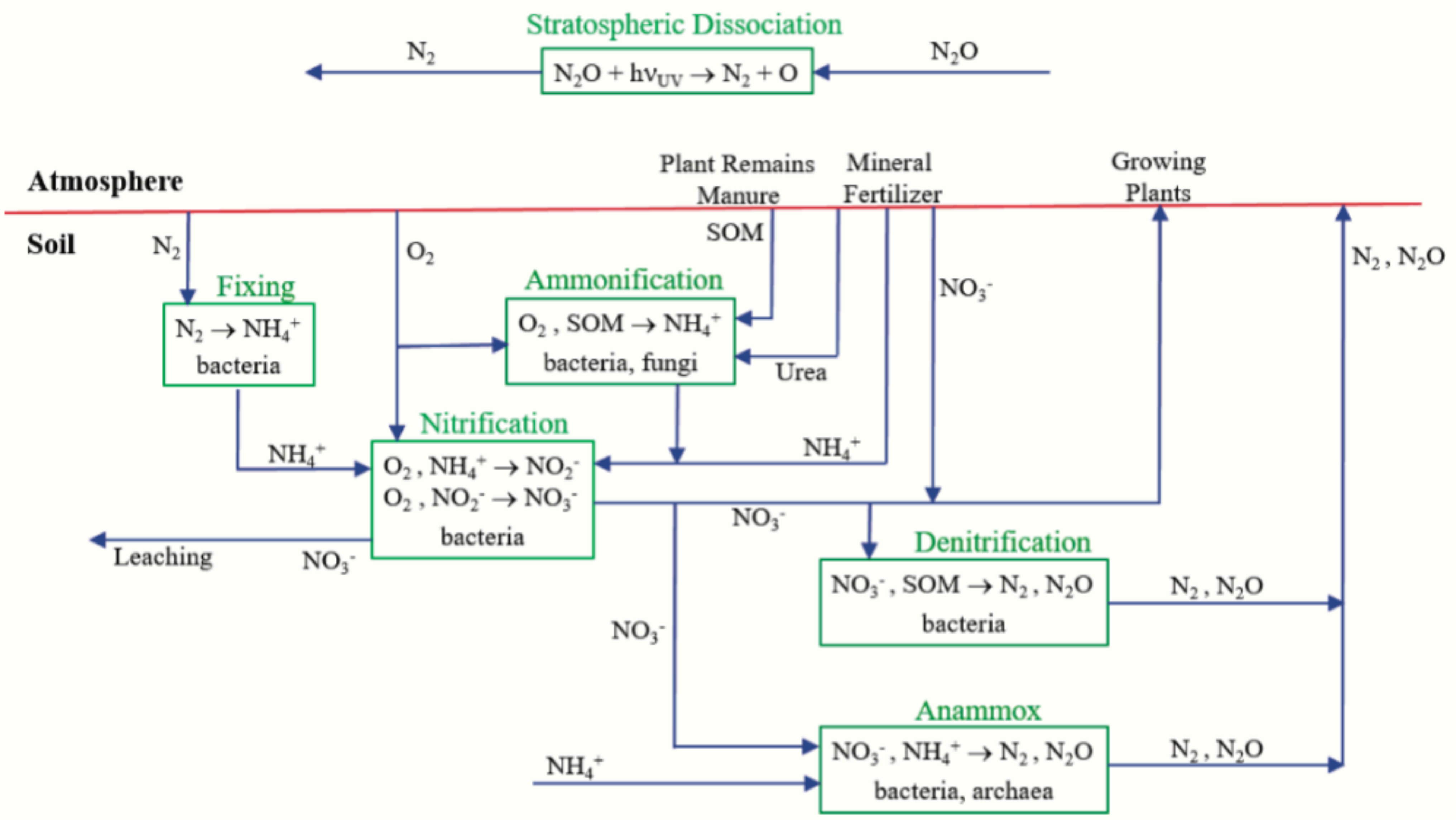


Biological nitrogen fixation



Compare with





Stratospheric Dissociation
N_2
$N_2O + h\nu_{UV} \rightarrow N_2 + O$
N_2O
Atmosphere
Plant Remains
Manure
Mineral
Fertilizer
Growing
Plants
Soil
N_2
O_2
SOM
NO_3^-
N_2, N_2O
Fixing
$N_2 \rightarrow NH_4^+$
bacteria
Ammonification
O_2, SOM $\rightarrow NH_4^+$
bacteria, fungi
Urea
Nitrification
NH_4^+
NH_4^+
O_2, $NH_4^+ \rightarrow NO_2^-$
O_2, $NO_2^- \rightarrow NO_3^-$
bacteria
NO_3^-
Leaching
NO_3^-
Denitrification
NO_3^-, SOM $\rightarrow N_2$, N_2O
bacteria
N_2, N_2O
NO_3^-
Anammox
NO_3^-, $NH_4^+ \rightarrow N_2$, N_2O
bacteria, archaea
N_2, N_2O
NH_4^+

Reactions in the soil (nitrification)

- In oxygenated soil ammonia is converted to nitrates by specialised microorganisms (ammonia oxidisers)

$$NH_4^+ + \frac{3}{2}O_2 + 2OH^- \rightarrow NO_2^- + 3H_2O.$$

$$NO_2^- + \frac{1}{2}\,O_2 \rightarrow NO_3^-.$$

Denitrification (loss of soil nitrogen to the atmosphere)

- Takes place in oxygen poor conditions
- Microbes use the reaction as a source of energy
- Without denitrification nitrates could reach toxic levels in the soil
- Important in treatment of sewage to prevent eutrophication
- Releases nitrogen back to the atmosphere.

$$8\,NO_2^- + 8H^+ + C_6H_{12}O_6 \rightarrow 4N_2 + 6\,CO_2 + 10\,H_2O,$$

Anaerobic ammonia oxidation

- Does not involve organic matter
- Source of energy for some anaerobic microbes

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

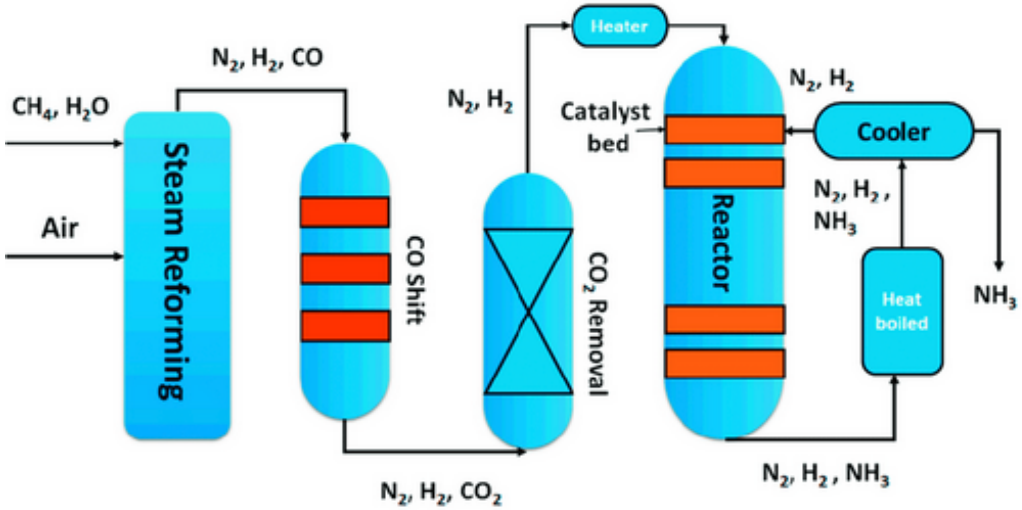
Sources of fixed nitrogen

- Prehuman world: creation of N_r from N_2
  - lightning
  - biological nitrogen fixation (BNF).
- Prior to human influence active N did not accumulate rapidly in environmental reservoirs: Microbial N fixation and denitrification processes were probably approximately equal

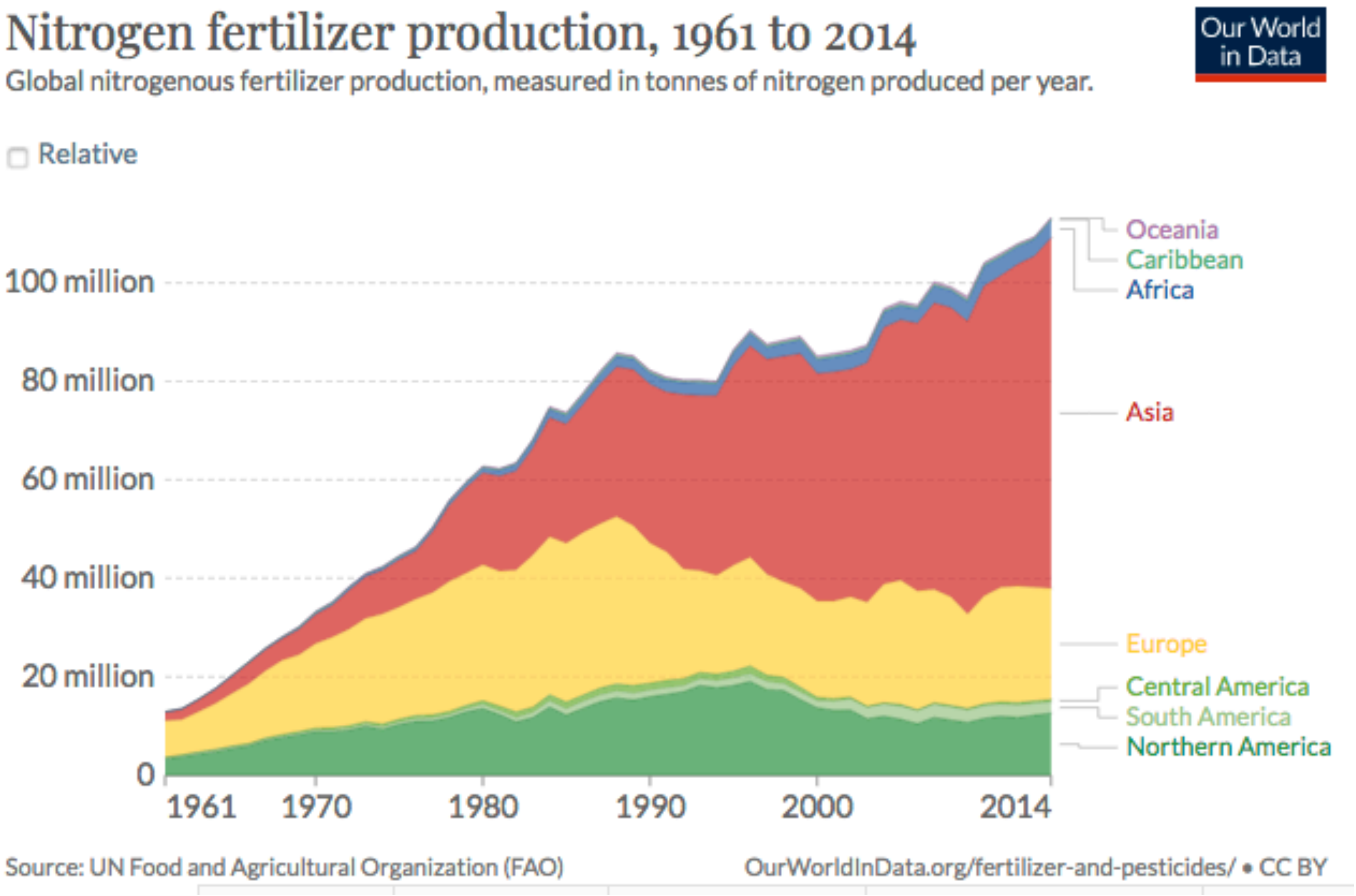
Sources of fixed nitrogen

- Production of N_r by humans now much greater than production from all natural terrestrial systems.
- Global increase in N_r production has three main causes:
  - Cultivation of legumes, rice, and other crops that promote conversion of N_2 to organic N through biological nitrogen fixation
  - Combustion of fossil fuels, which converts both atmospheric N_2 and fossil N to reactive NO_x;
  - The **Haber-Bosch** process, which converts nonreactive N_2 to reactive NH_3 to sustain food production and some industrial activities.

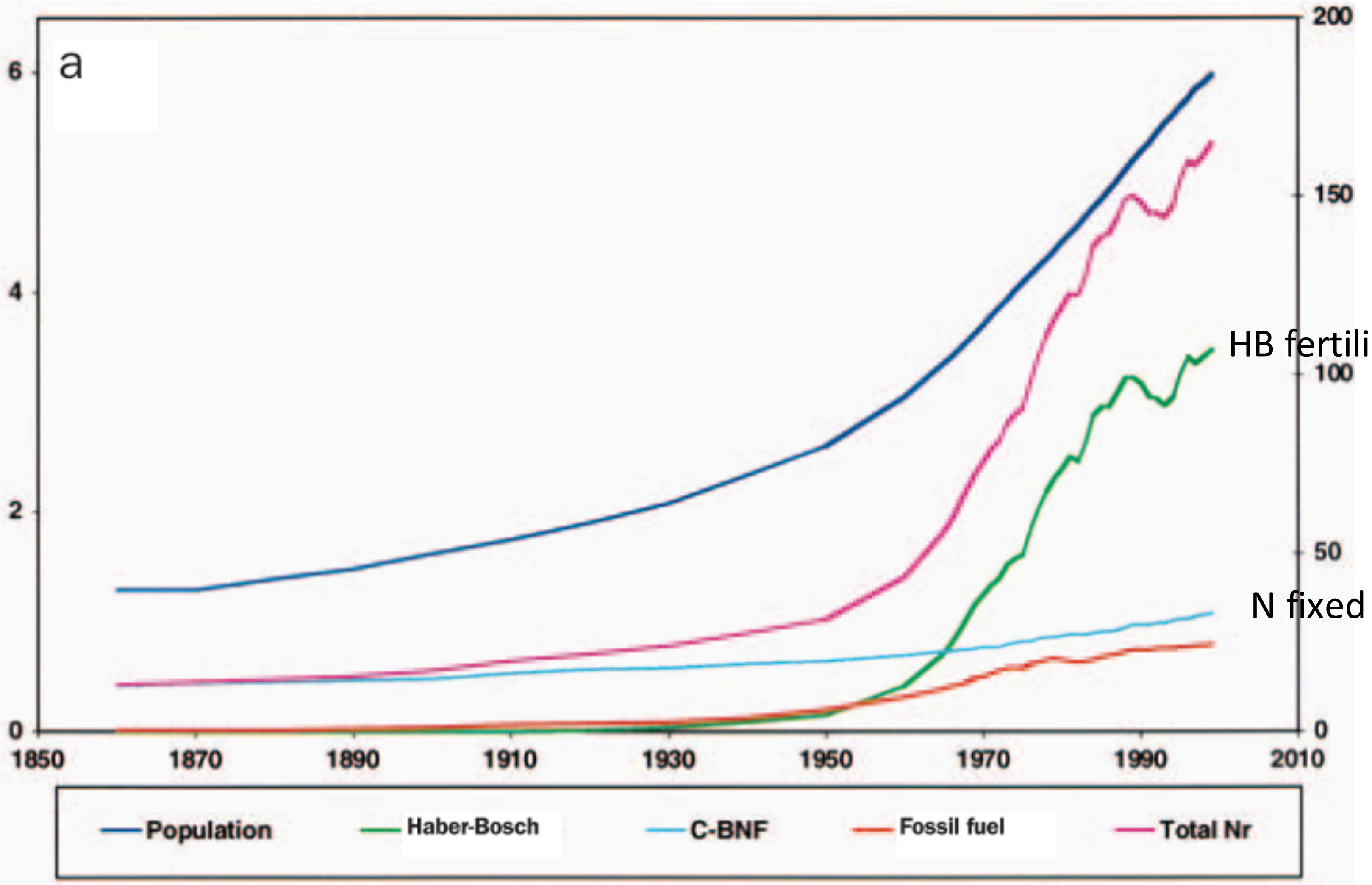
Haber Bosch process



Nitrogen fertiliser production



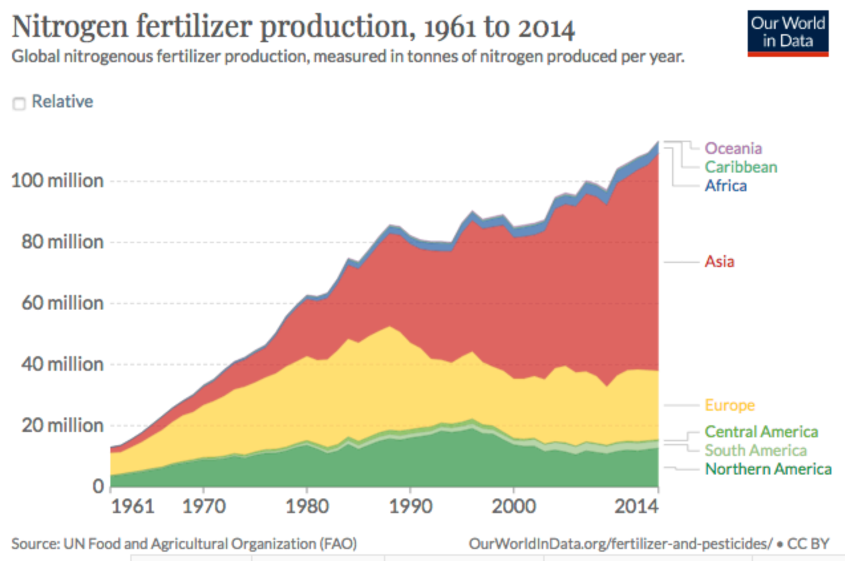
Haber Bosch nitrogen fixation

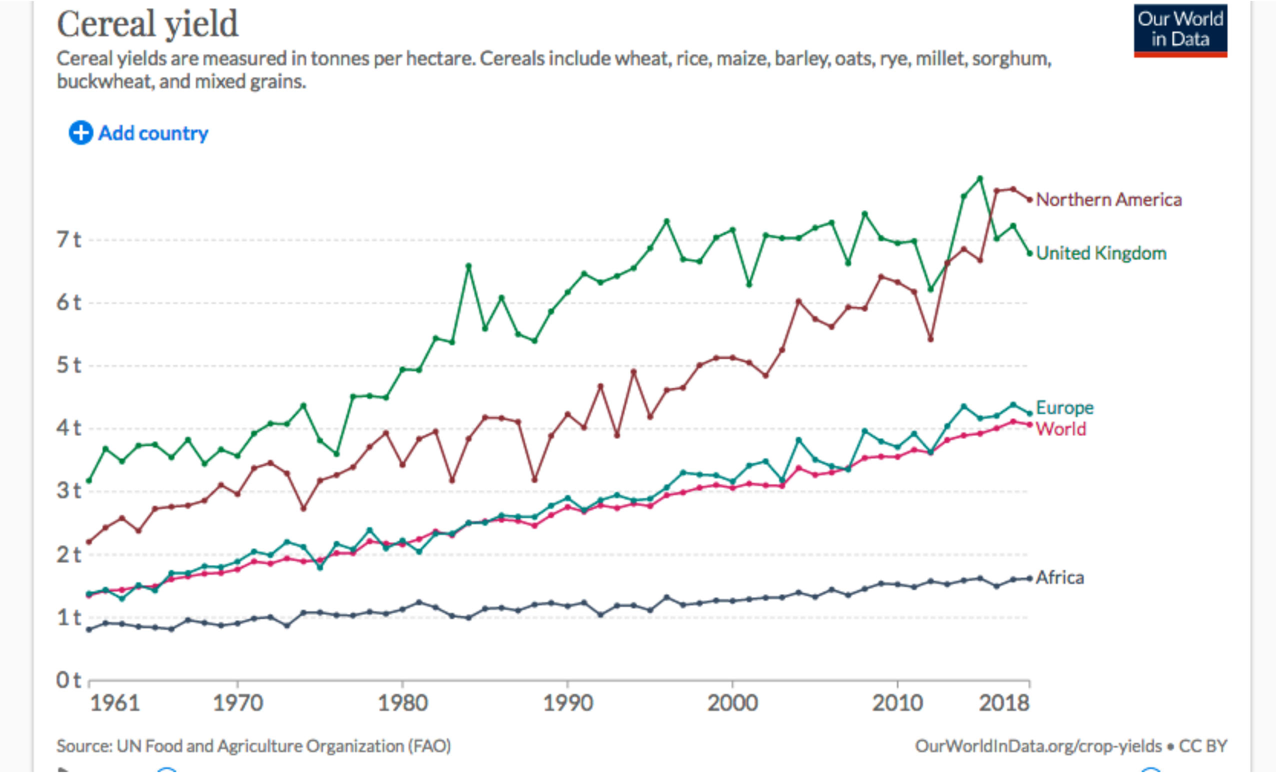


HB fertiliser

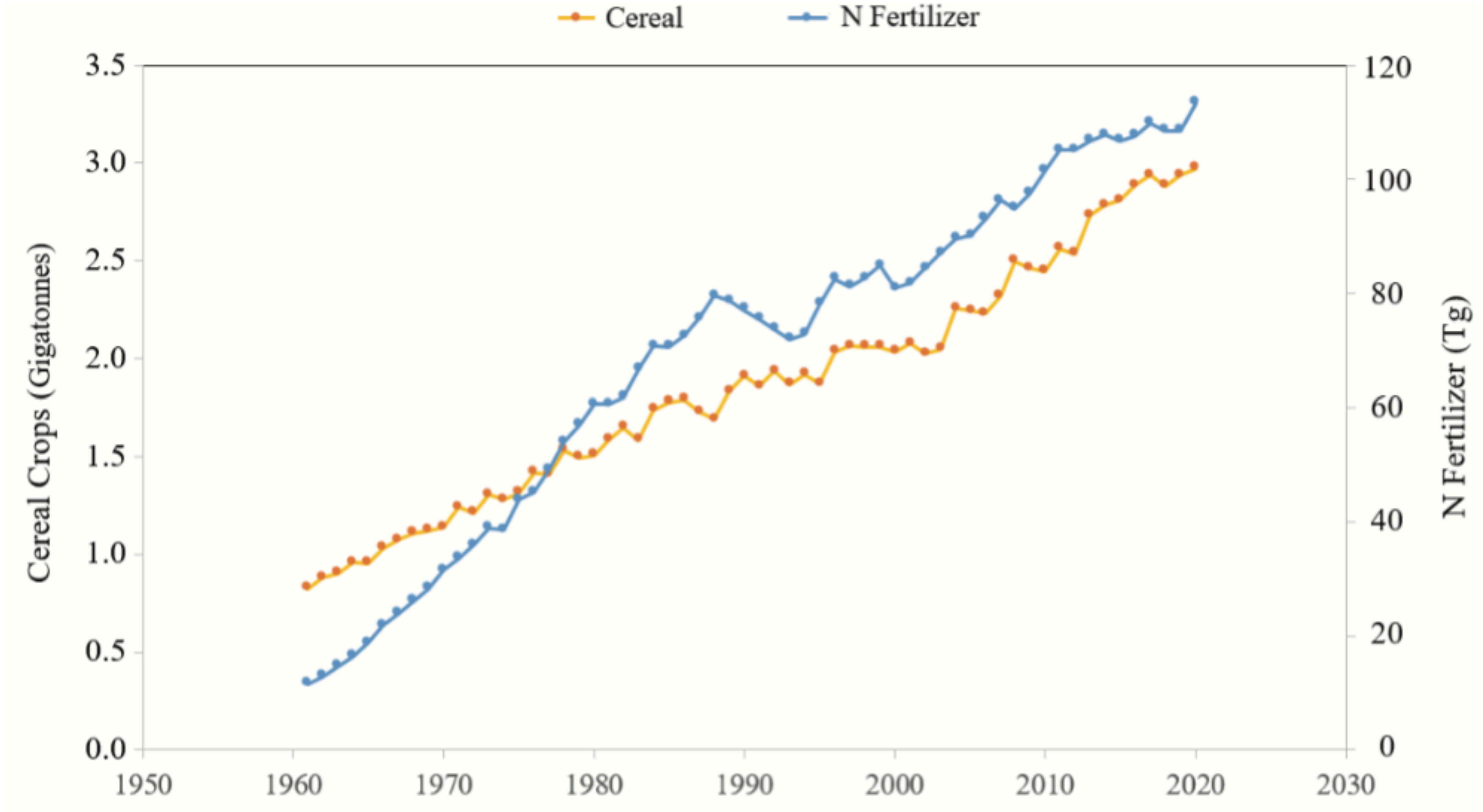
N fixed by legumes etc

Impact on crop yields





Cereal production and nitrogen fertiliser use




With nitrogen fertilizer
Without nitrogen fertilizer
'97 4 13

Carbon to nitrogen ratio

- There is always more carbon than nitrogen in organic matter.
- When an organic substrate has a C:N ratio between 1 and 15, rapid mineralization and release of N occurs, which is available for plant uptake.
- The lower the C:N ratio, the more rapidly nitrogen will be released into the soil for plant use
- 20–30 results in an equilibrium state between mineralization and immobilization.
- C:N ratio > 35 results in microbial immobilization.
- Soil microorganisms have a C:N ratio of around 8.

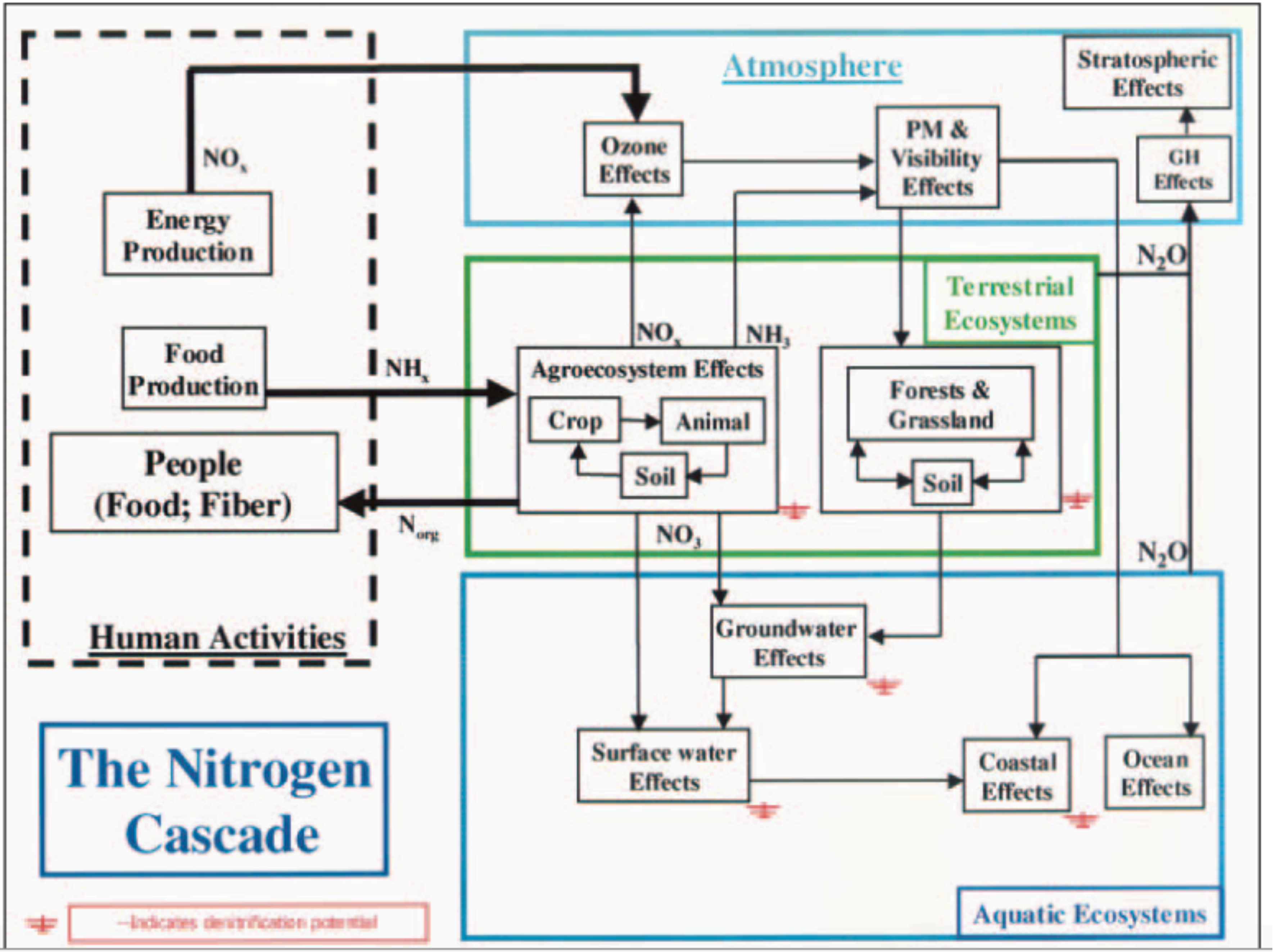
Very high C:N ratios lead plants to find alternative sources of nitrogen (e.g in Wareham forest)

Processes in Wareham forest

- Conifer plantations tend to add carbon to the soil, but relatively little nitrogen
- This can lead to acidification and difficulties in obtaining nitrogen
- Fire may make nitrogen temporarily more available
- Legumes such as gorse fix nitrogen
- Waterlogged soil (mires) lose nitrogen in anoxic conditions through denitrification.
- Conversion to agricultural land requires lowering C and raising N
- Changing pH through liming makes N more available.

The nitrogen cascade

- Fixed nitrogen can be thought of as “cascading” through terrestrial ecosystems
- Much is returned to the atmosphere through denitrification
- Some finds it way into rivers
- Rivers flow into estuaries
- Estuaries are joined to near shore maritime ecosystems
- Seas are linked to the large oceans.



Atmosphere
Stratospheric Effects
PM & Visibility Effects
Ozone Effects
GH Effects
NO_x
Energy Production
N_2O
Terrestrial Ecosystems
NO_x
NH_3
Food Production
NH_x
Agroecosystem Effects
Crop
Animal
Soil
Forests & Grassland
Soil
People (Food; Fiber)
N_{org}
NO_3
N_2O
Groundwater Effects
Human Activities
Surface water Effects
Coastal Effects
Ocean Effects
The Nitrogen Cascade
Aquatic Ecosystems
—Indicates denitrification potential

Table 1. Characteristics of different systems relevant for the nitrogen cascade.

System	Accumulation potential	Transfer potential	N_2 production potential	Links to systems down the cascade	Effects potential
Atmosphere	Low	Very high	None	All but groundwater	Human and ecosystem health, climate change
Agroecosystems	Low to moderate	Very high	Low to moderate	All	Human and ecosystem health, climate change
Forests	High	Moderate, high in places	Low	All	Biodiversity, net primary productivity, mortality, groundwater
Grasslands	High	Moderate, high in places	Low	All	Biodiversity, net primary productivity, groundwater
Groundwater	Moderate	Moderate	Moderate	Surface water, atmosphere	Human and ecosystem health, climate change
Wetlands, streams, lakes, rivers	Low	Very high	Moderate to high	Atmosphere, marine coastal systems	Biodiversity, ecological structure, fish
Marine coastal regions	Low to moderate	Moderate	High	Atmosphere	Biodiversity, ecological structure, fish, harmful algal blooms

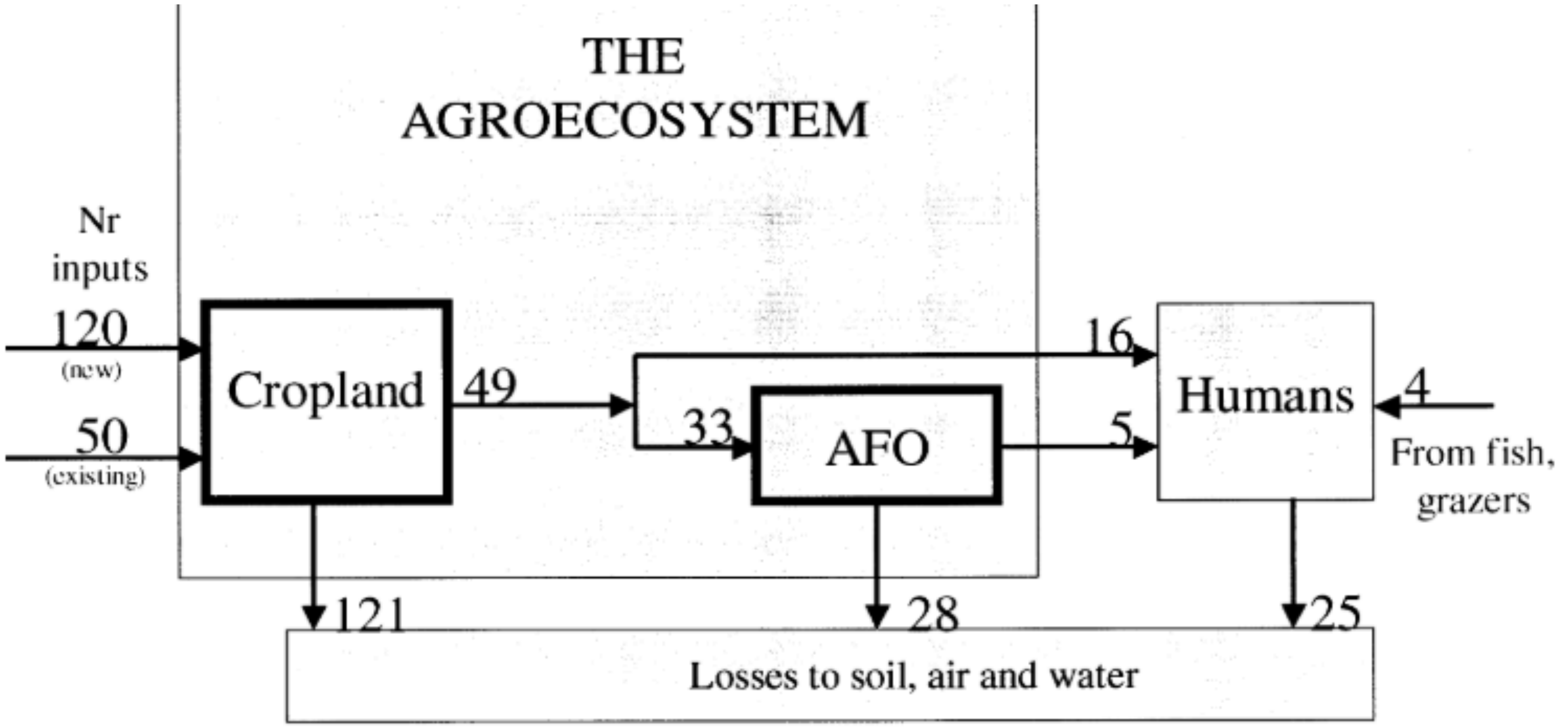


Figure 3. Major reactive nitrogen (Nr) flows in crop production and animal production components of the global agroecosystem. Croplands create vegetable protein through primary production; animal production utilizes secondary production to create animal protein. Reactive nitrogen inputs represent new Nr, created through the Haber-Bosch process and through cultivation-induced biological nitrogen fixation, and existing Nr that is reintroduced in the form of crop residues, manure, atmospheric deposition, irrigation water, and seeds. Portions of the Nr losses to soil, air, and water are reintroduced into the cropland component of the agroecosystem (Smil 2001, 2002). Numbers represent teragrams of nitrogen per year; AFO, animal feeding operations.

Points to note

- Most fixed N added to croplands is “lost” to soil air and water
- Losses can end up somewhere else if not denitrified
- Around 66% of the N in crops passes through livestock production, and 34% directly consumed by humans
- Human consumption of N is around 25% animal product derived and 75% directly from crops (highly variable between countries)
- All fixed nitrogen passing through humans ends up in soil, air and water

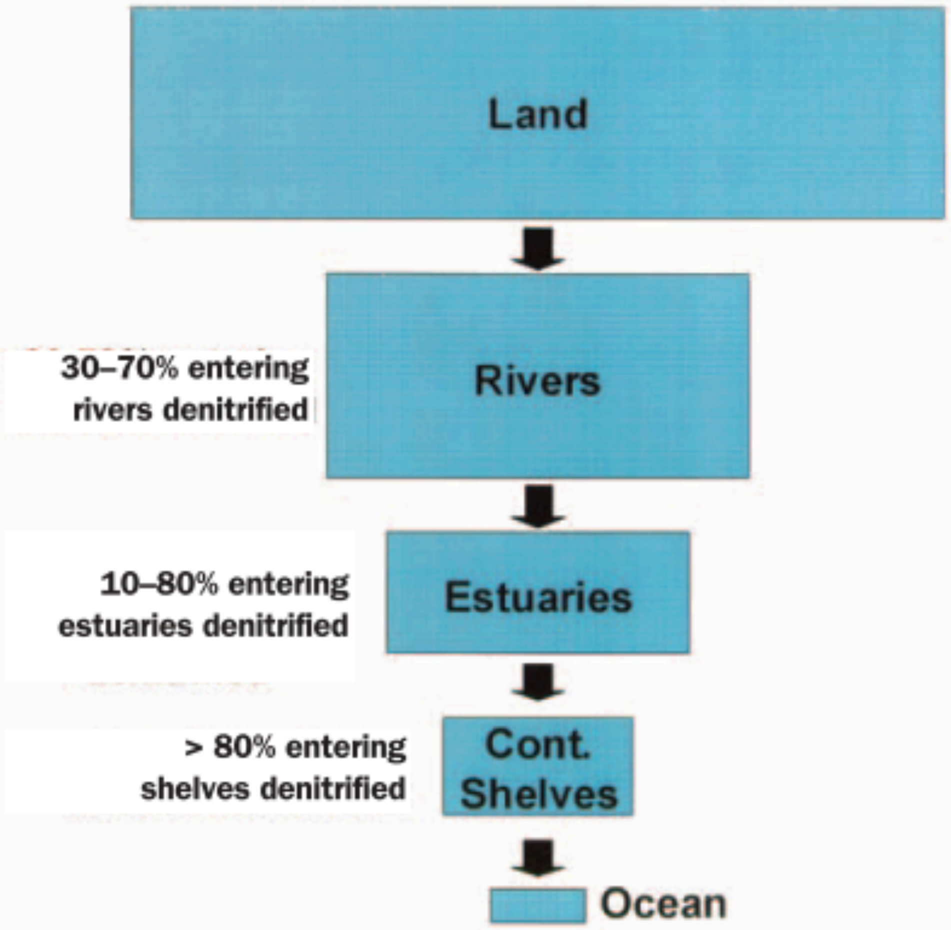
Improving nitrogen use efficiency

- Loss of fertilizer N results from gaseous plant emission, soil denitrification, surface runoff, volatilization, and leaching.
- Worldwide, nitrogen use efficiency (NUE) for cereal production is approximately 33%.
- The unaccounted 67% represented a $15.9 billion annual loss of N fertilizer (assuming fertilizer-soil equilibrium in 1999).
- Increased cereal NUE requires
  - Application of prescribed rates consistent with in-field variability
  - Low N rates applied at flowering, and forage production systems.
  - **Adjusting the fertilizer rate by soil mineral N before N application**

Nitrogen losses

- Denitrification occurs in all ecosystems
- Only a fraction of fixed nitrogen reaches the sea
- Coastal ecosystems at greatest risk of nitrogen enhanced eutrophication if sources are close by

Denitrification reduces the downstream transport of N



Return to neverland?

- Do ecosystems recover from eutrophication?
- In some cases recovery is rapid (short sharp shocks)
- In others it is very gradual and may not take the expected trajectory
- Return to “neverland” baseline may not be achievable
- Hysteresis and non linear trajectories of change

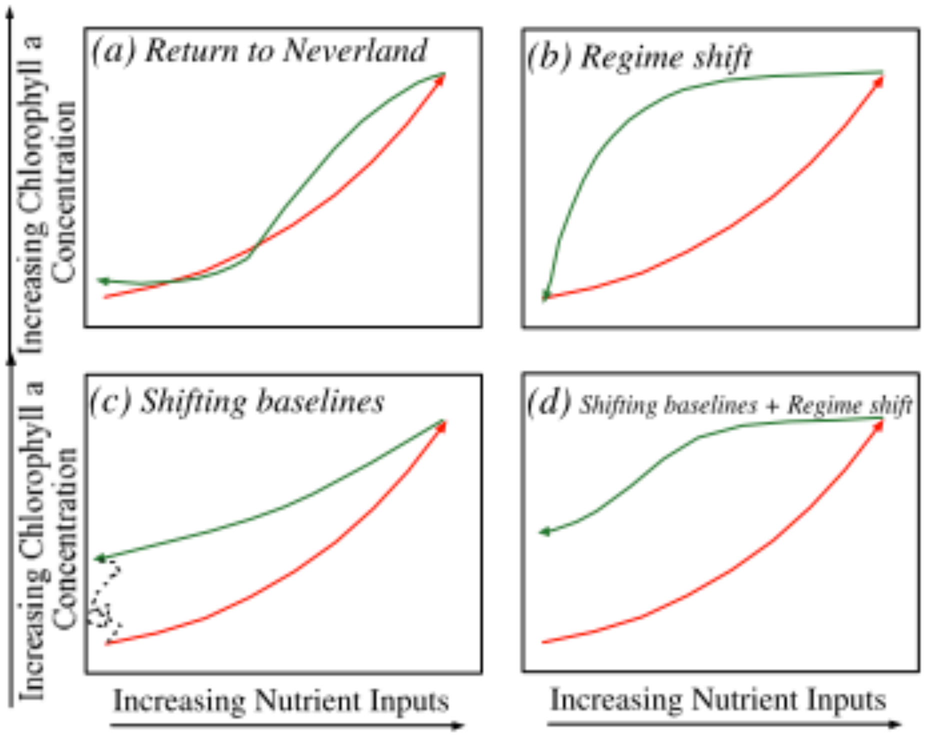
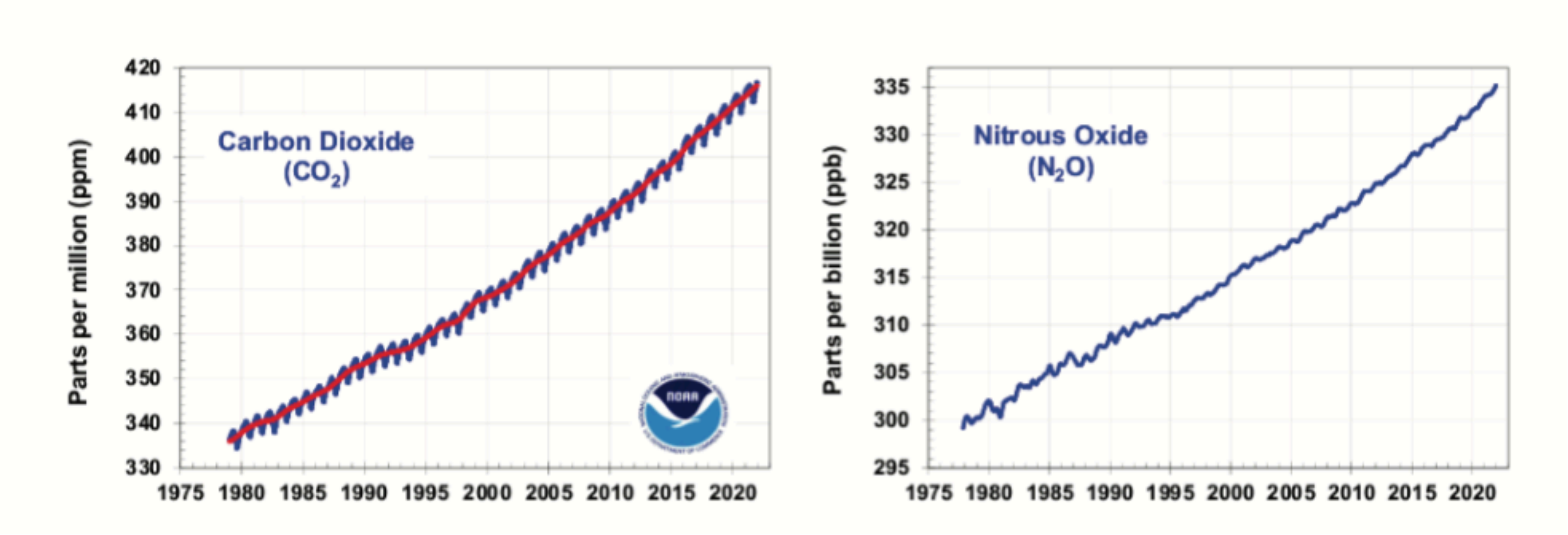


Fig. 1 Idealized trajectories of chlorophyll a concentrations, as an indicator of ecosystem status, and nutrient inputs to coastal ecosystems under increasing (*red line*) and decreasing (*green line*) nutrient inputs under different response scenarios: **a** "Return to Neverland" scenario implying a direct reversible relationship between chlorophyll a concentrations and nutrient inputs; **b** a trajectory resulting from a "Regime Shift" in ecosystem status in response to nutrient inputs. This trajectory results in an apparent time lag, or hysteresis effect, in the response to reducing nutrient inputs; **c** "Shifting Baselines" scenario, where changes in forcing factors other than nutrients (e.g., climate, food web structure) forces a trajectory for the ecosystem independent of that forced by nutrients, depicted by the *dotted line*, preventing the ecosystem to return to the "reference condition" after reducing nutrient inputs; and **d** a trajectory displaying "Regime Shift and Shifting Baselines" combined

Do nitrous oxides contribute to the greenhouse effect?

- Only N_2O has any noticeable greenhouse effect (levels of the other nitrous oxide concentrations are effectively negligible)
- N_2O concentrations have more or less tracked increases in CO_2



Comparative role of N_20

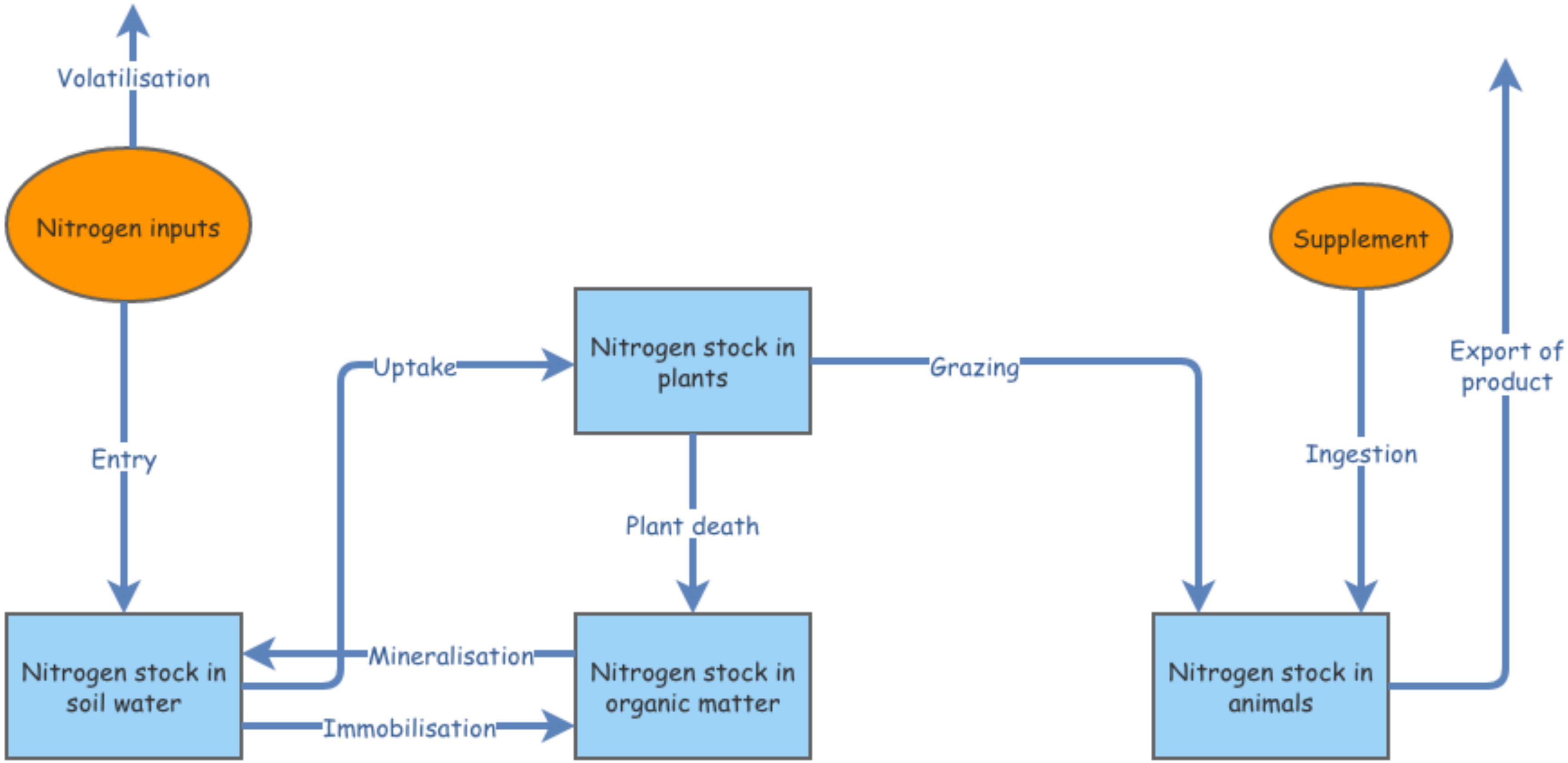
- Radiative forcing per added N_2O molecule is about 230 times larger than the forcing per added CO_2 molecule
- However, concentrations are much lower.
- The observed CO_2 rate of increase is about 2.5 ppm/year.
- This is about 3000 times larger than the N_2O rate of increase, which is about 0.0085 ppm/year.
- The contribution of nitrous oxide to the annual increase in forcing is therefore around 1/13 that of CO_2.

Conclusions

- The nitrogen cycle is **not** boring!
- It is **complex** and very challenging to understand.
- Fixed nitrogen levels in soil and water have a major impact on biodiversity.
- Most nitrogen tends to cycle locally but there is a cascade through ecosystems
- Like carbon, nitrogen is essential to primary productivity, including food production.
- Careful management of nitrogen is essential.

Ecosystem model

https://insightmaker.com/insight/172673/Clone-of-Story-of-nitrogen-dynamics-in-a-shallow-lake



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