

Definition: Nitrogen cycle

- The nitrogen cycle is the biogeochemical cycle that describes the transformations of nitrogen and nitrogen-containing compounds in nature.
- It is a cycle which includes gaseous components

Importance of Nitrogen

- All life requires nitrogen-compounds, e.g., Proteins and nucleic acids.
- Air, which is 79% nitrogen gas (N_2), is the major reservoir of nitrogen.
- But most organisms cannot use nitrogen in this form.

The Processes of the nitrogen cycle

- Conversion of N_2 - fixation
- Assimilation
- Ammonification
- Nitrification
- Denitrification
- Anaerobic ammonium oxidation

Conversion of N₂

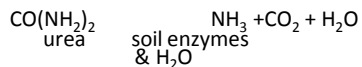
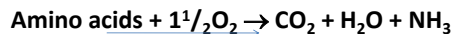
- The conversion of nitrogen (N₂) from the atmosphere into a form readily available to plants and hence to animals and humans is an important step in the nitrogen cycle, that determines the supply of this essential nutrient.
- There are four ways to convert N₂ (atmospheric nitrogen gas) into more chemically reactive forms
 - Biological fixation
 - Industrial nitrogen fixation
 - Combustion of fossil fuels
 - Other processes e.g. lightning

Assimilation

- Plants can absorb nitrate or ammonium ions from the soil via their root hairs.
- If nitrate is absorbed, it is first reduced to nitrite ions and then ammonium ions for incorporation into amino acids, proteins, nucleic acids (DNA), and chlorophyll

Ammonification

- When a plant or animal dies, or an animal excretes, the initial form of nitrogen is organic.
- Bacteria, or in some cases, fungi, convert the organic nitrogen within the remains back into ammonia, a process called ammonification or mineralization.



Nitrification

- The conversion of ammonia to nitrates is performed primarily by soil-living bacteria and other nitrifying bacteria.
- The primary stage of nitrification, the oxidation of ammonia (NH₃) is performed by bacteria such as the *Nitrosomonas* species, which converts ammonia to nitrites (NO₂⁻).
- Other bacterial species, such as the *Nitrobacter*, are responsible for the oxidation of the nitrites into nitrates (NO₃⁻).
- Nitrites need to be converted to nitrates because accumulated nitrites are toxic to plant life

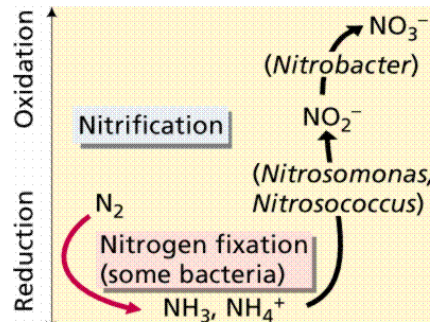
Nitrification...

- This involves two oxidation processes
- The ammonia produced by ammonification is an energy rich substrate for **Nitrosomas** bacteria
- They oxidise it to nitrite:

$$\text{NH}_3 + 1\frac{1}{2}\text{O}_2 \rightarrow \text{NO}_2^- + \text{H}_2\text{O}$$
- This in turn provides a substrate for **Nitrobacter** bacteria oxidise the nitrite to nitrate:

$$\text{NO}_2^- + \frac{1}{2}\text{O}_2 \rightarrow \text{NO}_3^-$$

Nitrification...



Denitrification

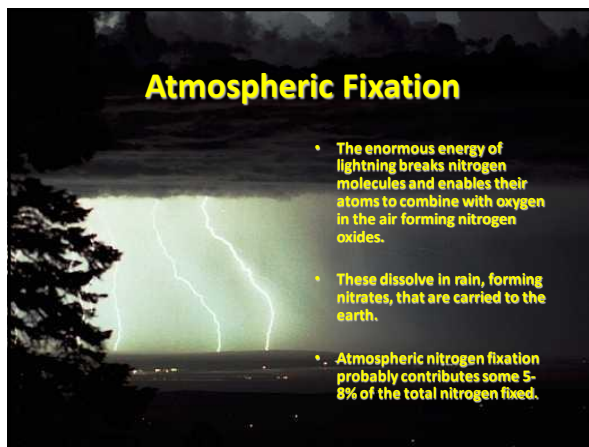
- Denitrification is the reduction of nitrates back into the largely inert nitrogen gas (N_2), completing the nitrogen cycle.
- This process is performed by bacterial species such as *Pseudomonas* and *Clostridium*.
- They live deep in soil and in aquatic sediments where conditions are anaerobic. These anaerobic bacteria can also live in aerobic conditions

Anaerobic ammonium oxidation

- In this biological process, nitrite and ammonium are converted directly into dinitrogen gas.
- This process makes up a major proportion of dinitrogen conversion in the oceans.

Conversion of N₂ (Nitrogen fixation)

- Nitrogen fixation is the process by which nitrogen is taken from its relatively inert molecular form (N₂) in the atmosphere and converted into nitrogen compounds such as:
- Ammonia (NH₃),
- nitrate (NO₃⁻) and
- nitrogen dioxide (NO₂)



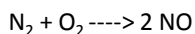
Atmospheric Fixation

- The enormous energy of lightning breaks nitrogen molecules and enables their atoms to combine with oxygen in the air forming nitrogen oxides.
- These dissolve in rain, forming nitrates, that are carried to the earth.
- Atmospheric nitrogen fixation probably contributes some 5-8% of the total nitrogen fixed.

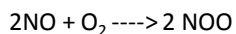
Atmospheric Fixation...

Lightning causes reaction with O₂ to form NO₃⁻ as follows:

- When a voltage of 30,000 volts passes through the air, nitric oxide is formed.

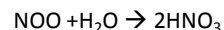


- This nitric oxide is next oxidised to nitrogen peroxide by atmospheric oxygen



Atmospheric Fixation...

- This peroxide when washed with rain water comes down as nitric acid, HNO₃ and is introduced into the soil.



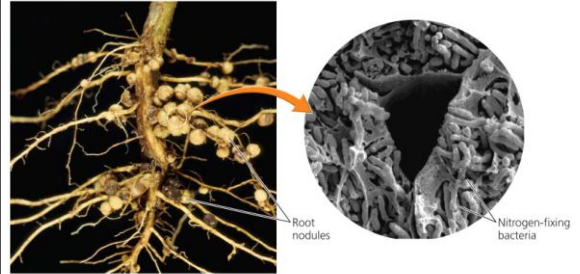
- This nitric acid reacting with CaCO₃, K₂CO₃, (NH₄)₂CO₃ are converted respectively to Ca(NO₃)₂, KNO₃ and NH₄NO₃.
- E.g. $2\text{HNO}_3 + \text{K}_2\text{CO}_3 \rightarrow 2\text{KNO}_3 + \text{CO}_2 + \text{H}_2\text{O}$
- Annually, 100 million tons of nitric acid are produced by lightning.

Biological Fixation

- The ability to fix nitrogen is found only in certain bacteria.
- Some symbiotic bacteria (most often associated with leguminous plants) and some free-living bacteria are able to fix nitrogen as organic nitrogen.
- An example of mutualistic nitrogen fixing bacteria are the *Rhizobium* bacteria, which live in legume root nodules.
- An example of the free-living bacteria is *Azotobacter*



Biological Fixation



Industrial Fixation

- Under great pressure, at a temperature of 600°C, and with the use of a catalyst, atmospheric nitrogen and hydrogen (usually derived from natural gas or petroleum) can be combined to form ammonia (NH₃).
- The Haber-Bosch Process

$$\text{N}_2 + 3\text{H}_2 \rightarrow 2\text{NH}_3$$
- Ammonia can be used directly as fertilizer, but most of its is further processed to urea and ammonium nitrate (NH₄NO₃).