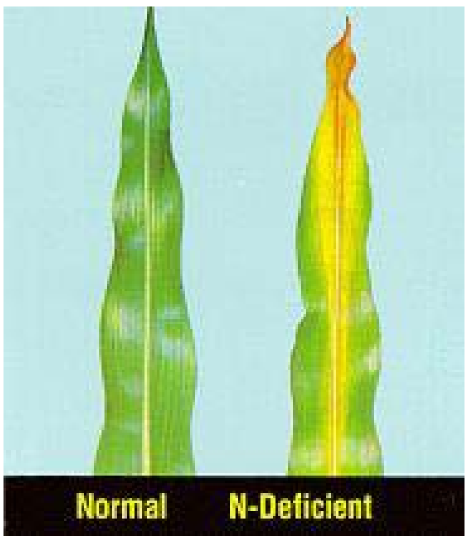
Nitrogen and Sulfur

Nitrogen

Influence of N on Plant Growth and Development

N is taken up as NH_4^+ or NO_3^-. It is essential as a component of many different biomolecules such as proteins, nucleic acids and chlorophyll. Deficiency results in chlorosis and poor growth. However, oversupply causes rank but abnormal growth and poor quality.



Origin and Distribution of Nitrogen

Most N is atmospheric. There is 10 to 20 x as much N in soil as in vegetative cover. Most soil N is in organic combinations and N comprises about 5 % of soil organic matter. Only about 1 or 2 % of the soil N is inorganic.

Immobilization and Mineralization

Mineralization is the conversion of organic-N to inorganic-N. About 2.5 % of the organic-N in soil mineralized annually. This represents a major source of N for plant growth.

Immobilization is the incorporation of inorganic-N into organic compounds. When the C / N ratio is high, immobilization > mineralization.

NH_4^+ Fixation

Entrapment of NH_4^+ between adjacent tetrahedral sheets of neighboring layers of 2:1 minerals. The tendency for fixation follows the sequence, vermiculite > illite > smectites. Fixed NH_4^+ is slowly released.

NH_3 Volatilization

$NH_4^+ + OH^-$ W $H_2O + NH_3$

Conditions favoring volatilization	Opposing volatilization
High pH	Low pH
Low CEC	High CEC
Surface application	Incorporation in soil
Dry soil	Moist soil
High temperature	Cool temperature

Nitrification

Microbial oxidation of NH_4^+

$2NH_4^+ + 3O_2$ 6 $2NO_2^- + 4H^+ + 2H_2O + E$
$2NO_2^- + O_2$ 6 $2NO_3^+ + E$

Nitrification is carried out by autotrophic bacteria

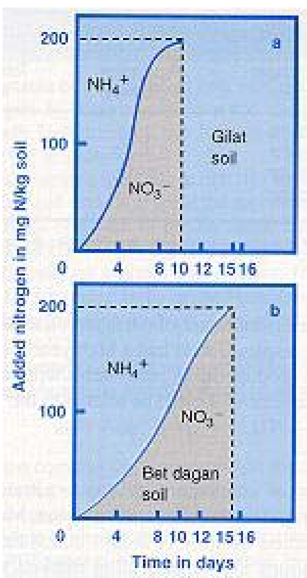
Step 1 *Nitrosomonas*
Step 2 *Nitrobacter*

Clearly, nitrification acidifies soil.

Soil environmental conditions affecting nitrification include:

High NH_3 concentration, which inhibits the process
O_2 required since nitrification is aerobic
Moist conditions favor nitrification but not so wet as to affect O_2 availability
Optimum temperature range is 25 - 35 C
Good soil fertility also favors nitrification

There are chemical inhibitors that reduce the activity of *Nitrosomonas* and, therefore, slow nitrification and the loss of N as NO_3^- by leaching or denitrification.



Nitrification is typically rapid.

NO_3^- Leaching

This is undesirable with respect to plant growth since it is a loss of N from the soil. Nitrate movement to ground and surface water also poses health and environmental risks. *Methemoglobinemia* (blue baby syndrome) is due to reduction of NO_3^- to NO_2^-, which reduces the capacity of hemoglobin to carry O_2. Enrichment of surface waters with NO_3^- may lead to *eutrophication* (especially marine systems).

Factors influencing NO_3^- leaching include:

Soil water drainage
NO_3^- concentration

Denitrification

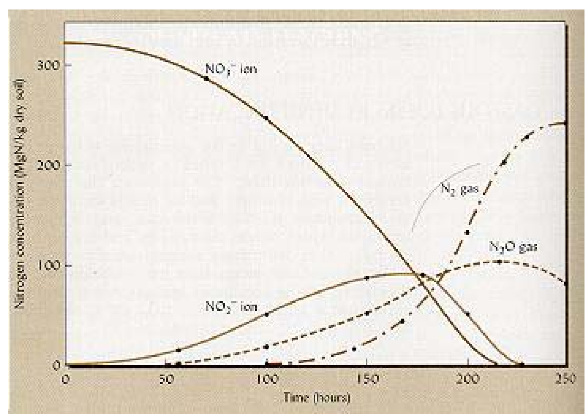
Reduction of NO_3^- to NO, N_2O or N_2

NO_3^- 6 NO_2^- 6 NO 6 N_2O 6 N_2
volatile losses

Denitrifying organisms include facultative anaerobes such as *Pseudomonas* and *Bacillus* that are heterotrophic and autotrophic *Thiobacillus denitrificans*.

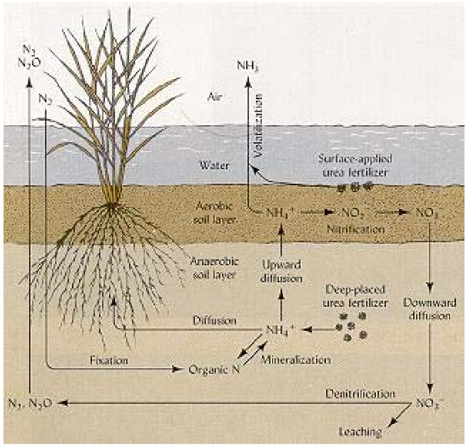
Factors affecting denitrification:

Presence of NO_3^-
Oxidizable substrates (for heterotrophs)
Anaerobic conditions
Optimum temperature 25 - 35 C
Low pH < 5 inhibits denitrification



Example of denitrification kinetics.

Denitrification occurs in wet soils like riparian zones; wetlands and rice fields; even in set areas of upland agricultural soils (spatially and temporally variable, up to 60 kg / ha annually).



Nitrification and denitrification in a paddy soil.

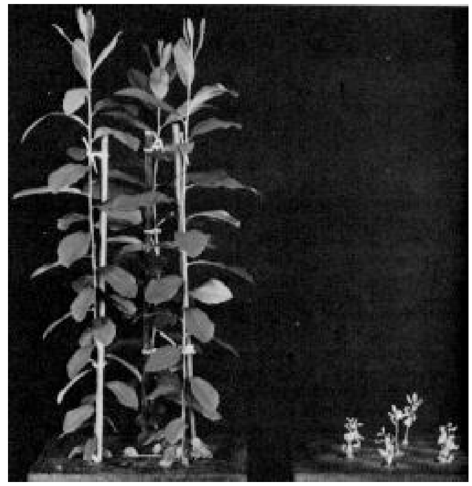
Denitrification contributes to acid deposition from HNO_3 formed from NO and N_2O. Also, N_2O is a greenhouse gas.

Biological N Fixation

$N_2 + 6H^+ + 6e$ 6 $2NH_3$

The NH_3 is incorporated into amino acids. Biological N-fixation is carried out by certain bacteria, actinomycetes, and cyanobacteria. About 139,000,000 Mg N is annually fixed in terrestrial systems.

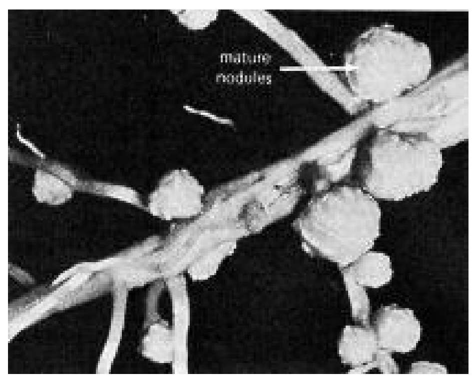
Nitrogenase is the enzyme complex responsible. It consists of two proteins. The smaller one supplies e^-s and larger traps N_2 and the larger supplies electrons for reduction. Since the reaction requires energy and it is aided by association with plants which supply photosynthetic products. Interestingly, nitrogenase is degraded by O_2 and is protected from O_2 by leghemaglobin. The formation of root nodules that contain the N-fixing bacteria is inhibited by soil NO_3^-. On the other hand, good Mo, Fe, P and S fertility is needed for N-fixation.



Growth with and without N-fixing organisms.

Symbiotic Fixation with Legumes

Rhizobium and *Bradyrhizobium* are the genera of bacteria involved. These form nodules on roots of legumes. The symbiosis is specific between legume and bacteria species. To ensure root nodulation one can inoculate if the right species is not present.



Nodulated root.

Symbiotic Fixation with Nonlegumes

Some form nodulated associations, like with actinomycetes of the genera *Frankia*. There are also non-nodulated associations, like the association of *Anabaena* within leaves of *Azolla.* Another non-nodulated symbiosis involves N-fixing organisms living in close, but external, association with plant roots in the rhizosphere.

Sulfur

This elemental is a component of certain amino acids and vitamins. Deficiencies in S result in chlorosis and stunted growth.

Sources of S include organic S; soil minerals such as $CaSO_4$ (arid regions), FeS (formed under reducing conditions) and, most commonly, SO_4^- adsorbed to colloids; and atmospheric forms.

S Oxidation and Reduction Reactions

Mineralization of organically bound S releases incompletely oxidized forms of S.

Oxidation to SO_4^- occurs chemically but is largely a biological process

$$H_2S + 2O_2 \rightarrow H_2SO_4$$

$$2S + 3O_2 + 2H_2O \rightarrow 2H_2SO_4$$

The autotrophic *Thiobacillus* does this.

Reduction is anaerobic.

$$SO_4^{-2} + 8H^+ + 8e \rightarrow S^{2-} + 4H_2O$$

It is carried out by *Desulfovibrio* and is coupled with oxidation of organic matter. Sulfide is subject to precipitation.

$$S^{2-} + Fe^{2+} \rightarrow FeS$$

Environmental Acidification Problems due to Inorganic Sulfur

Acid sulfate soils
Mined soils

Oxidation of FeS and FeS_2 leads to very low soil pH. Once soil containing reduced S is drained and aerated (or minerals containing reduced S are excavated), reduced S is subject to oxidation.

$$4FeS + 9O_2 + 4H_2O \rightarrow 2Fe_2O_3 + 4SO_4^{2-} + 8H^+$$

Acid deposition on forest soils

$$H_2SO_4 + HNO_3$$

These loadings of H^+, in addition to carbonic acid and organic and mineral acids from organic matter decomposition, accelerate natural leaching loss of nutrients.