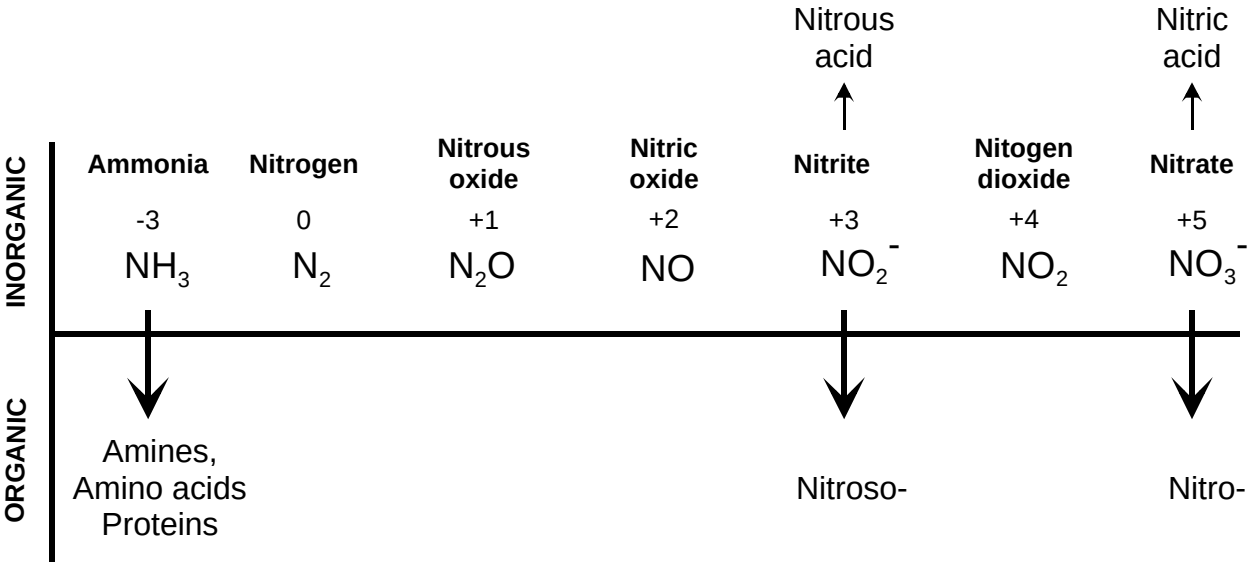
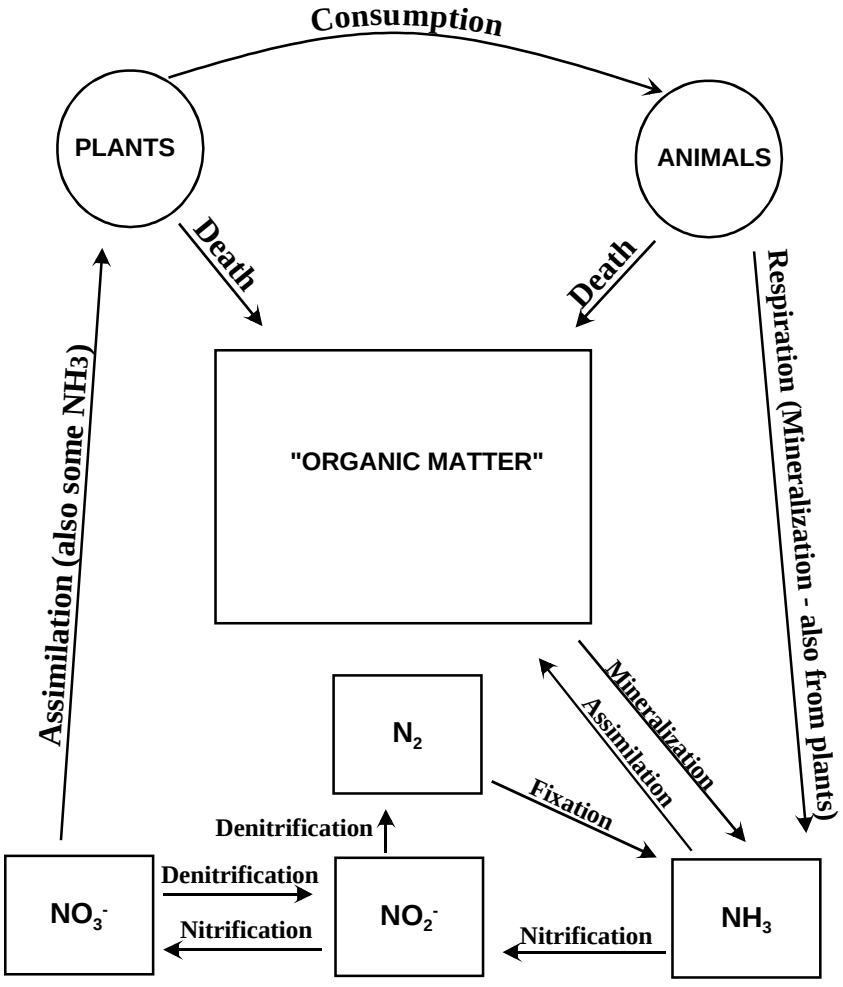

Nitrous acid
Nitric acid
INORGANIC
Ammonia
Nitrogen
Nitrous oxide
Nitric oxide
Nitrite
Nitogen dioxide
Nitrate
-3
0
+1
+2
+3
+4
+5
NH_3
N_2
N_2O
NO
NO_2^-
NO_2
NO_3^-
ORGANIC
Amines, Amino acids Proteins
Nitroso-
Nitro-


Consumption
PLANTS
ANIMALS
Death
Death
Respiration (Mineralization - also from plants)
Assimilation (also some NH_3)
"ORGANIC MATTER"
N_2
Mineralization
Assimilation
Fixation
Denitrification
NO_3^-
Denitrification
Nitrification
NO_2^-
Nitrification
NH_3

N in Soil

Note: soil concentrations can be anywhere, depending on vegetation, land use, etc. But a substantial amount - indeed most (ca. 99%)- soil nitrogen is organic

Free amino acids	**trace amounts**
Amino sugars	**5-10%**
Purine and Pyrimidine Bases	**trace amounts**
Bound amino acids	**20-50% of soil N**
Undescribed	**Lots - non-protein N**
	Crude proteins
	Lignin - N

NITROGEN MINERALIZATION / ASSIMILATION

Assimilation - incorporation of some substance into biomass
also referred to as immobilization

Mineralization - conversion of organic molecules to some inorganic form

e.g., $CH_2O + O_2 \rightarrow CO_2 + H_2O$

$H_2N\text{-}CH_2\text{-}COOH \rightarrow H_3C\text{-}COOH + NH_3$

Ammonia (um) is the <u>ONLY</u> inorganic N product of mineralization

NITRIFICATION

The conversion of ammonia(um) to nitrite then nitrate

I. Ammonium oxidation

$$NH_3 + 1.5O_2 \longrightarrow NO_2^- + H^+ (+H_2O)$$

$$\Delta G = -65 \text{kcal/mole}$$

Carried out by *Nitrosomonas*

II. Nitrite oxidation

$$NO_2^- + \frac{1}{2}O_2 \longrightarrow NO_3^-$$

$$\Delta G = -18 \text{kcal/mole}$$

Carried out by *Nitrobacter*

Ammonia / Ammonium Equilibrium

$$NH_3 + H^+ \rightleftarrows NH_4^+$$

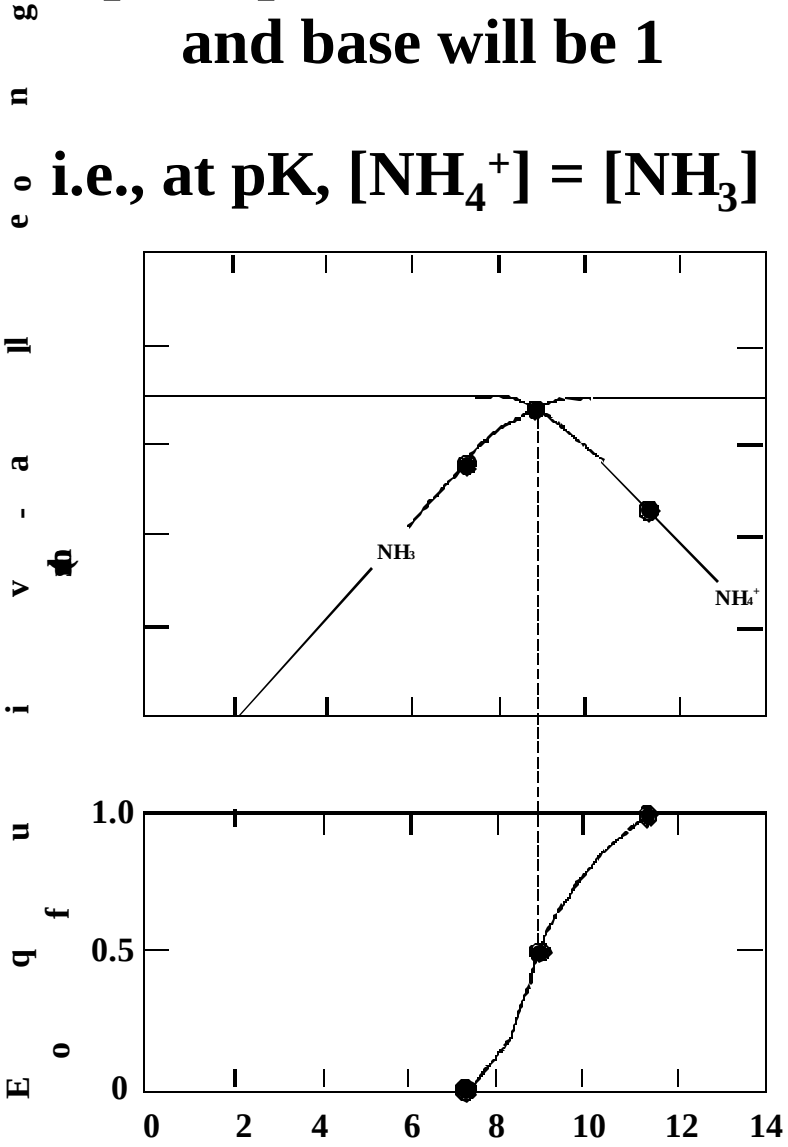
Dissociation constant (K_b) =1.79 ´ 10^{-5}

$$K_B = \frac{\left[NH_4^+\right]}{\left[NH_3\right] + \left[H^+\right]}$$

$K_w = K_A + K_B$ or $pK_A + pK_B = 14$

When pH = pK, the ratio of the acid and base will be 1

i.e., at pK, $[NH_4^+] = [NH_3]$



A recently published catalog of autotrophic nitrifiers

Soils: *Nitrosomonas*, *Nitrobacter*, *Nitrosospira*, *Nitrosococcus*, *Nitrosolobus*
Marine: *Nitrosomonas*, *Nitrosococcus*, *Nitrobacter*, *Nitrospira*, *Nitrospina*, *Nitrococcus*

also a *Nitrosovibrio*

Rates of nitrification by some heterotrophic and autotrophic nitrifiers

Organism	Substrate	Product	Rate of Formation (µg N/day/ g dry cells)	Max. product accumulation (µg N / mL)
Arthrobacter (heterotroph)	NH_4^+	NO_2^-	375-9000	0.2-1
Arthrobacter (heterotroph)	NH_4^+	NO_3^-	250-650	2-4.5
Aspergillus (heterotroph)	NH_4^+	NO_3^-	1350	75
Nitrosomonas (autotroph)	NH_4^+	NO_2^-	1-30 million	2000-4000
Nitrobacter (autotroph)	NO_2^-	NO_3^-	5-70 million	2000-4000

NITRATE REDUCTION
a heterotrophic process in 3 forms

Assimilatory nitrate reduction:

$$\text{glucose} + 3NO_3^- + 3H^+ \rightarrow 6CO_2 + 3NH_3 + 3H_2O$$

$$\Delta G = (-429 \text{kcal/mole})$$

Not oxygen sensitive - used by all organisms that assimilate NO_3^-

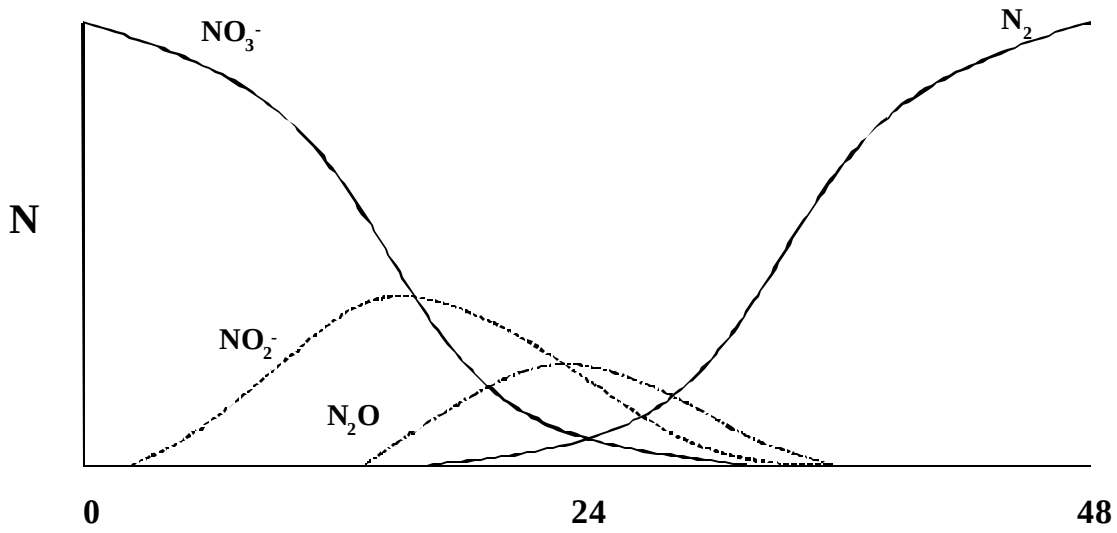
Dissimilatory nitrate reduction:

$$\text{glucose} + 3NO_3^- + 3H^+ \rightarrow 6CO_2 + 3NH_3 + 3H_2O$$

$$\Delta G = (-429 \text{kcal/mole})$$

Oxygen sensitive - used by a few facultative anaerobes - NH_3 is released to the environment - importance? Nitrate is "terminal electron acceptor" for glucose oxidation.

When nitrate and a suitable carbon source are placed together in an anaerobic zone, we see plenty of N_2, N_2O (occasionally some NO) and possibly some NO_2^-



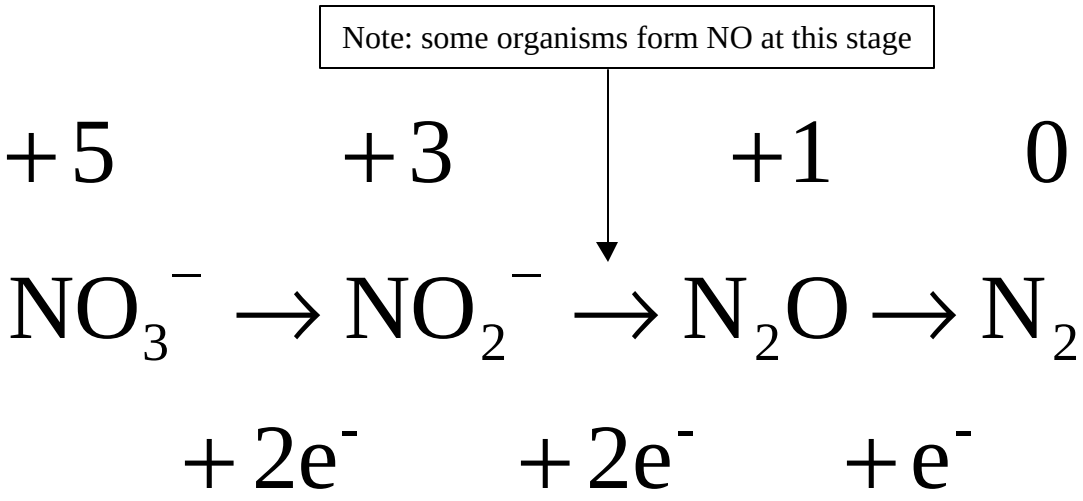
Denitrification is a heterotrophic process, conditions which favor heterotrophic processes in general will favor denitrification: pH 6-8, 15-30ºC

Denitrification

$$\text{glucose} + 4.8NO_3^- + 4.8H^+ \rightarrow 6CO_2 + 2.4N_2 + 8.4H_2O$$

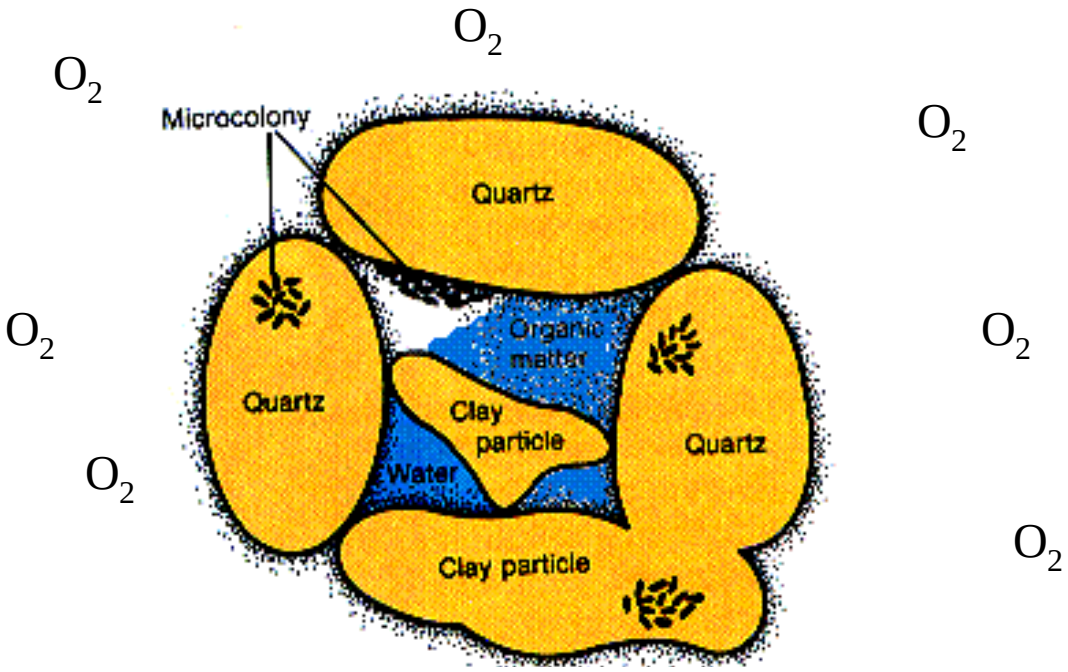
$$(\Delta G = \text{-}638 \text{ kcal/mole})$$

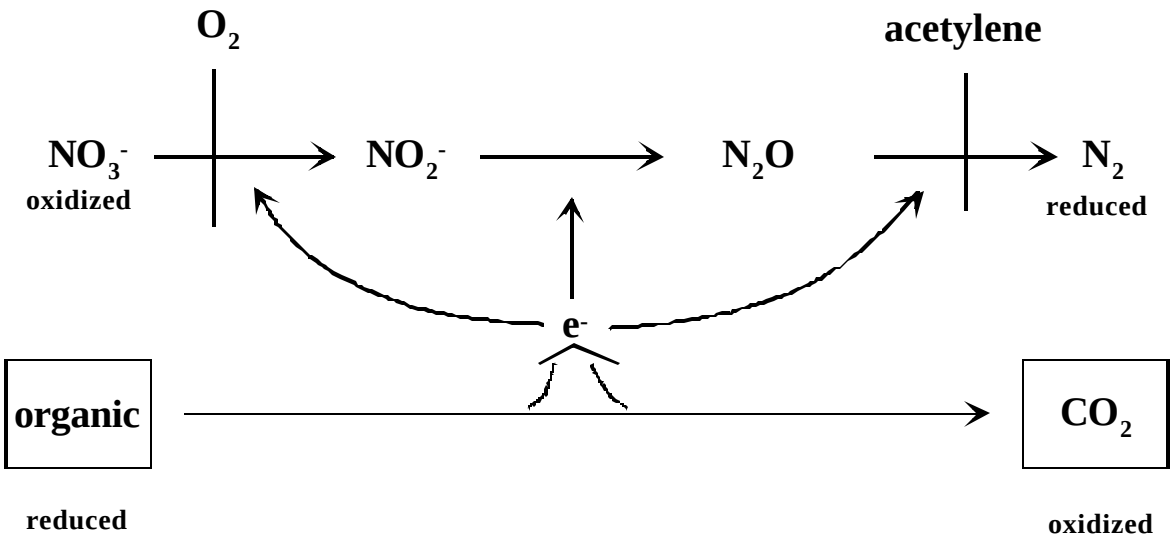
Oxygen sensitive - used by some facultative anaerobes to eliminate electrons from the oxidation of glucose



Denitrification is an anaerobic process

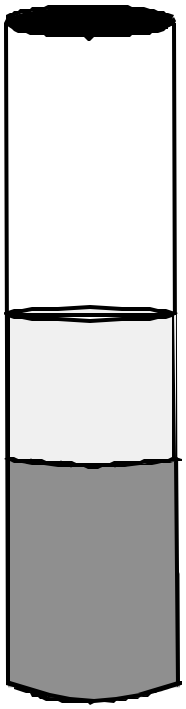
- Occurs in generally anaerobic environments if anaerobic microsites available

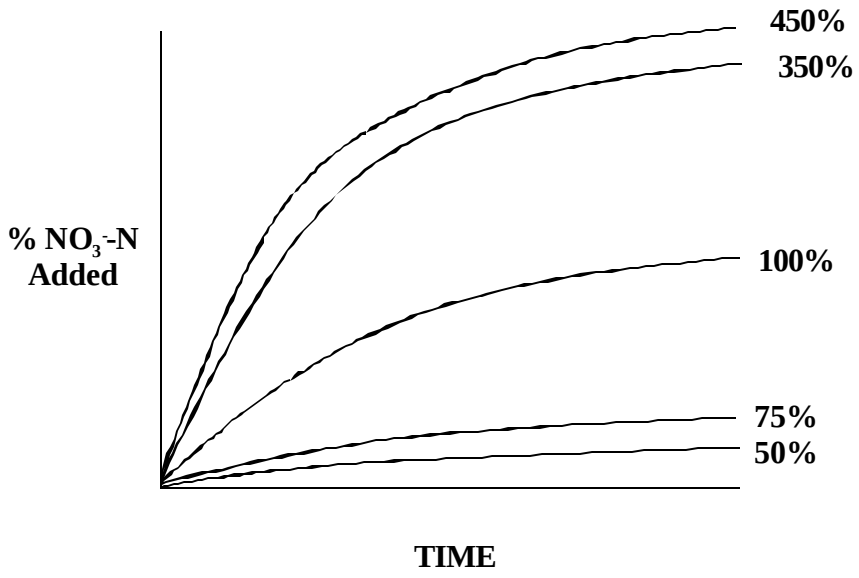




By adding a little acetylene to a soil or water sample, the denitrification rate can be determined by the accumulation of N_2O - simple analysis (acetylene block method)

N_2O Produced under varying conditions of soil saturation





Annual N loss to denitrification in nine forest soil classes in lower Michigan, 1985

Soil Drainage	N loss (kg ha -1 year -1) from profile texture:		
	Clay Loam	Loam	Sand
Well drained	18	10	0.6
Somewhat poorly drained	17	11	0.8
Poorly drained	40	24	0.5

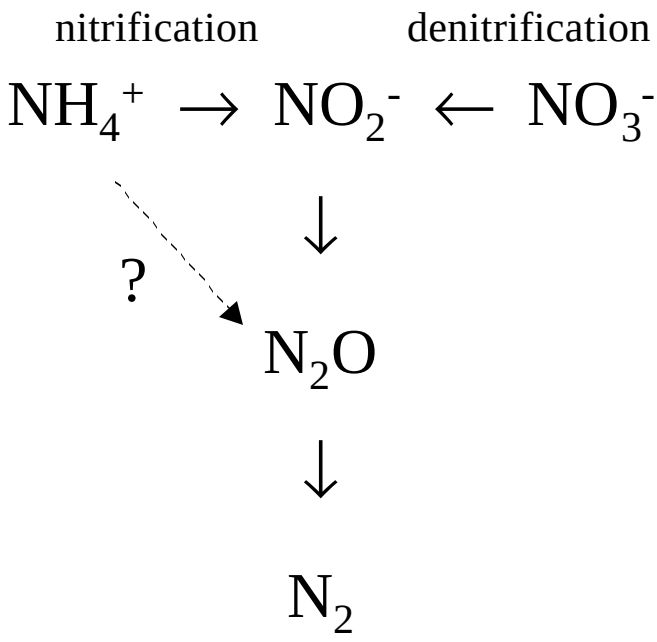
Adapted from Groffman and Tiedje (1989)

Land use and denitrification for different soil types in southern lower Michigan

Soil Type	% of region	% in agriculture	% in forest	% of regional forest	Annual denitrification (10^6 kg of N ha^{-1} $year^{-1}$)	% of regional denitrification
Clays	15	74	13	9	3.0	22
Loams	63	73	18	47	10.2	73
Sands	22	41	48	44	0.7	5
Total					13.9	

All soils south of approximately 44°N latitude. Total land area = 6.95×10^6 ha; total forest area = 1.71×10^6 ha. Adopted from Groffman et al.

Where does the N_2O (and N_2) come from?



Oxygen tolerance for some denitrifiers

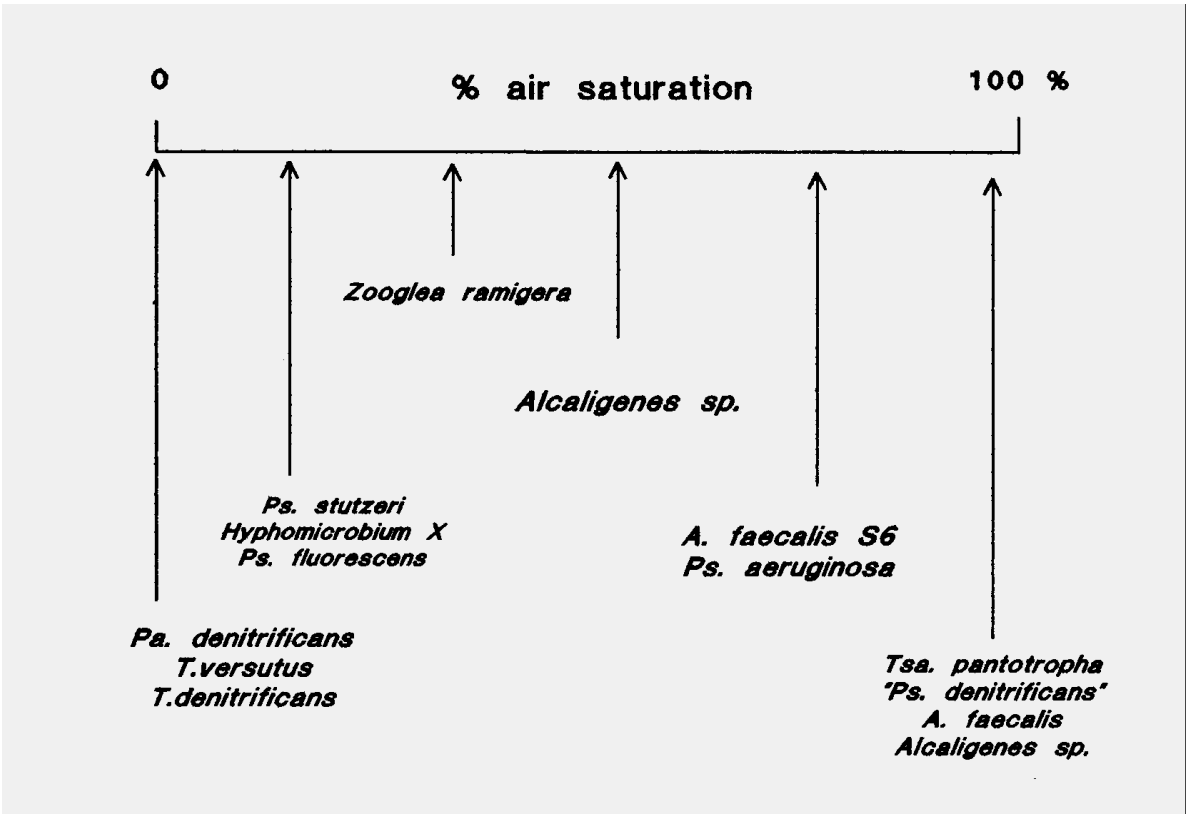


Table 5. Denitrification in tallgrass prairie[a]

Land use class	Denitrification (g of N ha^{-1} day^{-1}) in soil cores:		
	Unamended	Water amended	Water plus nitrate amended
Unburned	35 (7.2)	25 (8.5)	928 (107)
Burned	10 (3.9)	6 (1.9)	560 (78)
Burned/grazed	13 (4.3)	33 (5.4)	947 (116)
Cultivated	2 (0.98)	51 (16)	131 (51)

[a] Konza Prairie Research Natural Area near Manhattan, Kansas. Values are mean rates from four sample dates in 1987 and early 1988. Values are the mean (standard error in parentheses). Adapted from Groffman et al. (in preparation).

Haber-Basch Process:

$$N_2 + 3H_2 \rightarrow 2NH_3$$

300°-400°C, 500 Atm of pressure, No O_2, No H_2O

Energy (fossil fuel intensive)

Used as source of industrial N and about 65 million metric tons of fertilizer N each year

Cost is roughly $ 130 billion / year (global)

Remember - only about 1/3 of applied fertilizer is used by plants

Dinitrogen Fixation in Various Land-use Types[a]

Land use	ha ($\times 10^6$)	Nitrogen Fixed (kg ha^{-1} $year^{-1}$)	Nitrogen Tg
Legumes	250	140	35
Rice	135	30	4
Other cultivated crops	1,015	5	5
Permanent meadows, grasslands	3,000	15	45
Forest and woodland	4,100	10	40
Unused	4,900	2	10
Ice covered	1,500	0	0
Total land	14,900		139
Sea	36,100	1	36
	51,000		175

[a]Adapted from Burns and Hardy (1975).

BIOLOGICAL N FIXATION

$$N_2 + 3H_2 \rightarrow 2NH_3$$

- Same reaction as the Haber process
- Occurs at 1 Atm pressure and 15-35°C
- Catalyzed by enzyme NITROGENASE

•Nitrogenase

- Anaerobic Process
    - Protection by heterocysts
    - Protection by membrane binding
    - Protection by conversion in presence of oxygen
    - Protection by rapid respiration
    - protection by encapsulation of the organism
- Active on several other compounds including acetylene

Acetylene Reduction

Nitrogenase reduces Acetylene to Ethylene

Add a little acetylene to system,
measure nitrogenase activity as formation of ethylene

$$HC{\equiv}CH + H_2 \rightarrow H_2C{=}CH_2$$

Estimated Amounts of Nitrogen Fixed during a Year by Well-nodulated Legumes

Crop	Nitrogen fixed	
	Lb/ac	Kg/ha
Alfalfa	135	150
Sweet Clover	110	120
Red Clover	80	90
Soybeans	55	60
Field Beans	22	25
Field Peas	22	25

Source: **Averaged from several sources**