

# Nitrogen Transformations

This is the 4<sup>th</sup> module of a training course titled:  
*Submerged Soils for Rice Production*

An interactive version of this presentation can be viewed  
at this site:

<http://www.knowledgebank.irri.org/submergedsoils>

# Intro to Module 4

- Nitrogen (N) is an essential nutrient taken up in large amounts by rice
- The forms and processes of N differ between submerged and aerobic soils
- The purpose of this module is to provide the user with basic information about N, its forms, and its processes
- Organization:
  - Lesson 1 & 2 give an overview
  - The remaining 5 lessons are about N forms and processes.

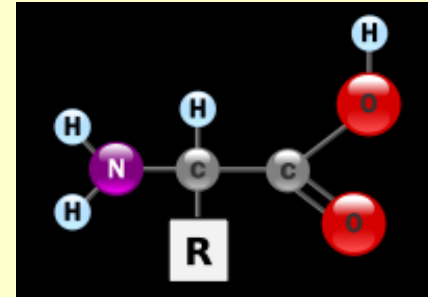


# Lesson 1 – Nitrogen around us

- Question: How is N important to the world around us?
- Objective: Become familiar with the various roles of N.

# Lesson 1 – Nitrogen: a part of life

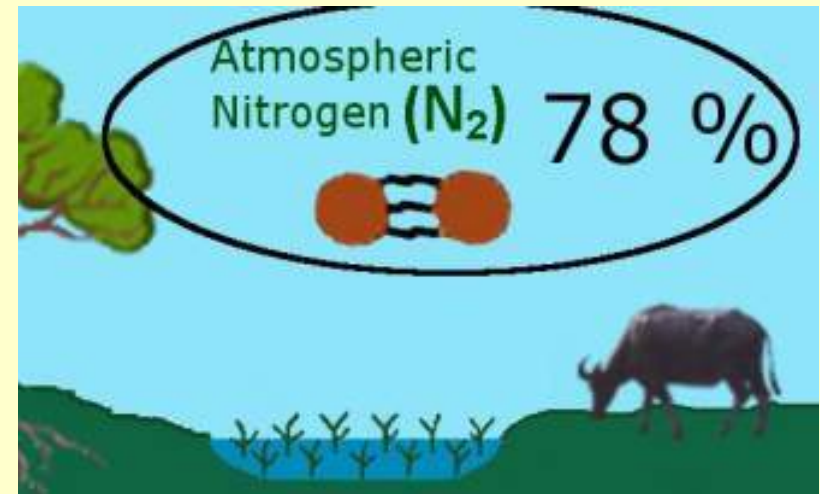
- N is an essential element for all life – it is in all amino acids, proteins, and enzymes
- It is the nutrient most often limiting rice production.
- N is found in all types of animal waste. N content ranges from 0.5-2%.



# Lesson 1 – Nitrogen around us

An abundant supply of N

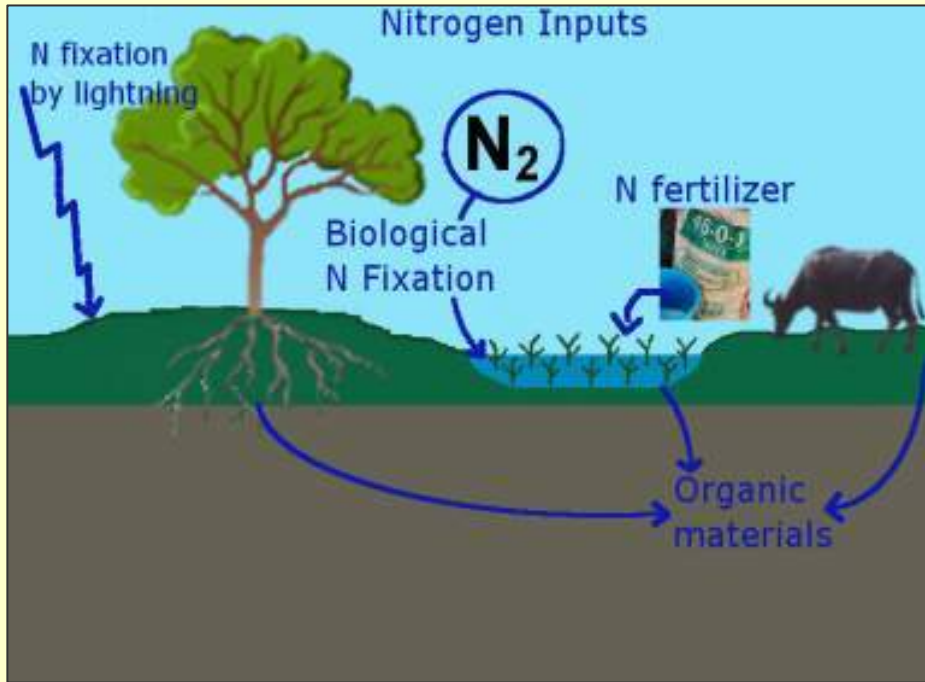
- 78% of earth's atmosphere is dinitrogen gas ( $N_2$ )
- However, much energy is required to break the triple bond between the atoms of N within  $N_2$
- Most living organisms can't use  $N_2$  from the atmosphere as a source of N



# Lesson 1 – An important scientific discovery

- In the early 1900's, two German scientists, Haber and Bosch, developed a process to convert  $N_2$  from the atmosphere into ammonia ( $NH_3$ ).
- In this process,  $N_2$  is reacted at elevated pressure and temperature with hydrogen gas, usually derived from natural gas (methane).
- This is still the main process used to create synthetic N fertilizer

# Lesson 1 – Nitrogen entering the rice production system

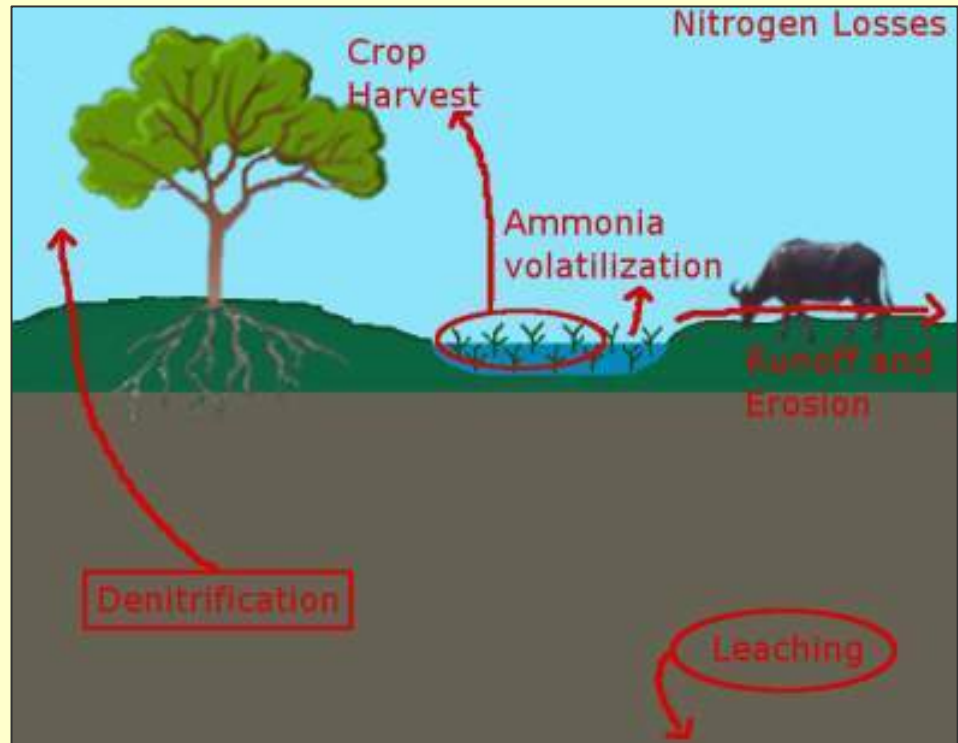


This diagram shows sources of N for the rice production system.

- N fertilizer – N<sub>2</sub> is converted into plant usable forms using fossil fuel energy
- Organic materials – N is made available to plants after decomposition
- Biological N fixation – microorganisms convert N<sub>2</sub> into a form usable by plants
- Lightning – energy from lightning converts N<sub>2</sub> into a form usable by plants

# Lesson 1 – Nitrogen leaving the rice production system

- Crop Harvest – N in the grain is removed at harvest
- Ammonia volatilization – N from fertilizer can be lost as a gas
- Denitrification – Nitrate converts to N gases escaping into the atmosphere
- Runoff – N is carried from the rice paddy by surface water
- Leaching – N moves with water down into soil becoming unavailable



This diagram shows how N is lost or removed from the rice production system.



# Lesson 1 – Summary slide

- N is found in the basic building blocks of life like amino acids and proteins
- N is abundant in the atmosphere as  $N_2$  but most living organisms can't use it
- A significant amount of fossil fuel energy is used to create N fertilizer from  $N_2$  in the atmosphere
- There are several ways which N flows in and out of the rice production system

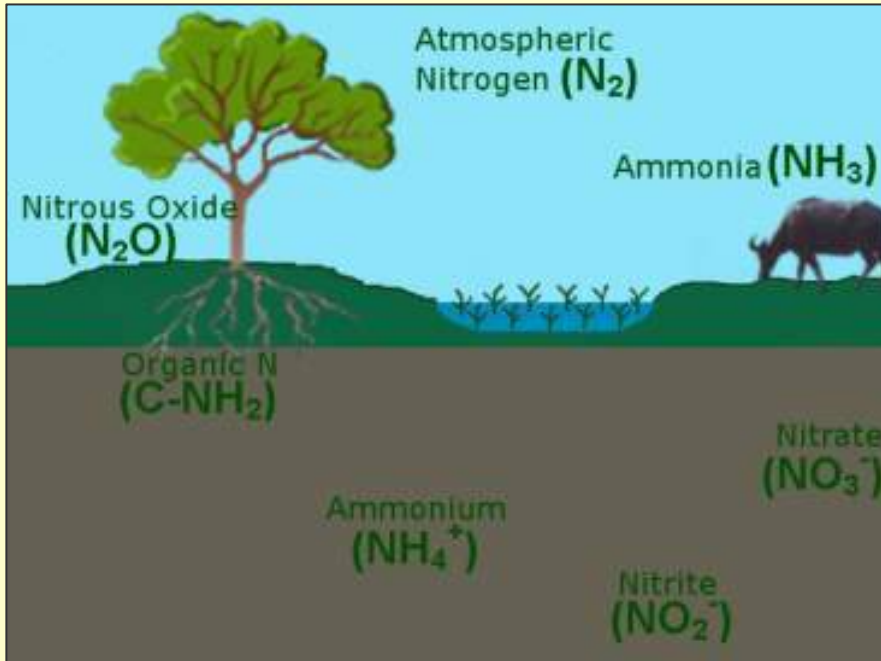
# Lesson 2 – Nitrogen forms and processes

- Question: What are common forms of N and the processes causing N to change forms?
- Objective: Be familiar with common N forms and processes.

# Lesson 2 – Nitrogen in soil

- Organic N
  - The N is bonded to a carbon atom
  - More than 95% of N in soil is in organic matter
- Inorganic N (also called mineral N)
  - Plants take up N in an inorganic form
  - Nitrate ( $\text{NO}_3^-$ ) and ammonium ( $\text{NH}_4^+$ ) are the main inorganic forms used by plants
  - $\text{NO}_3^-$  and  $\text{NH}_4^+$  represent a small fraction of total N in soil

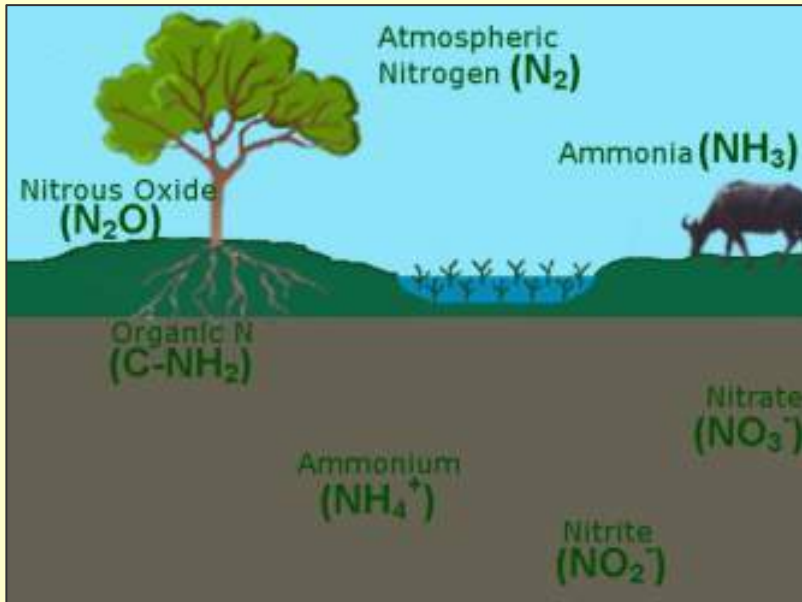
# Lesson 2 – Nitrogen forms (1)



7 nitrogen forms typically present where rice is produced in submerged soil

- Dinitrogen ( $N_2$ ) is the most abundant gas in earth's atmosphere; 2 N atoms triple bonded together make it stable and unusable by most plants.
- Ammonia ( $NH_3$ ) is a gas at normal temperature and pressure; it volatilizes into the atmosphere;
- Nitrate ( $NO_3^-$ ) is dissolved in water; it is the primary inorganic form of N in aerobic soil; and it is lost through leaching or runoff due to high solubility
- Nitrite ( $NO_2^-$ ) is dissolved in water; and it is an intermediary product of nitrification and denitrification

# Lesson 2 – Nitrogen forms (2)



7 nitrogen forms typically present where rice is produced in submerged soil

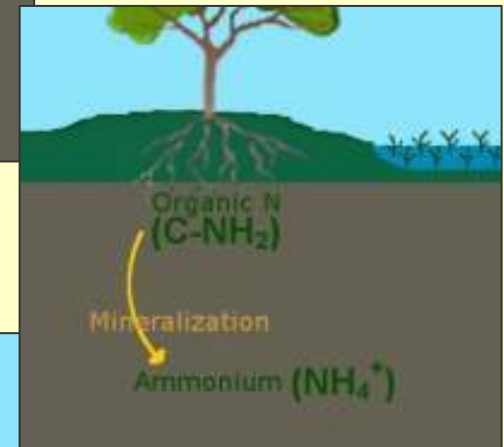
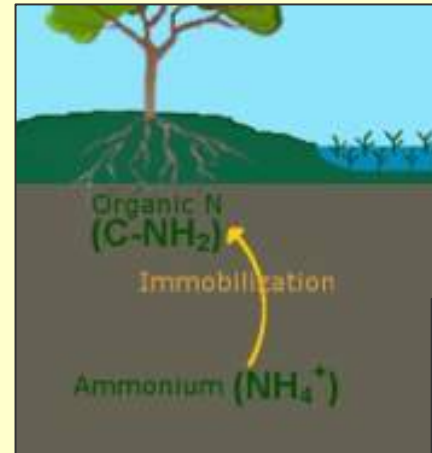
- Ammonium ( $NH_4^+$ ) the primary inorganic form of N in anaerobic soil; N is released from decomposing organic materials in this form
- Organic N ( $C-NH_2$ ) the most common form of N in soil; N is bonded to a wide variety of carbon structures; it must be mineralized before it is available to plants
- Nitrous oxide ( $N_2O$ ) is a potent 'greenhouse' gas that may be produced during nitrification and denitrification; it also acts as a catalyst in breaking down ozone in upper atmosphere.

# Lesson 2 – Reactive nitrogen

- Most forms of N in the environment are reactive:
  - They react chemically with other compounds and/or biologically with other organisms
  - N<sub>2</sub> is the primary exception to this
- The processes shown in the next 3 slides reflect how N reacts and is transformed into other compounds.

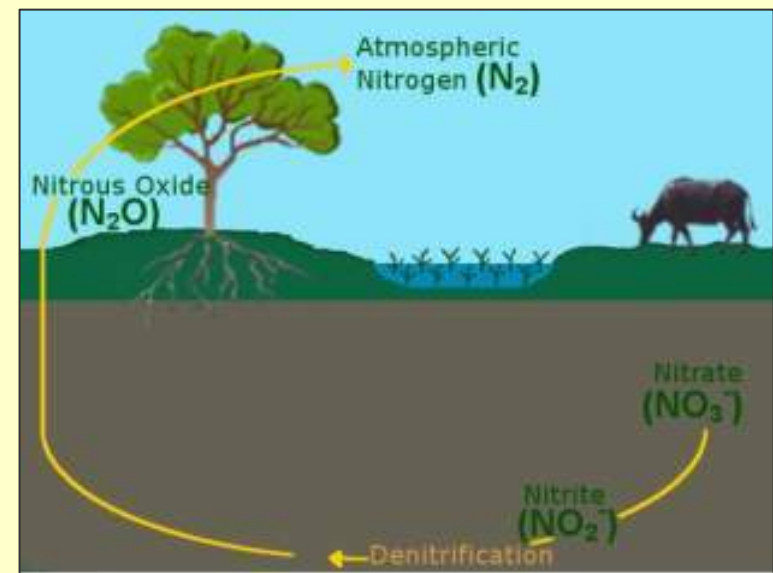
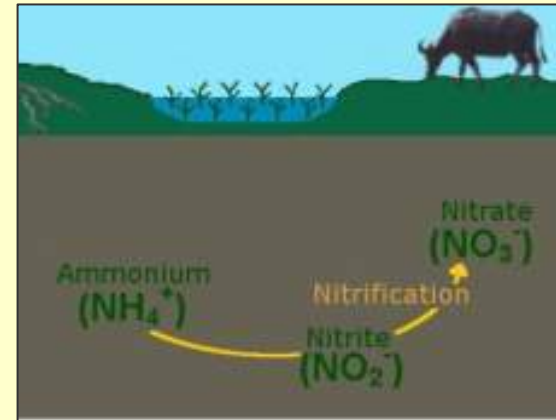
# Lesson 2 – Intro to Nitrogen processes (1)

- Immobilization – plant available forms of N are used by microorganisms; N becomes temporarily unavailable (Lesson 3)
- Mineralization – organic forms of N are transformed into a plant available form (Lesson 3)
- Ammonia volatilization - urea fertilizer converts to ammonia gas and is lost to the atmosphere (Lesson 4)



# Lesson 2 – Intro to Nitrogen processes (2)

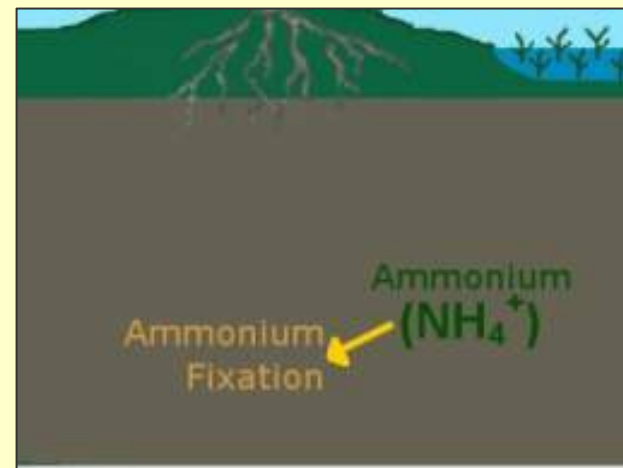
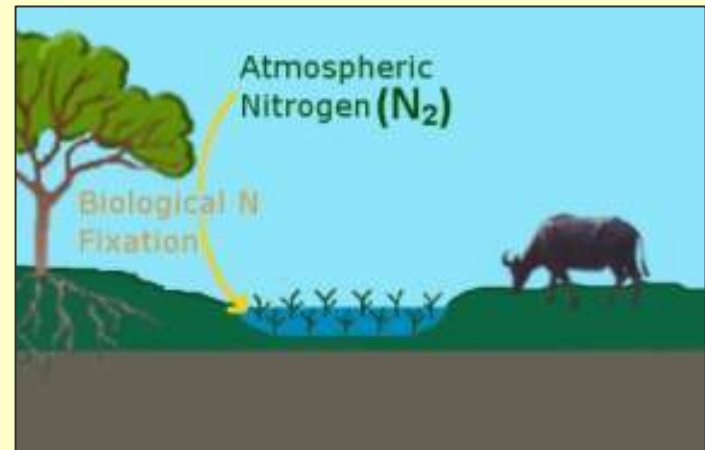
- Nitrification – in the presence of oxygen, ammonium is transformed into nitrate by microorganisms (Lesson 5)
- Denitrification – when nitrate moves into anaerobic soil, it is transformed into gaseous N forms like  $N_2$  (Lesson 5)





# Lesson 2 – Intro to Nitrogen processes (3)

- Biological N fixation – microorganisms convert  $N_2$  into a form plants can use (Lesson 6)
- Ammonium fixation – ammonium is trapped between clay particles and becomes unavailable (Lesson 7)



# Lesson 2 – Summary slide

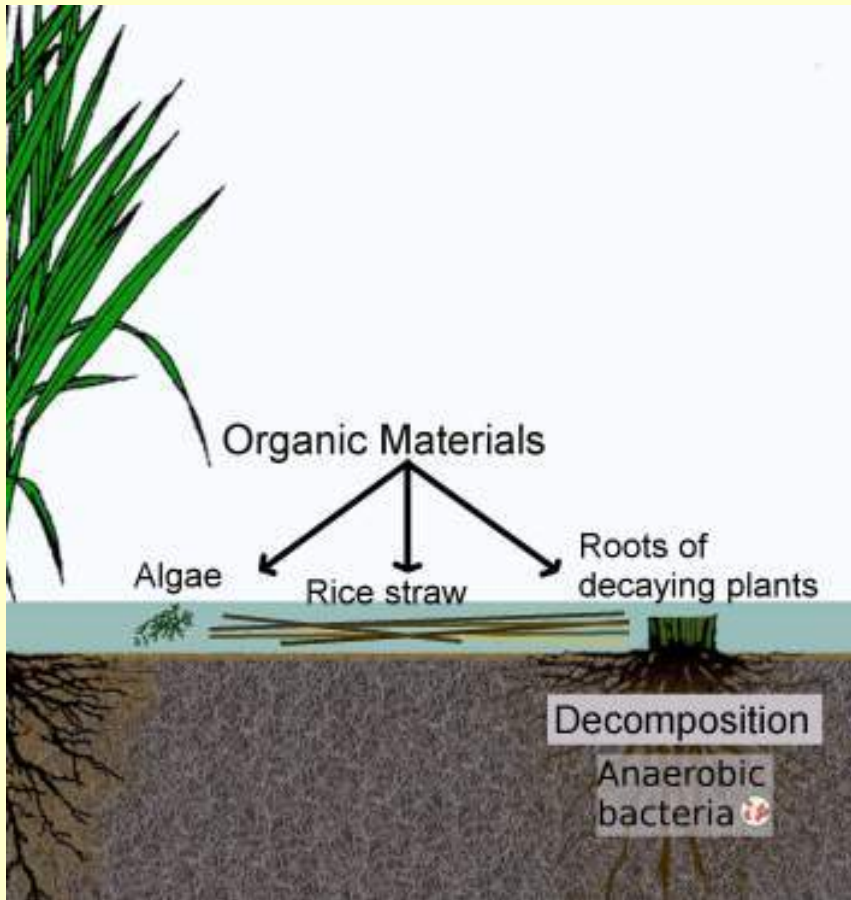
- Most N in soil is in organic matter
- Plants take up inorganic N as nitrate ( $\text{NO}_3^-$ ) and/or ammonium ( $\text{NH}_4^+$ )
  - $\text{NO}_3^-$  is the primary inorganic form in aerobic soil
  - $\text{NH}_4^+$  is the primary inorganic form in anaerobic soil
- Most forms of N in the environment are reactive
- There are many processes causing N to change forms. Several of these processes result in a decrease of available N for the rice plant

# Lesson 3 – Organic and inorganic nitrogen

Question: How does N transition from an organic form to a plant available form?

Objective: Be able to discuss the processes affecting the availability of N to rice.

# Lesson 3 – Microorganisms



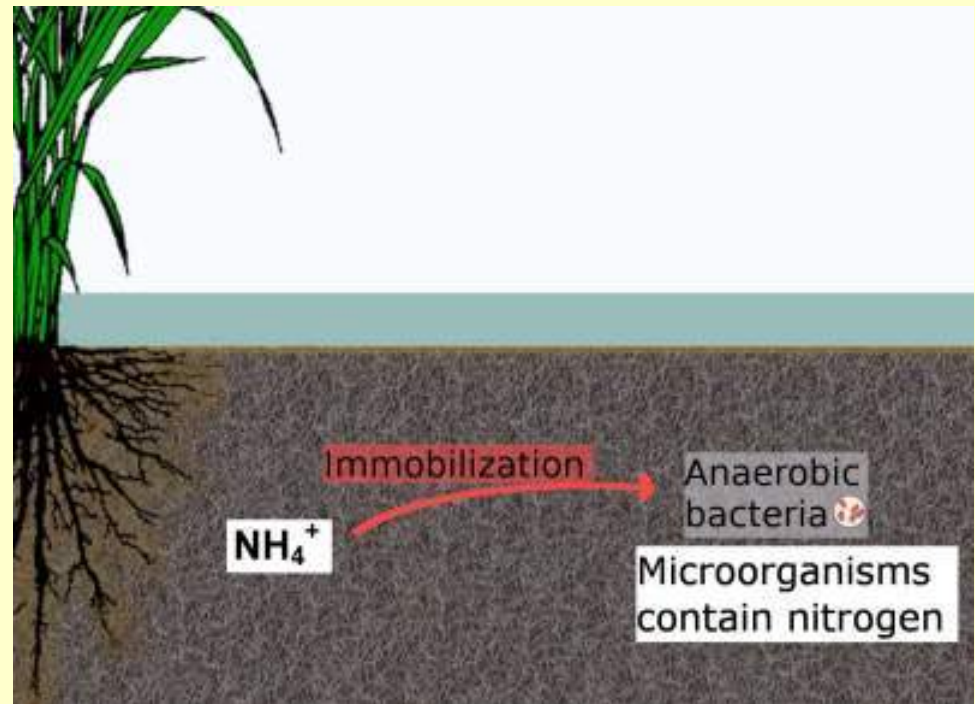
When organic materials are added to soil:

- The microorganism population grows to make use of this food supply

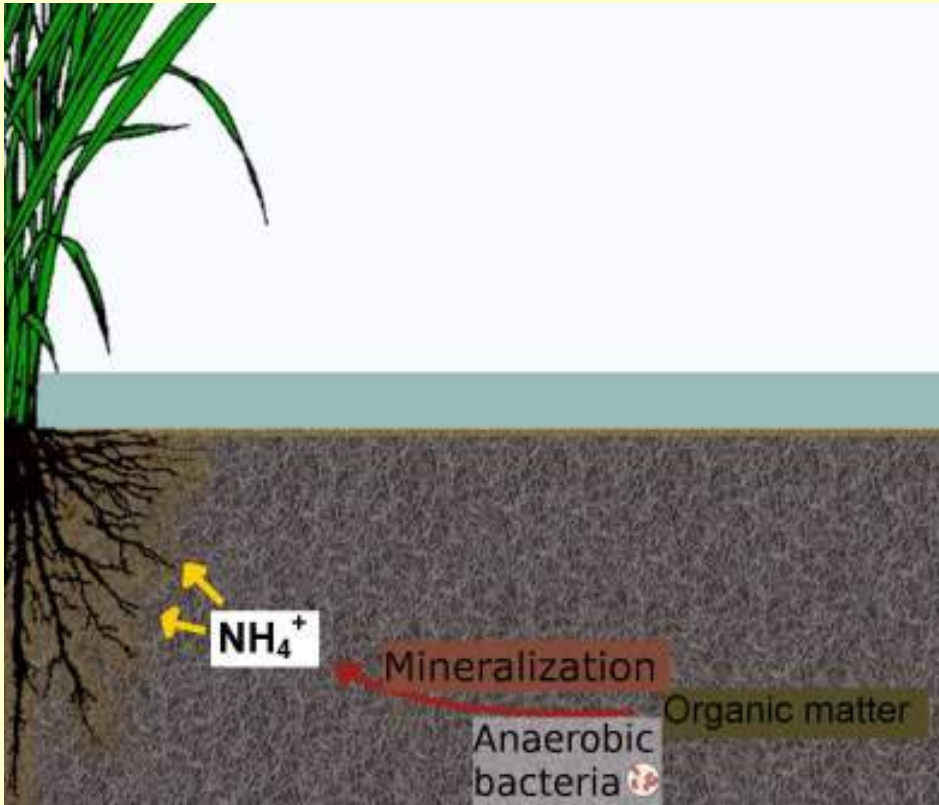
*Refer to Module 2 – Lesson 2 for more info about microorganisms*

# Lesson 3 - Immobilization

- Like rice plants, microorganisms need N for their life cycle
- As N is used by microorganisms, it becomes unavailable for plants
- This process is immobilization



# Lesson 3 – Mineralization



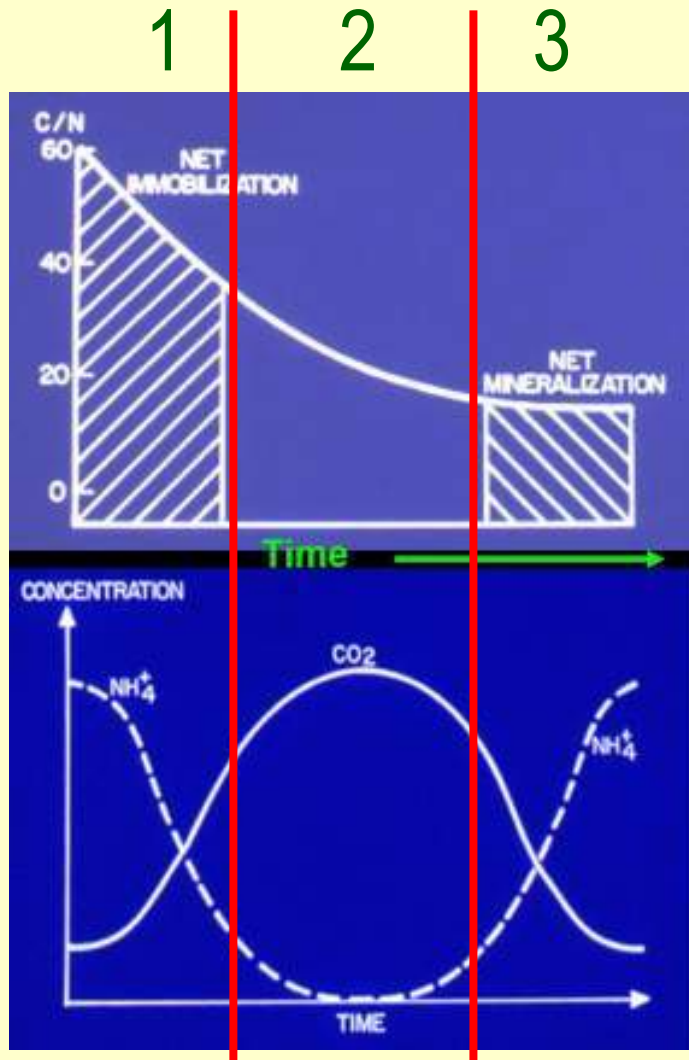
- Microorganisms break down complex N compounds in organic matter
- The final N product is  $\text{NH}_4^+$  which is available for plants
- This process is mineralization – also called ammonification

# Lesson 3 – Carbon to Nitrogen ratio

Carbon to nitrogen (C:N) ratio expresses the amount of N in a plant or in organic materials. When C:N ratio is:

- High - 30 or more parts C to 1 part N (like for rice straw)
  - The N in organic material is not enough to support decomposing microorganisms
  - Microorganisms will use N from surrounding soil to meet their needs
- Low - less than about 30 parts C to 1 part N (like for a legume)
  - Enough N is in the organic material to support decomposing organisms
  - N from organic material can be released into soil and be available for growing rice plants

# Lesson 3 – Organic materials with high C:N ratio (1)



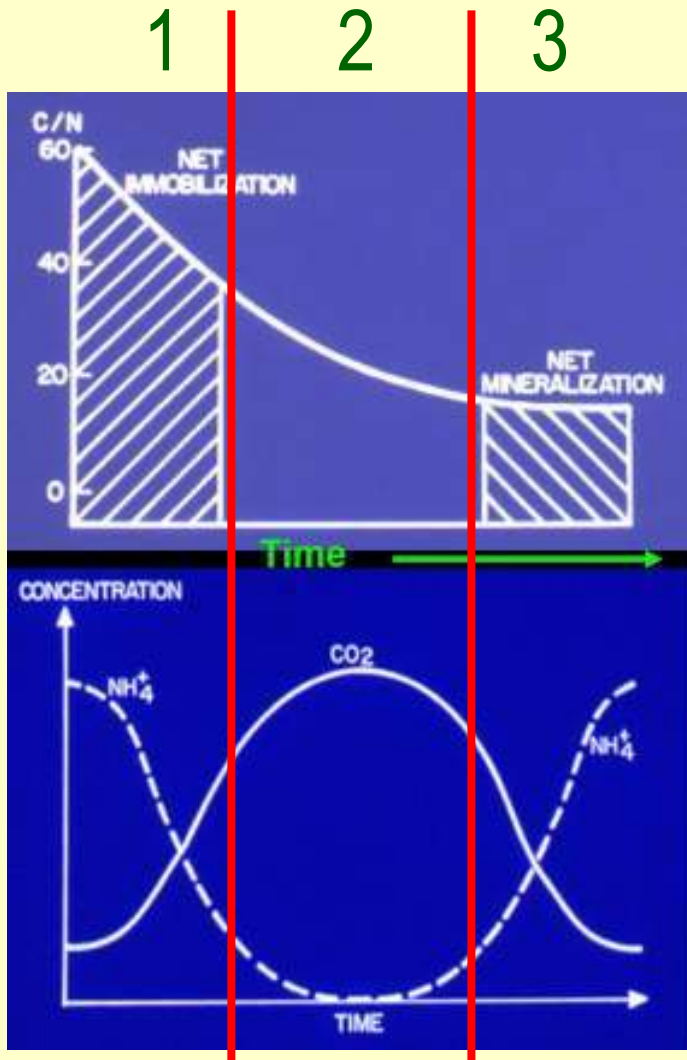
The 2 graphs at left show what happens when organic material with high C:N ratio like rice straw is added to soil. The graphs are divided into 3 time periods.

## 1) Initial phase – net immobilization

- ◆ Microorganisms consume N ( $\text{NH}_4^+$ ) causing  $\text{NH}_4^+$  to decrease (bottom graph)
- ◆ Microorganisms consume C products and release  $\text{CO}_2$  (bottom graph)
- ◆ C:N ratio is decreasing (top graph)



# Lesson 3 – Organic materials with high C:N ratio (2)



## 2) Intermediate phase

- ◆ Microorganisms have immobilized the available N ( $\text{NH}_4^+$ ) in soil (bottom graph)
- ◆ Maximum consumption of C products and production of  $\text{CO}_2$  (bottom graph)

## 3) Final phase – net mineralization

- ◆  $\text{NH}_4^+$  level is increasing – N in organic compounds is released and  $\text{NH}_4^+$  is now available in soil (bottom graph)
- ◆ C compounds are decomposed –  $\text{CO}_2$  production is low (bottom graph)
- ◆ C:N ratio is low (top graph)

# Lesson 3 – Net mineralization

The difference between the amount mineralized and the amount immobilized is called net mineralization.

*For submerged soil:*

- The total N immobilized and total N mineralized are typically less compared to aerobic soil
  - Fewer microorganisms are present in submerged soil
  - Those present operate at lower energy levels.
- Net mineralization is usually higher for submerged than aerobic soil

*Following decomposition, there is typically more N available for a rice crop in submerged soil compared to aerobic soil.*

# Lesson 3 – Summary slide

- Microorganisms responsible for decomposition require N for their growth
- Microorganisms feeding on organic matter low in N must get additional N from soil - immobilization
- Organic matter high in N may provide more N than what is needed by decomposing organisms. This excess N becomes available for plants - mineralization
- After decomposition, there is usually more N available to rice plants in submerged soil compared to aerobic soil

# Lesson 3 – Question to consider

If N is immobilized by microorganisms when organic material low in N like rice straw is added to soil...

- What are some practical considerations for a farmer planning to apply organic material to their field?

# Lesson 4 – Fertilizer lost as ammonia gas

- Question: What should a farmer know before broadcasting urea fertilizer in a submerged rice field?
- Objective: Be able to explain what can happen to the applied fertilizer and some of the controlling factors.

# Lesson 4 – Use of urea fertilizer

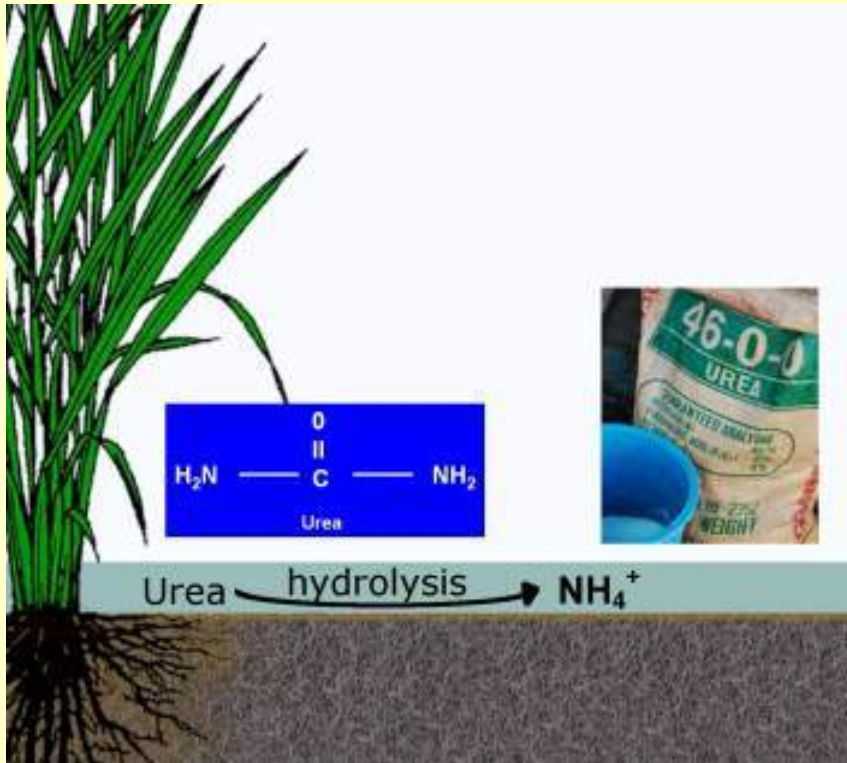


This farmer is broadcasting urea fertilizer on his growing rice plants.

Urea :

- is the most common N fertilizer for rice production
  - high percentage N - 46%
  - easy to use

# Lesson 4 – Hydrolysis of urea

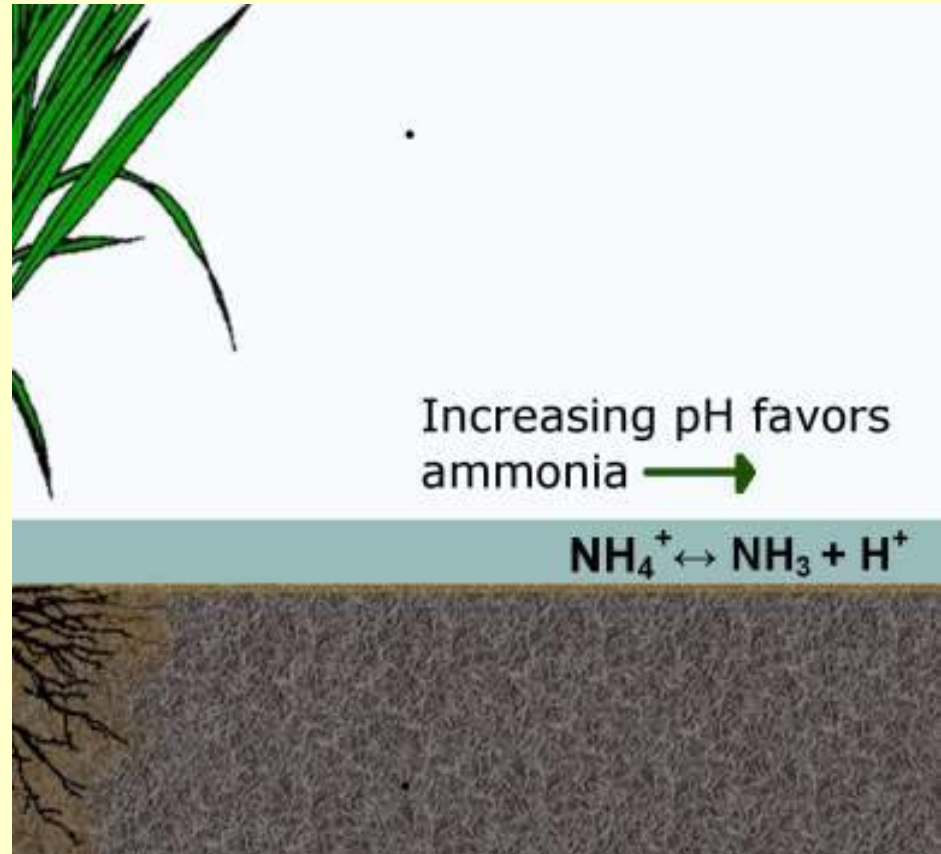


After urea is applied:

- It reacts with water and the enzyme urease in a process called hydrolysis
- $\text{NH}_4^+$  is a product of this reaction
- When urea is applied in submerged soil, this process is complete in a few days

# Lesson 4 – Ammonium and pH

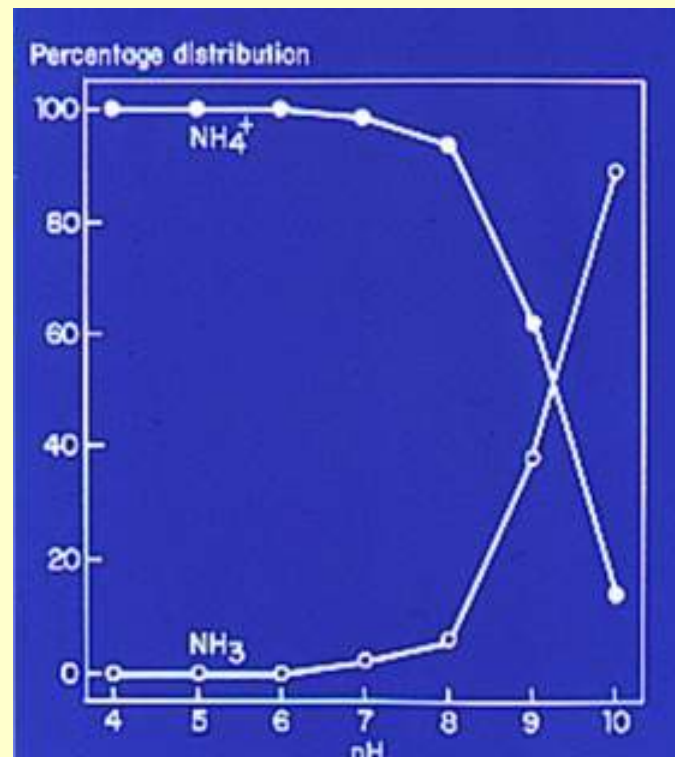
- $\text{NH}_4^+$  and  $\text{NH}_3$  are in equilibrium
- The ratio of  $\text{NH}_4^+$  to  $\text{NH}_3$  gas is affected by water pH
- At neutral pH,  $\text{NH}_4^+$  is strongly favored
- As pH increases, the amount of  $\text{NH}_3$  gas relative to  $\text{NH}_4^+$  increases





# Lesson 4 – Water pH and volatilization

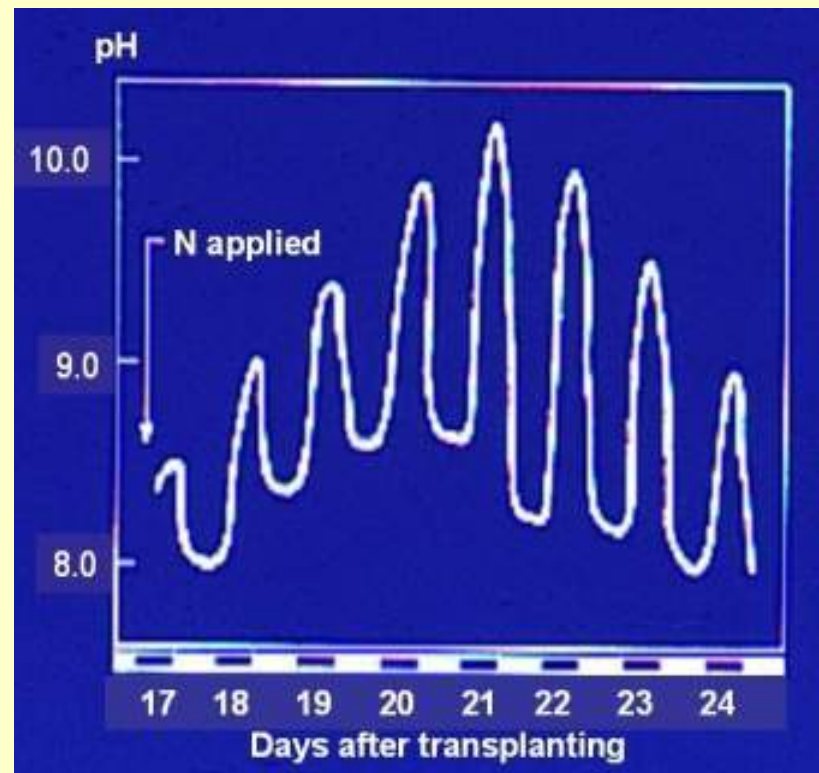
- Water pH influences the conversion of ammonium to ammonia gas.
- Conversion is slow when water pH is below 7.5.
- As water pH increases from 7.5 to 10, conversion increases rapidly (see the chart at right).



Effect of water pH on conversion of  $\text{NH}_4^+$  to  $\text{NH}_3$

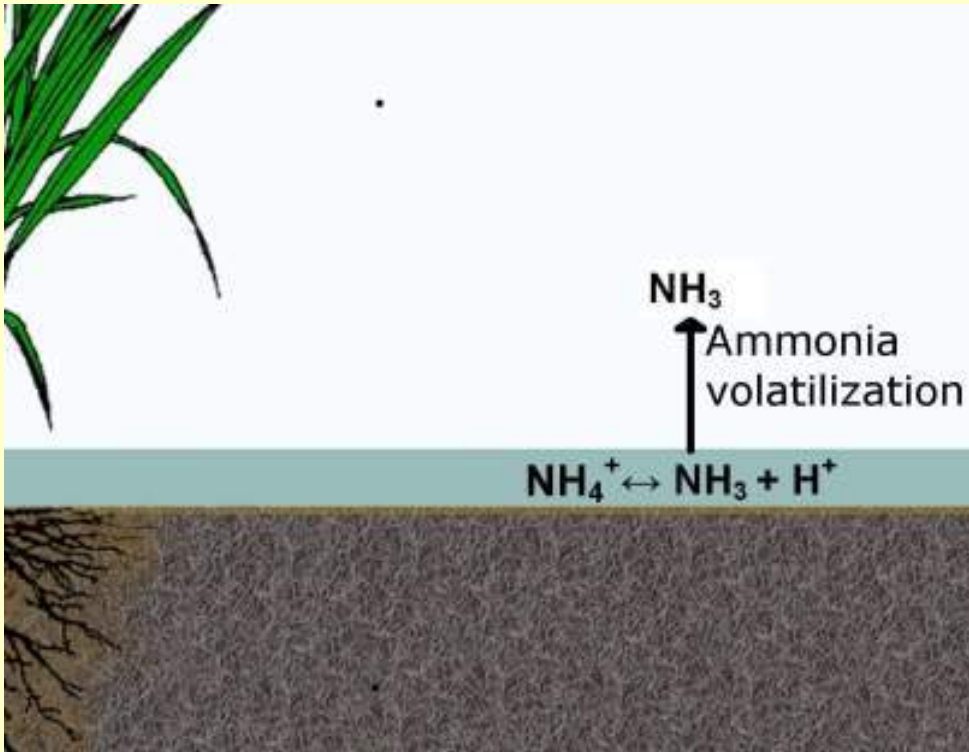
# Lesson 4 – Water pH and CO<sub>2</sub>

- Water pH changes with the amount of CO<sub>2</sub> in water:
  - As CO<sub>2</sub> goes up, pH goes down
- Algae growing in the rice paddy influences CO<sub>2</sub> in water
  - Photosynthesis by algae uses CO<sub>2</sub> and water pH goes up during the day
  - Respiration releases CO<sub>2</sub> and water pH decreases at night
- This is most pronounced in the week after applying fertilizer.



Daily rise and fall of water pH in a rice paddy caused by changes in CO<sub>2</sub>.

# Lesson 4 – Ammonia volatilization

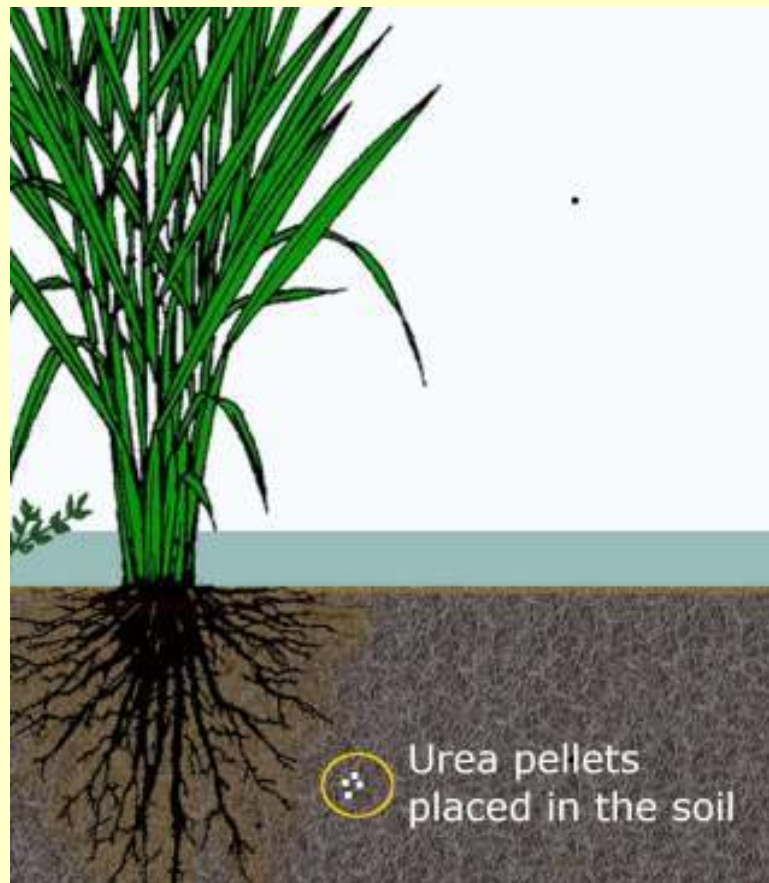


- Once  $\text{NH}_4^+$  is converted to  $\text{NH}_3$  gas, it can be lost into the atmosphere through volatilization
- This is a major cause of N loss for submerged rice fields
- Losses could even be as high as 50%
- Wind accelerates the transport of  $\text{NH}_3$  from the water surface and increases the loss of N

# Lesson 4 – Reducing volatilization

Reduce the buildup of  $\text{NH}_4^+$  in soil by:

- Applying urea according to need of the rice plant
- Placing urea in soil rather than broadcasting it on the surface



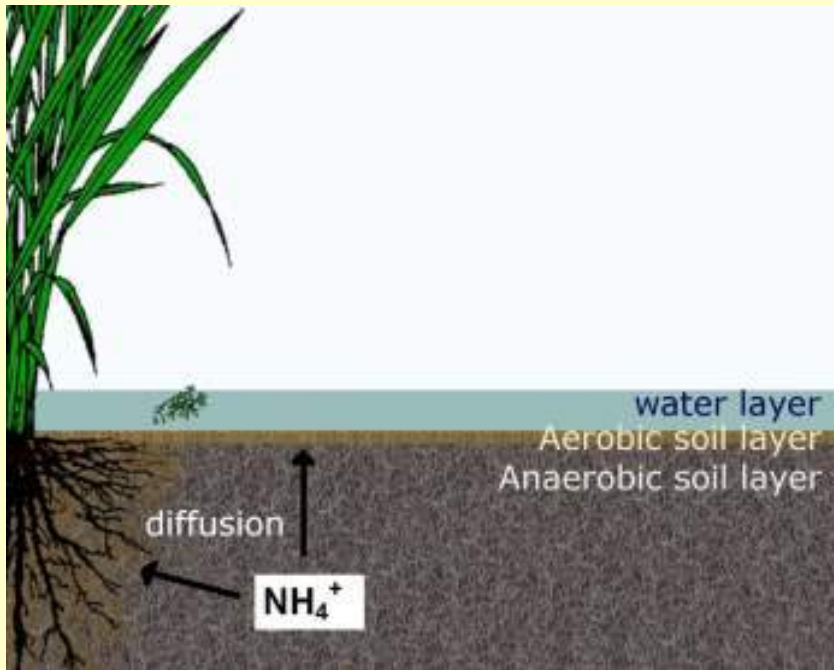
# Lesson 4 - Things to consider

- $\text{NH}_3$  volatilization is most significant in the week after applying N fertilizer
- $\text{NH}_3$  volatilization is greater when rice plants are small
  - Less shading from rice plants favors algae growth
  - Photosynthesis by algae can lead to increased water pH
- Rice plants require less N during first weeks after establishment
- Delaying N application until crop demand for N increases helps minimize  $\text{NH}_3$  buildup and loss through volatilization

# Lesson 5 – Nitrogen forms and oxygen zones

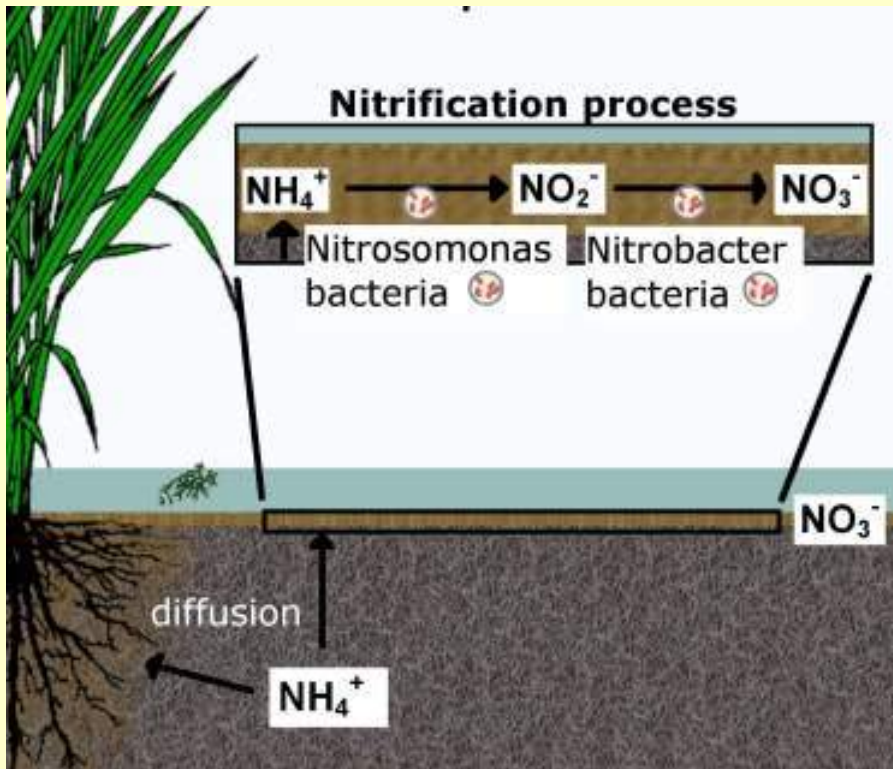
- Question: What can happen when N is exposed to aerobic and anaerobic environments?
- Objective: Be able to describe the two N processes involved and match them with their respective oxygen environment.

# Lesson 5 – Ammonium and aerobic soil



- NH<sub>4</sub><sup>+</sup> is the primary form of N in anaerobic soil
- Zones of submerged soil where O<sub>2</sub> can be present
  - rhizosphere
  - thin surface layer of aerobic soil
- NH<sub>4</sub><sup>+</sup> can move by diffusion into soil zones with O<sub>2</sub>

# Lesson 5 - Nitrification



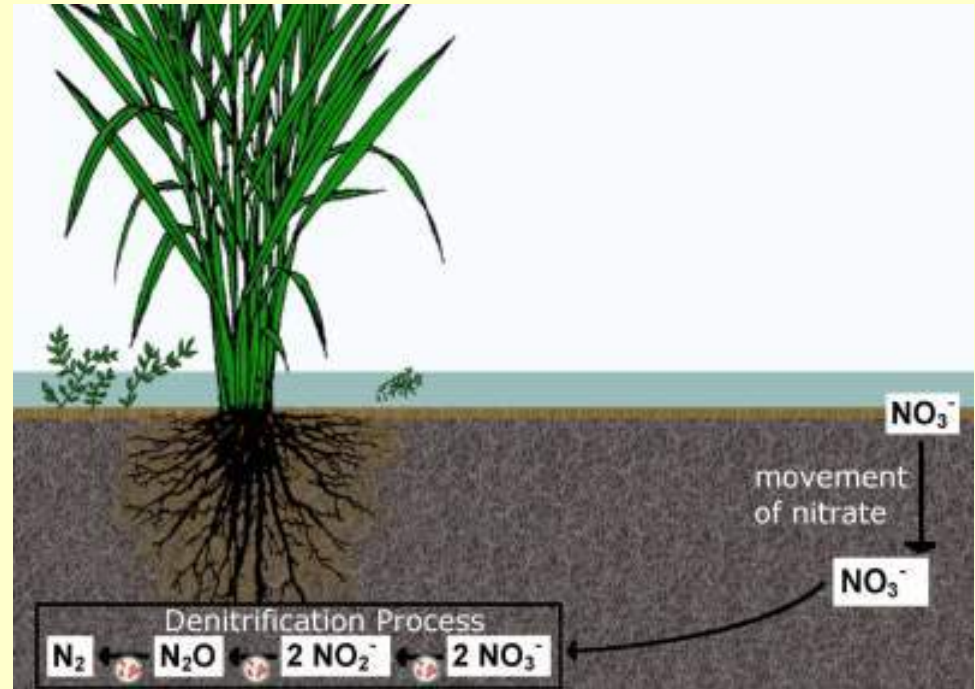
$\text{NH}_4^+$  in the presence of  $\text{O}_2$  may be changed:

- $\text{NH}_4^+$  may be oxidized to nitrite ( $\text{NO}_2^-$ ) by nitrosomonas bacteria
- $\text{NO}_2^-$  may be oxidized to nitrate ( $\text{NO}_3^-$ ) by nitrobacter bacteria
- These processes are both part of nitrification



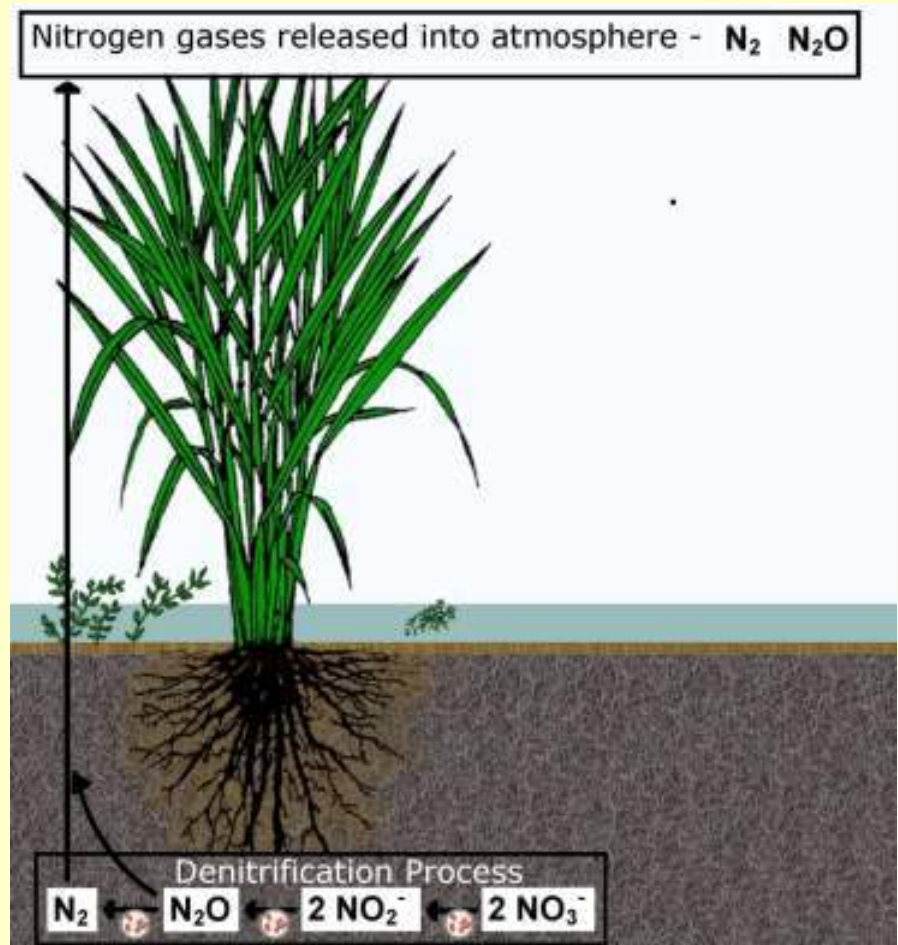
# Lesson 5 - Denitrification

- $\text{NO}_3^-$  is mobile because of its high solubility in water
- It may move via water flow or diffusion into anaerobic soil
- In anaerobic soil,  $\text{NO}_3^-$  may be reduced by bacteria to  $\text{N}_2$  or  $\text{N}_2\text{O}$
- This process is denitrification



# Lesson 5 – Release of N gases

- $N_2$  is the primary product of denitrification
  - It has no negative effects
- $N_2O$  can also be produced depending on conditions
  - It is a potent greenhouse gas
  - And it destroys ozone in the upper atmosphere



# Lesson 5 – Nitrification and denitrification can result in:

- Loss of N fertilizer applied by the farmer
  - Nitrification –  $\text{NH}_4^+$  that transforms to  $\text{NO}_3^-$  can be lost through runoff or undergo denitrification
  - Denitrification –  $\text{NO}_3^-$  in the anaerobic environment is transformed into N gases and lost in the atmosphere
- Loss of N fertilizer may result in reduced rice yield if there is not enough N for crop growth
- Harmful effects to the environment
  - Increased  $\text{NO}_3^-$  in the groundwater
  - Buildup of  $\text{N}_2\text{O}$  in the atmosphere

# Lesson 5 – Things to consider

- Avoid buildup of excess N
  - Apply N to meet crop needs (correct amount at correct time)
  - Deep placement of N reduces movement of  $\text{NH}_4^+$  to aerobic soil zones
- Minimize the amount of N remaining after the cropping season
- Alternate wetting and drying of a rice paddy can result in more N lost through nitrification-denitrification

# Lesson 6 – Biological nitrogen fixation

- Question: What is biological N<sub>2</sub> fixation and how do rice farmers benefit from it?
- Objective: Identify N<sub>2</sub> fixing organisms that can be used in a submerged rice production environment.

# Lesson 6 – What is a diazotroph?

- While  $N_2$  in the atmosphere is mostly unavailable to plants, a group of bacteria called diazotrophs convert  $N_2$  gas into a usable N form.

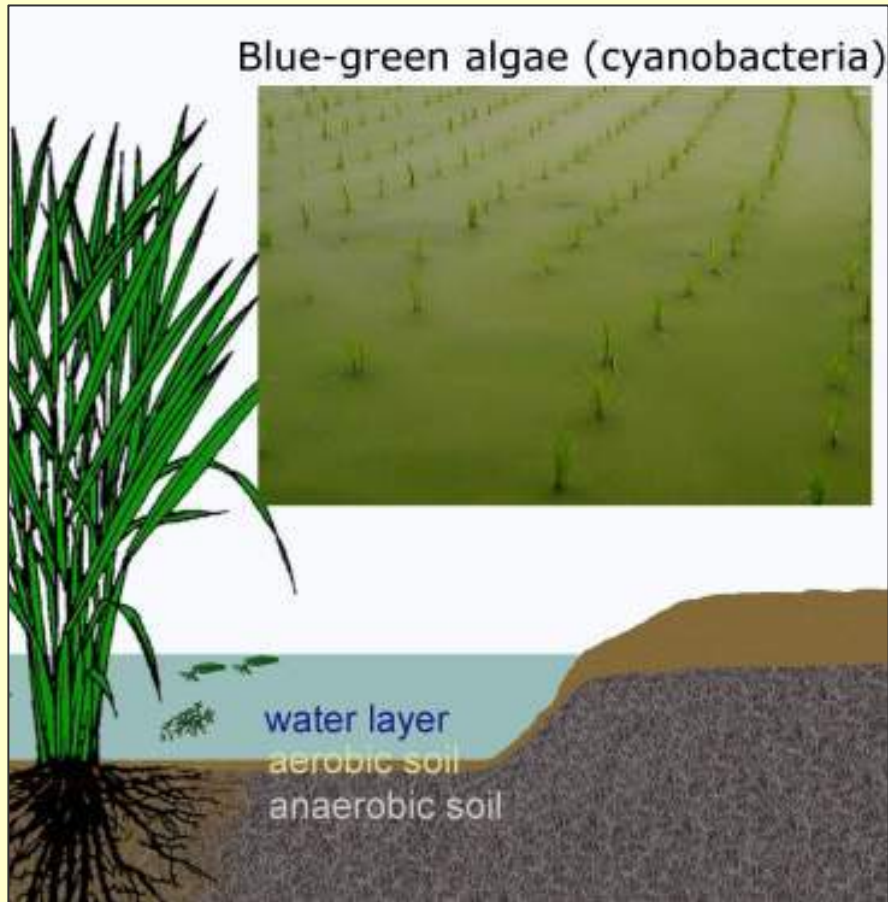
## Nitrogen fixing facts

- *On a global scale, the amount of  $N_2$  gas fixed by diazotrophs is comparable to what is fixed by industry and sold as synthetic fertilizer.*
- *In the tropics, lowland rice yields of 2-3.5 tons per hectare have been maintained for centuries with bacterial N fixation and mineralization of organic matter as the only sources of N.*

# Lesson 6 – Nitrogen fixing organisms

- There are several types of  $N_2$  fixing organisms - each has its unique requirements for growth
- The submerged soil supports several types since it contains zones of different  $O_2$  and light levels
- Some  $N_2$  fixing organisms are native to areas where rice is produced in submerged soil - others need to be established by the farmer
- The following 5 slides show examples of some  $N_2$  fixing organisms for submerged rice production

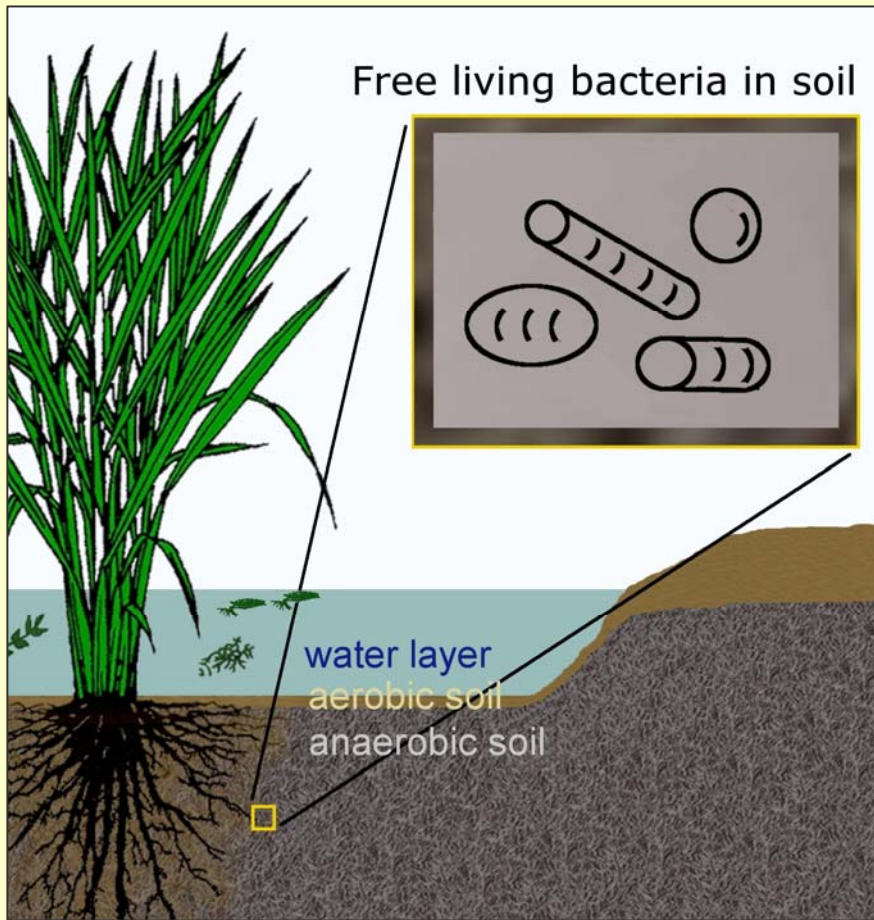
# Lesson 6 – Photosynthetic bacteria and cyanobacteria (blue-green algae )



- Single cell organisms living on the surface of water or plants in a submerged environment
- Produce their own food through photosynthesis
- Often native to the rice paddy
- 15-25 kg N per hectare can be fixed per crop



# Lesson 6 – Free living bacteria in soil



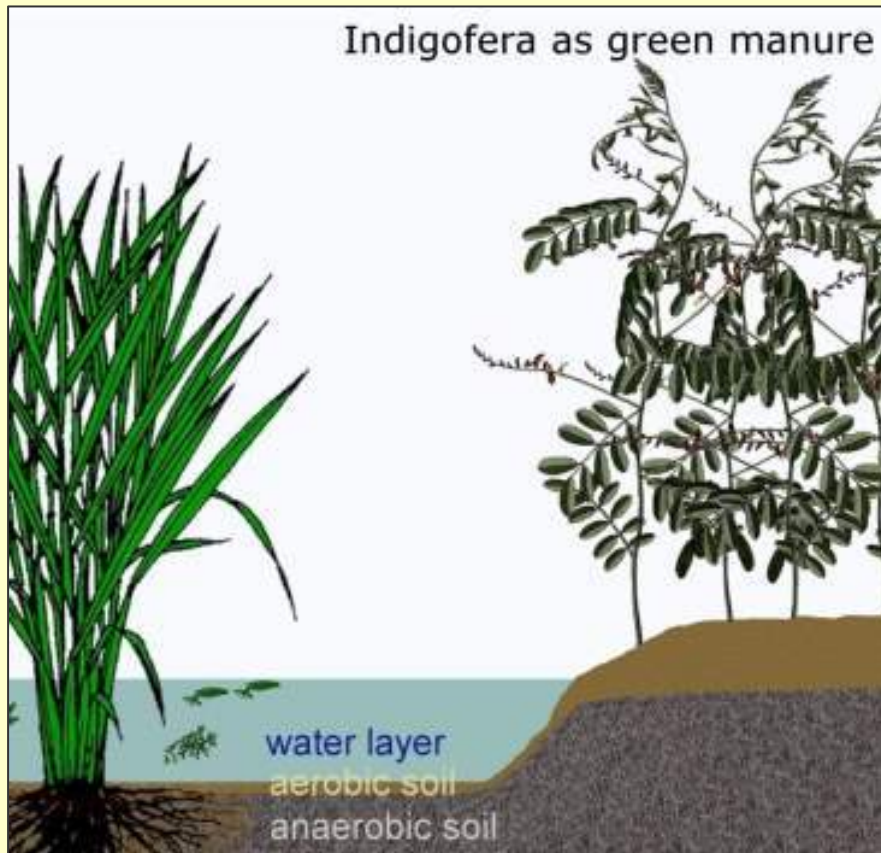
- Single cell organisms living within submerged soil and the root zone of rice
- Obtain their energy from breakdown of C compounds in soil
- Often native to the rice paddy
- Can result in 15 kg N per hectare per year
- Examples:
  - *Azospirillum* (aerobic)
  - *Azotobacter spp.* (aerobic)
  - *Clostridium spp.* (anaerobic)

# Lesson 6 – Azolla fern with *Anabaena azollae*



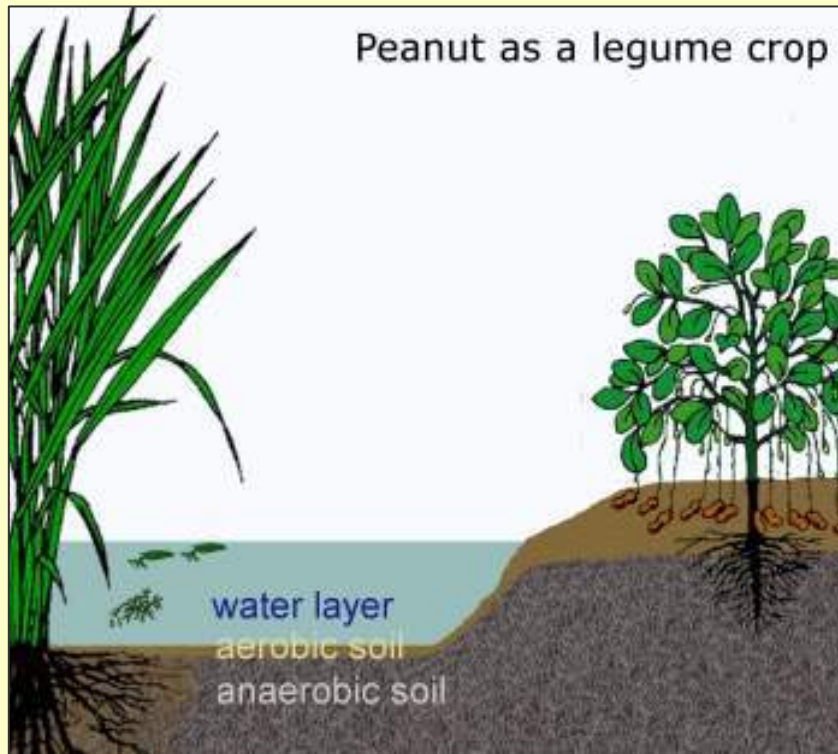
- Some species of azolla fern grow in association with *Anabaena azollae*, a blue green algae which fixes  $N_2$
- The azolla-anabaena combination has been used for centuries in rice paddies of China and Vietnam
- It can produce 20-40 kg N per hectare per rice crop
- It needs to be established each rice crop
- Can require additional P fertilizer for growth
- Susceptible to insect and fungal attack

# Lesson 6 – Legumes as green manure



- The rhizobia diazotroph fixes  $N_2$  for many species of legume
- In some rice-producing areas, a legume is grown during the period between rice crops and tilled into the soil to increase N
- They are capable of fixing 70 – 100 kg N per hectare per crop
- Can require P or other non-N fertilizer for good  $N_2$  fixation.
- Examples:
  - *Indigofera*
  - *Sesbania rostrata*
  - *Aeschynomene* species

# Lesson 6 – Grain legumes



- Some grain legumes are grown between rice crops as a source of food
- They are capable of fixing 50-90 kg N per hectare per crop
- Examples:
  - mungbean (*Vigna radiata*)
  - chickpea (*Cicer arietinum*)
  - groundnuts (*Arachis hypogaea*)
  - pigeon pea (*Cajanus cajan*)
  - soybean (*Glycine max*)

# Lesson 6 – Summary slide

- Several types of  $N_2$  fixing organisms can be used to increase available N for rice production in submerged soil
- Some of these are native to the rice environment and others must be introduced by the farmer
- They can require other fertilizer like P to promote good  $N_2$  fixation
- They can be labor intensive

# Lesson 7 – Leaching, runoff, and $\text{NH}_4^+$ fixation

- Question: How do leaching, runoff, and ammonium fixation affect N availability for rice?
- Objective: Be able to discuss these three processes and the N forms involved.

# Lesson 7 – Ammonium and nitrate respond differently

$\text{NH}_4^+$  and  $\text{NO}_3^-$  respond differently to leaching and runoff as a result of their different electrical charge.

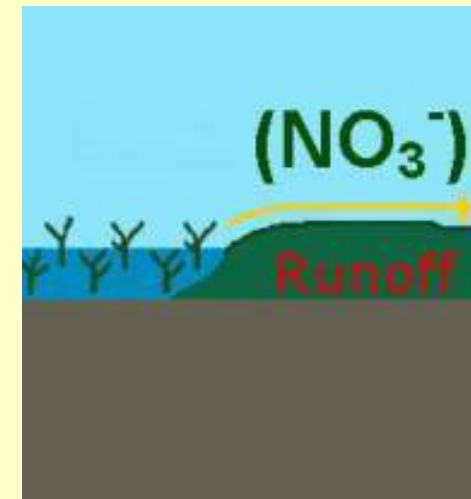
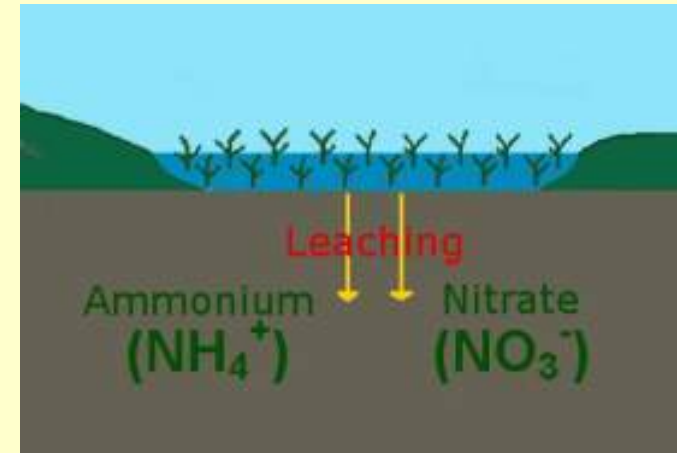
- The positively charged  $\text{NH}_4^+$  attaches more readily to soil particles than the negatively charged  $\text{NO}_3^-$
- For this reason,  $\text{NO}_3^-$  is more likely to be carried away

# Lesson 7 – Leaching and runoff

Leaching – Water moving down into the soil can carry ammonium and nitrate so they are no longer available to plants

- While puddling of soil helps to reduce leaching, it can continue especially in sandy soil

Runoff - Runoff contributes to loss of nitrogen when water carrying nitrate drains from the paddy or spills over the bund due to excess water.



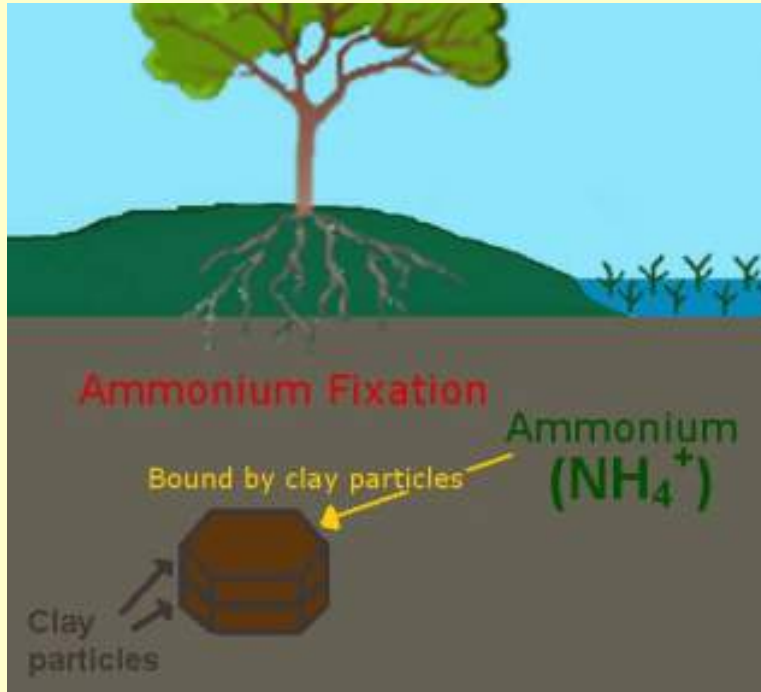


# Lesson 7 – Leaching and runoff may result in:

- Loss of fertilizer investment and yield because added N is no longer available for the rice crop
- $\text{NO}_3^-$  contributes to eutrophication, the prolific growth of plants and algae followed by decomposition and loss of dissolved  $\text{O}_2$  in water

# Lesson 7 – Ammonium fixation

Accumulation of  $\text{NH}_4^+$  in soil can result in fixation



- $\text{NH}_4^+$  ions get trapped between layers of clay particles
- $\text{NH}_4^+$  becomes unavailable to plants
- Influenced by soil moisture content, soil pH, organic matter, and soil temperature

# Lesson 7 – Ammonium fixation can result in:

- Loss of fertilizer investment and yield because added N is no longer available for the rice crop
- Reduced N loss through leaching since  $\text{NH}_4^+$  is held in soil
- A source of slow release N for plants

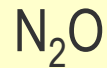
# Lesson 7 – Things to consider

- Avoid buildup of excess N
  - apply N to meet crop needs (correct amount at correct time)
- Minimize the amount of N remaining after the cropping season

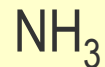
# Review Questions for Module 4

1) Match the name of the compound with its corresponding symbol:

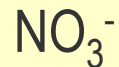
Nitrate



Ammonium ion



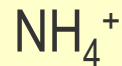
Dinitrogen gas



Ammonia gas



Nitrous oxide



2) Which of the following is true about diazotrophs:

- a) They fix  $\text{N}_2$  from the atmosphere and make it available to plants
- b) They include several species of bacteria
- c) They are abundant where rice is produced in submerged soil
- d) All of the above

# Review Questions for Module 4

## 3) True or False

When organic materials high in C and low in N (i.e. rice straw) are added to a rice paddy, mineralization takes place followed by immobilization.

## 4) Identify the correct statement about N in the atmosphere:

- a) It is plentiful in the atmosphere and plants can easily use this form of N for their needs.
- b) There isn't much N in the atmosphere making it difficult for plants to use.
- c) It is plentiful in the atmosphere but most plants can not use N in this form.

# Review Questions for Module 4

## 5) True or False

Up to 50% of N fertilizer applied as urea could be lost as  $\text{NH}_3$  gas when it is broadcast in a submerged rice paddy.

## 6) Match the term with its proper definition

Nitrification	The conversion of nitrate to dinitrogen gas in anaerobic soil
Denitrification	Ammonium ions get trapped between clay particles and become unavailable to plants
Ammonium fixation	The conversion of ammonium to nitrate in aerobic soil
Ammonia volatilization	In the presence of water, ammonium ions can convert to ammonia gas and are then lost in the atmosphere

# Review Questions for Module 4

- 7) Identify the correct statement(s) about nitrate:
- a) It is not as prone to leaching as ammonium
  - b) It is a positively charged ion
  - c) It can be carried away from a rice paddy via leaching and/or runoff
  - d) All of the above

This concludes the materials of Module 4.



# Answers to Review Questions

- |                |                      |
|----------------|----------------------|
| Nitrate        | $\text{NO}_3^-$      |
| Ammonium ion   | $\text{NH}_4^+$      |
| Dinitrogen gas | $\text{N}_2$         |
| Ammonia gas    | $\text{NH}_3$        |
| Nitrous oxide  | $\text{N}_2\text{O}$ |
- d) all of the above is correct
- False. When organic materials are low in N, microorganisms first immobilize N in soil in order to decompose organic materials. Once the materials have been decomposed, then N will become available through mineralization.

# Answers to Review Questions

4. *c) is correct. Dinitrogen gas is plentiful in the atmosphere but not usable by most plants.*
5. *True*
6. Nitrification - The conversion of ammonium to nitrate in aerobic soil  
Denitrification - The conversion of nitrate to dinitrogen gas in anaerobic soil  
Ammonium fixation – Ammonium ions get trapped between clay particles and become unavailable to plants  
Ammonia volatilization – In the presence of water, ammonium ions can convert to ammonia gas and are then lost in the atmosphere
7. c) it can be carried away from a rice paddy via leaching and/or runoff