اسمدة متقدم 5

L5 Gaseous losses of nitrogen

Nitrogen could be lost from soil in gases forms through :

1- Denitrification,

a- biochemical reduction of nitrate under anaerobic conditions.

b- chemical reactions involving nitrite under areobic conditions. (nitrogen deficit)

2 -Volatile losses of ammonia gas from surface of alkaline soils.

Dentrification

a- biochemical reduction :

when soils become waterlogged , oxygen is excluded and anaerobic decomposition take place. Some anaerobic organisms have the ability to obtain their oxygen from nitrates and nitrites with accompanying release of nitrogen and nitrous oxides. The probable pathways whereby these losses come about :

$$NO_3^- \longrightarrow NO_2^- \longrightarrow NO\uparrow \longrightarrow N_2O\uparrow \longrightarrow N_2\uparrow$$

* The organisms responsible for dentnitrification are : Pseudomonas, Micrococcus, Achromobacter, and Bacillus. Several autortrophs are also capable of reducing nitrates including , Thiobacillus denitrifcans and Thiobacillus thioparus.

* Energy relations :
  - under aerobic conditions microbes use O_2 as final electron acceptor

$$C_6 H_{12} O_6 + 6O_2 \longrightarrow 6CO_2 + 6H_2 O + energy$$

  - under anaerobic microbes use NO_3 as final electron acceptor

$$C_6 H_{12} O_6 + 4NO_3 \longrightarrow 6CO_2 + 6 H_2 O + \uparrow N_2 + energy$$

(nitrate respiration)

energy obtain in aerobic resp. > in anaerobic condition

(38 ATPS) (2ATPS)

* Factors affected biological denitrification

- pH

  determine kind of gases evolved. (show how?)

- O.M.

  ↑ O.M → ↑ dentrification (why?)

- NO_3

  take place under wide range

- Soil texture

soil type	N loss in 40 day
sand	11- 25
clay	16- 31
peat	19- 40

- O_2

  ↓ O_2 → ↑ dentrfication

- soil moisture content (water filled space, WFS)

most important factor among all.

↑ moisture ⟶ ↑ denitrification

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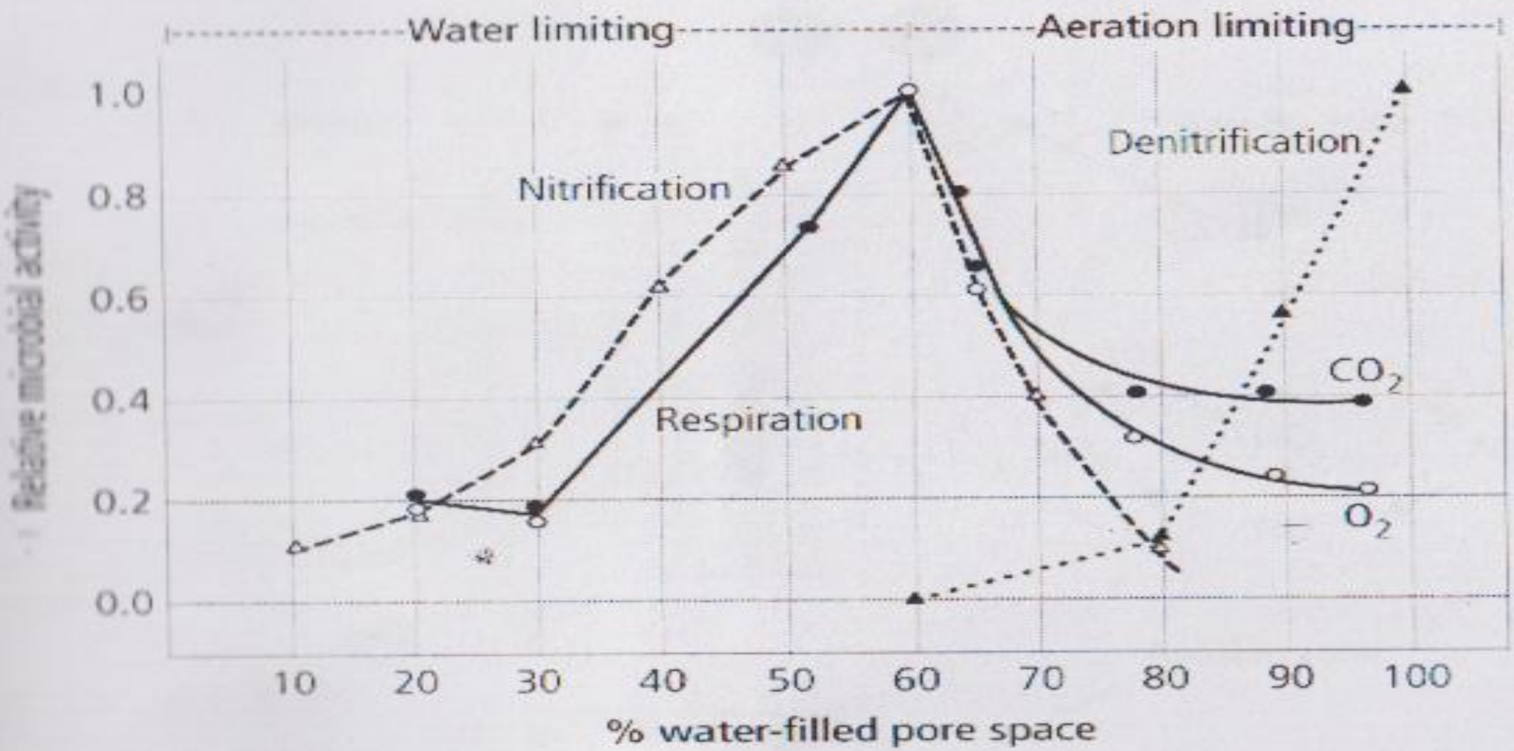
Figure 3.
Relationship between water-filled pore space and relative amount of microbial nitrification, denitrification and respiration (Linn and Doran, 1984)



* Nitrate and NO_2 are participating compounds in both dentrification and nitrifications through diffusion and mass flow can move from aerobic to anaerobic and vice versa. The co- existence of oxidized and reduced zones or layers is illustrated in fig below

Figure 4.
Illustration of the co-existence of oxidized and reduced zones/layers in flooded zones (a), in soil aggregates (b) and around roots of aquatic macrophytes (c)

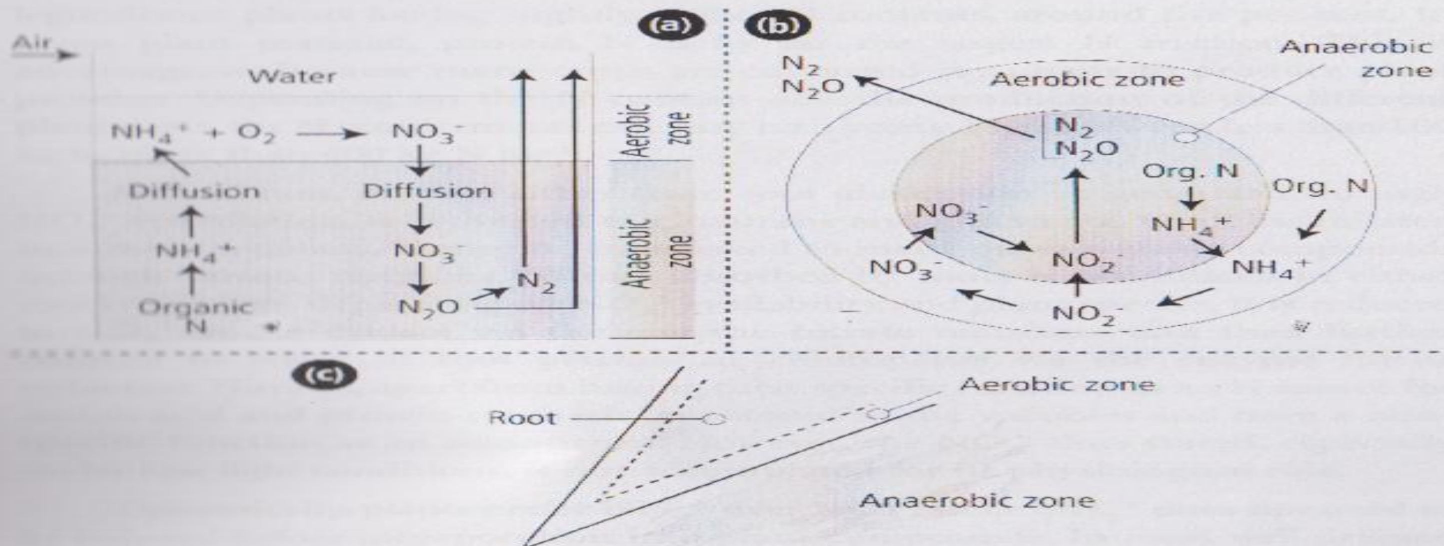
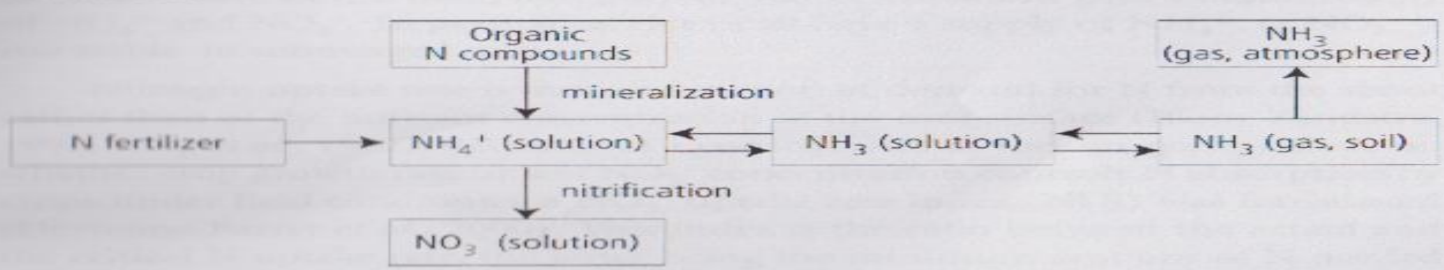


Figure 5.
Schematic presentation of the processes and equilibria of NH_4^+ in respect to NH_3 volatilization



b- chemodentirfication (N- deficit)

- it is not carried by microorganisms.
- important in acid soil and occur mostly in subsoil.
- at least three mechanisms have been suggested , all of which relate to NO_2 decomposition

i- decomposition of ammonium nitrite

$$NH_4NO_2 \longrightarrow 2H_2O + N_2$$

II- Van Slyke reaction

$$RNH_2 + HNO_2 \longrightarrow ROH + H_2O + N_2$$

III- spontaneous decomposition of nitrous acid

$$3HNO_2 \longrightarrow 2NO + HNO_3 + N_2$$

Volatilization of NH_3

When urea or any nitrogen fertilizers contain NH_4 added to alkaline soil its N could be subject to volatilization as NH_3 .

Terman & Hunt (1969) first suggest the chemical Rx. involved in NH_3 losses from inorganic N material.

Fenn and Kissel (1973) presented that Rx. as

$$X(NH_4)Y + DCaCo_3 \longrightarrow D(NH_4)_2CO_3 + Ca_nY_x$$

unstable compound

$$D(NH_4)_2CO_3 \xrightarrow{H_2O} NH_3 + 2H_2O + CO_2$$

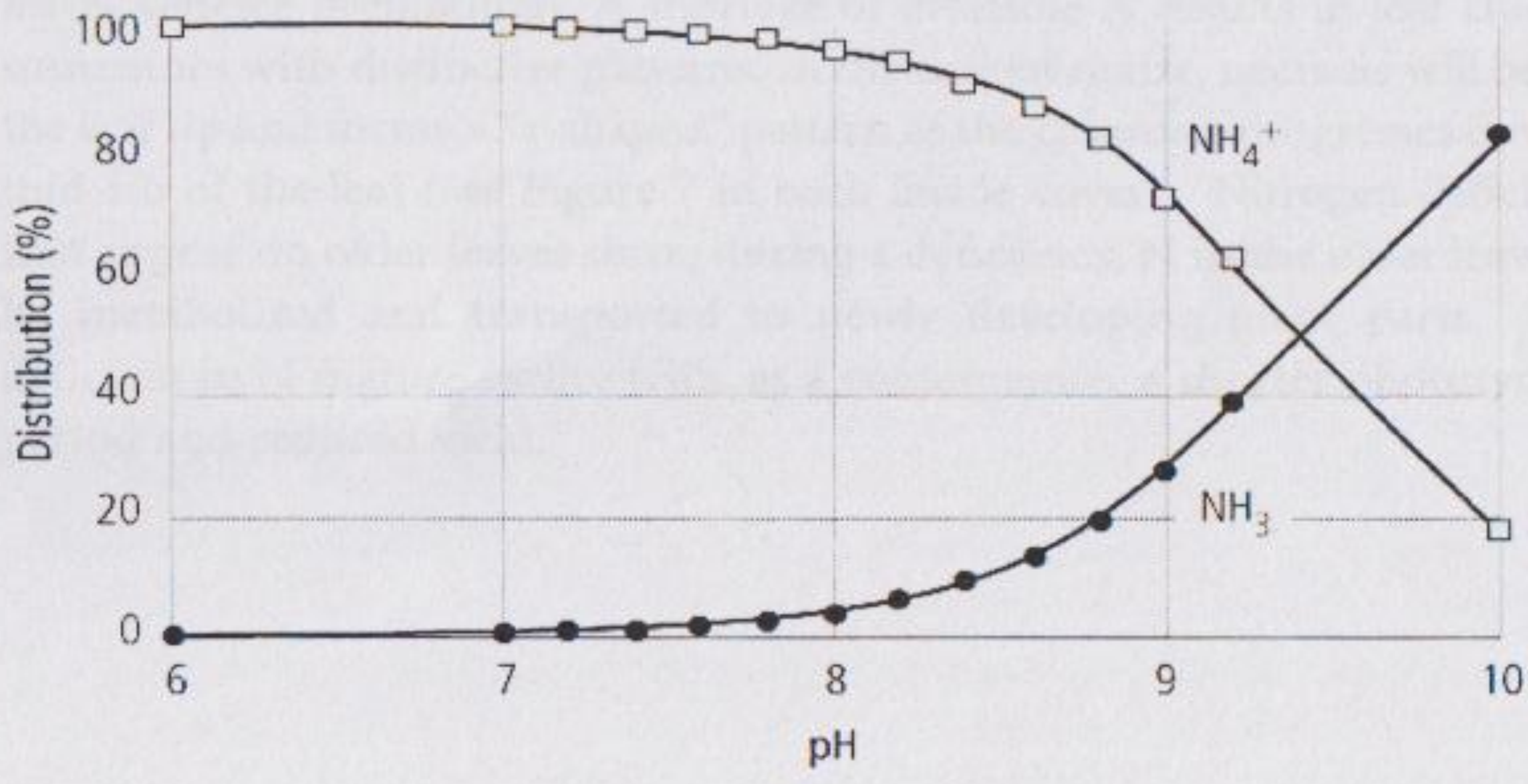
$$NH_3 \rightleftharpoons NH_4OH$$

amount of NH_4OH formed depends on the solubility of Ca_nY_x

Feagly & Hossner (1977) suggested that at soil with pH 8.5 or less the compound NH_4HCO_3 formed instate of $(NH_4)_2CO_3$.

- if the compound insoluble the Rx. shift to right so, more OH produce and pH of the soil increased which lead to more NH_3 volatilization .
- if the compound soluble the Rx. shift to left and pH of the soil depend on initial soil PH .

Figure 6.
Influence of the pH on the equilibrium between NH_4^+ and NH_3 (Court *et al.*, 1964)



* results of some experiments:

i- Feen and Miyamate (1981) , studied effect of using $(NH_4)_2SO_4$ on volatilization of NH_3

$$(NH_4)_2SO_4 + CaCO_3 \rightleftharpoons (NH_4)_2CO_3 + CaSO_4 \text{ (insoluble)}$$

$$(NH_4)_2CO_3 \rightleftharpoons NH_3 + 2H_2O + 2CO_2$$

II- other study :

effect of using NH_4NO_3 on volatilization of NH_3

$$2NH_4NO_3 + CaCO_3 \rightleftharpoons (NH_4)_2CO_3 + Ca(NO_3)_2 \text{ (soluble)}$$

iii- organic fertilizers (urea)

$$CO(NH_2)_2 \xrightarrow{\text{urease}} (NH_4)_2CO_3 + CO_2 + H_2O$$

* most of NH_3 volatilization occurs during the 3rd and 5th days after fertilizers application . Other studies showed that volatilization occur soon or after few hours of application.

- * Volatilization of NH_3 can be described in three steps:

  I- NH_4^+ / NH_3 equilibrium;

  ii- liquid / gas equilibrium;

  iii- mass transfer to the atmosphere .

  Steps I & ii involve a physio- chemical equilibrium. An important parameter is the equilibrium constant pk_a (being the negative log. of the equilibrium constant for the RX.)

$$NH_4^+ \rightleftharpoons NH_3 + H^+ \quad \text{-----------1}$$

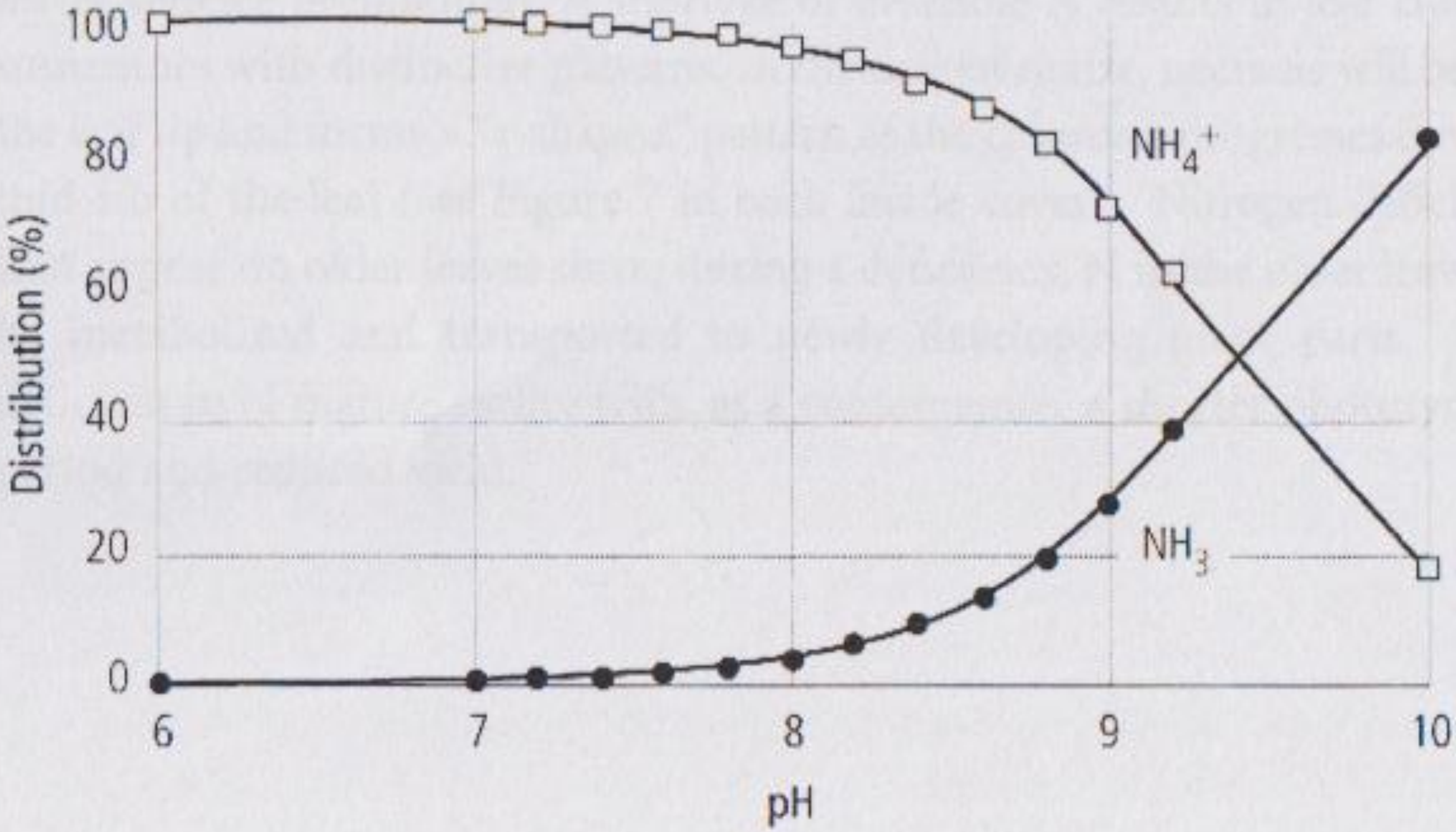
  * pk_a = 9.4 at 20º C in water solution. This means that NH_3
    - at pH 6 is only 0.04% of total N (NH_4 + NH_3)
    - at pH 7 is about 0.4% of total N
    - at pH 8 is about 4% of total N
    - at pH 9 is about 40%

  * Carbonate (CO_3^{-2}) and bicarbonate(HCO_3^-) can take up the H^+ emitted through NH_3 volatilization

$$CO_3^{-2} + 2H^+ \rightleftharpoons HCO_3 + H^+ \rightleftharpoons H_2CO_3 \rightleftharpoons CO_2\uparrow + H_2O \text{-------2}$$

  and thus push the rx. 1 to the right . Consequently , carbonate and bicarbonate partially neutralize acidity created by the formation of NH_3 leading to emission of CO_2 .

Figure 6.
Influence of the pH on the equilibrium between NH_4^+ and NH_3 (Court *et al.*, 1964)



Chemical and physical parameters that control absolute NH_3 volatilization :

1- Nitrogen application rate

Velks and Stumpe (1978) stated that NH_3 losses from solution is a 1^{st} order reaction . However, this is not necessarily applied to NH_3 losses from soils. Results of some studies:-

- Fenn and Kissel (1974)

used two sources for N fertilizers $NH_4 NO_3$ and $(NH_4)_2 SO_4$ at different rates to study NH_3 volatilization at different temps. Results obtained showed that volatilization differ for different sources.

$(NH_4)_2 SO4$ → losses ↑ with ↑ temp. and application rate.

$NH_4 NO_3$ → losses did not effected by rate , but increase with temp.

-Chin and Kroontje (1963)

after urea hydrolysis in soil NH_3 losses from $(NH_4)_2 CO_3$ is a first order Rx. application of energy source for urease increase hydrolysis rate .

*If urea hydrolysis slowly, eventhough,a high rate was applied , it will chemically appear as if low rate was applied. So, factors reduce urease activity could reduce NH_3 volatilization from urea fertilizer, these factors include:

a- urease inhibition : several urease inhibitors are available at market . Bremener and Douglase (1971) used heavy metals at conc. 50 ppm to reduce urease activity in soil. Results showed Ag > Hg > Au > Cu (high cost) .

- use of plants extracts as urease inhibitors.

b- high moisture content : urea movement downward the soil(irrigation time) .

c- nature of organic residue (C/N ratio).

d- if the soil surface is relatively dry , urea hydrolysis will occur at a reduced rate , this will allow downward movement of urea by subsequent irrigation. Hydrolysis of urea within soil does not results in substantial NH_3 losses. (Results of Dr. Ali thesis)

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2- Type of nitrogen fertilizers

effect of this factor on NH_3 volatilization has already been discussed.

3- Fertilizers placement site and application methods

$NH_3 NO_3$: - surface banding or dribble application in soil with low $CaCO_3$ buffering capacity NH_3 losses will reduced. If high $CaCO_3$ present application will not effect NH_3 volatilization.

- broad cast application will produce max. NH_3 losses under all conditions.

$(NH_4)_2 SO_4$: - broadcast application as liquid would be most effective application method. However, it's solubility does not allow to use it so.

Urea $(NH_2)_2CO$: -

- NH_3 losses under opt. conditions as high from acidic soil as from calcareous soil.
  - highest lost of NH_3 , if urea- based liquid broadcasted on undecomposed surface residue.
  - incorporation of urea into only a few surface mm of soil will substantially eliminate NH_3 losses due to exposure and reaction with adsorbed soil Ca^{+2} .
  - application of Ca or K with surfaced – placed urea (urea-Ca or urea- KCl) greatly reduced NH_3 losses, then any type of surface application will be secure.
  - use of acid with urea will reduce NH_3 volatilization BUT use of acid to reduce NH_3 losses in calcareous soil is questionable (find why is that ?). If such technique is used ratio of urea / acid must be more than 1 . Acids used are H_2SO4 and H_3PO_4 BUT HCl and HNO_3 is not recommended

urea-nitric acid → explosive

Hcl → toxic to plants

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4 – soil C.E.C.

has little effect on NH_3 volatilization , however, Fenn & Kissel,1973 found that NH_3 volatilization from soil with C.E.C of 58 meq/1oog was 50%, but in sandy soil losses reached 90% from $(NH_4)_2$ SO4 .

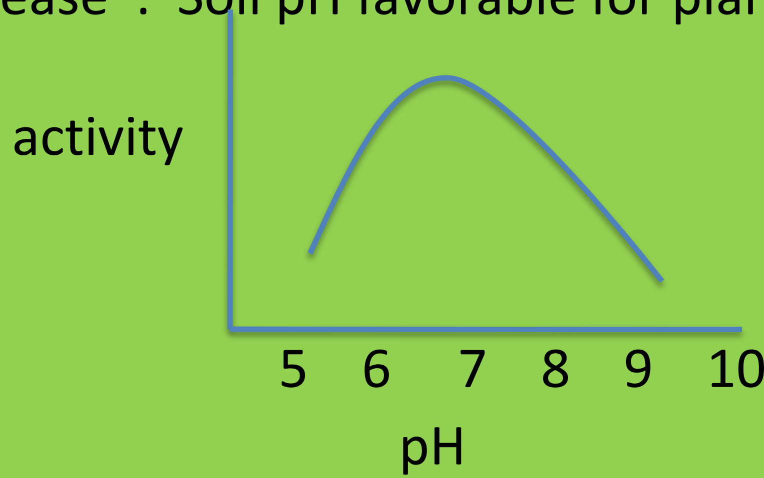
5- Temp.

volatilization increase as temp. increase

6- soil pH

plays a major role in NH_3 volatilization as already discussed.

Soil pH has significant effect on urease activity in soil . At $pH < 4$ urease activity decrease . Soil pH favorable for plant growth is so for uresae activity.



The Acidity and Basicity of Nitrogen Fertilizers L 6

- The equivalent acidity of fertilizers was expressed as the quantity of CaO_3 needed to neutralized the acidity produced by one unit of fertilizers nitrogen (9 Kg or 20 lb of N). In this regard, NH_4 NO_3 , urea, anhydrous ammonia or their solutions were considered to posses the same equivalent acidity . $(NH_4\ )_2$ SO4 and monoammomium phosphate require about three times as much $CaCO_3$ as the foregoing materials to correct acid- forming tendencies. The acidity due to N fertilizers arises when NH_4-N is converted to nitrate in soils. Additional acidity arises from presence of anions of ammonium fertilizers.

- Basic effect N- fertilizers include $CaNO_3$, $NaNO_3$, KNO_3, and calcium cyanamide. (WHY?)

Toxicity of N fertilizers to plants

urea

- $(NH_2)_2CO \xrightarrow{\text{urease}} (NH_4)_2CO_3 + CO_2\uparrow + H_2O$

$(NH_4)_2CO_3 \rightarrow NH_3 + CO_2 + H_2O$

$NH_3 \rightarrow$ gas (toxic)

$NH_3 \rightleftharpoons NH_4OH$

- buriet

buriet has toxic effect on seed germination and plant growth. (1.5 - 2%).

Sources of Nitrogen fertilizers

hand out : The of Nitrogen Fertilizers in Agriculture

Mrs. Farzna panhwar , 2004 (REQURIED)