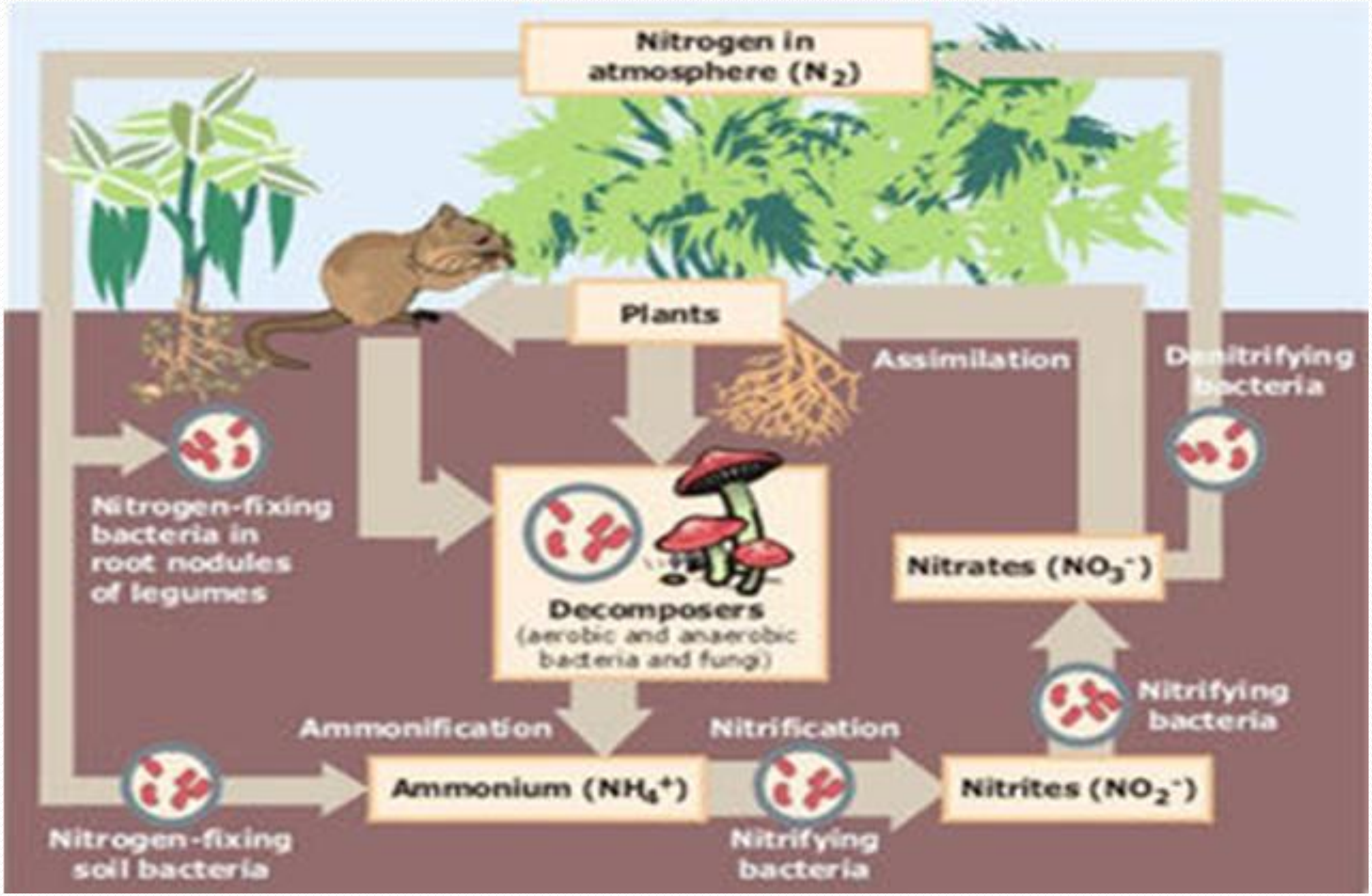
Nitrogen cycle

- The **nitrogen cycle** is the biogeochemical cycle that describes the transformations of nitrogen and nitrogen-containing compounds in nature.

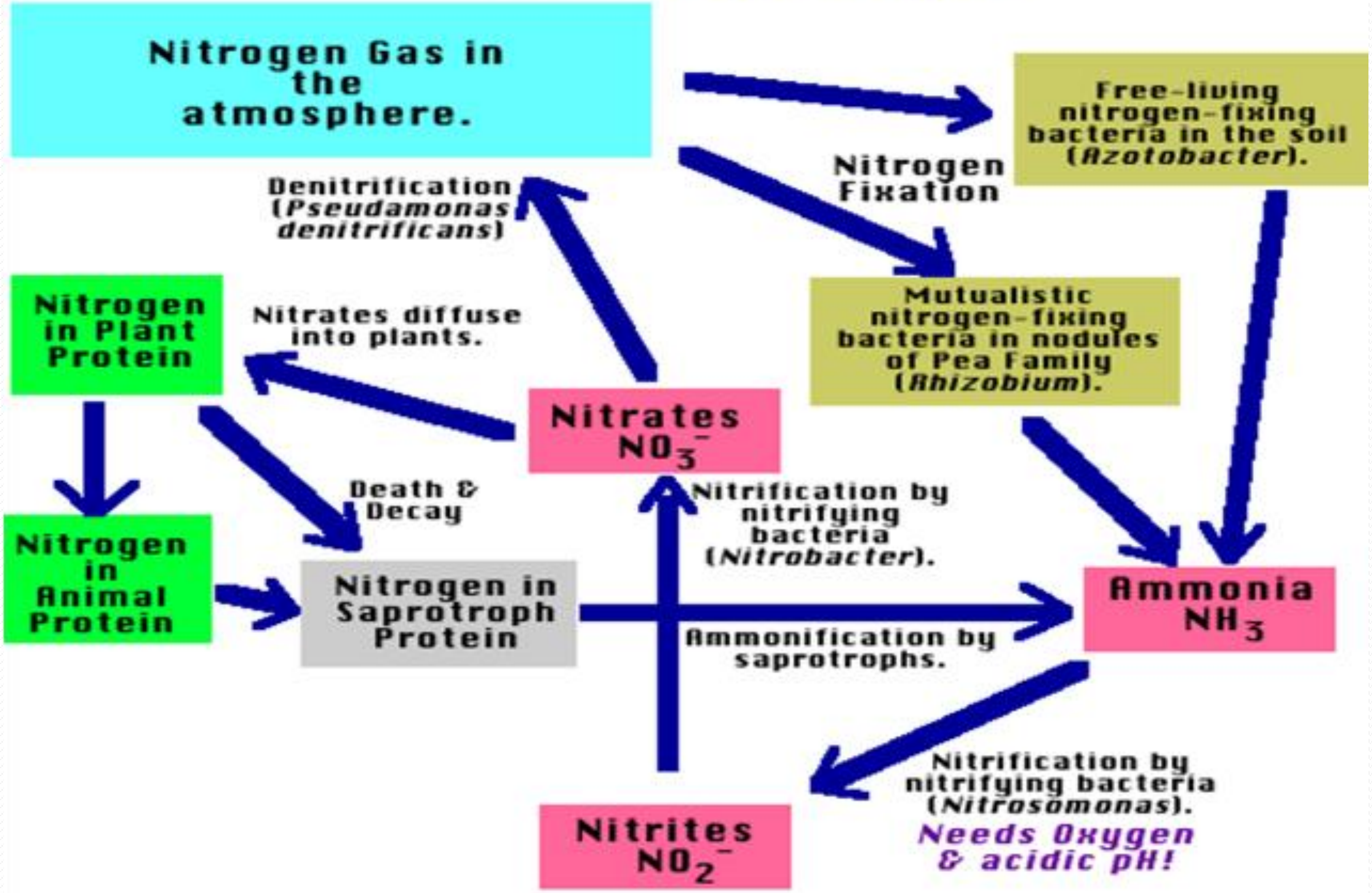
The basics

- Earth's atmosphere is about 78% nitrogen making it the largest pool of nitrogen
- Nitrogen is essential for many biological processes; it is in all amino acids, is incorporated into proteins, and is present in the bases that make up nucleic acids, such as DNA and RNA
- In plants, much of the nitrogen is used in chlorophyll molecules which are essential for photosynthesis and further growt.
- Processing, or fixation, is necessary to convert gaseous nitrogen into forms usable by living organisms.
- Some fixation occurs in lightning strikes, but most fixation is done by free-living or symbiotic bacteria.
- These bacteria have the nitrogenase enzyme that combines gaseous nitrogen with hydrogen to produce ammonia

Schematic representation of the Nitrogen cycle



The Nitrogen Cycle



Characteristics of the cycle

- **95 % of dissolved nitrogen is in the form of molecular nitrogen N_2**
- **Nitrogen has 9 oxidation states from -3 to +5**

+5	NO_3^-, N_2O_5
+4	NO_2
+3	HONO, NO_2^-, N_2O_3
+2	NO
+1	HONNOH, $HO_2N_2^-$, $N_2O_2^{2-}$, N_2O
0	N_2
-1	H_2NOH, HN_3, N_3^-
-2	H_2NNH_2
-3	RNH_2, NH_3, NH_4^+

- **Presence of internal processes such as , nitrogen fixation, nitrification and denitrification**
- **Unbalanced budget**
- **At the pH and pE of seawater all the nitrogen should be present as NO_3^-**

Nutrient Budget of the ocean (units: million metric tons)

	Nitrogen	Phosphorus	Silicon
Reserve in ocea	**920,000**	**120,000**	**4,000,000**
Annual use by plankton	**9,600**	**1,300**	**-**
Annual contribtion by:			
•Rivers (dissolved)	**19**	**2**	**150**
•Rivers (suspended)	**0**	**12**	**4,150**
•rain	**59**	**0**	**0**
Annual Loss to sediments	**9**	**13**	**3,800**

Nitrogen budget

- **Input is greater than the output by 70 M metric ton,**
- **Nitrogen present in the ocean represents 100 times the quantity needed by the phytoplankton,**
- **Nitrogen residence time in the ocean is 13000 year**
- **The unbalanced budget means that nitrogen escapes from the ocean as nitrogen gas**
- **This process keeps the nitrogen present in the atmosphere**
- **Denitrification in the sediments could not be entirely responsible for the return of nitrogen gas to the atmosphere,**
- **This process could only be responsible for 10 % of the nitrogen budget deficit,**
- **Denitrification might occur, in the water column, may happen in the presence of oxygen, in the water column, and may also happen inside some organisms**

Components of the nitrogen cycle

- **Addition and removal**
  - **Addition**
    1. **Volcanic activity,**
    2. **Atmosphere,**
       - **Gas exchange: Henry's law: $C = \alpha \times p$**

         C= equilibrium conc.;

         α = solubility constant;

         p = partial pressure of the gas in the atm.

       - **Rain water:**

     rain water contains variable conc. of amm. and nitrate

     Nitrate is most probably the result of amm. oxidation.

     Nitrate may also result from the oxidation of molecular nitrogen as follows:

$$\Delta + N_2 + O_2 \xrightarrow{\text{lighting}} 2NO$$

$$2NO + O_2 \longrightarrow 2NO_2$$

$$3NO_2 + H_2O \longrightarrow 2HNO_3 + NO$$

3. **Rivers**
   - Concentrations of NO_x in river water varies between 500-3700 μg l^{-1}
   - Average for major world rivers = 1000 μg l^{-1}
   - River input = 1/3 atmospheric input

- **Removal**

1. Loss with sedimented organic matter,
2. Loss of molecular nitrogen to the atmosphere

- **Internal processes**

all the processes leading to the transition between the different forms of nitrogen

Processes of the Nitrogen Cycle

- Nitrogen Fixation
- Nitrification
- Denitrification
- Ammonification
- Assimilation
- Anaerobic Ammonium Oxidation

Nitrification

- **Nitrification is the biological oxidation of ammonia with oxygen into nitrite followed by the oxidation of these nitrites into nitrates**
- **is performed by two different bacteria (nitrifying bacteria).**
- **The first step is done by bacteria of (amongst others) the genus *Nitrosomonas* and *Nitrosococcus***
- **The second step (oxidation of nitrite into nitrate) is (mainly) done by bacteria of the genus *Nitrobacter***
- **All organisms are autotrophs, which means that they take carbon dioxide as their carbon source for growth.**
- **Together with ammonification, nitrification form a mineralization process which refers to the complete decomposition of organic material, with the release of available nitrogen compounds.**
- **This replenishes the nitrogen cycle.**

Chemistry

- **Nitrification is a process of nitrogen compound <u>oxidation</u> (effectively, loss of electrons from the nitrogen atom to the oxygen atoms) :**

$$NH_3 + O_2 \rightarrow NO_2^- + 3H^+ + 2e^-$$

$$NO_2^- + H_2O \rightarrow NO_3^- + 2H^+ + 2e^-$$

- **Nitrification also plays an important role in the removal of nitrogen from municipal wastewater**
- **The conventional removal is nitrification, followed by denitrification.**
- **The cost of this process resides mainly in:**
  - **aeration (bringing oxygen in the reactor) and,**
  - **the addition of an extra organic energy source (e.g. methanol) for the denitrification.**

Nitrogen Fixation

- **Biological Nitrogen Fixation**
  - **Biological Nitrogen Fixation (BNF) occurs when atmospheric nitrogen is converted to ammonia by a pair of bacterial enzymes called nitrogenase**
  - **The formula for BNF is**

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

  - **Although ammonia (NH_3) is the direct product of this reaction, it is quickly ionized to ammonium (NH_4^+)**
  - **the nitrogenase-generated ammonium is assimilated into glutamate**

Denitrification

- **Denitrification is the process of reducing nitrate and nitrite, highly oxidised forms of nitrogen available for consumption by many groups of organisms, into gaseous nitrogen**
- **It can be thought of as the opposite of nitrogen fixation, which converts gaseous nitrogen into a more biologically available form.**
- **The process is performed by heterotrophic bacteria (such as *Paracoccus denitrificans*, *Thiobacillus denitrificans*, and various pseudomonads) from all main proteolytic groups**

Environmental conditions

- **Denitrification takes place under special conditions in both terrestrial and marine ecosystems**
- **In general, it occurs when oxygen (which is a more favourable electron acceptor) is depleted, and bacteria turn to nitrate in order to respire organic matter**
- **Because our atmosphere is rich with oxygen, denitrification only takes place in some soils and groundwater, wetlands, poorly ventilated corners of the ocean, and in seafloor sediments.**
- **Denitrification proceeds through some combination of the following steps:**
  - **nitrate → nitrite → nitric oxide → nitrous oxide → dinitrogen gas**
- **or expressed as a redox reaction:**
  - $2NO_3^- + 10e^- + 12H^+ \rightarrow N_2 + 6H_2O$

Nitrogen loss to sediments

- Nitrogen is lost to sediments buried with the organic matter
- It may also be lost due to ionic exchange on the surface of silicate particles
- Biological mineralization regenerates nitrogen and returns it to the water column
- Organic N decreases with depth in the sedimentary column while amm. N increases
- Organic N lost from sediments is less than inorganic N accumulating in the pore water
- Nitrogen is returned to the water column as, NH_3, NH_4^+, N_2, NO_2^-, NO_3^-
- Nitrogen generation from sediments is of great importance in the nitrogen cycle

Calculation of N loss due to denitrification in the water column

1- Use of Apparent Oxygen Utilization AOU

AOU: C : N : P = 270 : 106 : 16 : 1 **aerobic conditions**

AOU C : N : P = 235 : 106 : 16 :1 **anoxic**

$$\Delta N_2B(P) = 15[PO_4^{3-}] – \{[NH_4^+ + [NO_2^-] + [NO_3^-]\}$$

$$\Delta N_2B(O)\ \text{aerobic} = 0.056\ (AOU) - \{[NH_4^+ + [NO_2^-] + [NO_3^-]\}$$

$$\Delta N_2B(O)\ \text{anoxic} = 0.064\ (AOU) - \{[NH_4^+ + [NO_2^-] + [NO_3^-]\}$$

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Ammonification

- Mineralisation is the process by which organic matter is broken down into inorganic matter. Organic matter that is not eaten (and even matter that is eaten) is quickly broken down by bacteria which utilize some of the organic matter for their own use and release inorganic compounds. Mineralisation of organic nitrogenous compounds normally results in **ammonia** (NH_3 and/or NH_4^+) and is also called ammonification.
- The process of mineralisation of proteins can be summarised as follows:

protein <u>proteinases</u> peptides <u>peptidases</u> amino acids

<u>deamination</u> organic acid + ammonium (Herbert, 1999).