Global Circulation of Nitrogen related to Climate Change and Environment

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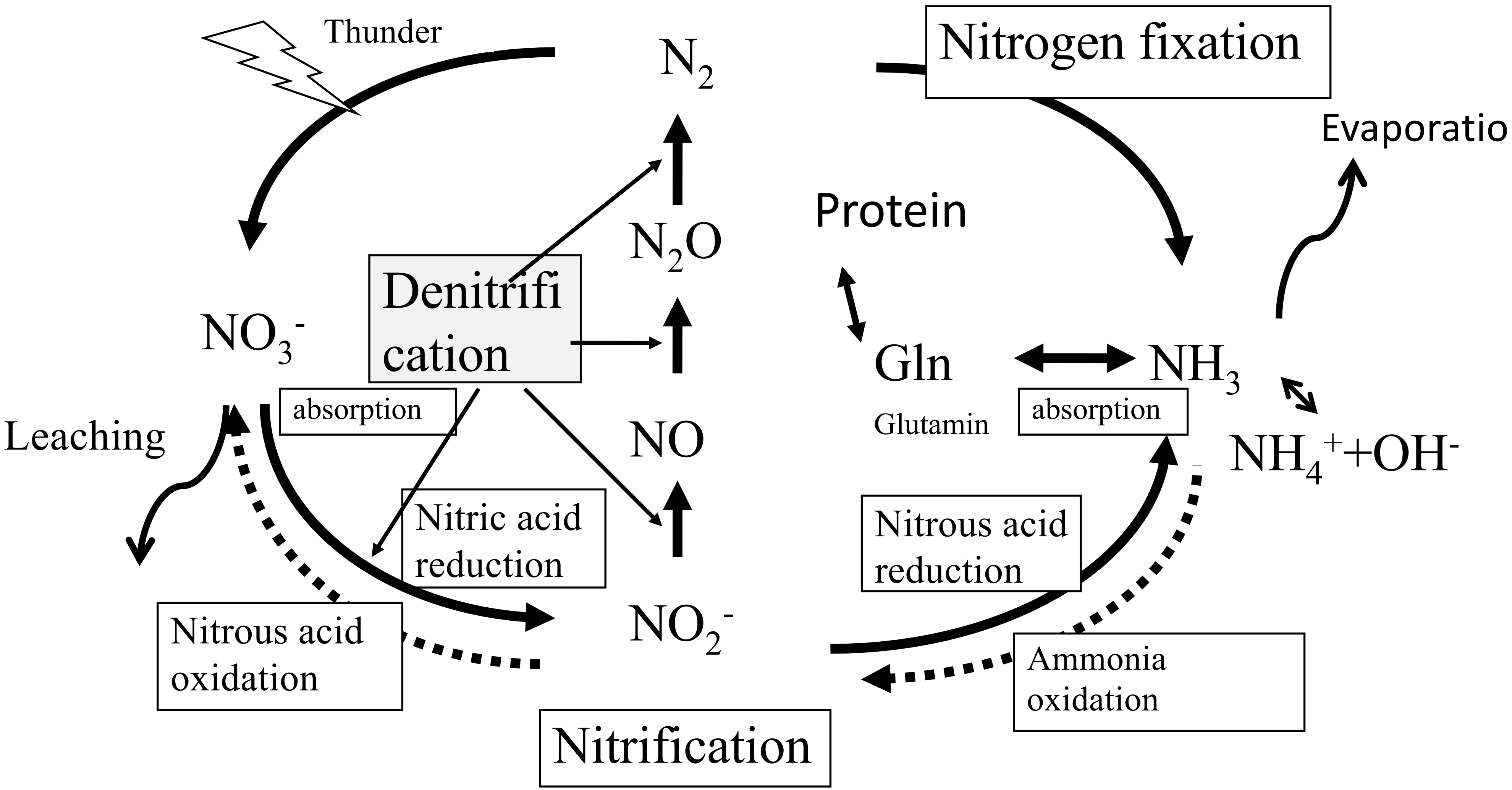
Circulation of Nitrogen



Nitrogen changes to many forms.

- NH_3 , NH_4^+ , R-NH_2 (N valency: -3)
- N_2 (N valency: 0 ）
- N_2O (N valency: +1 ）
- NO (N valency: +2 ）
- NO_2^- (N valency: +3 ）
- NO_2 (N valency: +4 ）
- HNO_3, NO_3^- (N valency: +5 ）
- N_2 is very stable. （Named from the meaning of suffocation in German and Japanese.）Stickstoff
- Compounds other than N_2 change readily.

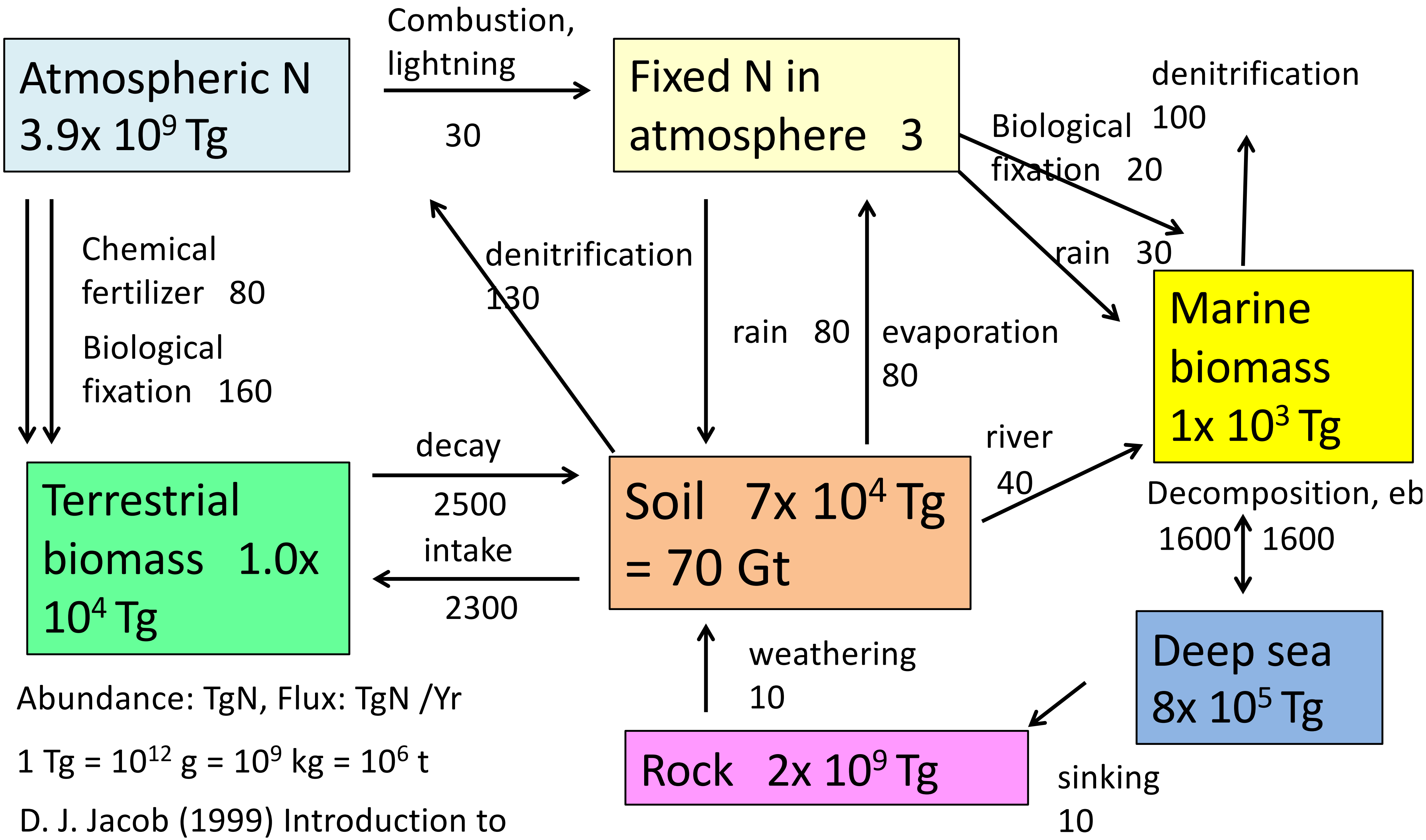
Abundance of nitrogen on earth.

Reservoir/ Pool Type	Metric Tons	% of Total
Biosphere	2.8×10^{11}	0.0002
Hydrosphere	2.3×10^{13}	0.014
Atmosphere	3.86×10^{15}	2.3
Geosphere	1.636×10^{17}	97.7

Items of nitrogen in geosphere.

Reservoir/ Pool Type	Metric Tons	% of Total
Crust	$0.13 - 1.4 \times 10^{16}$	0.78-8.4
Soils and Sediments	$0.35 - 4.0 \times 10^{15}$	0.21-2.4
Mantle and Core	1.6×10^{17}	95.6

Global circulation of nitrogen



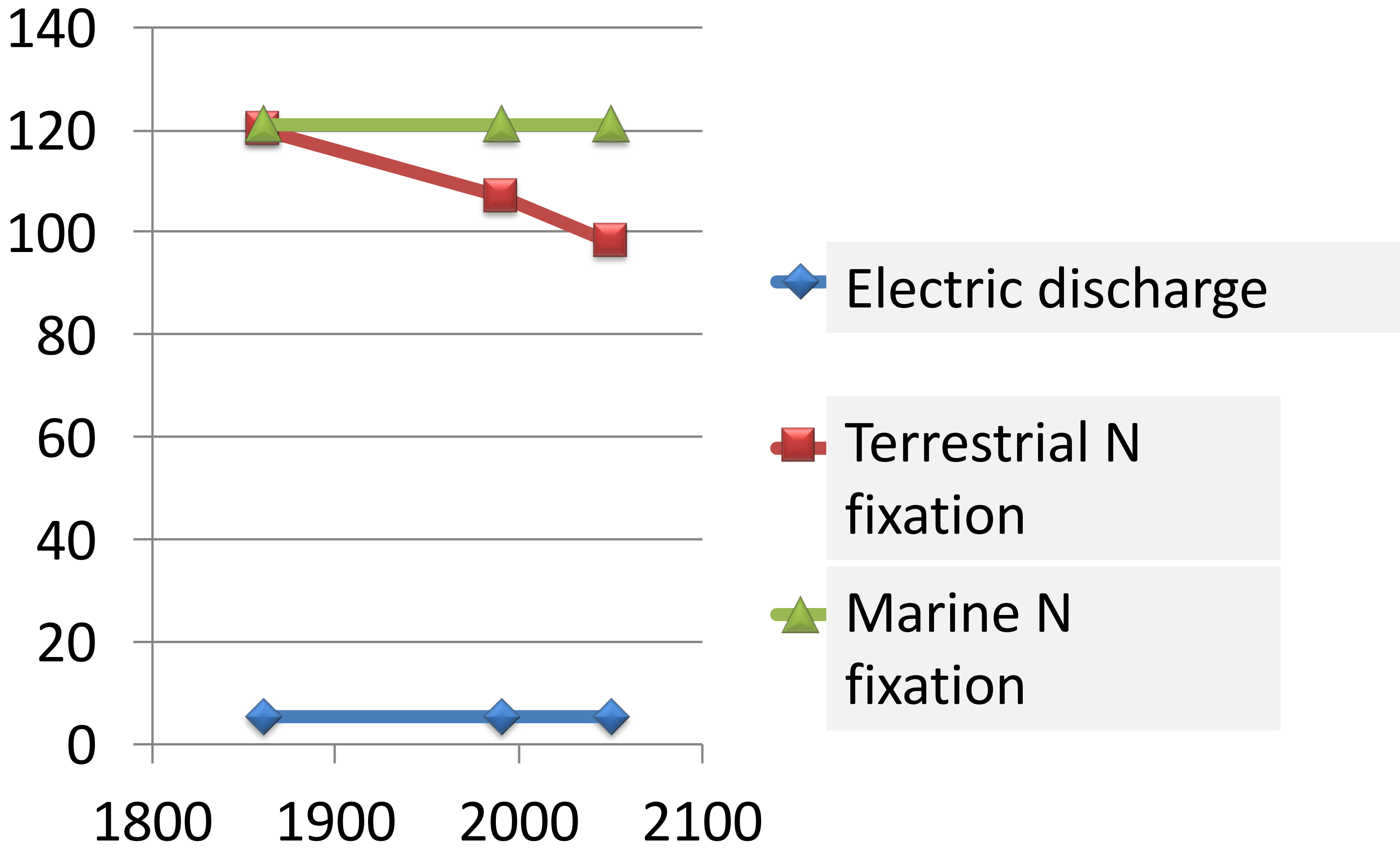
Abundance: TgN, Flux: TgN /Yr

1 Tg = 10^{12} g = 10^9 kg = 10^6 t

D. J. Jacob (1999) Introduction to atmospheric chemistry

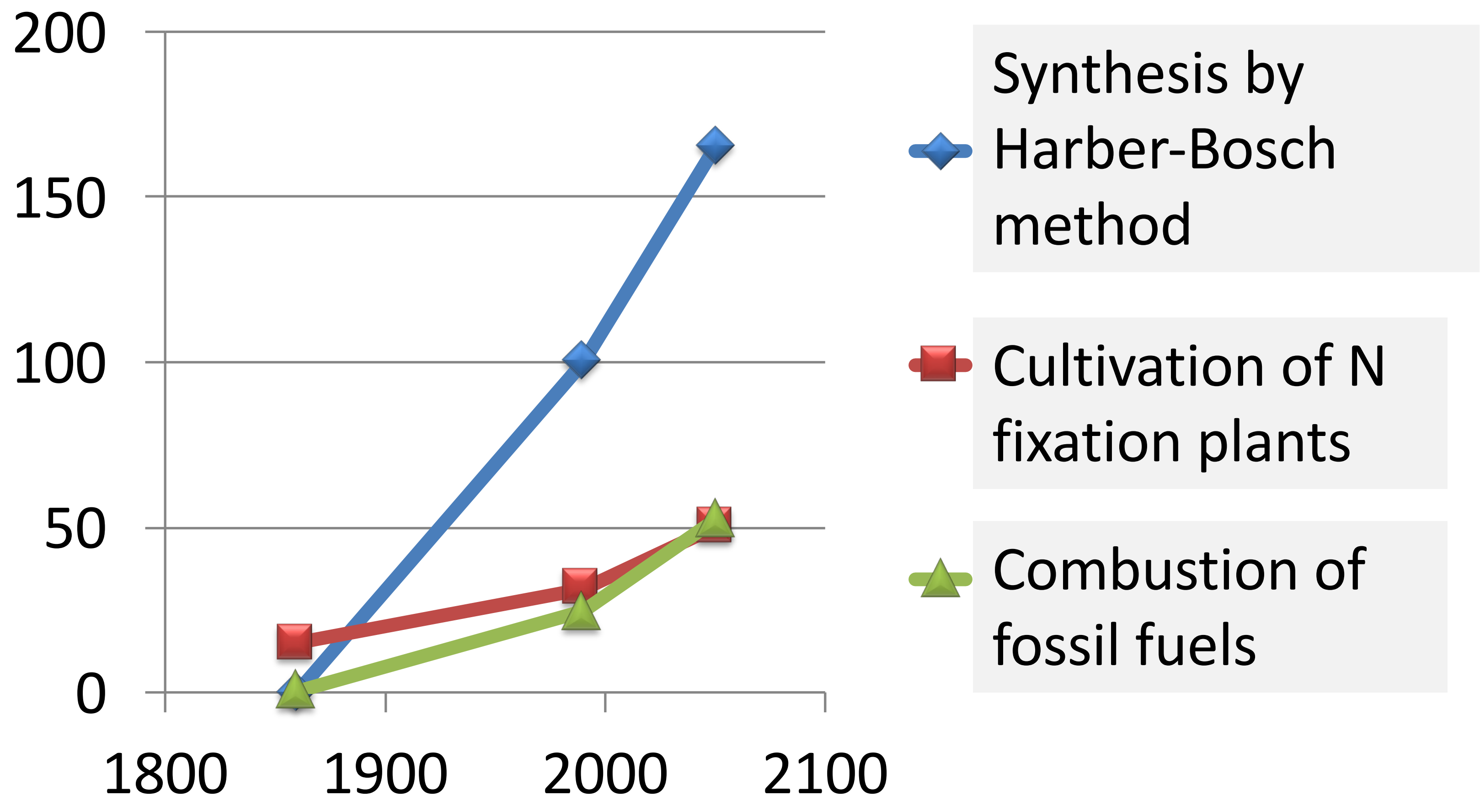
Change in natural origin N (TgN/Yr)

Galloway et al. 2004



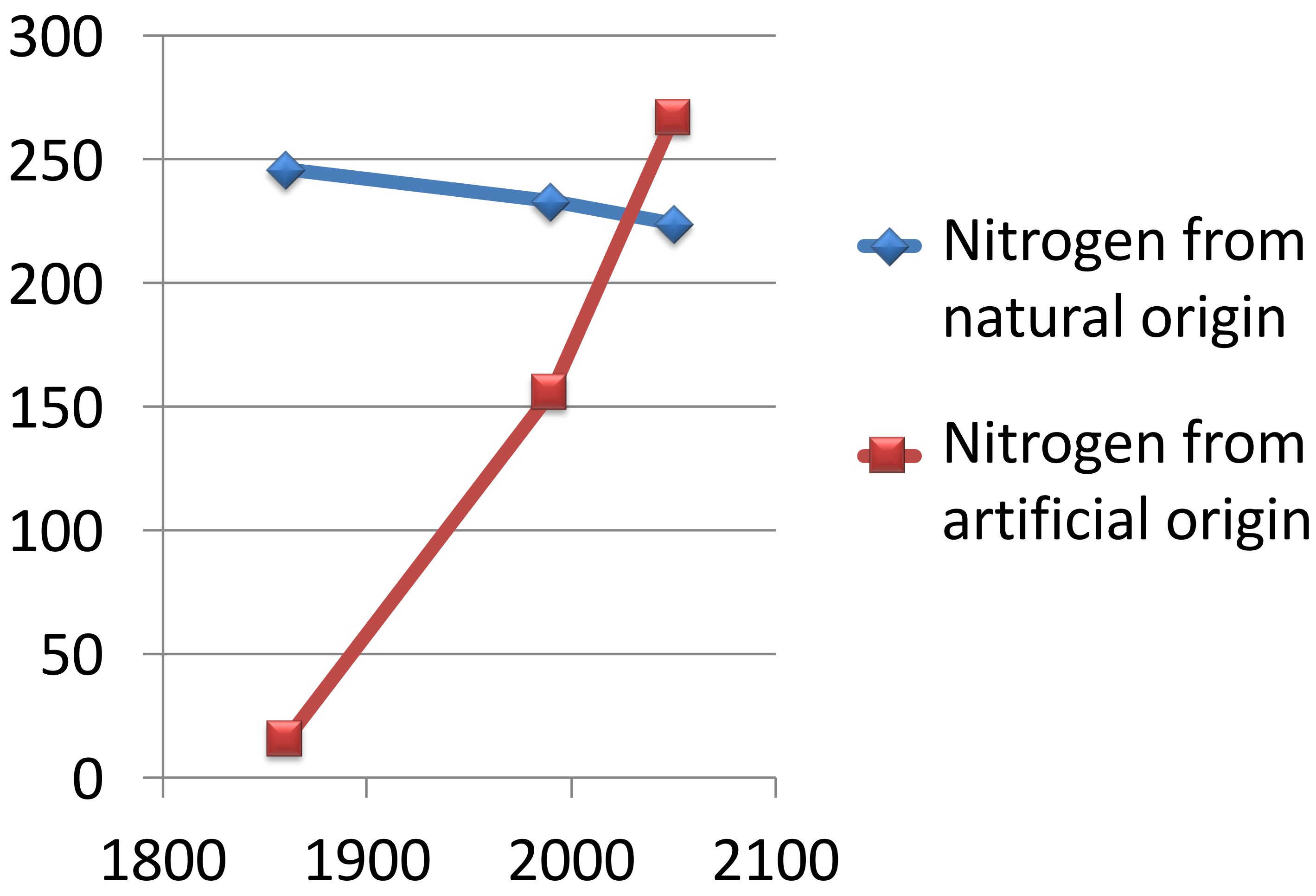
Change in artificial origin N (TgN/Yr)

Galloway et al. 2004



Change in reactive nitrogen (TgN/Yr)

Galloway et al. 2004



Supply of nitrogen into soil ecosystem

<table>
<tr><td rowspan="6">Non symbiotic N fixer</td><td rowspan="2">Heterotrophic microbes</td><td>Aerobic microbes</td><td>Azotobacter, Beijerinckia</td></tr>
<tr><td>Anaerobic microbes</td><td>Clostridium</td></tr>
<tr><td rowspan="4">Autotrophic microbes</td><td>Blue green algae</td><td>Anabaena, Nostoc</td></tr>
<tr><td>Photosynthetic bacteria</td><td>Rhodospirillum</td></tr>
<tr><td>Methanogenic bacteria</td><td>Methanosarcina</td></tr>
<tr><td>Sulfate reducing bacteria</td><td>Desulfovibrio</td></tr>
<tr><td>Associative N fixer</td><td colspan="3">Azospirillum: living in the root zone of rice and wheat.</td></tr>
<tr><td>Symbiotic N fixer</td><td colspan="3">Root nodule bacteria, actinomysetes (Frankia), fungi,
Blue green algae (Anabaena)</td></tr>
</table>

Loss of nitrogen from soil ecosystem

1. Volatilization: Heating, burning, and denitrification
2. Run off: Movement of water on the inclined ground surface
3. Leaching: Movement of water in vertical direction
4. Harvest of agricultural crops.

Feature of nitrogen circulation

- Carbon: Open circulation
- Nitrogen: Relatively closed circulation
- Input of nitrogen in the circulation is limited.

  → Once lost, it is difficult to recover.

For the rehabilitation of the ecosystem,

Securing of the input pathway is important.

To prevent the degradation of ecosystem,

Control of output pathways is necessary.

Nitrogen fixation

$N_2 + 2H^+ + 8e^- + 16ATP \rightarrow 2NH_3 + H_2 + 16ADP + 16Pi$

(Nitrogenase)

Large amount of energy (in the form of 16 ATP) is necessary to reduce nitrogen. Nitrogenase in the nitrogen fixing bacteria conveys this reaction. As nitrogenase is unstable under oxygen, nitrogen fixing bacteria have various mechanisms to keep away from oxygen.

Acetylene reducing ability (ARA) is used as a simple and sensitive detection method for nitrogen fixing ability, because acetylene and ethylene can be detected easily by gas-chromatography.

C_2H_2 (acetylene) $+ 2H^+ + 8e^- + 16ATP$

$\rightarrow$ C_2H_4 (ethylene) $+ H_2 + 16ADP + 16Pi$

(Nitrogenase)

Significance of biological nitrogen fixation

Molecular nitrogen comprising 78 % of global atmosphere can not be used directly by most of living things.
Living things can use only “Fixed nitrogen”.
Amount of biologically fixed nitrogen（13×10^{10} kg・yr^{-1}）is two times larger than the non-biologically fixed N amount（5×10^{10} kg・yr^{-1}）.
Living things have important roles in the circulation of nitrogen.

Nitrification

- Divided into ammonia oxidation and nitrous acid oxidation.
- Cooperation of ammonia reducing and nitrous acid reducing bacteria.

Denitrification
= Nitric acid reduction

Oxygen is removed from nitric acid by denitrification bacteria under reduced soil condition, and transformed to N_2 via NO and N_2O.

Features of denitrification bacteria.

- Wide range of microbes, including Eubacteria, Archaebacteria, and Eukaryotic microbes, have ability of denitrification, and occur widely in soil. Generally, more abundant in plowed soil than in unplowed soil. In paddy soil, nitrification occurs in the surface layer, and the formed NO_3^- leaches into the anaerobic reduced layer, where it is denitrified. Denitrifying ability in the root zone soil is much higher than that in the non-root zone soil.

Features of denitrification bacteria.

- Denitrification bacteria belong to facultative anaerobic bacteria and can use oxygen for the final electron acceptor. Therefore, denitrification does not occur under the existence of oxygen.
- However, due to the heterogeneity of soils, redox status of micro-site in and outside of the soil aggregates varies largely, and nitrification occurs even in the aerobic soils.

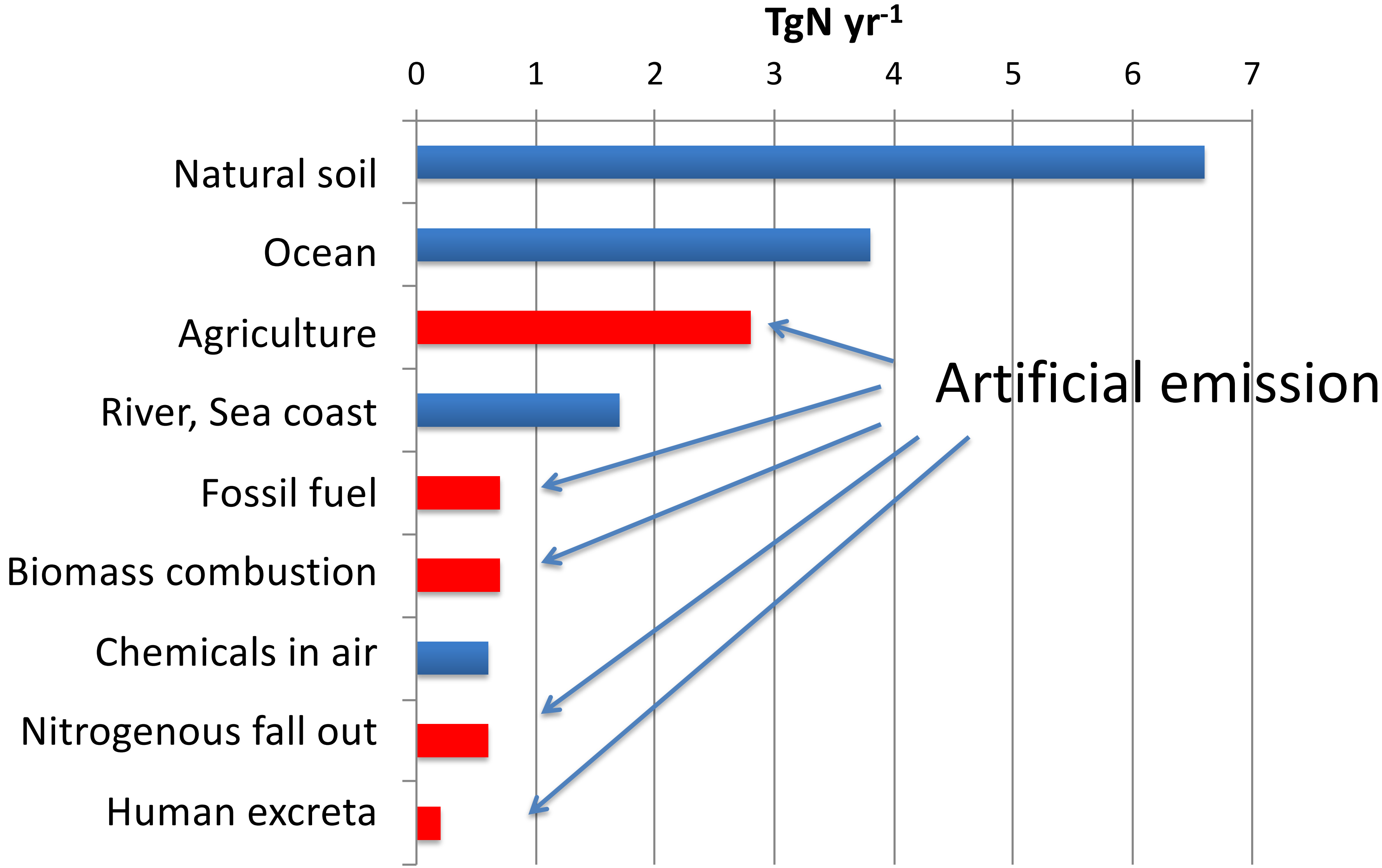
Significance of denitrification

- Denitrification contributes to the terrestrial nitrogen circulation. If denitrification does not occur, nitrogen distribution on the earth will be restricted in ocean.
- Removal of nitrate from the environment.

  Prevent the eutrophication of the aquatic ecosystem. Increase of nitrate concentration in water and crops is anticipated recently. Denitrification mitigates this tendency.

Items of global N_2O emission

Denman K. L. et al. (2007)



Emission of N_2O from the agricultural soil.

- Emission of N_2O from the fertilizer and domestic animal excrements treatment occupy 40 % of the global emission of N_2O.
- 0- few % of the applied fertilizer N are lost by volatilization.
- Emission is large from the soil with poor drainage.

Mechanism of N_2O formation

- Formed by both nitrification and denitrification.
- Causes global warming and the destruction of ozone layer.
- Contribution to the global warming is in the order of $CO_2 > CH_4 > N_2O$.
- Atmospheric N_2O concentration increased 16 % from 270ppb (before the Industrial Revolution) to 319ppb in 2005.

Nitrogen form transformation in paddy soils

Oxidized layer： NH_4^+ → NO_3^-
（Nitrifying bacteria
＝Ammonia oxidizer＋Nitrite oxidizer）

Oxidized layer to Reduced layer: Leaching of NO_3^-

Reduced layer： NO_3^- → NO_2^- → NO → N_2O → N_2
（Denitrifying bacteria）

Loss of fertilizer N due to denitrification and the deep application of fertilizer.

- Drs. Shioiri and Aomine (1937) clarified the mechanism of nitrification and denitrification in paddy soil, and developed the technique of deep layer application of ammonium sulfate to prevent the denitrification and loss of nitrogen from the paddy soil.

- If ammonium sulfate is applied directly to the reduced layer, nitrification and the following denitrification do not occur.

Reducing the emission of N_2O from the agricultural soil.

- Improve the drainage.
- Intermittent drainage during the growing season.
- Reduce the application of Nitrogen fertilizer.
- Fertilizer management

  Use slow release fertilizer

  Use fertilizer containing

  nitrification inhibitor agent.

Nitrogen transformation in compost (1)

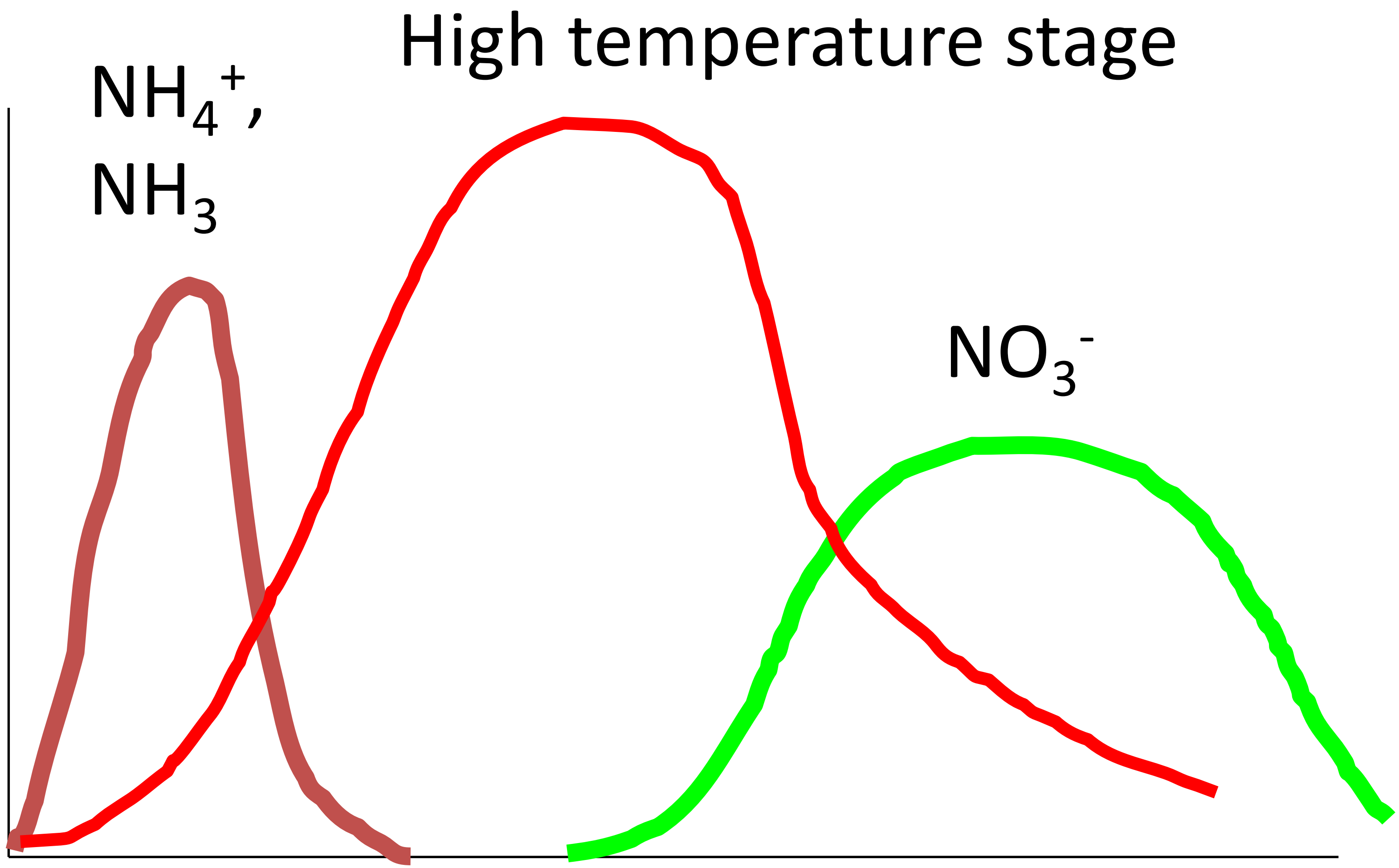
- Organic nitrogen is decomposed and ammonia is formed. （Occurs in the initial stage of composting. pH increases at the same time.）

- Volatilization of ammonia. （Causes the loss of nitrogen and air pollution. ）

Nitrogen transformation in compost (2)

- Change from ammonium to nitrate.

  （Occur in the late stage of composting. Indicating the maturity of compost.）



Process of composting and the formation of ammonia and nitrate.

Transformation of N in plants

- Absorption of ammonium and nitrate.
- Reduction of nitrate of ammonia.
- Immobilization of ammonia.

  Synthesis of amino acid and protein.

Immobilization

- Important functions of plants and autotrophic microbes.
- Nitrate is transformed via ammonium ion to a mino acids by the action of nitric acid reducing and ammonia assimilating enzymes
- Nitric acid reducing enzyme (NR). Nitrous acid reducing enzyme (NiR)
- Glutamine synthetase (GS),
- Glutamic acid synthetase (GOGAT)

Mineralization

- Conveyed by heterotrophic bacteria and facultative autotrophic bacteria.

- Microbial hydrolysis of amino acids and nucleic acids, de-amino reaction, and ammonification.

Transformation of N compounds related to organic matter application.

- Whether ammonium nitrogen is released from the applied organic matter depends on the ratio of C and N (C/N ratio) of the organic matter.

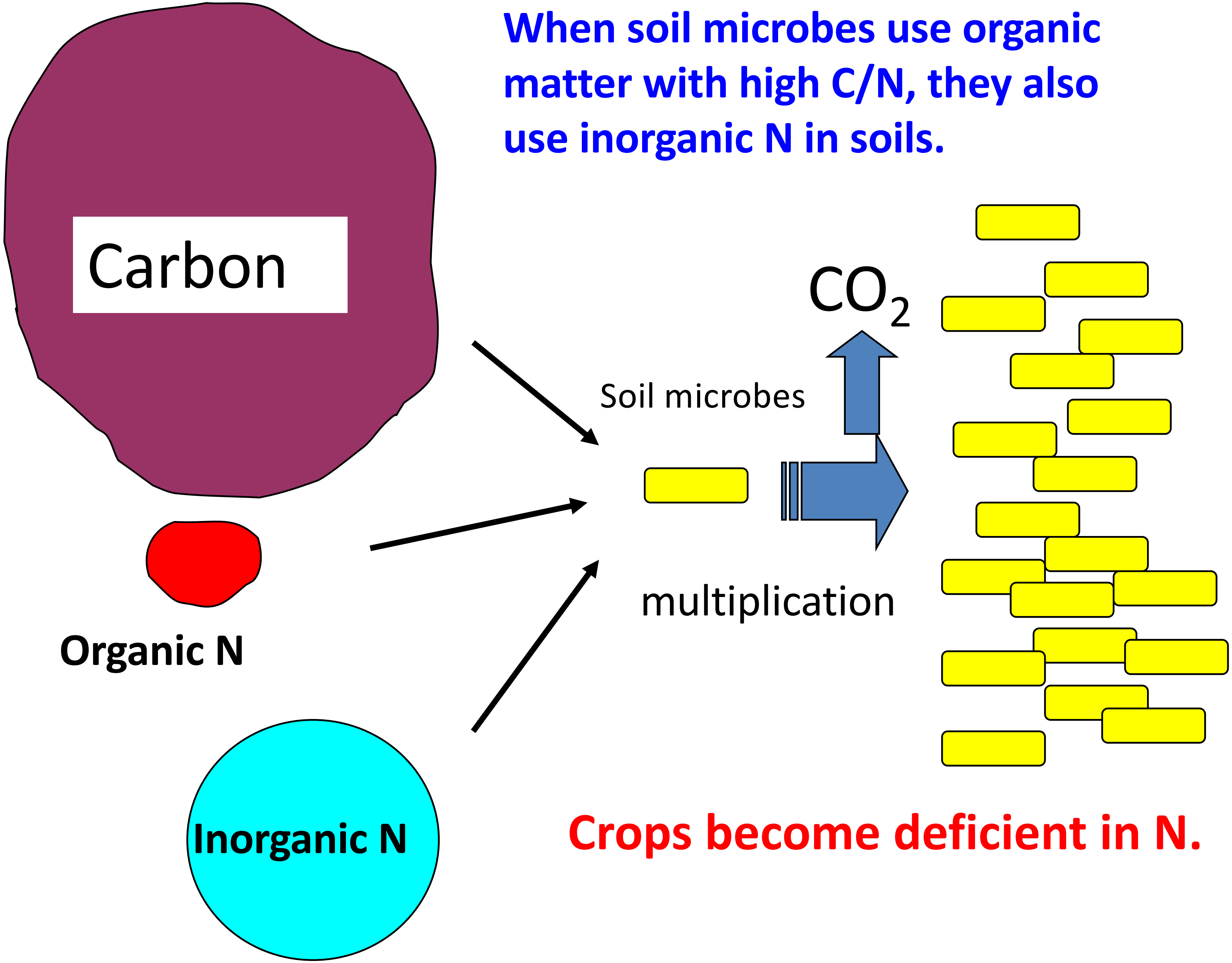
C/N ratios of various organic matter

Organic matter	C/N ratio
Microbes body	5 ～ 10
Young sweet clover	12
Matured compost	20
Matured clover	23
Green rye shoot	36
Rice straw	60 ～ 80
Saw dust	400

Relationships between C/N ratio and the mineralization of organic nitrogen.

When organic matter with C/N > 20 is added, mineralized N is used for the growth of microbes, and no nitrogen is released into soils. Competition for inorganic nitrogen between crops and microbes occurs, and crops become deficient in nitrogen. → **nitrogen starvation**

When soil microbes use organic matter with high C/N, they also use inorganic N in soils.



Crops become deficient in N.

Nitrogen starvation

- When microbes grow, they need 1/5 to 1/10 amount of N relative to C in its growth medium.
- When the C/N ratio of the organic matter is higher than 20, N in the organic matter will be incorporated into the microbial body, and the inorganic N in soil will be used in addition. This brings the N deficiency for the crops.

To avoid N starvation.

- Decrease C/N ratio by composting the organic matter.
- Grow crops after leaving enough duration after applying organic matter in the field.
- Apply necessary amount of N fertilizer.

Effect of organic matter application as nitrogen source.

- High C/N OM → Slow decomposition.
  → Slow effect.
- Low C/N OM → Fast decomposition
  → High and rapid effect.

“Good soil making” and organic matter application

“Good soil making” in old times:

Slow effect by fallen leaves and rice straw application.

Organic fertilizer in the recent agriculture,

such as the waste from animal husbandry:

Brings rapid effects

but causes environmental pollution at the same time.

Carrying capacity (Environmental capacity)

- The maximum load of pollutants carried by soil, water, and air without affecting the environment for living things.
- 200kg N/ ha of crop field with respect to nitrogen.
- It the total crop field in Japan is 5 million ha,

  Carrying capacity for nitrogen will be 1 million ton.

  When large amount of chemical N fertilizer is used,

  carrying capacity of soil for nitrogen from other sources will decrease.

Where goes the nitrogen emitted into the environment?

- In Japan, nitrogen emitted from agriculture, animal husbandry, and daily human life are already exceeding the carrying capacity of Japanese soils.
- Nitrogen which could not be carried by soil pollutes the environment and the ecological system.

How to decrease the nitrogen emission?

- Save the use of chemical fertilizer.
- Increase the efficiency of fertilizers and decrease the residual nitrogen.
- Do not decrease the valuable crop field.
- Increase the self support percentage of food.
- Decrease the import of forage, and use the domestic forage.
- Decrease the waste of food.