Soil and Plant Nitrogen

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Acknowledgments

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Symbols and Acronyms

ADAS	Agricultural Development and Advisory Service
AN	Ammonium nitrate
C	Carbon
$CaCO_3$	Calcium carbonate
CAN	Calcium ammonium nitrate
CO_2	Carbon dioxyde
CO_3^{2-}	Carbonate
CVR	Cost:value ratio
DCD	Dicyandiamide
DMPP	3,4-dimethylpyrazole phosphate
DON	Dissolved organic nitrogen
Fe	Iron
H^+	Proton
ha	Hectare
HCO_3^-	Bicarbonate
ISFM	Integrated Soil Fertility Management
K	Potassium
kg	Kilogram
km	kilometer
kPa	Kilo Pascal
MIT	Mineralization-immobilization turnover
N	Nitrogen
Na	Sodium
NBPT	N-butyl-thiophosphoric triamide
NDVI	Normalized difference vegetative index

NH_3	Ammonia
NH_4^+	Ammonium
NH_4^+-N	Ammonium nitrogen
N_{min}	Mineral nitrogen
NO	Nitric oxide
NO_2	Nitrogen dioxide
NO_2^-	Nitrite
NO_3^-	Nitrate
NO_3^--N	Nitrate nitrogen
NO_x	NO and NO_2
N_2	Dinitrogen
N_2O	Nitrous oxide
NUI	Nitrate uptake rate index
OM	Organic material
O_2	Dioxygen
$-NH_2$	Amide form
P	Phosphorus
ppb	Parts per billion
S	Sulphur
Si	Silicon
SOC	Soil organic carbon
t	Metric tonne
UAN	Urea ammonium nitrate
WFPS	Water-filled pore space
µg	Microgram

Abstract

Mineral and organic nitrogen (N) forms undergo a number of changes throughout the N-cycle. Nitrogen is easily transformed among various reduced and oxidized forms and is readily distributed by hydrologic and atmospheric processes. The amount of plant available N is positively influenced by N fertilization, mineralization of soil organic matter, biological N fixation and by precipitation. Negative influences result from immobilization, crop uptake and removal, denitrification (and to some extent nitrification), volatilization, leaching, run-off and erosion. The relative importance of these processes depends on environmental variables such as soil pH, topsoil texture, soil profile characteristics, soil aeration, water supply and temperature, as well as human activities such as type, amount, placement and timing of N fertilizers, available carbon, crop residue management, tillage, soil compaction, drainage, irrigation, land use change and stocking rate on grassland. A better knowledge of the above-mentioned processes has led to improved fertilizer N recommendations. Fixed rates as well as variable rates are common practices. Increased fertilizer N use levels in N-deficient crop production systems have positive effects on the environment through soil fertility maintenance and on human health through more and better food production. Increased N use at high levels, however, can lead to environmental risks that are not balanced by the beneficial effect of increased food supply and/or quality. In some parts of the world, the pressure for increased food production has resulted in nitrate enrichment of the water (nitrate pollution) and reduced air quality (tropospheric and stratospheric ozone, greenhouse effect, acid precipitation). The environmental mobility of reactive N creates an imperative for scientists and food growers to maintain and increase efforts to optimize N use from both inorganic and organic sources.

1. Introduction
The Importance of Nitrogen in Agriculture

Nitrogen (N) is widely distributed throughout the lithosphere, atmosphere, hydrosphere and biosphere. In contrast to the other two major plant nutrients, phosphorus (P) and potassium (K), rock deposits of N in the lithosphere do not exist, and therefore fertilizer N is made from the conversion of unreactive atmospheric dinitrogen (N_2) to reactive forms of N. It is striking that only a very small part of this N is present in the soil (approximately the first meter of the earth crust), mostly as organic forms. The total N content of surface mineral soils normally ranges between 0.05 and 0.2 per cent, corresponding to approximately 1750 to 7000 kg N ha^{-1} in the plough layer. Lower as well as higher amounts can be found, depending on the various soil-forming processes. Of this total N content only a small proportion, in most cases less than five per cent, is directly available to plants, mainly as nitrate N (NO_3^--N) and ammonium N (NH_4^+-N). Organic N, being the rest, gradually becomes available through mineralization.

Nitrogen is the most important plant nutrient for crop production. It is a constituent of the building blocks of almost all plant structures. It is an essential component of chlorophyll, enzymes, proteins, etc. Nitrogen occupies a unique position as a plant nutrient because rather high amounts are required compared to the other essential nutrients. It stimulates root growth and crop development as well as uptake of the other nutrients. Therefore, plants, except legumes which fix N_2 from the atmosphere, usually respond quickly to N applications.

In most ecosystems, N moves from the soil to the plant and from the plant (residue) back to the soil through the microbial biomass. It undergoes many transformations, which are all included in the "nitrogen cycle." In natural ecosystems, this cycle is more or less closed, i.e. N inputs are in equilibrium with N losses. In agricultural ecosystems, however, this cycle is disturbed by the export of substantial amounts of N with harvested products. As a consequence, the use of N fertilizers has been essential to keep and/or increase the productivity of the soil. In the past 50 years, increased fertilizer N use and better N management were the major contributors to large increases in global food production (Smil, 2001).

2. The Nitrogen Cycle

In agricultural and natural ecosystems, N occurs in many forms covering a range of valence states from –3 (in NH_4^+) to +5 (in NO_3^-). The change from one valence state to another depends primarily on environmental conditions and is mainly biologically mediated. Nitrogen is readily distributed by hydrologic and atmospheric transport processes. The transformations and flows from one form to another constitute the basis of the soil N cycle (Figure 1).

Figure 1.
A simplified N cycle
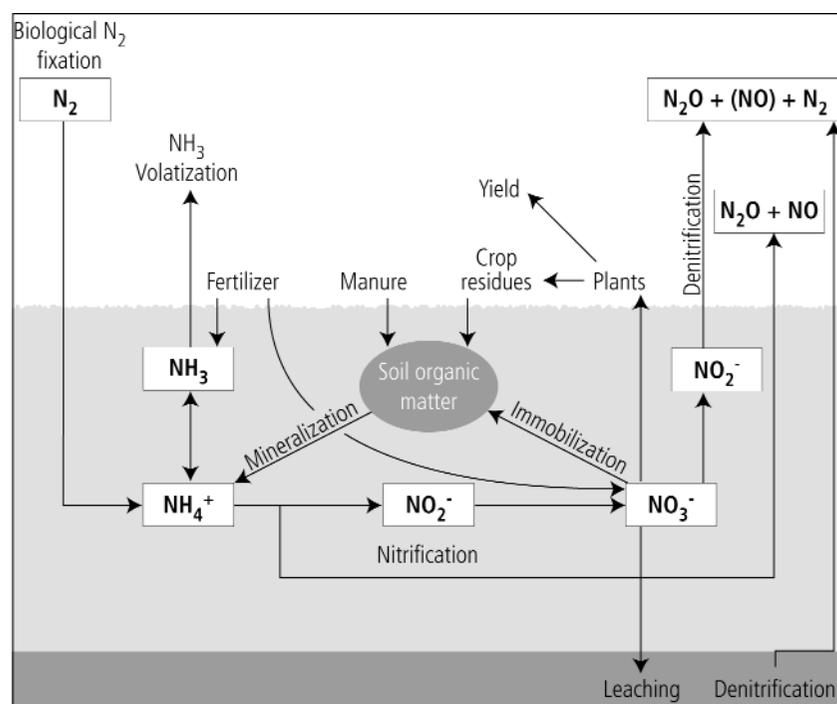
Lightning can convert atmospheric N_2 gas (valence 0) to various N-oxides and finally to nitrate (NO_3^-) (valence +5), which upon deposition can be taken up by growing plants. N_2 gas can also be converted to ammonium (NH_4^+) (valence -3) by biological fixation, a process more important than lightning. This NH_4^+ participates in a number of biochemical reactions in the plant. When plant residues decompose, the organic N-compounds undergo a series

of microbial conversions leading first to the formation of NH_4^+ (ammonification) and usually ending as NO_3^- (nitrification). Under anaerobic conditions NO_3^- can be converted to various N-oxides and finally to N_2 gas (denitrification), which is returned to the atmosphere and thus closes the N cycle. When inorganic or organic N fertilizers are used they undergo the same transformation processes and can influence the speed of the other N transformations.

With regard to the soil-plant compartment, there can be N gains (such as deposition, microbial fixation, animal manures and inorganic fertilizer inputs) as well as N losses (such as leaching, volatilization and denitrification) and N removal via harvested products. The relative importance of these parameters determines the need for fertilizers to sustain crop production.

3. Nitrogen Transformations in Soil

The principal forms of N in the soil are NH_4^+, NO_3^- and organic N-compounds. At any time, the inorganic N in the soil is only a small fraction of the total soil N. Most of the N in a surface soil is present as organic N. It consists of proteins (20 to 40 per cent), amino sugars, such as the hexosamines (five to ten per cent), purine and pyrimidime derivates (one per cent or less), and complex unidentified compounds formed by reaction of NH_4^+ with lignin, polymerization of quinones with N compounds and condensation of sugars and amines. These different N fractions are susceptible to various transformation processes.

3.1. Mineralization/Immobilization

Within the soil, N continuously cycles from organic to inorganic forms and vice versa. This cycling is mediated by the soil flora and fauna, thus, factors affecting soil biological activity have an influence on N transformation rates. Soil microbial biomass itself represents an amount of soil N of the order of 50 to 100 kg ha^{-1}. As already mentioned, most soil N is present in the soil organic matter. Organic N is composed of a continuum of organic matter stabilized against further degradation to different degrees by physical separation from the

soil microbial biomass and/or direct association with inorganic ions and clay surfaces (Hassink, 1992). Although there are several methods, chemical as well as physical, to characterize various pools of soil organic matter, a pragmatic approach subdividing it into old soil organic matter and freshly incorporated organic material is useful in terms of organic N transformations (mineralization/immobilization).

Micro-organisms slowly mineralize organic substances to NH_4^+, which will be further converted by other micro-organisms to NO_3^-. For example, this results in a background mineral N supply from "old" organic matter of the order of 0.5 to more than 1 kg N ha^{-1} day^{-1}, depending on soil type, former residue input and various environmental factors (Table 1). It corresponds with a mineralization ranging between two per cent to more than three per cent of the organic N on a yearly basis. On the other hand, micro-organisms can use both NH_4^+ and NO_3^- to satisfy their N need. This type of N transformation is called microbial immobilization.

Table 1.
N mineralization (kg N ha^{-1} day^{-1}) in the topsoil (0-30 cm) depending on field history and earlier inputs of organic material (OM) (Hofman *et al.*, 2001)

	OM yearly input	N mineralization
Agricultural land	Low	0.5-0.7
Agricultural land	Moderate	0.9-1.1
Agricultural land	High	1.1-1.3
Grassland		1.2-1.5

Immobilization of mineral N can occur (often quickly) by incorporation of fresh organic material, depending on the humification coefficient or effective organic matter content and the ratio of carbon (C) to nitrogen (C:N ratio) in the incorporated organic material. When utilizing organic material with a low N content, the micro-organisms need additional N, decreasing the soil mineral N pool with a resulting decrease in plant N availability. Thus, incorporation of organic matter with a high C:N ratio (e.g. cereal straw) results in immobilization. Incorporation of organic matter with a low C:N ratio (e.g. vegetable or legume residues) results in N-mineralization. A C:N ratio of 25 to

30 is often taken as the critical point range between immobilization and mineralization. Some examples of the input of organic material on N restitution/N immobilization processes are given in Table 2.

Table 2.
Examples of potential N restitution or N immobilization by incorporation of various kinds of organic material (OM)

OM type	Dry OM (kg)	Total N (kg N ha^{-1})	Effective OM[1] (kg)	N immobilization (kg N ha^{-1})	N restitution (kg N ha^{-1})
Farmyard manure 30 t ha^{-1}	4500	165	2250	112	53
Slurry 30 t ha^{-1}					
- Cows	1800	130	900	45	85
- Pigs	1800	195	900	45	150
Crop residues					
- Leaves and tops of					
sugarbeets 30 t ha^{-1}	4000	100	1000	50	50
- Straw	5000	30	1500	75	-45
Green manure Italian ryegrass	6000	120	1500	75	45

1. Effective OM is the amount of organic material left in the soil after one year of incorporation (Hénin and Dupuis, 1945)

In certain environments, the net available N in the soil can be lower because of possible volatilization losses (upon application of farmyard manure and slurry), denitrification losses (e.g. by incorporation of sugarbeet leaves and tops) and in general by leaching losses after excessive rain or irrigation.

3.2. Nitrification

Nitrification is a two-step process (Figure 2). In the first step NH_4^+ is converted to nitrite (NO_2^-) (valence +3) by a group of obligate autotrophic bacteria known as *Nitrosomonas* species. Another group of obligate autotrophic bacteria known as *Nitrobacter* species carries out the second step, where NO_2^- is converted to NO_3^-. Also a few heterotrophs can carry out nitrification, but usually at much lower rates than accomplished by the autotrophic bacteria.

During nitrification minor amounts of nitrous oxide (N_2O) (valence +1) and nitric oxide (NO) (valence +2) are formed. Both compounds have environmental consequences and are discussed in other sections of the paper.

Figure 2.
Nitrification and interaction with denitrification
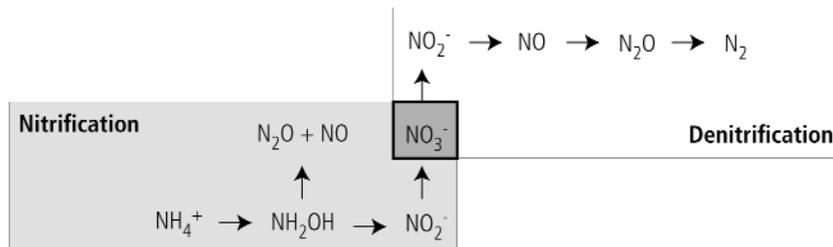
Nitrification is an aerobic process that requires O_2. As soil water reduces the diffusion of air into the soil, the moisture content of the soil has a great influence on the nitrification rate. At a water potential of 0 kPa (saturation) there is little air in the soil and nitrification ceases, due to the lack of oxygen. Nitrification is most rapid near field capacity (-33 kPa in medium to heavy textured soils to -10 kPa in light sandy soils). In dry soils, NH_4^+ and sometimes NO_2^- accumulate presumably because *Nitrobacter* species are more sensitive to water stress than other micro-organisms.

Nitrification is slow under acid conditions with an increasing rate as pH rises. Under alkaline conditions, nitrite also accumulates, because *Nitrobacter* is known to be inhibited by ammonia, which is formed under alkaline conditions. It means that NO_2^- might accumulate under dry and alkaline conditions, but this is generally not a widespread occurrence.

Nitrification is a process that acidifies the soil as protons (H^+) are liberated:

$$NH_4^+ + 2O_2 \rightarrow NO_3^- + 2H^+ + H_2O$$

There is a climatic (temperature) selection of species of nitrifiers, with those from cooler regions having lower temperature optima and less heat tolerance than species from warmer regions. Besides the above-mentioned factors, the population and activity of nitrifiers can also be reduced by the use of nitrification inhibitors, such as dicyandiamide (DCD), nitrapyrin, neem (*Azadirachta indica*) seed cake, etridiazole (Terrazole) and 3,4-dimethylpyrazole phosphate (DMPP). They are mostly used to retard the nitrification of ammonium in fertilizers. Their practicality is controversial and they are not extensively used. Although results from field studies vary widely. Yield responses to nitrification inhibitor use occur more often with early fall versus spring applied N, in coarse textured soils with a high leaching potential and in wet or flooded soils with a high denitrification potential (Peterson and Freye, 1989). Some nitrification inhibitors also have pesticidal properties and beneficial effects on the emission of greenhouse gases. More details about nitrification and nitrification inhibitors can be found in Prosser (1986) and McCarthy (1999).

3.3. Denitrification

In contrast to the nitrification process, denitrification is an anaerobic process. It is a heterotrophic process, needing organic substrate. There are two types of denitrification: biological denitrification and chemodenitrification. Biological denitrification refers to biochemical reduction of NO_3^--N to gaseous compounds. During denitrification, NO_3^- and NO_2^- are reduced to N oxides (NO, N_2O) and molecular N (N_2) by micro-organisms. These gaseous products are not available for plant uptake:

$$NO_3^- \rightarrow NO_2^- \rightarrow NO \rightarrow N_2O \rightarrow N_2$$

Several parameters influence the extent of biological denitrification: oxygen, moisture level, NO_3^- content, C supply, temperature, pH, soil texture, etc. The quantity and quality of incorporated C (harvest residues, organic manure and waste material) as well as its spatial distribution in the soil are especially important. Furthermore, weather conditions (drying/wetting, freezing/thawing) and management practices (physical disturbance, soil compaction, drainage, irrigation) can influence the amount of microbial available C.

Water-filled pore space (WFPS) is a soil parameter indicating whether nitrification or denitrification becomes dominant. The percentage of WFPS in a soil is a useful indicator of the relative potential for aerobic or anaerobic microbial activity in soil. This is illustrated in Figure 3 (Linn and Doran, 1984).

Figure 3.
Relationship between water-filled pore space and relative amount of microbial nitrification,
denitrification and respiration (Linn and Doran, 1984)
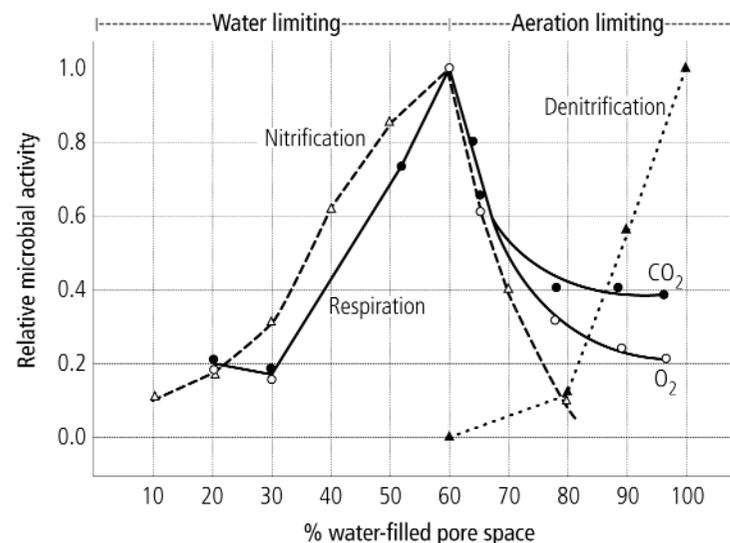
Oxygen availability is a major factor limiting microbial activity above 60 per cent WFPS, with aerobic processes (nitrification) declining most rapidly with increasing water in favour of anaerobic processes (denitrification). It has to be mentioned that N_2O is produced under sub-optimal conditions for both nitrification and denitrification.

Chemodenitrification refers to the same reduction pattern and end products, but it is not carried out by micro-organisms. This non-biological production is important in acid conditions. Chemodenitrification mainly occurs in the subsoil. Primary minerals formed under reducing circumstances, e.g. marine alluvia, release reduced components such as Fe^{2+} during weathering. Oxidized chemicals, such as O_2 and NO_3^-, infiltrating into this zone, will then be chemically reduced (oxidation-reduction reaction). The possibility of chemical NO_3^- reduction (chemodenitrification) in reduced subsoils was already suggested in the 1970s by Lind and Pedersen (1976a and b) and Pedersen and Lind (1976a and b). However, under field conditions, it seems reasonable to conclude that the chemical NO_3^- reduction takes weeks or

even months in order to proceed completely (Verdegem and Baert, 1985). Chemodenitrification can be important to decrease NO_3^- pollution in deep groundwater.

Microbial transformations of NH_4^+ and NO_3^- (Bouwman, 1998), in particular nitrification-denitrification (Lipschultz *et al.*, 1981, Wrage *et al.*, 2001) and NO_3^- reduction, but also chemodenitrification (Van Cleemput, 1998) and fungal transformations (Shoun *et al.*, 1992; Laughlin and Stevens, 2002) are considered to be the main processes producing N_2O in terrestrial ecosystems. The N_2O emitted from the soil surface via diffusion originates thus from a range of different processes.

Nitrate and NO_2^- are participating compounds in both denitrification and nitrification (Figure 2). Through diffusion and mass transport they can easily move from aerobic to anaerobic zones and vice versa. The co-existence of oxidized and reduced zones or layers is illustrated for flooded and upland conditions in Figure 4. Both zones can occur over large soil volumes, but on a microscale they can be near each other.

Nitrite accumulates in sites of high pH and can easily move to sites of low pH where it can undergo a number of reactions. Nitrous acid plays a key role in these reactions. Self-decomposition (at acid pH, below 5.5) and reaction with organic compounds (e.g. amines) or with a number of metals, of which ferrous iron is the most important one, lead to the formation of N_2 and a series of gaseous N oxides (NO, NO_2, N_2O) resulting in less plant available N.

3.4. Ammonia Volatilization

Ammonium N (NH_4^+-N) in the soil is either formed by mineralization of soil organic N and applied inorganic N or after hydrolysis of urea. This NH_4^+ can undergo several processes such as adsorption on soil colloids, fixation by clay minerals, nitrification, fixation by micro-organisms or volatilization. Ammonium in the soil is in equilibrium with atmospheric ammonia (NH_3) through different equilibria (Figure 5).

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)
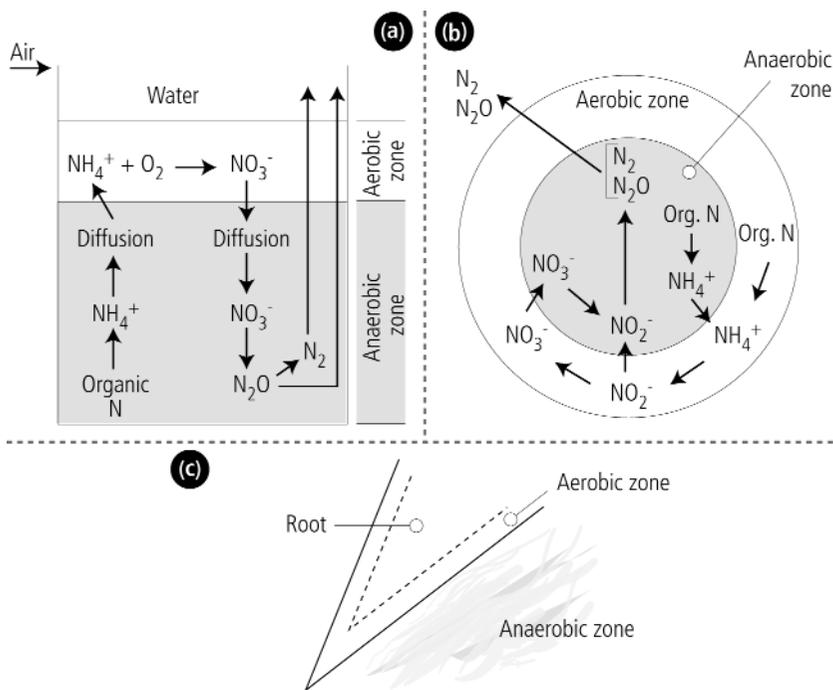
Figure 5.
Schematic presentation of the processes and equilibria of NH_4^+ in respect to NH_3 volatilization
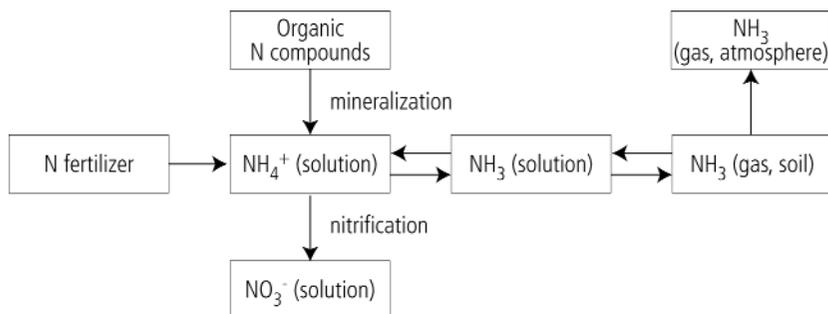
Volatilization of NH_3 can be described in three steps:

- NH_4^+/ NH_3 equilibrium;
- liquid/gas equilibrium;
- mass transfer to the atmosphere.

Step one and two involve a physico-chemical equilibrium. An important parameter is the equilibrium constant pka (being the negative logarithm of the equilibrium constant for reaction 1). This value is equal to 9.4 at 20°C in a water solution. This means that NH_3 is only 0.04 per cent of the total (NH_3 + NH_4^+)-N at pH 6, 0.4 per cent at pH 7, four per cent at pH 8, but 40 per cent at pH 9 as illustrated in Figure 6. Volatilization of NH_3 can be enhanced by the displacement of the NH_4^+/NH_3 equilibrium in favour of the NH_3 form (reaction 1). Carbonate (CO_3^{2-}) and bicarbonate (HCO_3^-) can take up the protons (H^+) emitted through NH_3 formation (reaction 2) and thus push the equilibrium of reaction 1 to the right. Consequently, carbonate and bicarbonate partially neutralize the acidity created by the formation of NH_3 leading to the emission of carbon dioxide (CO_2).

(1) $NH_4^+ \longleftrightarrow NH_3\uparrow + H^+$

(2) $CO_3^{2-} + 2H^+ \longleftrightarrow HCO_3^- + H^+ \longleftrightarrow H_2CO_3 \longleftrightarrow CO_2\uparrow + H_2O$
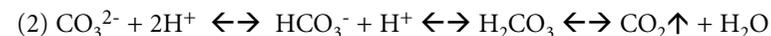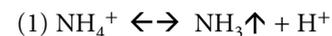
Figure 6.
Influence of the pH on the equilibrium between NH_4^+ and NH_3 (Court *et al.*, 1964)
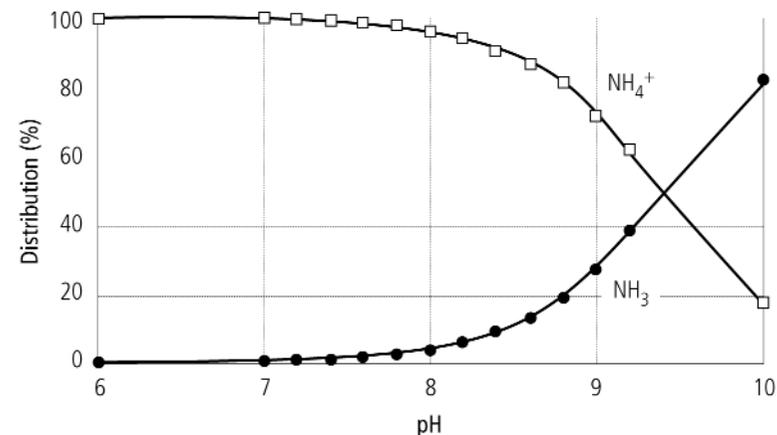
4. Role of Nitrogen in Plants

Generally, dry plant material contains between one and four per cent N, with leguminous plants having slightly higher N contents, around five per cent. In green plant material, protein N is by far the largest N fraction. This is advantageous because many crops are cultivated essentially to produce plant proteins. Depending on the N content and the production of the different plant parts, the N requirements can vary on a yearly basis between less than 100 kg to more than 400 kg N ha^{-1}.

Ammonium, derived either from root absorption or generated through NO_3^- assimilation, is converted to glutamine and glutamate. Once assimilated into these products, N may be transferred to many other organic compounds through various reactions. Nitrate absorbed by roots is assimilated in either roots or shoots, depending on NO_3^- availability and plant species. It is reduced to NO_2^- in the cytosol via the enzyme nitrate reductase and then further reduced to NH_4^+ in root plastids or chloroplasts via the enzyme nitrite reductase. Nitrates, apart from having their specific function as an N source for amino acid and protein synthesis, are stored in the vacuoles and have a non-specific function as an osmoticum. However, the NO_3^- thus stored, especially under low light conditions, is not accumulated for its physiological role.

Theoretically, plants prefer NH_4^+ over NO_3^-, since NH_4^+ does not need to be reduced before incorporation into plant compounds. In most well drained soils, oxidation of NH_4^+ is rapid and, as a consequence, NO_3^- is generally present in higher concentrations in soil than is NH_4^+. In addition, the relative ease of movement of NO_3^- through the soil facilitates its absorption by plants. Therefore, most plants have evolved to grow better with NO_3^- and, a number of studies have shown that plant growth may be enhanced with a mixed supply of NH_4^+ and NO_3^-. In particular, rice must have a supply of NH_4^+, as NO_3^- is not stable in submerged soils.

Nitrogen uptake rate is more a function of demand for N from the shoot rather than of the nutrient concentration at the root surface (Blom-Zandstra, 1990; King *et al.*, 1992). Recently, as a consequence of the on-going debate on whether crop growth rate or soil NO_3^- concentration controls N absorption by crops under field conditions, a NO_3^- uptake rate index (NUI) was introduced (Devienne-Barret *et al.*, 2000). This index is the ratio between the actual and the critical N uptake rate, the latter being the minimum amount of N needed for maximum growth rate. Below the critical N dilution curve (Greenwood *et al.*, 1990), NUI would be controlled both by the potential aboveground growth rate and the external NO_3^- concentration, which determines the actual growth rate. Above the critical dilution curve, NUI would be controlled only by the external N concentration.

A close relationship exists between the nutrient concentration in the soil solution in the vicinity of the roots and the rate of nutrient uptake by the plant. The ion concentration at the root surface depends on both the rate of movement of the ion from the bulk soil towards the root and the absorbing power of the roots. The transport itself is governed by two mechanisms, i.e. transport by mass-flow and transport by diffusion (Mengel, 1985; Barber, 1994). Mass-flow, related to the water used by the plant and the nutrient concentration of the soil water, is the major mechanism for moving NO_3^- towards the roots. On the other hand, NH_4^+ diffuses mainly along a concentration gradient, induced by depletion of nutrients at the root surface, and hence diffusion is the principal transport mechanism for it.

Inadequate available N reduces crop growth and production. A visual diagnosis is a valuable mean of assessing the nutritional status of a crop, but when visual symptoms are observed, plant stress has already occurred and may result in yield reductions. Deficiency symptoms are the consequence of metabolic disturbance and various causes can lead to similar syndromes. Visual diagnosis of deficiencies requires experience and can only successfully be practiced by experts (Mengel and Kirby, 1982). Nitrogen deficiency is characterized by stunted plants, less than optimum growth rate, and the older leaves senesce prematurely. A shortage of available N results in leaf chlorosis, sometimes with distinctive patterns. In the case of maize, necrosis will begin at the leaf tip and forms a "v-shaped" pattern as the chlorosis progresses down the mid-rib of the leaf (see Figure 7 in back inside cover). Nitrogen deficiencies first appear on older leaves since, during a deficiency, N in the older leaves will be metabolized and transported to newly developing plant parts. Crops deficient in N mature earlier with, as a consequence, a shorter photosynthetic period and reduced yield.

5. Nitrogen Fertilization in Crop Production

All soils in a natural state are deficient in N for crop growth. Soil nutrient depletion and decreasing yields are inevitable if crops are grown and harvested without replenishment of nutrients. Crop production cannot be sustained without the use of manufactured fertilizers, incorporation of N fixing crops and/or organic sources of N. The relative importance of these sources differs widely according to the region in question. Developing countries (mainly Asia) experience a steady annual growth of N fertilizer use. In developed countries, fertilizer use grew until 1989 at about 4.3 per cent per year, followed by a decline until 1993 further to the policy change in the Former Soviet Union and Central Europe. The use rate has remained fairly constant since 1993. The total amount of fertilizer N used in developing countries surpassed that of developed countries in the late eighties (IFA, IFDC, FAO, 1999).

5.1. Types and Characteristics of Nitrogen Inputs

Input of N for crop production occurs through inorganic and organic fertilization, through biological nitrogen fixation (BNF) and, to some extent, through atmospheric deposition.

5.1.1. Inorganic and Organic Fertilization

World fertilizer N production is based on the synthetic fixation of atmospheric N in the form of NH_3. The NH_3 produced is further used for the production of inorganic fertilizers, containing either NH_4^+, NO_3^-, a combination of both, or the amide form ($-NH_2$). In addition to these single (straight) N fertilizers, multinutrient (compound) fertilizers containing N together with other primary nutrients, such as phosphorous (P) and/or potassium (K), are widely used.

5.1.1.1. Inorganic Nitrogen Fertilizers

Three main forms of inorganic N fertilizers exist: ammonium (NH_4^+), nitrate (NO_3^-) and urea ($CO(NH_2)_2$). The effectiveness of inorganic fertilizers is influenced by the principles of ion exchange. Because of its positive charge, NH_4^+-N is adsorbed by the negatively charged soil colloids (clay and organic matter) and thus retained from leaching. The negatively charged NO_3^--N is subject to leaching, which is most important in sandy-textured soils.

Single Nitrogen Fertilizers

The most important single N sources are:

- **Anhydrous ammonia** (NH_3): 82 per cent N. Because it is a gas at atmospheric pressure, it has to be stored in pressurized vessels or under refrigeration. Special equipment is needed for injection into the soil to eliminate NH_3 vaporization. It is mostly used in North America.

- **Ammonium sulphate** ((NH_4)$_2SO_4$): 21 per cent N and 24 percent sulphur (S). This fertilizer is non-hygroscopic, with good handling and storage characteristics. It is especially suitable for use in the humid tropics and subtropics. After application, part of the NH_4^+ is normally transformed to NO_3^- and available for plant uptake or denitrification and loss. Ammonium can also be fixed on clay minerals and retained by soil colloids preventing it from leaching. Most ammonium sulphate results as a by-product of industrial processes. It has been widely displaced by urea.

- **Ammonium nitrate** (NH_4NO_3): 34-35 per cent N. Half of the N content of this fertilizer is in the NH_4^+ form and half is in the NO_3^- form. In Europe, ammonium nitrate is often used in the form of calcium ammonium nitrate (CAN) with 27 per cent N. Ammonium nitrate, when mixed with an organic C source (e.g. diesel fuel), confined and ignited is explosive (it is widely used in mining and construction for that purpose). For this reason, the transportation, storage and use of ammonium nitrate is becoming more regulated.

- **Urea** ($CO(NH_2)_2$): 46 per cent N, all in amide form ($-NH_2$). The relatively simple and less costly synthesis of urea and its high N content has made it the most commonly used N fertilizer in the world. In rice production, urea is dominant. Its comparatively high N content is advantageous for cost-effective transportation and storage, but it is hygroscopic. When applied to the soil, the $-NH_2$ is first converted to NH_4^+ and subsequently to NO_3^-. Before this conversion has taken place, the urea molecule is susceptible to movement with soil water, as it is not adsorbed by soil particles. When urea is applied, it rapidly hydrolyses, in 10-14 days, under well-drained conditions, unless a urease inhibitor has been applied to the urea granules. Upon hydrolysis by the urease enzyme, the soil pH increases. Depending on the buffer capacity of the soil, this may lead to volatilization of NH_3 in high pH soils, especially with surface application. Volatilization losses of 20 per cent are common, and up to 60 per cent

losses have been measured. To minimize this loss, urea should be incorporated into the soil as soon as possible after application with either tillage or irrigation water. If urea must be applied to soil surfaces, the use of a urease inhibitor should be considered. The inhibitor will reduce hydrolysis with the expectation that adequate rainfall will move the urea into the soil before hydrolysis occurs, thus reducing volatilization losses.

- **Calcium nitrate** ($Ca(NO_3)_2$): Prilled and granulated calcium nitrate contains 15.5 per cent N, while crystalline products contain 12 per cent N. Approximately two-thirds of world calcium nitrate fertilizer is used in Europe, but use is expanding in other parts of the world. It is extremely hygroscospic, which presents application difficulties, but the 100 per cent water-soluble nitrate form makes this relatively low-analysis fertilizer attractive for use in high-value crops such as vegetables.

- **Sodium nitrate** ($NaNO_3$): About 16 per cent N. This is also called Chilisalpeter because it was originally mined from natural deposits on the Chilean coast. It is useful for crops such as sugarbeets, which require sodium (Na).

- **Calcium cyanamide** ($CaCN_2$): 17 to 24 per cent N. All N is, upon hydrolysis, in the amide and cyanide forms. In soil, it is first converted to urea in the presence of water, and during the conversion, certain toxic products can be formed, which suppress weed growth. Because of the production of plant-toxic components, it must be applied so that the conversion to urea be completed prior to planting. Local recommendations should be carefully considered when using this fertilizer.

- **Ammonium bicarbonate** (NH_4HCO_3): 17.7 per cent N. This fertilizer is weakly hygroscopic and NH_3 volatilization during application is quite high. However, because of its low price and the high production capacity in China, ammonium bicarbonate is a commonly used N fertilizer in that country (about 5 million tonnes N, but following a downward trend), even though its efficiency is quite low.

Depending on their composition, fertilizers can provoke acidic or alkaline reactions in the soil. This is expressed as base equivalent and given as kg CaO per 100 kg of fertilizer. The base equivalent corresponds with either a negative value or neutralization capacity (by acidic reaction) or a positive value or alkalinization capacity (by alkaline reaction). The base equivalent for a number of fertilizers is calculated and given in Table 3. It shows, for example, that with

the application of 100 kg urea-N ha^{-1}, 46 kg CaO ha^{-1} would be theoretically required to neutralize the acid produced by the complete conversion of urea to NO_3^-.

Table 3.
Nitrogen content and base equivalent of some single N fertilizers

Fertilizer Material	N content	Base equivalent
Anhydrous ammonia	82%	- 82
Ammonium sulphate	21%	- 62
Urea	46%	- 46
Ammonium nitrate	35%	- 35
Calcium ammonium nitrate	27%	- 14
Calcium nitrate	15.5%	+ 12
Sodium nitrate	16%	+ 17
Calcium cyanamide	18%	+ 40

Multinutrient Nitrogen Fertilizers

- **Ammonium phosphates**: Production of these fertilizers is based on the reaction of NH_3 with phosphoric acid. Examples are mono-ammonium phosphate (10-11 per cent N), diammonium phosphate (18 per cent N), ammonium sulphate phosphate (13-16 per cent N) and liquid ammonium polyphosphate (10-11 per cent N). The granular fertilizers are all of low hygroscopicity. Ammoniated superphosphates can be produced using NH_4^+ to neutralize the free water-soluble phosphoric acid in superphosphate fertilizers. All of these fertilizes are used as P fertilizer sources, although the N is 100 per cent plant available.

- **Potassium nitrate** (KNO_3): 13 per cent N. This fertilizer is 100 per cent water soluble and is suited for application through irrigation systems used in greenhouse and container-grown nursery plant production systems that utilize low soil volumes. Both ions in the fertilizer are essential nutrients taken up by plants, resulting in low salt accumulation.

- A wide range of fertilizers can be obtained by mixing urea, ammonium sulphate or other N fertilizers with various P and K sources. Blending various fertilizer materials to obtain prescription fertilizer grades is widely practiced in North America and is becoming more common in other agronomic crop production regions of the world.

Time-Release Nitrogen Compounds

As N provided by commercial chemical fertilizers is subject to many different fates in soil, crop recoveries seldom exceed 60 to 70 per cent of the added fertilizer N. There is an on-going search for N fertilizers with a greater efficiency (e.g. slow-release products), enhanced by environmental concerns of N losses to groundwater, surface water and the atmosphere. There are also agronomic reasons for having sources with an extended period of N release, thus avoiding the need for repeated applications of conventional products. The ideal product is one that liberates N in accordance with crop needs throughout the growing period. Possibilities to reach these goals are the use of:

- substances of low water solubility and chemical and/or microbial decomposition before release of available N;
- sparingly soluble minerals;
- gradually decomposing substances;
- water soluble products treated to impede dissolution;
- ion exchange resins;
- nitrification and urease inhibitors (Havlin *et al.*, 1999).

5.1.1.2. Organic Nitrogen Sources

In addition to the inorganic fertilizers, the use of organic N through animal manure, sludge or other N-containing secondary products is quite important, in particular in countries with intensive cattle, poultry and swine feeding. Organic N sources can be extremely important N fertilizers in countries with developing agriculture, especially when inorganic fertilizers are not available or not affordable.

Organic manure can be of plant or animal origin or a mixture of both. However, most comes from dung and urine from farm animals. It exists as farmyard or stable manure, urine or slurry as well as compost. Because its composition is not constant and because plant material (catch or cover crops, legumes) is often added freshly cut (green manure) to the soil, crop nutrients available for the next crop range from less than 20 per cent to more than 50 per cent of what is applied. Legumes and manure can release quite high amounts of N in a rather short time. However, approximately 50 per cent of the total amount of N in slurry manures exists under NH_4^+ form, which will be volatilized to some extent, depending on the application procedure. Other organic N sources, like farmyard manure and some composts, release their N

slowly, avoiding excessive uptake and reducing potential losses by leaching and denitrification. On the other hand, N release from incorporated organic material can further occur after the crop is harvested, with the mineralized N being susceptible to leaching

5.1.2. Biological Nitrogen Fixation

Rhizobium species living in symbiotic relationship in root nodules of legumes (e.g. soybean, clover, alfalfa, peas, beans) can convert atmospheric N_2 gas to NH_3, which is further converted to amino acids and proteins. In exchange, the legumes provide the *Rhizobium* species with the energy they need to grow and to fix N_2. Some non-leguminous trees and plants (e.g. alder, sugarcane) also host N-fixing bacteria. Photosynthetic cyanobacteria are also N-fixing organisms and are especially important in rice paddies. The amount of N fixed varies greatly from crop to crop, ranging from a few kg to a several hundred kg N ha^{-1} year^{-1}. The process is depressed when other sources of N are abundant, and is also reduced in acid soils and in soils with low P availability.

5.1.3. Other Sources of Nitrogen Available to Crops

5.1.3.1. Atmospheric Nitrogen Deposition

Total atmospheric N (NH_4^+ and NO_3^-) deposition is of the order of 10-40 kg N ha^{-1} year^{-1} in much of northwestern and central Europe and some regions in North America. In less industrial areas, this amount ranges from 3 to 5 kg N ha^{-1} year^{-1}.

Nitrogen deposition is usually not directly included in calculations of N application rates. However, the deposition that takes place in winter will be part of the measured mineral N in spring. The amount deposited during the growing season will be considered as N being formed by mineralization of organic matter. Furthermore, this deposition contributes to acidification of agricultural soils, with possible impacts on biodiversity (Brussaert *et al.*, 2001; Gotelli and Ellison, 2002), and to eutrophication of sensitive ecosystems.

5.1.3.2. Nitrogen Input by Irrigation Water

Irrigation water can contain NO_3^- originating from sewage or leached from agricultural land. This input should be taken into account when calculations are made with regard to fertilization practices, although these amounts will be limited. For example, a total irrigation of 100 mm and a concentration of 20 mg NO_3^--N L^{-1} provides an input of 20 kg N ha^{-1}.

5.1.3.3. Nitrogen Availability from Mineralization of Soil Organic Matter

Mineralization of soil organic matter is generally of the order of less than 50 kg N ha⁻1 year⁻¹ for low organic matter content soils to greater than 200 kg N ha⁻¹ year⁻¹, depending on climatic conditions, organic matter content and tillage practices. To keep steady state conditions, this N release has to be compensated by inputs of organic N and/or immobilization.

5.2. Nitrogen Fertilizer Recommendations

The mineral N (NH_4^+, NO_3^-) pool (available N) in soil is only a small proportion of the soil's total N. Figure 8 illustrates positive and negative factors and processes influencing this pool. The pool size ranges from tenths of kilograms to a few hundred kg N ha⁻¹. Most of the mineral N is in NO_3^--N form because NH_4^+-N is quickly nitrified in most arable soils. This quantity of plant-available N is of paramount importance for fertilizer recommendations.

Figure 8.
Factors influencing the mineral N pool
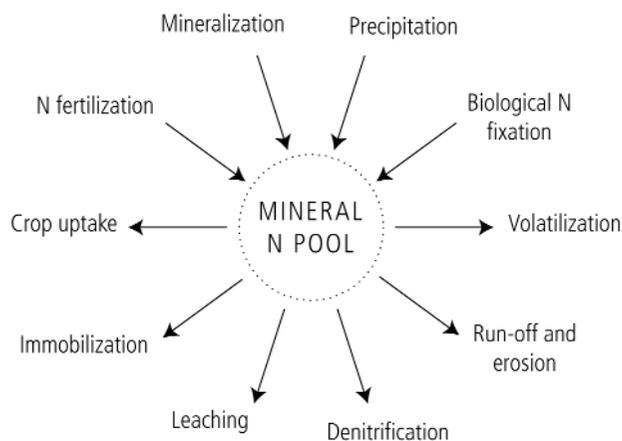
Until the seventies, results of field trials with various N levels over different years were used to identify the optimum N level for a certain crop in a specific region. This approach was unsatisfactory because the potentially available N in the rooting zone of the crop was unknown. Further, because the

N requirement is related to the level and quality of production, the 'answer' changes each year, especially with varying weather conditions.

Optimal N fertilization will normally result in crops with good quality. A better timing of N fertilization, e.g. a supplementary N fertilization at flowering stage of wheat, can enhance the protein content of the grain. Most consumers prefer leafy vegetables, like lettuce, with a dark green color that can only be obtained with adequate available N. On the other hand, the quality of the harvested products can be reduced by excessive N contents as well. Sap purity and sugar extractability from sugar beets, dry matter and starch content in potatoes and nitrate contents in leafy vegetables are examples of traits that can be affected by high levels of available N in the soil. In addition, excessive N availability can lead to yield reductions, e.g. due to cereal lodging, decreased sugar content in sugar beet and sugarcane, and a higher risk for diseases and pests in many crops. The need for field- and season-specific N fertilizer recommendations is recognized throughout the world. However, the data and/or the technology to implement a programme to determine the optimum N rates on a site-specific basis are not always available.

Rapid and accurate determination of mineral N in the soil profile, as well as the availability of plant tissue testing and computer simulation modeling have led to science-based N recommendation systems for many crops in various parts of the world (Hofman and Salomez, 2000). These recommendations can roughly be split into fixed rate recommendation programmes and variable rate recommendation programmes.

5.2.1. Fixed Nitrogen Rates

The simplest type of fertilizer recommendation specifies a fixed rate for the crop in all situations, regardless of soil type, field characteristics, cultivar, etc. Though easy and without costs for soil or plant analysis, this method is completely inadequate as it ignores factors such as mineralizable organic N, residual N from previous fertilizer applications, rainfall variation and the variation in leaching potential for soils with different textures, to name only a few factors.

A refinement of this method is the ADAS (Agricultural Development and Advisory Service) N index method (Anonymous, 1994) utilized in the United Kingdom. On the basis of past management practices and on information of the previous grown crop, fields are attributed an index, ranging from 0 (low amounts of mineral N (N_{min}) expected) to 2 (high amounts of N_{min}

expected), giving an indication of expected N_{min} residues, the exact N_{min} amount being unknown. N_{min} is the amount of mineral N, expressed in kg ha^{-1}, in the soil profile to the mean rooting depth of the specific crop at the start of the growing period. The recommended N rate further depends on soil type and the organic matter content of the soil as presented in Table 4 for winter wheat.

The lack of precision in such a system is recognized and, thus, is only to be used under conditions where soil sampling is not possible due to the presence of stones and in situations where N_{min} at the start of the growing period is not likely to fluctuate among fields and years. In all other situations, a method which includes soil analysis is recommended (Neeteson, 1995).

Table 4.
ADAS N recommendation system for winter wheat (kg N ha^{-1}) [spring N top-dressing] (Anonymous, 1994)

	Index		
	0	1	2
Sandy soils	175	140	80
Shallow soils	225	190	130
Deep silty soils	180	90	0
Clays	190	110	0
Other mineral soils	210	150	70
Organic soils	120	60	0
Peaty soils	80	20	0

5.2.2. Variable Nitrogen Rates

N_{min} method sensu stricto

The results of Van der Paauw (1963) and others, concerning the effect of residual N, were the forerunners for the investigations into inorganic N in the soil profile. Later on, research in different countries led to N fertilization recommendations based on the linear relationship between the N_{min} in the rooting zone of the crop at the start of the growing period and the optimum N fertilization for the crop. Figure 9 shows this relationship for potatoes. This method, with some adaptations, is still used in several parts of Germany and in The Netherlands.

Table 5 gives an overview of the current Dutch N fertilizer recommendations for potatoes, as a function of soil type, whereby a and b represent the coefficients of the linear relationship between N fertilizer recommendations and soil N_{min}.

Table 5.
Current Dutch N fertilizer recommendations (N_{rec}) for potatoes (Anonymous, 2000)

	$N_{rec} = a - b \times N_{min}$		Sampling depth for N_{min}
	a	b	(cm)
Ware potatoes			
Clay and loam soils	285	1.1	0-60
Sandy soils	300	1.8	0-30
Starch potatoes	275	1.8	0-30
Seed potatoes	140	0.6	0-60

Although the linear regression is significant in Figure 9, there is still large variation around the calculated regression line. To reduce this variation, other systems that take more factors into account have been introduced.

Figure 9.
Relationship (N appl. = 300-1.8 x N_{min}) between the amount of mineral N in the 0-30 cm soil layer at the end of the winter period and the economically optimum application rate of N fertilizer for potatoes (*Solanum tuberosum* L.) on sandy soils in The Netherlands (Neeteson *et al.*, 1984)
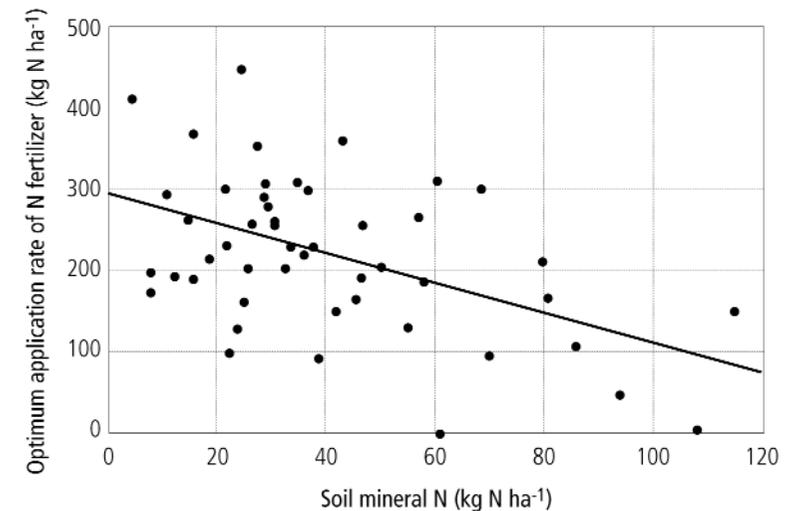
N-index method

The Pedological Service of Belgium proposed the N-index method in the early 1980s (Boon, 1981). Besides the N_{min} amount, other factors, up to a maximum of 18, were included into the N-index system. Depending on the history of the field, one or more of these factors could be omitted.

N-index = $X_1 + X_2 + X_3 + …. + X_{16} + X_{17} + X_{18}$

Whereby X_n represents the various factors.

These factors can be divided into three groups (Vandendriessche *et al.*, 1992):

- N_{min} (X_1):

> is the mineral N in the soil profile to the mean rooting depth of the crop at the beginning of the growing period;

- Mineralization (X_2-X_9):

> are the factors responsible for the N release from soil organic matter and various types of incorporated material, e.g. green manure, crop residues, animal manure, compost, etc.

- Negative factors (X_{10}-X_{18}):

> are factors that have a negative effect on the N availability, e.g. compaction, less than optimum pH or possible N leaching.

The optimum N fertilization recommendation is calculated as follows:

N recommended = a – b x N-index

Whereby a and b depend on the cultivar and destination of the harvested products.

The relationship between the N-index and the optimum N fertilizer rate is less variable than the one shown in Figure 9 and it results in more precise N fertilizer recommendations.

Nitrogen balance sheet method

The N balance sheet method was first developed in France and in the United States (Hébert, 1973; Carter *et al.*, 1974) and is, with some minor adjustments, also used in Belgium and The Netherlands (Hofman, 1983; Neeteson *et al.*, 1988).

The theoretical N fertilization is calculated as follows:

N need of the crop + Residual N_{min} in the soil profile at harvest*	=	N_{min} before planting + N mineralization + N fertilization

*The residual N_{min} in the soil profile at harvest to the mean rooting depth is the amount of mineral N which remains in the rooting zone at optimum N fertilization and at the time of maximum N uptake

The practical N fertilization recommendation is also adjusted according to expected losses. These potential losses are estimated to range between 5 and 20 per cent, mostly depending on soil texture.

The balance sheet method has also been applied in China with the following approach whereby all the parameters are expressed in kg N ha^{-1}:

$W_{input} = W_{output} - \Delta W - (W_n - W_{n+m})$

Where:
W_{input} = N requirement

W_{output} = N requirement of target yield

ΔW = (N mineralized + subsoil mineral N + dry deposition N + wet deposition N) – volatilized N

W_n = available N before planting

W_{n+m} = available N after harvest

This method requires significant amounts of soil specific data, but does provide a means for making field and season-specific N fertilizer recommendations (J. Jin, Chinese Academy of Agricultural Sciences, personal communication 2004).

The above-mentioned methods do not take into account (fixed rate and N_{min} method) or only estimate (N-index method and N balance sheet method) the amount of N that will be mineralized from soil organic matter during crop growth. In order to better cope with post-planting mineralization, other methods are in use, all of which try to determine whether or not to make an additional N application during the growing season. For example, the Pre-

Sidedress Soil Nitrate Test (PSNT) developed by Magdoff *et al.* (1984) has been widely utilized to estimate the need for supplement N fertilizer in fields planted to maize where large amounts of organic N sources have been applied. This test prevents over-application of N and provides assurance that adequate N is available to the crop from the organic sources, but does require the capacity for top-dressing of N to the growing crop. Other reasons to use a top dressing are possible improvements in fertilizer N use efficiency, possible yield increase, improvement of quality and the decrease in potential adverse environmental impacts. Better N management usually results from split N application programmes, because it is difficult to predict achievable yields and N losses at the start of the growing season.

KNS-system

The crop-aided N_{min} norm system (in German: "Kulturbegleitenden N_{min} Sollwerte-System", KNS-system), introduced in Germany by Lorenz et al. (1985) and taken over in The Netherlands as the additional N fertilization system (in Dutch: "N-BijmestSysteem", NBS-system) (Breimer, 1989) has been developed as an aid for the N fertilization of vegetables. It involves the measurement of the residual N_{min} at fixed intervals during the growing period and comparison with target values (Pannier *et al.*, 1996). The advantage of this system is that one can adapt a supplementary N dose according to N mineralization and the performance of the crop in the early stages of development. When irrigation possibilities are provided, splitting the N dose becomes even more important.

Simulation models

With simulation models, it is possible to calculate, on a daily basis, the availability of N to the crop and the N uptake and growth of a crop, using average or actual weather data and soil, crop and field parameters as inputs. Simulation models can thus be used to estimate the fertilizer N requirements of a crop at any time during the growing season. Also, the environmental side effects of N fertilizer applications can be estimated. In order to keep these models as simple as possible and to keep the number of parameters and input data to a minimum, they have to be simplified as much as is justified by the soil, crop and climatic conditions in a given environment (Neeteson, 1995). The main disadvantages of (simplified) models are that they require extensive data, which are not always readily available, and that extrapolation is difficult as the models are mostly developed for specific soil and climatic conditions.

However, such models can form the basis for determining research needs associated with improving N fertilizer recommendations in areas that are beginning to use more fertilizer N, as well as to determine the environmental factors (mainly rainfall) influencing optimum N rates from season-to-season (Montaner *et al.* 1997).

Plant analysis (petiole sap analysis, chlorophyll-meter readings…)

Plant analysis is used to check the N status of a crop during the growing period. The idea behind plant analysis is that the crops themselves are the best indicators of the supply of N by the soil, as well as of the crop's N demand and its ability to absorb the N available in the soil. When the N status appears to be inadequate, additional fertilizer N can be applied. Plant analysis methods have the advantage that a second N fertilization can be delayed and that the mineral N supply from soil organic matter can at least partly be introduced into the recommendation system. However, the 'translation' of values obtained into amounts of fertilizer N to be applied to compensate for the N deficiency has been, until now, very difficult, and optimal timing for a second N fertilizer application is not easy to define.

Site-specific and real-time N management

During the mid-1990s, nitrogen omission plots were used to develop a site-specific approach to N fertilizer management in rice in Asia (Buresh *et al.*, 2004). The system involves determination of the N fertilizer need as the difference between the supply of N from indigenous sources (measured with an N omission plot) and the demand of the rice crop for N as estimated from the total N required by the crop to achieve a target yield for average climatic conditions. A calibrated leaf color chart is used to estimate crop N demand through the growing season and applications are made at pre-determined critical growth stages. The site-specific approach was evaluated over six crops in three years (205 on-farm experiments) with the following results: it increased (1) rice grain yield by 0.4 t ha^{-1}, (2) agronomic N efficiency from 6.8 to 12.5 kg grain kg^{-1} N applied, (3) apparent N recovery efficiency from 0.19 to 0.31 kg N taken up kg^{-1} N applied and (4) returns above fertilizer costs by US\$ 89 ha^{-1}.

The 'real-time' N management approach to determining N needs in rice production in Asia utilizes leaf color measurements at 7-10 day intervals from 15 to 20 days after planting to flowering (Buresh *et al.*, 2004). Nitrogen fertilizer is applied whenever the leaf color values fall below critical threshold

values. Preliminary evaluation indicates significant improvement in fertilizer use efficiency in these highly fertilized, irrigated rice production systems. A key component to both the site-specific and real-time management approaches is that other elements such as P, K, and S must be above yield-limiting levels in order for N fertilizer to be used efficiently.

In the United States, research groups in Oklahoma and Nebraska have worked with the application of optical sensors to estimate winter wheat N needs. Sensors measure the normalized difference vegetative index (NDVI) computed from red and near infrared reflectance values. These data are coupled with temporal estimates of N responsiveness and spatial variability in NDVI readings in 0.4 m^2 areas of the field (Raun *et al.*, 2004). Their research has shown N use efficiency increases of 15 per cent for winter wheat. The principles supporting this technology should also apply to estimating N fertilizer requirements for other crops.

5.2.3. Nitrogen Recommendations in Developing Countries

Under tropical and subtropical climates, mineralization of soil organic matter is accelerated by prevailing high temperature. Moreover, crop residues are generally removed from the field for other purposes or are burned in order to facilitate fast and easy land preparation. Although substantial efforts have been made to enhance fertilizer use, it is still marginal and nutrient balances are often negative. There is a substantial variability in N fertilizer use between regions, villages and even fields. Current use of fertilizers is usually sharply below recommended rates. The many reasons behind the low fertilizer use include cost, limited availability, lack of knowledge on the appropriate and efficient use and often low and/or unstable produce prices, which limit farmers' interest in fertilizer use (IFDC, 2003). Over-attention to organic N might also have resulted in a negative approach towards inorganic N. Organic inputs play an important role, but they will not be able to supply enough N for acceptable crop production levels. Integrated Soil Fertility Management (ISFM) advocates the combined use of organic and inorganic N sources thereby exploiting the potential of positive interactions between both inputs (Vanlauwe *et al.*, 2002).

5.3. Nitrogen Use Efficiency

Nitrogen use efficiency by crops can be defined differently according to various view points (Bowen & Zapata, 1991):

(1) fertilizer N use efficiency: the yield increase (grain or tubers or other plant parts) per unit of applied N. This can also be considered as the agronomic approach and defined as yield efficiency;

$(Y_N-Y_0)/F_N$

(2) N uptake efficiency: the increase of N absorbed in above-ground biomass at physiological maturity per unit applied N. This is an ecophysiological approach;

$(U_N-U_0)/F_N$

(3) physiological N use efficiency: the yield increase per unit of N absorbed. This is a physiological parameter;

$(Y_N-Y_0)/(U_N-U_0)$

(4) the N utilization efficiency: yield per unit of applied N;

Y_N/F_N

Whereby:

Y_N and Y_0 are yield with and without N application, respectively

U_N and U_0 are plant N uptake, with and without N application, respectively

F_N is fertilizer N applied

The agronomic approach is most useful for understanding the factors governing N uptake and fertilizer efficiency and to compare different N management options. For cereals, it is often in the range of 10-25 kg grain kg^{-1} N applied. The ecophysiological index is within the 30-50 per cent range, although values of up to 80 per cent can be reached. The physiological index represents the ability of a plant to transform the N taken up into yield. This is a characteristic of the plant and also depends on external factors. The most important index for farmers, however, is the N utilization efficiency as it integrates the use efficiency of both indigenous and applied N resources. The N utilization efficiency in cereal crops is often within the 40 to 60 kg grain kg^{-1} N applied, but it can reach values of more than 100 kg grain kg^{-1} applied N.

The term efficiency can be further extrapolated and defined in other ways including the increase in the well-being of man or the increase in food production. Needless to say that for economic as well as for environmental reasons, the uptake or efficiency of fertilizers should be as high as possible. In addition, quantification and location of the non-efficient part of the fertilizer N use is a necessity in order to be able to introduce the proper measures to protect the environment.

There are different methods to determine fertilizer N use efficiency or N uptake efficiency. The difference method uses the difference in N uptake between fertilized plants and non-fertilized plants. Also the slope of the linear regression relating the N content in the plants and the rates of applied fertilizer N can be used. With this method, different levels of fertilization (possibly also zero fertilization) must be used. The use of isotopes also allows the determination of fertilizer N use efficiency. The isotopic method directly determines the amount of N derived from the applied labelled N fertilizer in the plant. The slope of the regression line between the labelled N uptake against the amount of applied labelled fertilizer N is also used to estimate efficiency. The use of isotopes also allows an estimation of the residual effect of the fertilizer because the labelled fertilizer N can be followed through both soil and plants. In addition, the amount of biological N fixation can be evaluated as well as the fate of the non-efficient portion of the applied N. Both the indirect method (difference method) and the direct method (use of isotopes) have advantages and disadvantages, but they usually provide results that are closely correlated (Bowen and Zapata, 1991). When comparing both techniques, a number of considerations should be taken into account. Because the difference method compares data obtained from different levels of fertilization, the assumption is made that all fertilizer levels have the same influence on soil N. This is seldom true because of its influence on soil N turn-over and on root development. The isotope method, on the other hand, assumes that no biological interchange occurs between the labelled and non-labelled N. Jenkinson *et al.* (1985), in their review on the 'priming' effect discussed this shortcoming. In soils with a low amount of soil N, the indirect method is preferred, while in soils with a high amount of native N, the isotope method is favoured. In addition, the isotopic method provides more accurate information on a shorter period of time.

Across all regions and crops a range of 5 to 90 per cent for fertilizer N recovery has been observed. Smil (1999) estimated that, on the world scale, 50 per cent of all input N was recovered. Sheldrick *et al.* (2002) calculated a slightly higher figure of 57 per cent. Most recovery data refer to uptake during the first growing season, while an amount remains available for subsequent crops. However, this amount seldom reaches more than five per cent of the applied fertilizer N. The "non-efficient" amount is for the greater part dissipated in the wider environment, including the atmosphere, groundwater and surface waters. This induces a number of side effects, which may be of serious environmental and ecological concern.

The lowest fertilizer N recovery is found in Africa (Smil, 1999). This may not be surprising because of growth limiting factors such as lack of water, acid soils and/or deficiencies of other nutrients such as P. It is generally accepted that the recovery decreases with increasing fertilizer N rates because of increased chances for N losses through run-off, erosion, leaching and gaseous emissions. These loss processes depend on soil, climate and agricultural practices. A number of measures can be taken to minimize these losses and to increase N use efficiency:

- no excess inorganic or organic N fertilizer should be applied;
- N fertilization should be synchronized with plant needs;

  In practice, these conditions can be fulfilled through:

- application of fertilizer N at optimal rates, taking into consideration all N sources;
- when appropriate, fertilization should be split-applied, in order to be timed with the crop needs and development stage;
- avoiding fertilization outside the growing period and certainly not before a fallow period;
- adjustment of the fertilization plan for conditions whereby unexpected losses occur (e.g. excessive rainfall) or with deviations from the forecast crop development;
- N uptake by the crop should be fostered by balanced fertilization with the other essential plant nutrients;
- application techniques should be as professional as possible (e.g. precision farming, sub-surface application, band or point application). For example, deep placement of urea or of NH_4^+ containing fertilizers has long been known to reduce substantially the N loss from paddies. Nitrogen loss is retarded both by placement of the fertilizer particles in

the reduced zone and by increasing the particle size, which gives a smaller active surface area and a higher NH_4^+ concentration in the microsite. Also, in order to avoid excessive NH_3 losses and maximize N use efficiency, liquid manure (slurry) should be injected below the soil surface (Figure 10).

Figure 10.
Example of sub-surface application of slurry to maximize manure N recovery and use



5.4. Economics of Fertilizer Nitrogen

The economic use of N fertilizer is based on whether the N rate increases yields enough to pay for the extra N input (Black, 1993). The economic optimum is then the N level at which the yield response falls to the cost:value ratio (CVR). This is given by the following formula:

CVR = Cost of 1 kg manufactured N fertilizer / purchase price of 1 kg harvested product = X

As long as 1 kg supplementary manufactured N fertilizer produces more than X kg harvested product, the N application is economically justified. The critical point is thus a yield increase by X kg as a consequence of 1 kg supplementary N supply. It means that the economic optimum can be lower than the optimum for maximizing the yield. This is illustrated in Figure 11, showing the relationship between the optimal N application for sugarbeets as a function of available N (N Index) for maximum root production, maximum

sugar production or the economic optimum. As the sugar content is negatively correlated with the available N, it is clear that the optimum N fertilization for sugar production will be lower compared to the optimum N for root production. As payment for the farmers is based on sugar production and charges or benefits are given in relation to the sugar content (eventually increased by other quality parameters such as sap purity and extractability of the sugar), the economic N optimum is still substantially lower.

Figure 11.
Schematic optimum N fertilizer recommendations for sugarbeets as a function of N-index (available N) and production criteria: (1) root production; (2) sugar production; (3) economic optimum
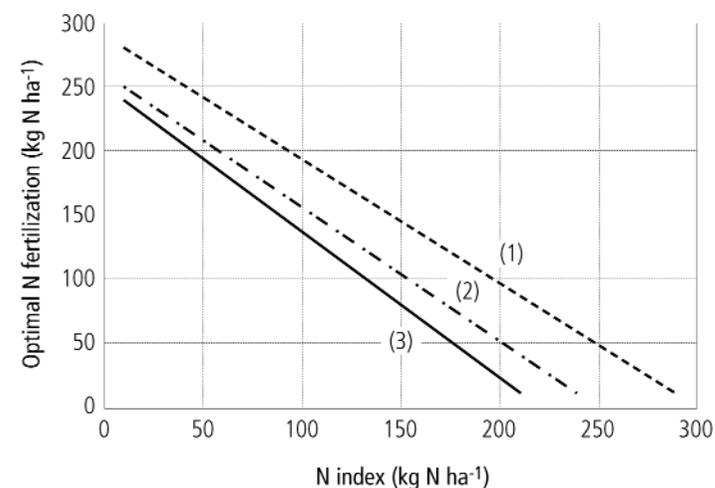
6. Nitrogen Fertilization and Environmental Issues

The most important pathways that remove N from terrestrial ecosystems are loss of N gases by transformation-dependent processes, losses of N as a consequence of temporal or spatial heterogeneity in the amount of N fertilization versus the demand for available N in the ecosystem, and the loss of dissolved organic N (DON).

Process-dependent losses mainly refer to nitrification and denitrification. Leaching easily occurs with imprecise synchronization between N supply and

N demand coupled with excess rainfall or irrigation. Mineralization-immobilization turnover (MIT) as well as soil organic carbon (SOC) availability are major factors determining fertilization effects on the environment. Temporary excess of supply over demand can occur on time scales from day-to-day, season-to-season and for longer time periods. Year-to-year variations in climate can drive temporary imbalances in N supply and demand, particularly in water-limited systems.

Hedin *et al.* (1995) suggested that losses of DON could represent an uncontrollable leak of fixed N from natural/pristine ecosystems, one that could balance the very low atmospheric N deposition. DON losses appear to be much less dependent on the N status of an ecosystem than is NO_3^- leaching.

6.1. Atmospheric Emissions of Nitrogen Oxides and Ammonia

6.1.1. Emission of Nitrogen Oxides (N_2O, NO) and Molecular Nitrogen

Nitrous oxide (N_2O) emitted from the soil surface via diffusion originates most likely from a mixture of N_2O produced by a range of different microbial processes. Microbial nitrification and denitrification are also responsible for the emission of nitric oxide (NO) (Bremner, 1997). Both N_2O and NO are by-products in nitrification and intermediates during denitrification. During the industrial era, the atmospheric concentration of N_2O has steadily increased. It is now 16 per cent (46 ppb) larger than in 1750. In 1998, the concentration of N_2O amounted to 314 ppb. Between 1980 and 1998, it has increased at a rate of 0.8 ppb per year, which is equal to about 0.25 per cent per year, and is thought to be causing five to six per cent of the enhanced greenhouse effect (IPCC, 2001).

Probably about 0.5 to 0.8 per cent of fertilizer N applied is emitted as NO (Veldkamp and Keller, 1997; IFA/FAO, 2001) and 0.8 per cent as N_2O (Mosier *et al.*, 1998; IFA/FAO, 2001; Xiaoyuan Yan *et al.*, 2003). These values are significantly lower than with the application of manure. Intensification of arable agriculture and of animal husbandry has made more N available in the soil N cycle, increasing the potential for emission of N oxides. The relative percentage of NO and N_2O formation very much depends on the moisture content of the soil. At water-filled pore spaces (WFPS) below 50 per cent, mainly NO is produced from nitrification. Between 50 and 80 per cent WFPS,

formation of N_2O from denitrification is important. From 75 per cent on, the formation of dinitrogen (N_2) by denitrification is dominant (Bouwman, 1998). Next to the water content, the most important determining factors for N_2O formation are availability of N, temperature and decomposable organic matter (Stevenson & Cole, 1999).

In the presence of sunlight, NO_x (NO and NO_2) reacts with volatile organic compounds from evaporated petrol and solvents and from vegetation, to form tropospheric ozone which is, even at low concentration, harmful to plants and humans.

The major gaseous end-product of denitrification is N_2, which is a loss to plant availability, but without negative environmental effects. The ratio of N_2O to N_2 produced by denitrification depends on many environmental conditions. Generally the more anaerobic the environment the greater the N_2 production. Denitrification N loss is usually lower than 15 per cent of the fertilizer N input and is more important on grassland and when manure is applied (von Rheinbaben, 1990; Mosier *et al.*, 2002). Peoples *et al.* (1995) reported losses of 1 kg N ha^{-1}day^{-1} under conditions of high soil NO_3^-, temperature and water content. A literature review by Meisinger and Randall (1991) showed 2 to 25 per cent loss of fertilizer N applied in well-drained soils, compared to 6 to 55 per cent on poorly drained soils.

6.1.2. Atmospheric Emission and Deposition of Ammonia

Losses of N from the soil by NH_3 volatilization has been estimated to amount globally to 54 Mt year^{-1} and 75 per cent is of anthropogenic origin (Sutton et al., 1998). The background concentration in the atmosphere over land is about 2 µg NH_3 m^{-3}. Ammonia is a plant metabolite and plants can both emit and take up NH_3 from the air. Net emissions of NH_3 from plants are in the order of 1-2 kg N ha^{-1}. Emissions from plant residues during decomposition vary with the N content and can be substantial from N-rich materials. According to ECETOC (1994), the dominant source is animal manure and about 30 per cent of N in urine and dung can be lost as NH_3. The other major source is surface application of urea or ammonium bicarbonate and, to a lesser degree, other NH_4-containing fertilizers. As urea is the most important N fertilizer in the world, it may lead to important NH_3 losses (especially if surface applied) upon hydrolysis and subsequent pH rise in the vicinity of the urea prill. Ammonia losses depend on various factors such as pH, soil moisture, soil temperature, soil composition, soil texture and structure, weather conditions, etc. The

Table 6.
Influence of pH, $CaCO_3$ content, moisture content and temperature on NH_3 volatilization of various NH_4-containing fertilizers (Hofman and Van Cleemput, 1995)

pH	$CaCO_3$ content	Moisture content	Temp.	Ammonium sulphate	Ammonium nitrate	Urea	UAN Solution*
L	L	L	L	-	-	+	+
L	L	L	H	-	-	++	++
L	L	H	L	-	-	±	±
L	L	H	H	-	-	+	+
H	L	L	L	+	±	+	±
H	L	L	H	++	+	++	+
H	L	H	L	±	±	±	±
H	L	H	H	+	±	+	±
H	H	L	L	++	+	++	+
H	H	L	H	++	+	++	+
H	H	H	L	+	±	+	±
H	H	H	H	++	±	++	+

* Urea ammonium nitrate solution: ½ urea + ½ NH_4NO_3
L: low - H: high
Volatilization: - low, ± moderate, + high and ++ very high

influence of pH, $CaCO_3$ content, moisture content and temperature on NH_3 volatilization of some NH_4-containing chemical fertilizers is given in Table 6.

Urease inhibitors have been used to reduce NH_3 volatilization. Rice *et al.* (1995) reported an 18 to 36 per cent increase in irrigated and dryland corn yield, respectively, with urea + NBPT (n-butyl-thiophosphoric triamide) compared to urea or ammonium nitrate alone.

This volatilized N will be deposited afterwards. According to Lekkerkerk *et al.* (1995), 20 per cent of NH_3 is deposited within one km from its source. Within 5 km, 30 per cent of the total NH_3 is deposited and 70 per cent (mainly after conversion to NH_4^+) is deposited between 5 and 1000 km from the source. High N deposition originates from previously emitted NH_3 and NO_x from agricultural and industrial activities, as well as automobile use. It is

expected that the total N deposition from agricultural sources will decrease in the future as NH_3 losses from concentrated livestock feeding farms is reduced and as direct incorporation of manures on agricultural land increases. Subsurface placement of manure and urea reduces NH_3 volatilization from the field, but does not eliminate it completely. This is clearly illustrated in Table 7.

Table 7.
Percent N loss upon addition of four different fertilizers at a rate of 200 kg N ha^{-1} to a clayey soil at three different depths at 16°C (Hofman and Van Cleemput, 1995)

Fertilization	Depth (cm)	% N loss of the applied fertilizer (200 kg ha^{-1})
Ammonium sulphate	0	37.3
	2	3.8
	4	0.5
Ammonium nitrate (AN)	0	12.3
	2	1.3
	4	0.7
Urea (U)	0	30.8
	2	6.1
	4	0.6
UAN solution*	0	20.4
	2	3.9
	4	0.5

*Urea ammonium nitrate solution: 50% U + 50% AN

Depending on the area, atmospheric N can be deposited in different ways. Total deposition includes dry, wet and fog deposition. Dry deposition is defined as the deposition or absorption of gases and/or particles directly from the atmosphere. The contribution of dry deposition to total deposition is estimated to be about 38 per cent for NO_3^--N and 24 per cent for NH_4^+-N (Erisman and Bleeker, 1995; Erisman *et al.*, 1995). The remainder is deposition from gases and/or particles dissolved in rain or other kinds of precipitation and is called wet and fog deposition depending on the carrier.

Next to economic consequences, NH_3 volatilization is also indirectly responsible for acid precipitation. In the atmosphere, NH_3 reacts with sulphuric oxides, forming ammonium sulphate, which is deposited onto the soil. This NH_4^+ is microbiologically transformed to NO_3^-, producing protons. As a result the pH of the soil decreases.

6.2. Leaching

Both applied NO_3^- and NO_3^- formed via nitrification from manufactured NH_4^+ and from NH_4^+ from soil organic matter and incorporated organic material can leach from the rooting zone. It is possible that this leached NO_3^- can be denitrified at other places and return to the atmosphere. The amount and intensity of rainfall, quantity and frequency of irrigation, evaporation rate, temperature, soil texture and structure, type of land use, cropping and tillage practices and the amount and form of fertilizer N are all parameters influencing the amount of NO_3^- movement to groundwater and surface waters.

Even though some scientists doubt the effect of dietary NO_3^- on human health (Leifert *et al.*, 1999; L'hirondel and L'hirondel, 2002), there are other arguments for enforcing a reasonable limit for the NO_3^- level in ground and surface waters used as drinking water supplies (Townsend *et al.*, 2003). A rise of the N content of ground and/or surface waters is a symptom of improper use of N sources, inorganic as well as organic, and/or poor agricultural management practices. In the European Union (EU), the Nitrate Directive (91/676/EEC) (European Commission, 1991) and the Water Framework Directive (European Commission, 2000) strive to attain reasonable ground and surface water quality in the near future in the EU. The main objective of the Nitrate Directive is "to reduce water pollution caused or induced by nitrates from agricultural sources and prevent further such pollution". The purpose of the Water Framework Directive is much broader and has the objective of establishing a framework for the protection of inland surface waters, transitional waters, coastal waters and groundwater. It includes not only a reduction of pollution, but also the promotion of sustainable water use and mitigating the effects of flooding and drought (De Clercq and Sinabell, 2001). As a result, it is necessary to continually improve scientifically-based N fertilization recommendation schemes.

6.3. Nitrogen Losses by Run-off and Erosion

In hilly regions, large amounts of N can be transported by surface run-off and erosion. Two important fractions can be distinguished: dissolved N and particulate N, i.e. N adsorbed on sediment particles.

In general, only small amounts of dissolved N are found in run-off water, as compared to other pathways of N losses. Indeed, because of its high solubility, the largest amounts of NO_3^--N will be found in subsurface run-off and groundwater, while the upper layer (0-5 cm) will be depleted of soluble N. However, large amounts of particulate N can be transported by erosion of arable land. Because N, especially organic N and NH_4^+, is mainly adsorbed on clay-sized particles, the eroded sediment is often enriched in N, due to the selective erosion of finer particles at low erosion intensities. According to Sharpley (1985), an enriched ratio between the N content in the eroded sediment compared to the N content *in situ* of 1.5 and 3 is quite common. These losses are, together with the N leaching losses, co-responsible for the euthrophication of surface waters. An increased input of plant nutrients results in an excessive primary biomass production of algae and aquatic weeds. N and P are responsible for algal growth while the presence of silicon (Si) determines the composition of the algal community (Laegreid *et al.*, 1999). Depending on the N/P/Si ratio, various organisms become important, some of them producing toxins. Run-off of fertilizer N varies greatly with the N application method and time of run-off events. These N losses can be reduced to a large extent by the use of grass filters (Daniels and Gilliam, 1996). Dissolved N can be removed in these riparian buffer strips by denitrification while the particulate N is deposited in these strips.

7. Conclusions

Nitrogen application is necessary for sustainable crop production. The level of fertilization depends on the type of plant and the expected yield. The final crop yield, however, depends on soil chemical, physical and biological characteristics, environmental conditions and field management. Some variables (amount and distribution of rainfall, temperature, soil profile characteristics, socio-economic conditions of the farmer, availability and type of fertilizer) are difficult or not at all manageable, while others (crop and crop rotation, fertilization, irrigation, land preparation) are manageable, but require knowledge and specific skills.

A critical point is to determine the correct N fertilization requirement for each field and for each location in the field, taking into account a variable fertilizer use efficiency. Nitrogen mineralization-immobilization turnover

(MIT), nitrification, denitrification, as well as volatilization and leaching frequently occur simultaneously, but have a different influence on plant available N, depending on the environment.

"Good agricultural practices" or "best management practices" refer to those actions whereby the above-mentioned processes positively affect the amount of available N and minimize the contribution of reactive N into the atmospheric, terrestrial and aquatic environments. In developed countries, where fertilizer N use has reached a plateau, techniques should be applied and further developed to increase fertilizer use efficiency while maintaining soil organic matter content. In developing countries, important attention must go to integrated nutrient management that maximizes positive interactions between organic N sources and inorganic N fertilizers. Increased use of fertilizers in these deficient situations, even at low levels, will have beneficial effects on health (more and better food production). Increased use at high levels of plant available N, on the other hand, presents environmental risks.

Crop yield per unit land must increase worldwide as populations increase on the limited amount of additional land that is available for crop production. N use and N use efficiency must increase to sustain adequate food production. However, enhanced knowledge of the factors influencing soil and plant N will lower potential environmental problems from N fertilizer use in the future.

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Figure 7.
Nitrogen deficiency of maize (Whalen, 2004)