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# Nitrogen Sources and Cycling in the Ecosystem and its Role in Air, Water and Soil Pollution: A Critical Review

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## Abstract

The natural cycle of nitrogen involves several biological and non-biological process including: mineralization, nitrification, denitrification, nitrogen fixation, microbial and plant uptake of nitrogen, ammonia volatilization, leaching of nitrite and nitrate and ammonia fixation. Nitrogen exists naturally in the environment and is constantly being converted from organic to an inorganic form and vice versa. Production of commercial fertilizer adds up to the natural source of nitrogen. The main source of nitrogen include: atmospheric precipitation, geological sources, agricultural land, livestock and poultry operations and urban waste. Agricultural emissions show a strong increase due to the application of fertilizer to agricultural soils, grazing of animals and spreading of animal manure. Emissions from agricultural practices and animal manure wastes are the major source of nitrogen pollution in surface and underground water. Soil erosion and runoff from fertilized land as well as domestic and industrial wastes contribute to the enrichment of lakes and streams with nutrients. Nitrates concentration exceeding certain limits in drinking water is toxic to animals and humans, especially infants. Nuisance of algal bloom and fish kills in lakes and rivers occurs due to eutrophication. Obnoxious colours and smells are developed as a result of organic matter decay and are destroying the natural beauty of the environment. The water born contaminants affect human health from both recreational use of contaminated surface water and from ingestion of contaminated drinking water derived from surface or ground water sources. The methods for abatement of nitrogen pollution must follow multi pathways. First, the source and amount of pollution must be detected and defined. Second, the possible ways to treat animal and domestic wastes should be carefully investigated. Third, better agricultural practices should be developed that include: proper storage and application of slurry and solid manure, rapid incorporation of slurry and solid manure into the soil, use of band spreading machineries such as trailing house and trailing shoe and sub-surface applicators, use of specifically made round covers fitted to above ground tanks and slurry lagoons, applying fertilizers during periods of greatest crop demand at or near the plant roots in smaller amounts with frequent applications, using multiple cropping systems such as using crop rotations or intercropping to increase the efficiency of nitrogen uses and changing current livestock production techniques.

**Keywords:** Nitrogen cycle; Organic nitrogen; Nitrogen dioxide; Ammonium; Nitrification; Volatilization; Denitrification; Nitrogen fixation; Leaching; Fertilizer; Manure; Air; Water; Soil

# Introduction

Water is an indispensable resource on which human existence depends. About 73% of the fat free body weight in healthy human adults is water which is equivalent to 60% of body weight for non-obese subjects [1]. Although three quarters of the earth is covered with water, only one percent of which is fresh water that is considered safe for use to meet our daily needs. Water that cannot be used because it is polluted: (a) reduces present and future supply, (b) inhibits local, regional and national economic growth, (c) poses known and unknown dangers to the public health, (d) curtails expansion of recreational activities and (e) further dislocates the already badly disrupted balance of nature [2].

Water pollution may be defined according to the usage of water and the presence of certain constituents and their effects on human health and the surrounding environment. One of the widely accepted definition of water pollution is "the introduction into water substances of such character and in such quantity that alter its natural quality as to impair its usefulness or render it offensive to the human senses of sight, taste or smell" [3,4]. A substance may not appear by itself as pollutant, but may indirectly (by its effect upon other materials or living organisms) lead to an offensive effect. The determination of whether a certain constituent creates a nuisance, impairs the usefulness of the water or interferes with nature's balance depends on the subsequent use of the water. Water can be polluted from many human activities and pollutants not only reduce the water quality and quantity but may act as harmful media to other living organisms. Polluted water can contain excess nutrients, pathogens, toxic materials and dangerous chemical which can affect human health, destroy marine species and disturb the ecological cycle [5,6].

Nitrogen in its elemental form is the major component of the air constituting about 78% of the gases in the earth atmosphere. There are also different nitrogen gaseous compounds that exist in the atmosphere including  $NH_3$ , NO and  $N_2O$ . The importance of nitrogen to life is that it constitutes (with carbon, hydrogen and oxygen) the major part of proteins of all living materials. All living organisms, except few microorganisms (nitrogen fixing bacteria, algae and fungi), cannot use  $N_2$  as a source of nitrogen and need different forms of fixed nitrogen ( $NH_4$  and  $NO_3$  for plants and organic nitrogen for animals and humans) as a supply for their requirement of protein synthesis.

The elemental form of nitrogen (N<sub>2</sub>) is very unreactive and hard to

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extract from the environment although there are approximately five billion metrics tons of nitrogen around the earth [7]. Some forms of nitrogen are considered poisonous to plants, animals and humans if they exceed certain concentration in their environment. The presence of higher quantities of fixed nitrogen ( $NH_4$  and  $NO_3$ ) in the water or soil will encourage vegetative growth of plants beyond the favourable level. Nitrogen pollution means pollution due to the fixed forms of nitrogen (bonded with carbon, oxygen or hydrogen) also known as reactive nitrogen [8].

Nitrogen fixation is being done in nature in several ways and passed to the rest of living organism. Nitrogen will return back to the soil after the death of these organisms through the activities of soil microorganisms which provide the nitrogen in its ready form again to plants and then to animals and humans. Certain amounts of this fixed nitrogen are liable to be lost to the atmosphere in elemental form. However, the significant increase in human population increased the demand for food which leads to mass production of synthetic nitrogen fertilizers for agricultural activities. Human activities such as production and use of commercial fertilizer, production and use of fossil fuels in industrial processes, energy generation and transportation altered the nitrogen cycle and caused disturbance to the total environment (Air, soil and water) [9].

# Natural Cycle of Nitrogen

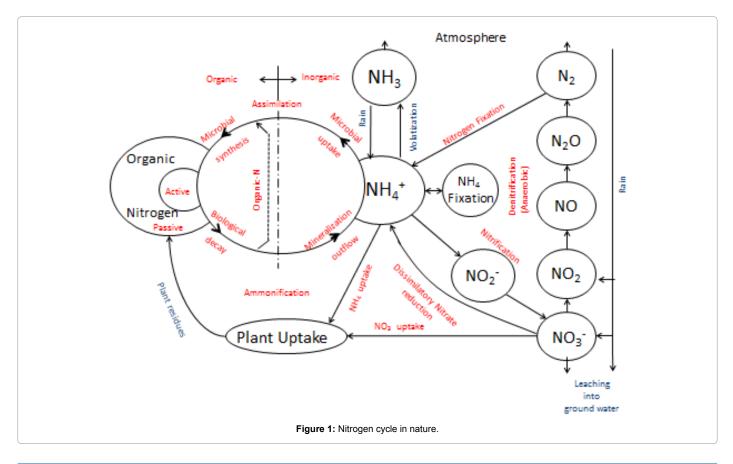
The importance of nitrogen from the standpoint of fertility of the soil has long been recognized and our knowledge concerning the nature, distribution and transformations of nitrogen compounds in soil is extensive. A schematic diagram depicting the cycle of nitrogen in nature is shown in Figure 1. The nitrogen cycle includes several biological and non- biological processes. The biological processes are: ammonification/ mineralization, nitrification, denitrification, nitrogen fixation, nitrogen assimilatory reduction and microbial synthesis of ammonium and organic nitrogen into microbial cells, plant uptake and conversion of ammonium and nitrate nitrogen into plant proteins. The non-biological processes are ammonia volatilization, leaching of nitrite and nitrate nitrogen to ground water, ammonium fixation into soil clay minerals, precipitation of nitrate and ammonium nitrogen.

### Mineralization

Mineralization (or ammonification) of soil nitrogen is the term used for the process by which nitrogen in organic compounds  $(C_aH_bO_cN_d)$  is converted by soil microorganisms into ammonium ion  $(NH_{+})$  as follows [10,11].

Complex organic nitrogen 
$$\rightarrow$$
 Ammonium (1)

The soil microflora typically produces ammonium from organic compounds when they set free more nitrogen from the organic matter on which they are living than they can assimilate into their own protoplasm. This concept of the ammonium production (being the nitrogen waste product in the conversion of organic matter into microbial tissue and use of vital energy) is fundamental for understanding the effect of adding different types of organic matter on the mineralization of nitrogen in the soil [12]. Thus, when an animal protein (such as dried blood) is added to a soil, about 80% of the added nitrogen is liberated as ammonium and the remainder of the nitrogen is retained in microbial tissue. However, by increasing the quantities of a carbohydrate, such as cellulose mixed in with the protein, the amount of microbial tissue that can be built up is increased, with the consequence that the proportion of nitrogen liberated as ammonium



decreases until the ratio of carbohydrate to protein reaches a value of about 5:1 when all the nitrogen in the dried blood is needed by the microorganisms [13].

The accumulation of ammonium in the soil is affected by: (a) the rate of mineralization of organic nitrogen in the soil, (b) uptake of ammonium by microbes as a source of nitrogen for growth, (c) uptake of ammonium by plants as a source of nitrogen for growth, (d) volatilization of ammonia, (e) nitrification (biological conversion of ammonium to nitrate), (f) loss of nitrate by leaching (which increases the rate of nitrification) and (g) plant uptake of nitrification). Therefore, a low concentration of ammonium in the soil does not indicate low mineralization and may indicate high rates of nitrification, volatilization or microbial and plant uptake. Nonetheless, net mineralization will be directly affecting the organic nitrogen content in the soil and the availability of carbon for microbial growth. Thus, vegetation with high C: N ratio will result in a low rate of nitrogen mineralization [14].

## Nitrification

Nitrification is the oxidation of ammonium nitrogen to nitrites and nitrates. It is the result of metabolism by chemoautotrophic (or chemolithotrophic) organisms. The two groups of organisms that are considered to be the primary nitrifying bacteria are *Nitrosomonas* Sp. and *Nitrobacter* Sp. *Nitrosmonas* carry out the oxidation of ammonium to nitrite to obtain energy (E) and *Nitrobacter* oxidizes nitrite to nitrate for the same purpose. The general oxidative processes involved can be represented by the following equations [15,16]:

$$NH_4^+ + 1\frac{1}{2}O_2 \xrightarrow{\text{Nitrosomonas}} NO_2^- + H_2O + 2H^+ + Energy$$
(2)

$$NO_2^- + \frac{1}{2}O_2 \xrightarrow{\text{Nitrobacter}} NO_3^- + Energy \tag{3}$$

Both genera use  $CO_2$  as their sole carbon source for growth as follows, as they are obligate autotrophs and strict aerobes [17].

$$NH_{4}^{+} + 5CO_{2} + 2H_{2}O \rightarrow C_{5}H_{2}O_{2}N + H^{+} + 5O_{2}$$
(4)

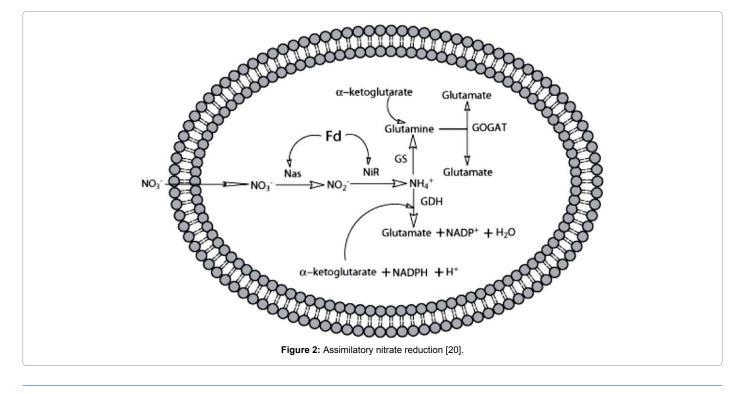
Nitrifying bacteria have a low activity level compared with heterotrophs. For example, it takes *Nitrosomonas* nearly an hour to produce twice its weight in  $NO_2$  whereas some heterotrophic bacteria produce one thousand times their own weight in products in the same time. Under aerobic conditions, the endogenous respiration of the organisms results in the breaking down of cellular nitrogen and its release as ammonium [18,19].

## Denitrification

Denitrification (or nitrate reduction) is a more complex and less understood process than nitrification. Nitrification and denitrification are redox processes involving nitrogen compounds to obtain energy. There are two processes of nitrate reduction: assimilatory and dissimilatory.

Assimilatory nitrate reduction: Assimilatory nitrate reduction (ANR) is one of the main processes in the nitrogen cycle in which nitrate  $(NO_3^{-1})$  is used as nitrogen source for the growth of new cells. At first, the nitrate  $(NO_3^{-1})$  is incorporated into the cells by a high affinity transporter which is then reduced to nitrite  $(NO_2^{-1})$  by the enzymes nitrate reductase which is further reduced to ammonium  $(NH_4^{+1})$  by the enzyme nitrite reductase. The ammonium which is produced in incorporated into the carbon skeltons by glutamine synthetase or glutamine synthase pathway as shown in Figure 2 [20].

Bonete et al [20] reported that the assimilatory nitrate reduction takes place in three steps: (a) nitrate  $(NO_3^{-})$  uptake, (b) reduction of nitrate  $(NO_3^{-})$  to nitrite  $(NO_2^{-})$  and (c) reduction of nitrite  $(NO_2^{-})$  to ammonium  $(NH_4^{-+})$ . In the first step, the nitrate  $(NO_3^{--})$  uptake into the cells takes place using ATP-dependent ABC transporter. In the second step, after the nitrate is being imported into the cells, it is reduced to nitrite  $(NO_2^{--})$  by ferredoxin dependent assimilatory nitrate reductase (NR). In the third step, the nitrite is reduced to ammonium  $(NH_4^{++})$  by ferredoxin dependent assimilatory nitrate reductase is described as follows:



 $NO_3^-uptake \xrightarrow{ABC \text{ transporter}} NO_3^- \xrightarrow{Nitrate reductase} NO_2^- \xrightarrow{Nitrite reductase} NH_4^+$  (5)

**Dissimilatory nitrate reduction:** Dissimilatory (or respiratory nitrate) reduction is the process in which nitrate (specifically the oxygen in nitrate) serves as the terminal hydrogen acceptor in energy yielding reactions. It has been shown that nitrate reduction by this process closely follows the same steps as when molecular oxygen is used. It is tied in with the cytochrome system for electron transport. Thus, when the dissolved oxygen level drops to low levels for the aerobic metabolism of facultative organisms they can turn to nitrate reduction for oxygen fairly easily. The term denitrification is assigned to dissimilatory nitrate reduction. The general simplified equation for the denitrification process is postulated as follows [21-24]:

$$NO_{3}^{-} \xrightarrow{\text{Nitrate reductase enzyme}} NO_{2}^{-} \xrightarrow{\text{Nitrite reductase enzyme}} N_{2}O_{2}$$

$$\xrightarrow{\text{Nitrous oxide reductase enzyme}} N_{2}O \xrightarrow{\text{Nitric oxide reductase enzyme}} N_{2}$$
(6)

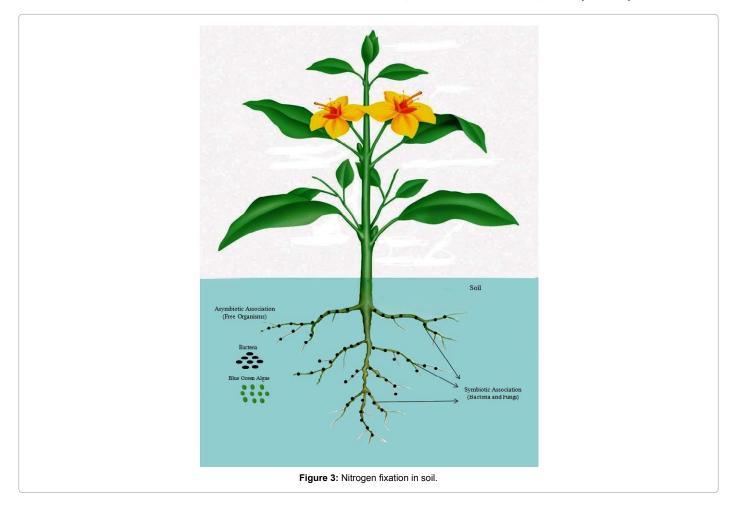
The nature of the intermediates is not generally known although many workers have suggested  $N_2O_2$  and  $N_2O$  which themselves may involve other complicated reactions [14,25]. There are a great many genera of bacteria that can accomplish denitrification among them are *Pseudomonas* Sp., *Thiobacillus denitrificans* (an autotroph) and *Micrococcus denitrificans*. The presence of dissolved oxygen has been found to inhibit the denitrification process to various degrees. This point out the need for low or zero dissolve oxygen levels before denitrification can occur [26,27].

# Nitrogen fixation

Although atmospheric nitrogen  $(N_2)$  is abundance in the atmosphere, it is not in a ready from of nitrogen to be used by most organisms. Strong triple bond which links the nitrogen element in  $N_2$  is hard to break. In Harber process, in which chemically synthesized nitrogen is formed, red hot magnesium or a catalyst is used at elevated pressures and temperatures to make  $N_2$  reactive [28]. However, in the biological nitrogen fixation process, nitrogen is fixed by the microorganisms that are capable of breaking the bond at ambient temperatures and pressures and is called diazothrophic [28,29]. The dizaotrophs are available in soil both as free living and in symbiotic association with plants. Diazothrophic microorgainsms use the enzyme nitrogenase to carry out the fixation process. There are about 100 species of enzymes but they are very similar in their activities [28]. Nitrogenase reduces dinitrogen to ammonium (NH<sub>4</sub><sup>+</sup>). The enzymatic reaction can be described as follows:

$$N_2 + 4H_2O \xrightarrow{\text{Nitrogenase}} 2NH_4^+ + 2O_2 \tag{7}$$

Soils can gain small amounts of nitrogen from the rain which falls on them. However, the most important natural process for increasing the nitrogen content of soils is nitrogen fixation by microorganisms living in the soil on and around the roots (Figure 3). A functional classification of the range of nitrogen fixing bacteria is soil is shown in Table 1 [30]. The estimates of nitrogen fixed by different microorganisms are shown in Table 2 [31]. Nitrogen fixation is inhibited in the presence of high level of available nitrogen (NH<sub>4</sub><sup>+</sup> or NO<sub>3</sub><sup>-</sup>). The process is



also controlled by N: P rations as phosphorous activate the gene for synthesis of [31]. Nitrogen can be fixed in the soil through symbiotic fixation and asymbiotic fixation. The rate of nitrogen fixation is related to the rate of photosynthesis (plant growth). A comparison between nitrogen fixation and photosynthesis is shown in Table 3.

Asymbiotic fixation of nitrogen: Soils contain a number of free-living, nitrogen-fixing organisms such as bacteria (Azotobacter, Bejerinckia, some Clostridium, and Aerobacter, Achromobacter and Pseudomonas), blue-green algae and yeast which possess the enzyme nitrogenase needed for nitrogen fixation [32]. The processes take place in soils high with organic matter that provide a ready source of energy. Nitrogen fixation goes on more actively under conditions of poor rather than good aeration, when the level of available nitrogen salts is low [33]. Asymbiotic nitrogen fixing bacteria are extremely diverse occurring in nine subdivision of the eubacteria, four subdivision of archeabacteria. Free living prokaryotes such as diazotrophs which have the ability to fix atmospheric free nitrogen are ubiquitous in the soil. The ability of free living diazotrophs to perform nitrogen fixation depends upon various conditions such carbon, nitrogen and oxygen partial pressures. The diazotroph populations depend upon the C: N ratio which is potentially used as bioindicators of nitrogen status of the soil. The contribution of assymbiotic nitrogen fixing bacteria in

Туре	Nitrogen fixing bacteria	Symbiont
	Heterotrophs	
Free living		
Anaerobic	Clostridium	
Microaerophilic	Frankia, Azospirullum	
Aerobic	Bradyrhizobium, Azotobacter, Derxia	
	Root-associated	
Microaerophilic	Azospirullum, Herbaspirullum	
Endophytic	Acetobacter	Sugar cane (Saccharum sp.)
Symbiotic	Frankia	Casuarina sp. Alnus sp.
	Rhizobium, Bradyrhizobium	Many legumes
	Azorhizobium	Sesbania rostrata
	Autotrophs	
Free living		
Anaerobic		
Microaerophilic	Rhodospirillum, Bradyrhizobium	
Aerobic	Cyanobacteria	
Symbiotic	Cyanobacteria	Fungi (lichens), Cycads
	Anabaena azollae	Azolla sp.
	Bradyrhizobium	Aeschynomene sp.

 Table 1: Classification of nitrogen fixing bacteria which contribute to agriculture [30].

Nitrogen fixing system	Nitrogen (N <sub>2</sub> ) fixed (kg N ha <sup>.1</sup> )
Free living	
Rice-blue green algae	10-80
Rice-bacterial association	10-30
Sugarcane bacterial association	20-160
Symbiotic	
Rice-Azolla	20-100
Legume-Rhizobium	
Leucaena leucocephala	100-300
Glycine max	0-237
Trifolium repens	13-280
Sesbania rostrata	320-360
Non-legume-Frankia Casuarina sp.	40-60

Table 2: Estimation of dinitrogen fixed by different nitrogen fixing systems [31].

Parameters	Nitrogen fixation	Photosynthesis
	Differences	
Medium	In soil	Above soil
Substrate	N <sub>2</sub>	CO <sub>2</sub>
Delivery point	Root	Leaves
Machinery	Enzyme nitrogenase	Chlorophyll
End Product	NH4	CH₂O
Energy	Chemical	Solar
Organism	Bacteria, Fungi, Blue green algae	Plant, Algae
Organic-C	Decomposed	Produced
	Similarities	
By product	O <sub>2</sub>	0 <sub>2</sub>
Need for P	For nitrogenase	For ATP
Rate	Affected by nutrients	Affected by nutrients

Table 3: A comparison between nitrogen fixation and photosynthesis.

terrestrial ecosystem is much higher than symbiotic nitrogen fixing bacteria [34-36]. It is estimated that free living prokaryotes are capable of fixing nitrogen in the range of 0 to 60 kg/ha/y.

**Symbiotic nitrogen fixation:** Certain leguminous plants and a few other non-legumes possess nodules in their roots. These nodules contain bacteria (belong to the genus Rhizobium) and fungi living symbiotically with the plant. They have the ability to fix nitrogen and provide the plant with nitrogen compounds while they receive their source of energy (carbohydrate) from the plant.

Some of the symbiotic nitrogen fixing bacteria such as *Azolla* in symbiosis with *Anabaema azollae* can fix 2-4 kg N/ha/day. There are other benefits of *Azolla* including: (a) they can be used as weed suppressor, (b) potassium (K) scavenger from floodwater, (c) can be used in animal feed and fish feed, (d) phosphorous (P) scavenger in sewage treatment and (f) suppressor of ammonia volatilization [31]. Heterotrophs such as *Azotobacter chroococcum* and *Azotobacter vinelandii* are excellent symbiotic nitrogen fixing bacteria but they have strict requirement for neutral pH conditions and, therefore, their availability in tropical soils is very rare. However, other symbiotic bacteria such as *Beijerinckia indica*, *Bejierinckia fluminensis*, *Azospirullum sp.* and *Herbaspirullum sp.* are more tolerant to low pH and have wide range of ecological adaptation to fix nitrogen [30].

The nitrogen uptake by free living bacteria and blue green algae takes place in soils high in organic matter that provided ready source of energy. The reduction of N2 to  $NH_4$  has large metabolic costs (respiration of organic carbon in the soil) as follows:

$$Organic - C + O_2 \rightarrow CO_2 + H_2O + Energy$$
(8)

The energy cost of nitrogen fixation links the biogeochemical process to the availability of organic carbon provided by photosynthesis. Asymbiotic are an important source of nitrogen for terrestrial ecosytems. The requirement of molybdenum (Mo) and iron (Fe) as structural components of nitrogenase links nitrogen fixation to availability of these elements in nautral ecosystems. Phosphorous is also required for the production of the enzyme nitrogenase.

The symbiotic association between fungi and higher plants are found in most ecosystems and is important for the nutrition of plants. Many trees harbor the ecotrophic mycorrhizal fungi which form a sheath around the active fine roots and extend their hypae into surrounding soil. Because of their large surface area, fungi obtain soil nutrient and transfer then to plants thereby contributing to weathering of soil minerals through the release of organic acids. Fungi in return, depend on plants for carbohydrate as source of carbon energy [37]. Nodulated legumes are used in cropping systems for centuries and they are used as primary source of food, fuel, fiber and fertilizer to other plants or to enrich the soil with nitrogen [31]. After removing the crop from the field, plant nodules will be a good source of nitrogen in the soil.

## Microbial uptake of ammonium

The ammonium uptake across the biological membranes is generally facilitated by ammonium transporters (Amt). The ammonium transporters (Amt) are a class of membrane-integral transport proteins which are found in archaea and bacteria and even in eukaryotes [38,39]. The ammonium produced from nitrite reduction is assimilated by several microorganisms using glutamine synthetase-glutamate synthase (GS-GOGAT) pathway or glutamate dehydrogenase (GDH) pathway. The GS-GOGAT pathway requires ATP but has higher affinity towards ammonium. The GDH pathway does not require ATP and is less effective in growing cells in nitrogen limited conditions [20].

Most microorganisms use both pathways for ammonia assimilation. However, when the microorganisms which are able to assimilate nitrate are exposed to ammonium, the nitrate assimilation by the cells are drastically inhibited. Ammonium inhibition can be long or short term. Prolonged incubation of cells to ammonium can lead to repression of transporter genes and nitrate reductase (Nas) and nitrite reductase (Nir) enzymes. Shorter incubation of cells in ammonium inhibits nitrate and nitrite uptake without affecting the genes or enzymes [40].

#### Plant uptake of ammonium and nitrate

Most of the plant species absorb and assimilate nitrate  $(NO_3)$ , ammonium (NH<sup>+</sup>), urea and amino acids as nitrogen sources, but the specifity of these sources vary with different plants. Crawford and Glass [41] reported that the optimal ratio of nitrate : ammonium is 3:1 for tomato roots and the growth is inhibited if the ratio of ammoium is increased, but for white spruce prefer more ammonium in the soil and some artic sedges prefer more amino acids in the soil. Both nitrate  $(NO_3^{-})$  and ammonium  $(NH_4^{+})$  possess some common features including: (a) both ions (NO<sub>3</sub> and NH<sub>4</sub><sup>+</sup>) are absorbed by the roots at low external concentrations, (b) there are high affinity transport systems (HATS) in the roots for both nitrate (NO<sub>3</sub><sup>-</sup>) and ammonium  $(NH_{4}^{+})$  (c) the HATS for nitrate is double the HATS for ammonium and (d) the influx of both ions is responsive to plant N status and is subject to diurnal regulation [42].

Meyer et al. [43] and Stitt [44] reported that plants, unlike bacteria or fungi use ammonium as a nitrogen source and show better growth in the presence of nitrate. Nitrate can get accumulated in the leaves of the edible plants or in drinking water and may affect both the environment and human health. After nitrogen uptake, nitrate is either stored in the plant root system or translocated to aerial parts via the xylem. High concentrations are usually found in the vacuoles as a nutrient source and plays an important role in the maintanence of osmoticum. Nitrate reduction in plants takes place both in roots and shoots. The nitrate reduction takes place in cytoplasm and the nitrite reduction takes place in plastids/chloroplasts. The reduction of nitrate to nitrite is catalyzed by the enzyme nitrate reductase (NR) enzyme. The nitrite after nitrate reduction is translocated to the chloroplast where it is reduced to ammonium by nitrite reductase (NiR) enzyme.

Ammonium obtained after nitrite reduction and also from photorespiration or amino acid recycling is assimilated in the plastid/ chloroplast by GS/GOGAT cycle. The glutamine synthetase (GS) fixes ammonium on a glutamate molecule to form glutamine. The

glutamine formed reacts with 2-oxuglutarate to form two molecules of glutamate in the presence of glutamine 2-oxyglutrate amino transferase (GOGAT) enzyme [45,46]. There are two different forms of GOGAT enzymes present in plants: Fd-GOGAT and NADH-GOGAT. Fd-GOGAT uses ferredoxin and NADH-GOGAT uses NADH as electron donors, respectively. Fd-GOGAT is usually localized in the plant leaves, whereas NADH-GOGAT is localized in plastids of non-photosynthetic tissues such as roots, etiolated leaf tissues and companion cells. The ammonium formed in the plastids are converted to carbomylphosphate which is a precursor of citrulline and arginine in the presence of carbamoylphosphate synthase (CPase) as shown in Figure 4 [46,47].

Both  $NO_3^{-1}$  and  $NH_4^{+1}$  are absorbed by plants in the form of amino group (-  $NH_2$ ). The availability of  $NH_4^+$  or  $NO_3^-$  depends on the environmental conditions that affect the production of NH4+ and the conversion of  $NH_4^+$  to  $NO_3^-$ . However, many plants species show preferences to NO<sub>3</sub> over  $NH_4^+$ , although thermodynamic analysis suggests that the metabolic energy cost of reducing NO<sub>3</sub> to NH<sub>2</sub> is significantly greater. There are several reasons for plants showing preference towards  $NO_{a}^{-}$  over  $NH_{a}^{+}$ : (a)  $NH_{a}^{+}$  interacts with soil cation exchange where NO, is slightly soluble and mobile, (b) the rate of NO<sub>3</sub> delivery by diffusion is higher than that of  $NH_4^+$ , (c) plant that uses NH<sub>4</sub><sup>+</sup> have to compensate for the difference in diffusion by investing more energy in the root growth, (d) uptake of NO<sub>3</sub> avoids the competition that occurs in root enzyme carriers between NH<sub>4</sub><sup>+</sup> and other positively charged ions and (e) relatively high concentration of  $NH_4^+$  is toxic to plants.

The amino group (-NH<sub>2</sub>) is attached to soluble organic compounds and the nitrogen absorbed by the roots is transported to the xylem in the steam (capillary system) as amides, amino acids or uried before its eventually incorporated into proteins in leaves. There are two types of amides: (a) metallic derivatives of  $NH_4^+$  in which  $NH_2^-$  group is retained and (b) organic derivative. The following are examples of the different types of amides, amino acids and uride.

Metallic Amides: (a)

$$K^{+} + NH_{4}^{+} \rightarrow K (NH_{2}) + 2 H^{+}$$

$$\tag{9}$$

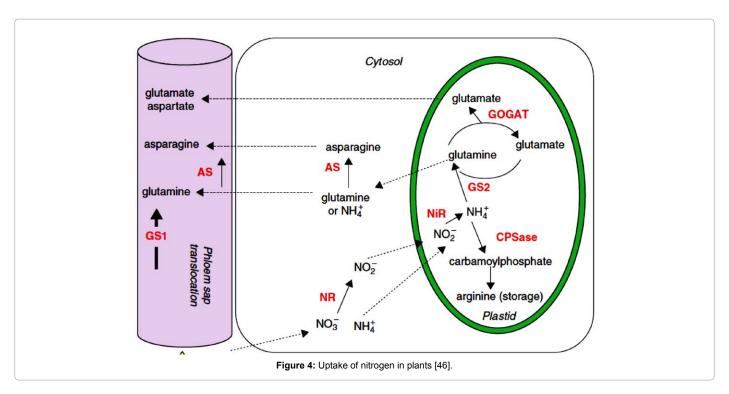
$$Na^{+} + NH_{4}^{+} \rightarrow Na(NH_{2}) + 2H^{+}$$
(10)

(b) Organic Amides:

- C

$$COOH + NH_4 \rightarrow COO(NH_2) + 2 H^+$$
(11)

In case of NO<sub>3</sub> uptake by plant, it is first reduced to amino group which is then interacts with CO<sub>2</sub> to form amine. The amine interacts with organic acid to form aminoacid as follows.



(a) 
$$NO_3 + H_2O \rightarrow NH_2 + 2O_2$$
 (14)

(b) 
$$\operatorname{NH}_2 + \operatorname{CO}_2 \rightarrow \operatorname{COONH}_2 + \frac{1}{2} \operatorname{O}_2$$
 (15)

# Ammonia volatilizaiton

Ammonium exists in two forms: free or unionized form  $(NH_3)$  and ionized form  $(NH_4^+)$ . Ionised ammonium is soluble in water while unionised ammonia is volatile and could be easily removed from water. The process of volatilization carries the free ammonium from the water into the atmosphere. un-ionized ammonia is volatile and could be easily removed. Ammonium volatilization occurs when ammonium ions are present in an alkaline medium and gets dissociated into gaseous ammonia which then gets released into the atmosphere [48].

$$NH_4^+ + OH^- \to NH_3 \uparrow + H_2O \tag{17}$$

The overall process of ammonia volatilization could be comprised into four major steps: (a) conversion of iodized ammonium into free ammonium by dissociation, (b) diffusion of free ammonia to the waterair interface, (c) volatilization or releasing the free ammonium to the atmosphere at the interface and (d) diffusion of free ammonium from the water-air interface into the atmosphere which is carried out by mass transfer [48-50].

Various agricultural activities including livestock production and fertilizer application are the main sources of atmospheric ammonia emisson. Ammonia emission occur from livestock buildings, open feedlots and maure storage facilities as well as manure handling and application to the land. In livestock facilities, the urea present in the urine is broken by the enzyme urease which is present in the feces to release ammonia into the atmosphere. There are several factors affecting ammonia volatilization including: (a) manure type and characteristics, (b) temperature, (c) wind speed, (d) pH and (e) method and timing of manure application [51,52].

Rochette et al. [53] reported that the impact of urea application rate on the nitrogen loss in the form of ammonia  $(NH_3)$  is variable as shown in Table 4 [54-64]. The large variability in the results reported from several studies has been due to the nonlinear response of the ammonia to variation in pH and the availability of ammonia in the soil. Ammonia volatilization occurs in a soil when the pH is high (>7.5) [48]. Sommer et al. [65] reported that pH affects the ammonia loss and is affected by climatic and soil conditons.

Manure type and characteristics such as total nitrogen (TN), ammonium nitrogen (NH<sub>4</sub>-N) and percentage dry matter (%DM) play an important role in the ammonia volatilization during manure application. Liquid manure (slurry) used for agricultural purposes have high rate of ammonia loss when compared to soil manure. Slurries with lower solids have greater fluidity and can infiltirate soil more readily, where ammonium is protected from volatilization by adsorption onto soil colloids [52,66]. Sommer and Hutchings [66] reported that the composition of animal maure varies widely between animal species and manure types. The animal manure contains a mixture of faeces, urine, blood, split feed, split drinking water and water used in washing and it is collected as slurries. In some animal housing systems, the soild manure containing only faeces and straw and liquid manure containing urine, water and dissolvable faecal components are separated. The typical composition of different types of animal manure are shown in Table 5 [66].

Ammonia volatilization increases with increases in temperature because at higher temperature the solubility of ammonia ( $NH_3$ ) gas is reduced in soil by increasing the proportion of total ammonia nitrogen (TAN) as  $NH_3$  gas [67,68]. Sommer and Hutchings [66] reported that TAN is produced by the hydrolysis of urea by ureic acid. Therefore, the ammonia ( $NH_3$ ) emissions from the polutry manure is influenced by

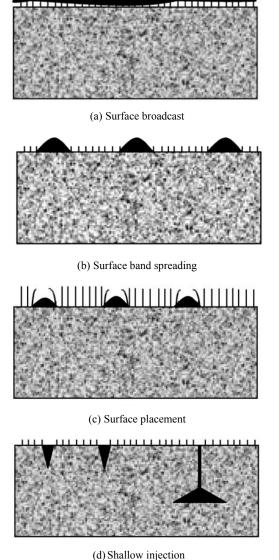
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Conditions	Soil pH	N rate (kg ha <sup>-1</sup> )	NH <sub>3</sub> loss (% appl. N)	N placement	References
Laboratory	9.0	15	56		
		30	48		
		60	41	Surface broadcast	[54]
		120	34	Dioducasi	
		240	29		
Field	8.7	89	14		
		178	16	Surface broadcast	[55]
		255	20	Dioducasi	
Field	8.6	75	44	Surface	1501
		200	48	broadcast	[56]
Greenhouse	8.0	55	58		
		110	58		
		275	61	Surface	
		550	67	broadcast	[57]
		1100	63		
		2200	61		
Greenhouse	8.0	55	55	Surface	
		165	67	broadcast	[57]
Greenhouse	8.0	55	68	Surface	
		165	66	banded	[57]
Greenhouse	7.6	25	22		
		50	21	Surface	[58]
		100	22	broadcast	
Field	7.2	135	15	Surface	
		225	19	broadcast	[59]
Field	6.3	40	11	Surface	
		80	9	broadcast	[60]
		120	8	(moist)	
Field	6.1	30	10		
		100	17	Surface broadcast	[61]
		300	33	Dioaucasi	
Laboratory	6.1	50	13		
		100	14		
		150	16	Surface	[52]
		200	17	broadcast	
		300	16	-	
Field	5.9	70	24	Sub-surface	
		140	20	Banded (2	[53]
		250	15	cm)	L 3
Field	5.2	80	14	Surface	
				Junaou	[54]

ammonia volatilization. There are four types of application techniques (Figure 5) [67]: (a) surface broadcast, (b) surface band-spreading (via trailing hoses), (c) surface placement (via trailing shoes) and (d) shallow

Manure	Animal	Dry matter (g/Kg)	N. tot (g/Kg)	TAN (g/Kg)	Ureic acid-N (g/Kg)	P (g/Kg)	K (g/Kg)	рН
	Cattle	74.23	3.95	1.63		0.63	3.46	7.20
Slurry	Pig	34.50	9.35	3.66		0.74	3.62	6.72
	Poultry	218.00	12.00	5.93				7.23
	Cattle	181.50	4.85	1.33		1.45	3.85	7.80
Solid Manure	Pig	222.00	10.45	4.40		3.70	5.25	7.70
Manure	Poultry	574.60	29.60	5.49	6.0	5.98	6.53	8.50
	Cattle	261.00	5.20	0.90		1.40	9.70	8.60
Deep Litter	Pig	412.00	11.20	2.80				8.90
	Poultry	570.00	27.10	6.48	7.54	9.25	15.50	9.1
Liquid Manure	Cattle	1.68	2.60	2.05		0.03	4.33	8.70

Table 5: Typical composition of animal manure [66].



(d) Shallow injection Figure 5: Schematic representaion of slurry application techniques [70].

 Table 4: Impact of urea application rate on ammonia losses [53].

water content and temperature. Sommer and Hutchings [65] reported that there is a linear relationship between ammonia volatilization rate and temperature in the range of 15-25°C. Agrifacts [51] reported that 50% of the total nitrogen is volatilized as ammonia at 30°C compared to 25% at 25°C. Therefore, manure applications should not be carried out at higher temperatures.

Thompson et al. [69] reported that wind speed had a positive effect on ammonia  $(NH_3)$  volatilization but less significant compared to other factors affecting the loss of nitrogen. Increasing the wind speed from 0.5 to 3.0 m/s increased the total 5 day loss by 29% and the loss of nitrogen was more pronounced in the first 24 h after application of manure. Meisinger and Jokela [52] reported a linear relantionship between ammonia volatilization and wind speeds to about 2.5 m/s.

Application of slury on the soil plays an important role in the

slot injection (500 mm depth). During surface broadcaset application the slurry is applied by tanker with a single outlet and splash plate. The surface band spreading involves multiple hoses depositing slury bands 5-10 cm wide on the ground with approximately 30 cm between each bands. The surface placement technique involves placing slurry in bands approximately 3 cm wide and 20 cm apart, between and below the crop canopy. The shallow injection techniquee involves the injected beneath the soil surface either via open slot, shallow injection (to 50 mm) or deep tines (to>150 mm). Misselbrook et al. [70], Smith et al. [71], Huijsmans et al. [72] and Bussink and Oenema [73] observed direct loss of nitogen fertilizer in the form of ammonia during manure application on soil surface which could be prevented by carrying out shallow injection technique or band spreader technique. Bussink and Oenema [73] stated that there are other factors such as moisture content, rainfall, soil texture and cation exhange capacity of the soil that affect the volatilization of ammonia druing manure application. The range of measured losses of ammonia at different steps is shown in Table 6 [73].

# Leaching of NO<sub>2</sub> and NO<sub>3</sub>

Leaching of nitrite or nitrate refers to the removal of nitrite or nitrate from the plant root zone by the movement of water through the soil. Since nitrite  $(NO_2^{-})$  and nitrate  $(NO_3^{-})$  are negatively charged, they are found to move freely with the water unless soils have a significant anion exchange capacity. It was estimated that 55Tg of nitrate are leached from agricultural soils every year [74]. Leaching of nitrogen form soil reduces the bioavailability to plants and impacts the environmental quality.

## Ammonium fixation

Soils are found to have the ability to bind ammonium  $(NH_4^+)$  in such a way that it would not be readily recovered by extraction with alkali or dilute acids. This form of ammonium is referred to as nonexchangeable or fixed and is held in between the lattice of clays. It is generally not affected by cations on the clay surfaces or by addition of KCl [75]. However, if ammonium gets exposed due to clay expansion, the exposed ammonium is made available for plant growth [76].

## Sources of Nitrogen

Nitrogen exists naturally in our environment and is constantly being converted from organic to an inorganic form and vice versa. Production of fertilizer adds up to the natural source of nitrogen [77]. Naturally occurring and anthropogenic production of nitrogen make up the whole nitrogen cycle today. Human activities are the biggest contributor of nitrogen and have a major influence on the nitrogen cycle nowadays. The changes in the cycle can affect other natural cycle such as carbon, sulfur and oxygen cycles. Global nitrous oxide emissions are mainly caused by agricultural activities and large scale biomass burning. Agricultural emissions show a strong increase due to the application of fertilizer to agricultural soils and due to grazing of animals and spreading of animal manure. The inter annual variability of agricultural N<sub>2</sub>O emission is caused by the annual savannah burning. Table 7 summarize the global N<sub>2</sub>O emissions from number of resources around the world [78]. Table 8 shows the N<sub>2</sub>O emission by source in Canada in 2010 [79]. Overall, approximately 140TgNy<sup>-1</sup> was fixed by

Compartment	Ammonia loss	Factors affecting NH <sub>3</sub> loss
Artificial fertilizer	6-42% of urea N applied	T, SWC, CEC, pH, fertilizer type, N input, CaCO <sub>3</sub> , vegetation
Application slurry	1-100% of $NH_4$ -N applied on grassland 3-70% $NH_4$ -N applied on arable land	T, rainfall, CEC, SWC, pH, %DM, amount applied, application technique, vegetation
Farm yard manure	45-100% of NH <sub>4</sub> -N applied	T, CEC, SWC, pH, %DM, amount applied, application technique, vegetation
Grazing	0-18% of the N excreted per grazing or 3.1-8.5% of the N excreted per year	T, CEC, SWC, N input grassland management, urease activity, rainfall
Housing slurry	0-70% of N excreted	T, stable type, N content of urine, residence time, ventilation
Storage of slurry	0-20% of total N	Time, T, N content, storage type, aeration
Crops	<0-156 g N ha-1 d-1	N status, crop type

\*T: Temperature; CEC: Cation Exchange Capacity; SWC: Soil Water Content; N: Nitrogen

Table 6: Range of ammonia (NH<sub>3</sub>) losses [73].

Source	1992	1995	1997	2002	2008
Manure management	317.81	320.40	304.14	313.00	336.00
Direct soil emissions	2231.80	2296.46	2370.49	2480.00	2690.00
Manure in pasture/range/paddock	1672.96	1727.17	1731.01	1810.00	1980.00
Indirect N <sub>2</sub> O emission from agriculture	746.26	767.57	780.44	819.00	894.00
Savanna burning	897.03	629.10	582.99	503.00	907.00
Agricultural waste burning	31.81	32.45	33.86	35.30	40.90
Forest fires	424.66	287.48	305.94	285.00	185.00
Grassland fires	97.92	96.32	87.02	117.00	23.80
Peat fires and decay of drained peatland	85.28	17.26	310.67	70.70	2.22
Forest Fires-Post burn decay	275.18	290.19	285.81	292.00	276.00
Wastewater handling	268.56	285.83	297.43	320.00	342.00
Waste incineration	6.16	6.36	6.49	6.77	7.39
Other waste handling	8.49	11.74	13.83	19.10	25.70
Fossil fuel fires	0.75	0.75	0.75	0.75	0.75
Indirect N <sub>2</sub> O from non-agricultural NOx	536.54	520.04	536.71	536.00	603.00
ndirect N <sub>2</sub> O from non-agricultural NH <sub>3</sub>	273.97	137.00	558.50	224.00	117.00
Total	7875.18	7426.12	8206.09	7831.62	8430.76

**Table 7:** Global  $N_2O$  emissions in Tg  $N_2O$  [78].

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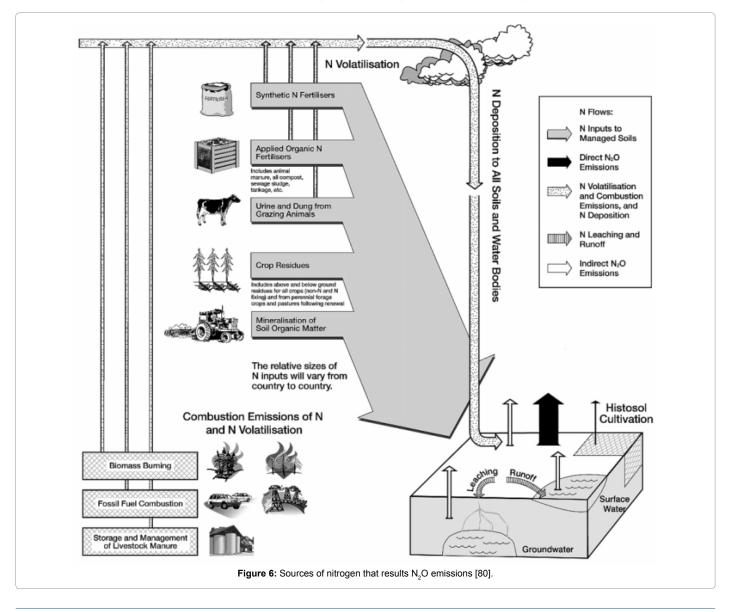
Source	Nitrous Oxides (Kilotonnes)
Transportation	680.0
Off-road vehicles	458.1
Oil and Gas industries	457.5
Fuel for electricity and heating	277.5
Other industries	174.6
Home firewood burning	10.1
Incineration and miscellaneous	2.4

human activity in terrestrial ecosystem [9]. The sources and pathways of nitrogen that result in direct and indirect  $N_2O$  emissions from soils and water are shown in Figure 6 [80].

## Atmospheric precipitation

Most of the nitrogen in the atmosphere is in the molecular form of  $N_2$ . However, there are small amounts of ammonia (NH<sub>3</sub>) as well as various nitrogen oxides (NO<sub>2</sub>), such as nitric oxide (NO) and nitrous oxide (N<sub>2</sub>O) and their hydration products nitric acid (HNO<sub>3</sub>), present in the atmosphere [81]. Most atmospheric nitrogenous compounds are attributed to industrial air pollution. Small amounts are released from the decomposition of organic matter in the soil and photochemical reactions in the atmosphere [80,82]. Most of dissolved inorganic N in rain water is ammoniac nitrogen. Cape et al. [83,84] reported that organic nitrogen makes up 24-40% of the total amount of dissolved nitrogen in rain and snow across UK (Table 9). Maximum concentration of ammonium and nitrate occur during spring while late summer rain contains more water-soluble organic nitrogen. Goldberg [85] stated contribution from rainwater to nitrogen added to soil or runoff water vary greatly depending upon time of the year and the location which have great implication on the amount of fertilizer used by farmers and the consequent air and water pollution.

Production of nitrous oxide ( $N_2O$ ) is one of the greatest concerns today as it is one of the main greenhouse gases. Earlier estimation of the global budget of  $N_2O$  production, suggested that the emission of  $N_2O$  to the atmosphere by agricultural activities was relatively small [86-88]. However, recent investigation suggested that agricultural activities can actually contribute a lot more  $N_2O$  emission than was thought earlier [89]. If total agricultural emission is to be considered,



0:44	Nitra	te-N	Ammon	ium-N	Organ	ic-N	Total	
Site	(µM)	(%)	(µM)	(%)	(µM)	(%)	(µM)	
		Cair	ngorm					
North-east Scotland	30	52	14	24	14	24	58	
		В	ush					
East Scotland	15	33	16	35	15	33	46	
		Merl	ewood					
North-west England	17	19	27	31	35	40	87	
		Moor	house					
North-west England	20	24	32	38	31	37	84	
		Cli	moor					
North Wales	22	30	33	45	29	39	73	
	No	orwich	Universit	ty				
South-East England	38	29	58	45	3	26	129	
		Wii	nfrith					
South-west England	23	31	26	35	23	31	75	

 $\label{eq:table_transform} \begin{array}{l} \mbox{Table 9: Concentration } (\mu M) \mbox{ of inorganic and total nitrogen in precipitation across} \\ \mbox{United Kingdom during the period of 2000-2002 [84].} \end{array}$ 

 $N_2O$  emission can be produced not only from fields fertilized with synthetic nitrogen fertilizer but also includes animal production system [90]. Volatilization, runoff and leaching are some of the mechanisms through which nitrogen is being release back to the environment from agricultural activities. However, with human population exceeding seven billion people in 2012, the nitrogen emission from agricultural activities needs a further investigation [91]. As human population continues to increase rapidly, it is only a matter of time that nitrogen pollution from agricultural production systems will be our biggest concern of all.

The most abundant oxide of nitrogen is probably nitrogen tetroxide  $(N_2O_4)$ , produced by internal combustion engines. More than 20 Tg of N is fixed or mobilized during fossil fuel combustion and other high temperature process which is emitted in a form of NO. Ion molecule reactions, which occur in the stratosphere and upper ionosphere, account for formation of nitrogen molecules other than N<sub>2</sub> [92].

$$N_2 + O_2 \xrightarrow{Heat} 2NO$$
 (18)

$$NO + \frac{1}{2}O_2 \xrightarrow{\text{Heat}} NO_2 \tag{19}$$

The formation of ammonia in the atmosphere is mainly due to the effect of lighting. Some of this ammonia is oxidized to some oxides of nitrogen. Butcher et al. [93] reported that formation of two molecules of NO from collision of  $N_2$  and  $O_2$  in a direct heat process is relatively slow reaction compared to the formation of NO in the presence of lightening which results in a series of simple steps comprising of Zeldovich mechanism as shown in the following reaction:

$$N_2 + O \xrightarrow{\text{Lightning}} NO + N \tag{20}$$

$$N + O_2 \xrightarrow{\text{Lightning}} NO + O$$
 (21)

# **Geological sources**

A very good example of geological sources of nitrate is the sediments

of nitrate of soda on the plateau of Tarapacá, a part of Atacama Desert in Chile. The nitrate deposits in Chile have probably been developed since the ancient times. Evans et al. [94], Noble [95] and Ehleringer et al. [96] stated that Atacama Desert had to go through decades of intervals of rainfall. The almost no-existence moisture in that area causes Atacama Desert to be known as the driest places on Earth. Since nitrate is soluble in water, the absence of water allow nitrate to deposits in layers forming *caliche*, type of sedimentary rock that consists layers of sodium nitrate. Holloway et al. [97] and Blatt et al. [98] reported that 75% of rocks exposed at the Earth's surface are sedimentary in nature containing 10<sup>21</sup> g of fixed nitrogen globally which is a lot more than the amount of fixed nitrogen in the total biosphere of 10<sup>19</sup> g. The formation of nitrogen in the bedrocks was derived from burial of organic matter in marine and freshwater sediments [99].

Other sources of nitrate are igneous rocks, metamorphic rocks and coal. These fixed forms of nitrogen in rocks may amount in some estimation to a total 50 times greater than the amount of fixed nitrogen in the atmosphere. Although rocks contain significant amount of fixed nitrogen, it was not thought as a ready source due to access problem [97,99]. Morford [99] suggested that nitrogen rich bedrocks may influence the forest ecosystem ability to store carbon and nitrogen. Bedrocks rich in nitrogen might have been feeding the forest, enhancing its growth. Nitrogen content of soils and forest foliage on nitrogen rich sedimentary rocks is 50% more than the soil and forest foliage on nitrogen poor bedrocks. Forest associated with nitrogen rich bedrocks also have 42% more carbon in above ground tree biomass and 60% more carbon in the upper 30 cm of the soil in comparison to similar sites on top of poor nitrogen bedrocks. These findings may explain why the nitrogen budget for forest is always imbalanced.

The role of nitrogen as a nonpoint sources to the contamination of surface water was reported by Holloway et al. [97] who observed increased nitrogen content in stream water in certain California watersheds caused by bedrock lithology. The Mokelumne River watershed in the central Sierra Nevada of California experienced consistently low nitrogen concentration in its stream water at its lower watershed that has diorite lithology. While for other streams that have biotite schist lithology, the concentration of nitrogen in the streamwater was highest during the rainy season and decreasing during the spring period before the end of the stream flow. Lower watershed that contained geological nitrogen was the source of 90% of nitrogen in the streamwater in comparison to upper watershed. Although upper watershed had 90% of watershed area, the nitrogen flux was only 0.12 kg N ha-1 yr-1 while the lower watershed had nitrogen flux of 10-20 kg N ha<sup>-1</sup> yr<sup>-1</sup> during the 1995-96 water year. Significance difference between the two parts of watershed suggested that geological nitrogen would be the only source.

# Agricultural land

Agricultural sources of nitrogen result primarily from organic and inorganic materials added to soils as a source of crop nutrition. Since fertilizers are now one of the lowest-cost "inputs" in crop production, the use of synthetic nitrogen is growing rapidly in areas where natural

Nitronon	20	08	20	09	20	10	20	11	20	12
Nitrogen	Fertilizer	Nitrogen	Fertilizer	Nitrogen	Fertilizer	Nitrogen	Fertilizer	Nitrogen	Fertilizer	Nitrogen
Total supply	206431	131106	212225	136252	219930	140732	230334	147748	240711	154199
Total demand	197004	127820	201482	130409	205947	133059	211230	136198	216019	139140
Surplus	9427	3286	10473	5843	13983	7673	19104	44550	24692	15059

Table 10: Supply and demand of fertilizer and nitrogen (thousand tonnes) in the world for the duration of 2008-2012 [103].

soil phosphorus, potassium and calcium are inadequate and limit growth [100]. Kjaergaard [101] reported that synthetic nitrogen was added to the soil in Europe when the area of fallow land was decreasing, limiting the available nitrogen for the crops.

Increasing world population causes more than ever a demand for food and boosts up the production of synthetic nitrogen for agricultural land. Galloway [102] stated that for food production per capita basis to increase, additional nitrogen must be added to agro-ecosystem to keep up with the demand. Supply and demand of fertilizer in the world has steadily increased since 2007 and the trend is predicted to be the same for the next fifty years [103]. The supply and demand balance for the nitrogen has also increasing (Table 10) [103]. The total world nitrogen fertilizer supply increased form 131.106 Tg/year in 2007 to 154.199 Tg/ year in 2012.

Table 11 shows the top ten countries with highest fertilizers application per a hectare of land [104]. China, one of the largest agricultural countries in the world, increased the use of chemical fertilizer from  $1.74 \times 10^7$  Mg N in 1990 to  $2.2 \times 10^7$  Mg N in 1995 and used 54 million tonnes of fertilizers in 2011 [105]. The fertilizers used in China alone accounted for one fourth of the world total fertilizers [103,106]. The rapid increase in fertilizer use in China is polluting ground water and surface water and causing many environmental and health problems. Besides synthetic fertilizers.

In the 17<sup>th</sup> century, the animal manure collected from animal in grazing season and the biological nitrogen fixation were enough to provide about 20 Kg N ha<sup>-1</sup> for grain production of 1999 kg ha<sup>-1</sup> in Western Europe [107]. Currently, synthetic fertilizers have been used to provide much higher crop yield. Artificial fertilizers are widely used to provide three types of primary plant nutrients: nitrogen (N), phosphate ( $P_2O_5$ ) and potash ( $K_2O$ ). Table 12 shows the use of fertilizer in USA from 2007 to 2010 for agricultural activities [108].

Different forms of added nitrogen as fertilizers could be lost from the soil to the surface water and underground water causing pollution problems. The nitrogen salts ( $NO_2$  and  $NO_3$ ) carried by the runoff are in a direct relation to the amount of water applied and land use practice. Drainage water contains nitrogen concentrations of 1-60 mg/L, mostly in the form of nitrate [109]. Sediment suspended in the flowing water may carry relatively high amounts of ammonium nitrogen as well as particulate organic nitrogen [110-112].

The lateral and vertical movements of nitrogen in the soil are quite different in their effect as a source of pollution. Iqbal [113] indicated that the vertical movement of nitrogen is more significant than the lateral movement as a source of pollution. Nitrate dissolves easily in water and moves through soil pores, contaminating ground water as shown in Table 13 [113]. Nitrate horizontal potential movement in soils is negligible and can be negative in shallow subsoil. Platzer [114]

Country	Amount of fertilizers used (Kg/ha)
Ireland	594.5
Netherlands	450.2
Egypt	385.8
Costa Rica	385.0
Slovenia	369.4
Japan	301.0
United Kingdom	285.8
Vietnam	285.3
Israel	256.0
China	255.6

The fertilizer use was calculated by dividing fertilizer consumption in kilograms by hectares of arable and permanent cropland. The fertilizer consumption includes nitrogenous, phosphate and potash fertilizers.

 Table 11: List of countries with the highest consumption of fertilizers in the world [104].

Veer	1000 tonnes							
Year	Nitrogen	Phosphate (P <sub>2</sub> O <sub>5</sub> )	Potash (K <sub>2</sub> O)	Total				
2007	13194	4572	5133	22899				
2008	12561	4247	4660	21468				
2009	11461	3138	3090	17689				
2010	12285	4099	4458	20843				

Table 12: Fertilizer use in USA for the years of 2007-2010 [108].

stated that the vertical flow has a very high nitrogen capacity while the horizontal flow associates effectively with denitrification.

Subsurface drainage of gravitational water from the soil through tiles is commonly used in the agriculture to improve crop production in poorly drained soils. The drainage water from the crops contains significant amounts of nitrate-N ( $NO_3$ -N) [115]. Bolton [116] conducted a tile drainage experiment at Woodslee, Ontario, Canada on a Brookston clay soil and estimated the nutrient losses through tile drains under three different cropping systems mainly in the nitrate form with and without addition of fertilizers. They found that the greatest losses of nitrogen occurred with corn grown continuously or in rotation. They reported that the losses were increased by fertilizer application and were associated with the total and average effluent flows as shown in Table 14 [116].

Randall et al. [117] studied the nitrate losses through subsurface tile drainage in four cropping systems including: continuous corn, a corn-soybean rotation, alfalfa and conservation reserve program. The conservation reserve program (CRP) was carried out in United States of America as part of converting highly erodible and environmentally sensitive agricultural land to permanent grassland cover to reduce soil erosion and produce row crops [118]. The results from the study indicated that average NO<sub>3</sub>-N concentrations from continuous corn, corn-soy bean rotation, alfalfa and conservation reserve program

Fertilizer		Nitrate vertical leaching (mg)							Nitrate lateral leaching	
application		30 cm				6	60 cm		Amount	
kg ha	I	F	S	Т	I	F	S	Т	(mg/L)	Movement (mg/m)
0	50.13	134.74	43.95	101.13	57.12	75.39	43.95	123.63	5.79	1.22 × 10 <sup>-3</sup>
90	102.62	58.87	-	128.24	72.60	119.54	47.84	143.24	8.97	3.24 × 10 <sup>-3</sup>
180	142.23	102.49	-	185.17	112.47	61.49	85.27	147.31	5.06	-1.50 × 10-3
270	129.00	125.73	92.38	209.35	63.57	89.17	77.88	212.39	13.43	7.58 × 10 <sup>-3</sup>
360	230.28	83.11	88.43	196.71	146.37	43.88	88.43	214.89	4.92	-1.06 × 10 <sup>-3</sup>

\*I: Irrigation; F: First rain; S: Second rain; T: Third rain

 Table 13: Vertical and lateral nitrate leaching in a wheat farm [113].

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Cron	N Losses	(Kg/ha/y)	Effluent from drains (ppm)				
Crop	No Fertilizer	Fertilizer	No Fertilizer	Fertilizer			
Rotation							
Corn	5.6	15.1	8.5	14			
Oats and alfalfa	4.3	5.7	6.4	8.5			
Alfalfa (1st year).	4.8	3.9	6.3	5.8			
Alfalfa (2 <sup>nd</sup> year)	4.7	8.6	9.3	10.1			
		Continuous					
Corn	6.6	14	4.4	8.9			
Bluegrass sod	0.3	0.7	3.5	1.1			
Mean	4.4	8.1	6.4	8.1			

 
 Table 14: Nitrogen annual losses through tile drains and concentration in effluent of tile drains on Brookston clay soil [116].

(CRP) were 32, 24, 3 and 2 mg/L, respectively. Nitrate losses from continuous corn and corn-soybean were 37 times and 35 times more than alfalfa and CRP systems, respectively.

Kladivko et al. [119] summarises the results from the study conducted over 15 years on nitrate leaching to subsurface drains. The results indicated that the mean nitrate concentration decreased from 28 mg/L in the period of 1986-1988 to 8 mg/L in the period of 1997-1999. The results also showed that the annual nitrate leaching decreased from 38 kg/ha in the period of 1986-1988 to 15 kg/ha in the period of 1997-1999, respectively. The reduction in the concentration of nitrate loss was due to reduction in the fertilizer N rates and addition of a winter cover crop as a trap crop after corn-soybean rotation. The author concluded that nitrate concentrations and nitrate losses in the tile drains vary with soil organic matter, yearly weather conditions, fertilizer N rates and timing, drain spacing, cover crop growth, cash crop yield and water table control practices.

Randall and Goss [120] reported that some non-controllable factors such as precipitation and mineralization of soil have great impact on the drainage volume and nitrate loads which put limits on the concentrations and loads that can be achieved by row-crop agriculture.

# Livestock and poultry operations

In 2009, Luxembourg recorded the highest meat consumption per capita (194.2 kg/year) followed by U.S (190.6 kg/year). Canada was in the 16<sup>th</sup> place with meat consumption per capita of 152 kg/year. The top 20 meat consumption countries are shown in Table 15 [121]. Currently, chicken is the highest available stocks in the world, followed by cattle and pigs as shown in Table 16 [122]. Today, China leads the total meat consumption in the worl by consuming 71 million tonnes of meat per year. Half of the pork in the world is in China. China's pork consumption rose to 52 million tonnes in 2012 [123]. Canada has 12.5 million cattle on their farms in 2012. The beef cows were 4.2 million, the beef replacement heifers were 554,300, the dairy cows were 1.4 million and the cattle and calf slaughter totalled 3.5 million [124]. The Canadian cattle inventories from 2006-2012 are shown in Table 17.

Animals are not breed solely for the meat but also for milk, eggs and fibers. The high demand for meat based foods changed the way food is produced today [125,126].

The system known as concentrated animal feeding operation (CAFO) allows for growing thousands of animals on strict diets. Phang [127] reported that animal feeding operation is an agricultural operation where animals are kept and raised in confined areas. Feed is bought to the animals rather than the animals grazing for their feed. A farm reaches the status of CAFO when it houses at least 300 cattle, 750

pigs or 25,000 chickens. In the CAFO system, animals are fed with high nutrients diet including nitrogen rich foods.

Olson et al. [128] reported that increasing meat consumption around the world justifies the needs of having CAFO as this system provide the meat needed in large amount with lowest cost. There are several advantages of CAFOs including: (a) low-cost source of meat, milk and eggs, (b) efficient feeding and housing of animals, (c) increased facility size and (d) animal specialization. There are also major environmental risks involved in this method of housing animals. The most health related issue is the production of large amounts of manure which contains plant nutrients such as nitrogen and phosphorous, pathogens such as *E. coli*, growth hormones, anitbiotics, chemical additives used to clean manure, animal blood, leachate from corn feed and copper sulfate used in the footbath for cows [13,125,129,130].

Rank	Country	Per Captia (kg/yr)
1	Luxembourg	194.2
2	United States of America	190.6
3	Austria	185.1
4	Australia	183.4
5	New Zealand	179.0
6	Oceania	173.4
7	Denmark	170.6
8	Spain	163.0
9	Argentina	161.8
10	Bahamas	160.3
11	Italy	158.4
12	Portugal	157.0
13	Bermuda	156.8
14	Germany	156.3
15	French Polynesia	155.4
16	Canada	152.0
17	Mongolia	151.1
18	Slovenia	149.6
19	Ireland	147.8
20	France	146.5

Table 15: Meat consumption per captia of top 20 countries in 2009 [121].

Animal	Number in × 10⁴		
Asses	4,323.0700		
Beehives	7,841.1600		
Buffaloes	19,539.7500		
Camelids, other	839.1900		
Camels	2,663.5400		
Cattle	1,42,638.9000		
Chickens	2,070.8000		
Ducks	132.38500		
Geese and guinea fowls	38.1200		
Goats	92,414.5900		
Horses	5,847.2100		
Mules	1,045.7100		
Pigeons, other birds	3.2500		
Pigs	96,716.4600		
Rabbits and hares	89.5000		
Rodents, other	1.8400		
Sheep	1,09,356.6700		
Turkeys	46.7600		

Table 16: World stocks of live animals in 2011 [122].

Cattle	2006	2007	2008	2009	2010	2011	2012
Bulls	264.0	244.6	246.8	243.9	232.1	222.2	221.2
Beef cows	5,247.2	5,020.1	4,981.9	4,649.5	4,391.0	4,273.0	4,228.4
Dairy cows	1,019.1	994.8	984.3	978.5	981.0	983.1	985.3
Heifers, dairy	495.1	480.1	471.1	450.6	450.7	443.1	444.1
Heifers, beef	628.3	587.1	595.0	537.0	516.4	531.6	554.3
Heifers, slaughter	986.8	963.5	982.9	834.5	899.8	844.0	839.5
Steers	1,146.8	1,145.2	1,101.6	1,067.6	1,141.7	1,081.7	1,098.1
Calves	4,867.7	4,719.6	4,506.4	4,433.4	4,292.3	4,078.3	4,144.1
Total	14,655.0	14,155.0	13,870.0	13,195.0	12,905.0	12,457.0	12,515.0

Table 17: Cattle inventories of Canada from 2006-2012 [124].

Burkholder et al. [131] stated that growing the animal in CAFO systems is unnatural and unhealthy. The animals are confined in a very limited space where they cannot even turn around. They are fed with enormous amount of corn and soy beans to increase their weight significantly in the shortest time. High density, limited space and continuous supply of food will produce large volume of manure. Sherman [132] stated that manure confined feeding operations is heavier because the manure is a mixture of faeces and urine with additional water used to pump it to the storage facility. The heavy manure is hard to be transported and disposing it has caused a major form of concern because of its impact to the environment).

Table 18 shows the number of farm animals slaughtered for human consumption in the world [133]. Table 19 shows the amount of manure produced by different animals [134-136]. USDA [137] estimated the manure production to be more than 335 million tonnes/year on the farms in United States, which was 100 times more than the manure produced by humans. It is estimated that the amount of manure produced by 2,500 cows are equal to the waste produced by 411,000 humans (1 cow=164.4 persons).

Manure from concentrated animal feeding operations is usually collected in a lagoon near the feedlots. The manure is disposed either by pumping the liquefied manure onto nearby "sprayfields" (crops, pasture or forage fields fertilized and irrigated by nutrient rich liquid) or being transported to another location with a high cost of transportation [138,139]. These practises increase the amount of nitrogen released freely into the environment which results in air, soil and water pollution. However, in recent years, the economic advantages of commercial fertilizers have made the use of animal wastes unprofitable to many farmers. The cost of handling and treating manure reduced the popularity of using it as organic fertilizer. The large automated feeding operations further magnified the problem by concentrating thousands of animals in localized areas [125].

Air pollution is mainly caused by various emissions from CAFOs such as ammonia, hydrogen sulfide, volatile organic acids, methane and particulate matter. The type of air pollutants surrounding CAFOs are shown in Table 20 [125]. Varel [140] reported on the nitrogen loss from feedlots via volatilization of nitrogen gases, primarily ammonia, into the atmosphere. Ammonia volatilization has contributed to soil and water pollution, where 90% of the nitrogen in urine exerted in cattle feed yards may escape into the air as ammonia. The authors found that a significant amount of ammonia volatilized from cattle feedlots is returned from the air to water bodies in the vicinity of the feedlot, and so the magnitude of nitrogen enrichment of lakes via this pathway can be significant.

Ndegwa et al. [141] reported that ammonia volatilization is one of the major pathways for nitrogen loss from agricultural feeding operations.

This process of losing nitrogen not only affects agricultural production but can adversely affect the environment. Ammonia deposited in the atmosphere in lower amounts are beneficial to plants as a nutrient source for growth but when excess N is deposited, it gets oxidized and reduced and causes various environmental issues including: (a) exposure to high concentrations of fine particulate aerosols (PM2.5) causes respiratory diseases, (b) contamination of drinking water with nitrate, (c) eutrophication of surface water bodies causing algal blooms and decreased water quality; (d) higher concentrations of N causes changes in vegetation and ecosystem, (e) climatic changes associated with increases in nitrous oxide (N<sub>2</sub>O), (f) saturation of forest soils with nitrogen and (g) acidification of soil through nitrification and leaching.

Water pollution results mainly due to the insufficient land used to contain the volume of manure. Runoff and leaching from feedlots have always been a threat to the nearby water bodies but a lagoon failure can send tens of millions of liters of untreated manure directly into water bodies. Minimal leaching and accumulation of nitrogen below the feedlot pens can possibly occur from denitrification of the poorly aerated layers [131,142]. In a study of soil and groundwater quality under a cattle feedlot in Southern Alberta, Olson et al. [128] reported that denitrification may have prevented an increase in NO<sub>3</sub>-N concentration in the groundwater. However, concentration of NH<sub>4</sub> N increased in the shallow groundwater beneath the pens although it did not accumulate in the sub soil layer during the four years of study.

Westerman et al. [138] evaluated swine lagoon seepage in sandy soils. They investigated two swine manure anaerobic lagoons on coastal sandy soil. Both lagoons had significant seepage after 3.5-5 years. The authors reported that manure lagoons constructed in sandy soils with high water tables have resulted in some groundwater pollution and about 3-6 mg nitrate NO<sub>3</sub>/L were found in surface runoffs from spray fields. They concluded that too much variability of NH<sub>3</sub>-N and NO<sub>3</sub>-N with time which made it difficult to determine the factors affecting the pollutant transport.

Stone et al. [139] conducted a 5 year research study on a watershed stream with intensive agricultural practices of crop, swine, poultry and cattle production. The results from the study indicated that most of the streams in the watershed had acceptable water quality. The nitrogen mass balance calculations and comparisons of the N loadings in the streams showed that 26% of the excess nitrogen applied is lost to stream water. The streams adjacent to swine effluent spray fields had 6-8 mg total inorganic N/L and 0.7-1.3 mg P/L.

Mahmoodabadi et al. [143] studied the effect of sheep manure leaching on soybean root characteristics and soil salinity. The results from the study indicated that the sheep manure significantly increased N, Fe, Cu, Zn and Mn concentrations. There was no significant increase in the pH of the soil (from 7.8 to 7.9). The leaching manure helped in

Animals	Heads		
Buffalo	57,681,750.00		
Cattle	609,729,971.76		
Ass	2,461,800.00		
Camel	2,031,008.00		
Goat	879,124,344.00		
Horse	4,504,308.00		
Mule	542,600.00		
Camelids	655,712.00		
Pig	1,382,927,239.95		
Sheep	1.046.814.221.65		

 Table 18: Total number of farmed animals slaughtered for human consumption in 2011 [133].

Animal	Average body weight (kg)	Urinary N (g/d)	Fecal N (g/d)	Total N (g/d)
Cattle	400	90.0	70.0	160.0
Sheep	40	7.0	3.0	10.0
Goats	15	5.0	3.0	8.0
Horses	400	49.0	27.0	76.0
Pigs	80	15.0	3.0	18.0
Chicken	4	7.2	3.4	10.6

Table 19: Nitrogen content in animal excretion [134-136].

increasing the number and dry weight of root nodules. Applying sheep manure increased the net nitrogen fixation in root nodules to 1.81 mg/Kg compared to 0.54 mg/Kg in the control pot. The sheep manure also reduced the salinity in the soil by 2%.

Dikinya et al. [144] studied the effect of chicken manure on three different soils including: luvic calcisol, ferralic arenosol and vertic luvisol that were classified as sandy clay loam, loamy sand and clay, respectively. The experiment was conducted for 63 days and the results indicated that there was substantial increase in pH. The highest pH recorded was 7.75 for ferralic arenosol soil and the lowest pH recorded was 7.01 for vertic luvisol soil. For most of the time the pH for the soil treated with chicken manure remained neutral or slightly alkaline. Lopez-Mosquera et al. [145] also reported that soil pH treated with chicken manure remained in the range of 7-7.9.

Whalen et al. [146] studied the effect of cattle manure on the pH of two acid soils obtained from Beaverlodge and Fort Vermillion in the Peace River Region of Alberta, Canada. The results obtained from the 8 week study indicated that the pH of Beaverlodge and Fort Vermillion soils increased from 4.8 to 6.0 and 5.5 to 6.3, respectively. The availability of minerals such as N, P, K, Ca and Mg increased immediately after manure application and were 3 to 4 times higher than untreated soils.

Plaza et al. [147] studied the effect of annual additions of pig slurry on soil pH at the rate of 30, 60, 90, 120 and 150  $m^{3h}a^{-1}y^{-1}$  over a 4 year

period under semiarid conditions. The control soil had a pH of 6.0. After slurry application the pH of soil increased significantly and the highest pH of 7.6 was observed. The soil had greater P and K contents and slightly higher total N content in it. However a significant decrease in the organic C was observed in soil treated with high slurry rates. The effect of animal manure of the pH of the soil from several other studies is shown in Table 21 [148-157].

## Urban waste

Domestic waste water effluents without specific treatment for nitrogen removal have nitrogen concentrations in the range of 20-85 mg N/L [158,159]. A typical composition of domestic wastewater is shown in Table 22 [160]. Ammonium is the predominant from of nitrogen in effluents from primary and high rate treatment plants. Storm water from residential areas can supply some nitrogen to rivers. Analysis of Wei River in China showed that it contains 7.31 mg NH<sub>4</sub>/L [161]. Zhang et al. [162] noted down ammonium concentration of 10-28 mg/L when examined the Yellow River in China.

Several substances containing nitrogen are commonly found in industrial wastes. Ammonia is a waste material from gas and coke manufacturing and other chemical manufacturing processes. Cyanide  $(CN^{-})$  is evolved during gas manufacture, plating, case hardening and metal cleaning. Nitrogen compounds also originate from explosive factories and other chemical works. There are some cases recorded of severe nitrogen pollution from industrial sources. Haber Bosch process does not only produce ammonia for fertilizer, it also provides ammonia as a raw material to create multiple products. Production of nylon, resins, plastics and melamine require ammonia [163]. Approximately 23 Tg N produced from Haber Bosch process was used for chemical production [164]. Unfortunately, little is known about the fate of this nitrogen in the environment.

Severe ammonia pollution in the Tolka River in Ireland is due to poor discharge qualities of Clonee, Co [165]. The pollution caused chemical burn to the vegetation, absence of aquatic flora and fauna, shortness of breath, skin and eye irritation and live fish and invertebrates were not observed in that area. Thousands of dead fishes were also observed. Nitrogen inputs to rivers, lakes and ocean originate either from point or non-point sources (Table 23) [166]. The point sources of nitrogen pollution include effluent pipes from municipal sewage treatment plant and factories. The non-point sources include the runoff from urban runoff from areas having a population of less than 100,000. These point sources are continuous and can be easily identified, monitored and controled. The non-point sources arise from suite of activities across large areas and are difficult to control [166,167].

Rouse et al. [168] reported that industrial effluents and wastewater treatment plant discharges from urban areas are a substantial source of nitrogen to aquatic ecosystems. Initially, these discharges contribute

CAFO emissions	Source	Traits	Health risks
Ammonia	Formed when microbes decompose undigested organic nitrogen compounds in manure	Colorless, sharp pungent odor	Respiratory irritant, chemical burns to the respiratory tract, skin and eyes, severe cough, chronic lung disease
Hydrogen Sulfide	Anaerobic bacterial decomposition of proteins and other sulfur containing organic matter	Odor of rotten eggs	Inflammation of the moist membranes of eye and respiratory tract, olfactory neuron loss, death
Methane	Microbial degradation of organic matter under anaerobic conditions	Colorless, odorless, highly flammable	No health risks. Is a greenhouse gas and contributes to climate change
Particulate matter	Feed, bedding materials, dry manure, unpaved soil surfaces, animal dander, poultry feathers	Comprised of fecal matter, feed materials, pollen, bacteria, fungi, skin cells, silicates	Chronic bronchitis, chronic respiratory symptoms, declines in lung function, organic dust toxic syndrome

Table 20: Air Pollutants from CAFO emissions [125].

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Type of		Characteristics (gKg <sup>-1</sup> DM)							рН	Reference
manure	С	N	Р	К	Са	Na	Mg		change	
Poultry(L)	250.0	39.0	205.0	26.9	110.7	5.4	11.0	6 weeks	4.0→6.5	[148]
Poultry(B)	343.0	25.0	188.0	19.0	34.8	3.5	17.0	6 weeks	4.0→5.0	[148]
Poultry	211.5	13.7	13.0	5.2	69.5	2.0	19.5	3 weeks	4.7→5.8	[149]
Poultry	239.0	63.0	21.0	20.0	77.0	2.6	5.7	6 weeks	4.2→5.4	[150]
Poultry	252.0	39.0	20.5	26.9	110.7		11	3 days	4.1→6.3	[151]
Poultry	131.0	32.8	43.0	29.3	27.0		5.7	30 days	4.3→4.6	[152]
Poultry	296.3	3.6			12.4		8.9	3 weeks	4.6→6.4	[153]
Poultry	252.0	38.5	20.5	26.9	110.7	5.4	11.0	7 weeks	4.1→6.5	[154]
Poultry	252.0	38.5	20.5	26.9	110.7	5.4	11.0	25 weeks	4.1→5.0	[154]
Cattle	114.0	10.0	1.8	0.60	0.3		0.1	3 days	4.1→4.6	[151]
Cattle	249.3	22.8	7.0	22.7				25 weeks	4.8→6.0	[155]
Cattle	313.0	4.9			11.2		19.9	3 weeks	4.6→5.9	[153]
Cattle	194.0	16.3	3.8	4.8	2.4	0.1	0.8	7 weeks	4.1→4.6	[154]
Cattle	194.0	16.3	3.8	4.8	2.4	0.1	0.8	25 weeks	stable	[154]
Pig	340.0	25.4	34.5	12.4	50.9	4.0	11.5	7 weeks	4.1→5.0	[154]
Pig	340.0	25.4	34.5	12.4	50.9	4.0	11.5	25 weeks	4.1→4.2	[154]
Pig (RL)		28.8	0.66	1.1				28 days	5.8→5.3	[156]
Pig (RL)		28.8	0.66	1.1				120 days	5.8→5.2	[156]
Pig (ADL)		30	0.78	1.1				28 days	5.8→5.3	[156]
Pig (ADL)		30	0.78	1.1				120 days	5.8→5.2	[156]
Pig	271.3	5.2			13.7		13.0	3 weeks	4.6→6.4	[153]
Pig		24.2	39.0	16.5	38.6		9.9	8 weeks	4.0→4.8	[157]

L: Layer; B: Broiler; RL: Raw Liquid; ADL: Anaerobically Digested Liquid

# Table 21: Effect of animal manure application on soil pH.

Question in secto		Concentration (mg/L)	
Contaminants	Low strength	Medium strength	High strength
Solids, total (TS)	390	720	1230
Dissolved, total (TDS)	270	500	860
Fixed	160	300	520
Volatile	110	200	340
Suspended solids, total (TSS)	120	210	400
Fixed	25	50	85
Volatile	95	160	315
Settleable solids	5	10	20
Biochemical oxygen demand			
5-d, 20°C (BOD <sub>5</sub> , 20°C)	110	190	350
Total organic carbon (TOC)	80	140	260
Chemical oxygen demand (COD)	250	430	800
Nitrogen (total as N)	20	40	70
Organic	8	15	25
Free ammonia	12	25	45
Nitrites	0	0	0
Nitrates	0	0	0
Phosphorous (total as P)	4	7	12
Organic	1	2	4
Inorganic	3	5	10
Chlorides	30	50	90
Sulfate	20	30	50
Oil and grease	50	90	100
Volatile organic compounds (VOCs)	<100	100-400	>400
Total coliform (no./100 mL)	10 <sup>6</sup> -10 <sup>8</sup>	10 <sup>7</sup> -10 <sup>9</sup>	10 <sup>7</sup> -10 <sup>10</sup>
Fecal coliform (no./100 mL)	10 <sup>3</sup> -10 <sup>5</sup>	10 <sup>4</sup> -10 <sup>6</sup>	10 <sup>5</sup> -10 <sup>8</sup>
Cryptosporidum oocysts (no./100 mL)	10 <sup>-1</sup> -10 <sup>0</sup>	10 <sup>-1</sup> -10 <sup>1</sup>	10 <sup>-1</sup> -10 <sup>2</sup>
Giardia lambia cysts( no./100 mL)	10 <sup>-1</sup> -10 <sup>1</sup>	10 <sup>-1</sup> -10 <sup>2</sup>	10 <sup>-1</sup> -10 <sup>3</sup>

 Table 22: Typical composition of untreated domestic wastewater [160].

Point Sources	Nonpoint Sources
Wastewater effluent, both municipal and industrial	Runoff from agriculture (including return flow from irrigated agriculture)
Runoff and leachate from waste disposal site	Runoff from pasture and range
Runoff and infiltration from animal feed lots	Urban runoff from unsewered areas and sewered aread with a population of less than 100,000
Runoff from mines, oil fields and unsewered industrial sites	Septic leachate and runoff from failed specifications
Strom sewer outfalls from cities with a population of greater than 100,000	Runoff from construction sites smaller than two hectares and abandoned mines
Runoff from construction sites larger than two hectares	Atmospheric deposition over a water surface
Overflows of combined storm and sanitary sewers	Activities on land that generate contaminants, such as logging, wetland conservation, construction and development of land or waterways

Table 23: Sources of point and nonpoint pollution [166].

only a small percentage of total nitrogen released to the environment but long term discharges into the water systems cause detrimental effect on stream ecosystems.

Another source of nitrogen contaminations in the urban areas is precipitation. Rain, snow and fog contain various amounts of nitrogen. Motor vehicles and industrial exhausts contribute nitrogen oxides (NO and  $NO_2$ ) to the atmosphere which are deposited in the water systems through precipitation. Precipitation causes problem in the watersheds which do not have an extensive ground cover of natural vegetation such as in urban areas [169].

# **Effect of Nitrogen Pollution**

# Lake eutrophication

Eutrophication was considered a natural biological aging process of aquatic ecosystems where nutrients increase produce more plants leading to the formation of pond and finally into a marsh [170]. However, the term eutrophication is currently used to describe a rapid nutrient enrichment process that take place in water bodies as a result of human activities that add up the nutrients. Present knowledge indicates that the fertilizing elements most responsible for Lake Eutrophication are nitrogen and phosphorus. Iron, silica and certain trace element are also important [171].

Although the increase in yield of a crop after fertilization is desirable in terrestrial situations, the effects of eutrophication of waters are undesirable. Generally, the aesthetic value of a lake is lowered through excessive growth of aquatic weeds and algae and production of floating algal scums which are a nuisance to those who used the water for recreational purposes. Other effects include undesirable odors and tastes, depletion of dissolved oxygen, destruction of aquatic life and impairment of water treatment operations such as clogging of filters by algae [172,173].

The stage of lake eutrophication is not controlled solely by the quantities of nutrients present or entering the receiving body of water, but also the interrelationship of climatic, physical, biological and chemical factors which affect lake metabolism are very important and significant and must be considered. However, nitrogen is the most important nutrient that limits primary production of photosynthetic organisms in temperate and coastal marine waters [174,175]. At the estuarine area, nitrogen often becomes the first nutrient to limit primary

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production. Excess inorganic nitrogen that flows to the estuarine will support a larger bloom in that area [176-177].

Different forms of nitrogen compound (organic or inorganic) reach the streams and subsequently the lakes through: (a) surface runoff, (b) groundwater interflow and (c) domestic and industrial wastes disposed of into the river. In the last four decades, nitrogen flux entering Mississippi River in USA had increased four folds and more than ten folds into the North Sea [77,150,178].

Besides agricultural activities, aquaculture industry (growing resources) also contributes nutrients to streams. Fish farms in developing countries are often located in a shallow bay area, allowing nutrients to accumulate and stimulate algal growth [179]. Romdhane et al. [180] described aquaculture activities in lagoons as a hazardous business as lagoons may function as a trap for toxins or other exudates from algal.

Other source of nutrients includes nitrous oxides in wet and dry deposition. About 50-100% primary production of harmful algal blooms in Yellow Sea, China is generated by typical rain event containing nitrogen, phosphorus and silica [181].

The level of nitrogen which will produce algae blooming is quite varied and depends on many factors, the most important of which are the available phosphorus and organic carbon. Nutrient ratios play an important role in influencing the algal growth. Hodgkiss et al. [182] reported algal bloom in Tolo Harbour in Hong Kong increases whenever the ratio N: P decreases. The authors recorded that the ration of N: P between 1982 and 1989 in Tolo Harbour and found it to decreases from 20:1 to 11:1 as the number of dinoflagellate red tides increased. Hodgkiss [183] demonstrated that whenever N: P ratio fell below approximately 10:1 in Tolo Harbour, the dinoflagellate cell number increased. Algal bloom of dinoflagellate red tides result in prominent colouration of the water bodies. Microflagella dinoflagella blooms when nitrogen concentration is low while some other species such as marine diatoms exploits nitrate-rich conditions through physiological adaptations [184-187].

Smith et al. [188] reported that in Northern Ireland, soil P reserves have accumulated at a rate of 1000 kg P km<sup>-2</sup> yr<sup>-1</sup> over the past 50 years and these increases have resulted in increases in the losses of inorganic P runoff at a rate of 2 mg m<sup>-3</sup> yr<sup>-1</sup>. The average of characteristics of water bodies with various levels of nitrogen and phosphorous loading is shown in Table 24 [188]. McGarrigle [189] reported that annual dissolved inorganic P concentration should be lessern tha 47 mg m<sup>-3</sup> to prevent the growth of algae and to preserve water quality suitable for salmonoid fish, in Irish rivers. Miltner et al. [190] reported that the total inorganic nitrogen (TIN) and dissolved inorganic phosphorus

Water bodies	Trophic state	Total nitrogen (mg m <sup>-3</sup> )	Total phosphorus (mg m <sup>-3</sup> )	Chl a (mg m <sup>-3</sup> )
	Oligotrophic	<350	<10	<3.5
Labaa	Mesotrophic	35-650	10-30	3.5-9
Lakes	Eutrophic	650-1200	30-100	9-25
	Hypertropic	>1200	>100	>25
	Oligotrophic	<700	<25	<10
Streams	Mesotrophic	70-1500	25-75	10-30
	Eutrophic	>1500	>75	>30
	Oligotrophic	<260	<10	<1
Marine	Mesotrophic	260-350	10-30	1-3
	Eutrophic	350-400	30-40	3-5
	Hypertropic	>400	>40	>5

 Table 24: Average characteristics of lakes, streams and marine waters [188].

(SRP) concentrations exceeded 610 and 60 mg m<sup>-3</sup>, respectively causing deleterious effects to marine organisms in Ohio streams, USA.

Xiangcan et al. [172] studied the eutrophication in various freshwater lakes in China and reported that a total nitrogen concentration of 5.45 mg/L in Lake Nanhu which is higher than the permitted level of 0.6 mg/L. The author also reported that the total phosphorous in Lake Dianchi was 0.529 mg/L which is higher than the permitted level of 0.02 mg/L.

Anderson et al. [191] reported that nitrogen and phosphorus are two major limiting factors in water bodies. In freshwaters, phosphorous are least available in large quantities for the photosynthetic organisms and can limit or co-limit the growth of algae in estuarine and marine environments that are sustaining high nitrogen inputs. In some tropical and highly eutrophic temperate lakes, nitrogen may be a more important limiting factor than phosphorus. Duan et al. [192] reported that the nutrient sources for eutrophication are mainly sewerage, livestock drainage, soil nutrients and loss of fertilizers in drained agricultural lands, which could be associated with human population and economic development.

Mackenthum [193] reported that a concentration of 0.30 mg/L inorganic nitrogen is considered critical for stimulation of algal growth in the presence of adequate phosphorus in Lake Michigan, where total inorganic nitrogen averaged 1.56 mg/L and reached as high as 3.14 mg/L in Indiana Harbor. The source of pollution in this example was from the discharged domestic waste. However, excessive growth of plants and algae in polluted water can be avoided if the concentration of nitrate nitrogen is kept below about 0.3 mg/L and the concentration of total nitrogen is not allowed to rise much more above 0.6 mg/L. Certain species of algal are classified as harmful algal blooms because toxic compounds are released from this type of algal. Anderson [194] suggested that there is a relation between the toxicity of the harmful algal blooms with nutrients content in the water. Toxicity can increase or decrease significantly depending on the limiting nutrients of the species. For example, saxitoxin production by A. tamarense can be 5-10 folds higher in phosphorus limited environment in comparison to nitrogen limited environment [194,195].

The algal bloom may affect fish, by lowering the dissolved oxygen (DO) in water during the night. This algae oxygen demand can deplete the DO sufficiently and lead to fish kills. Fish may also find it hard to feed if the algae color the water and obscure their vision. Algal blooming at the surface of water will block the sunlight from reaching the bottom of the water bodies. Lack of sunlight can disturb the photosynthesis process of plankton and may lead to another ecological problems such as loss of biodiversity [6,196].

Carpenter et al. [166] reported that the adverse effects of eutrophication are: (a) increased phytoplankton biomass, (b) shifts in phytoplankton to bloom forming species which are toxic or inedible, (c) increases in blooms of gelatinous zooplankton in marine environment, (d) increases in biomass of benthic and ephiphytic alage, (e) changes in macrophyte species composition biomass, (f) death of coral reefs, (g) decreased transparency of water, (h) depleted oxygen levels, (i) increased incidence of fish kills and (j) reduced harvest of fish and shellfish.

# Human and animals health

Webb et al. [197] reported that animal wastes are rich in organics and high in biochemical oxygen-demand (BOD). The treated human sewage contains 20–60 mg BOD/L, raw sewage contains 300–400 mg BOD/L, and swine waste slurry contains 20,000–30,000 mg BOD/L. Skinner et al. [198] reported that agricultural wastes such as cattle slurry contain 50 times greater BOD (10,000-20,000 mg/l) than domestic sewage. The ranges of BOD concentrations for various wastes in shown in Table 25 [111].

Burkholder et al. [131] and Mellon et al. [199] reported that animal wastes carry parasites, viruses, and bacteria as high as 1 billion/g. Swine wastes contain >100 microbial pathogens that can cause human illness and disease. About one-third of the antibiotics used in the United States each year is routinely added to animal feed to increase growth. This practice is promoting increased antibiotic resistance among the microbial populations present and, potentially, increased resistance of naturally occurring pathogens in surface waters that receive a portion of the wastes. The pathogens in the animal manure are capable of causing various diseases to humans. Some of the select pathogens found in animal manure are shown in Table 26 [125].

Burkholder et al. [131] reported that waterborne contaminants affect human health from both recreational use of affected surface water and from ingestion of drinking water derived from either contaminated surface water or groundwater. Generally, the very young, elderly, pregnant women and immune compromised individuals are at great risk of infection. Accidental ingestion of contaminated water that may result in diarrhoea or other gastrointestinal tract distress from waterborne pathogens and dermal contact during swimming that may cause skin, eye, or ear infections. Drinking water exposures to pathogens could occur in vulnerable private wells; under normal

Source	BOD (mg/L)
Silage effluents	30,000-80,000
Pig slurry	20,000-30,000
Cattle slurry	10,000-20,000
Liquid effluents draining from slurry stores	1000-12000
Dilute dairy parlour and yard washing (dirty water)	1000-5000
Milk	140,000
Untreated domestic sewage	300-00
Treated domestic sewage	20-60
Clean river water	<5

Table 25: Ranges of BOD concentrations for various wastes [111].

Pathogen	Disease	Symptoms
Bacillus anthracis	Anthrax	Skin sores, headache, fever, chills, nausea, vomiting
Escherichia coli	Colibacilosis, Coliform mastitis- metris	Diarrhea, abdominal gas
Leptospira pomona	Leptospirosis	Abdominal pain, muscle pain, vomiting, fever
Listeria monocytogenes	Listerosis	Fever, fatigue, nausea, vomiting, diarrhea
Salmonella species	Salmonellosis	Abdominal pain, diarrhea, nausea, chills, fever, headache
Clostirdum tetani	Tetanus	Violent muscle spasms, lockjaw, difficulty breathing
Histoplasma capsulatum	Histoplasmosis	Fever, chills, muscle ache, cough rash, joint pain and stiffness
Microsporum and Trichophyton	Ringworm	Itching, rash
Giardia lamblia	Giardiasis	Diarrhea, abdominal pain, abdominal gas, nausea, vomiting, fever
Cryptosporidium species	Cryptosporidosis	Diarrhea, dehydration, weakness, abdominal cramping

 Table 26: Pathogens found in animal manure [125].

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circumstances community water utilities disinfect water sufficiently before distribution to customers.

WHO [200] and Carmichael et al. [201] reported that cyanobacteria (blue green algae) released from animal manure into the surface can produce toxins such as microcystins that are neurotoxins and hepatotoxins. Acute and chronic health impacts are bound to occur on exposure to these toxins.

High concentrations of nitrites in water consumed by infant causes methemoglobinemia. Heldin [202] reports that methemoglobinemia was found in young bottle-fed infants in parts of Neapawa and Portage le Prairie in Manitoba, Canada, and Health Service traced it to be caused by high nitrate content of water in local wells. Also, at about the same time, nitrate poisoning of cattle was reported by local veterinarian. High nitrate in forage can be contributing factor in livestock production. The drinking water standards (1962) of the U.S. Public Health Service list 10 ppm nitrate nitrogen (45 ppm NO<sub>3</sub>) as the level that should not be exceeded for infants.

Cornell et al. [203] reported that applying synthetic nitrogenous fertilizer onto land has pronounced effect on the local and global environment. Ammonia (NH<sub>3</sub>), nitrous oxide (N<sub>2</sub>O) and nitric oxide (NO) are the main nitrogen gas species emitted to the atmosphere from agricultural activities. Nitrous oxide (N<sub>2</sub>O) and nitric oxide (NO) are very minor contributors, but ammonia (NH<sub>3</sub>) contributes significantly to the atmospheric nitrogen deposition. Ammonia and nitrogen oxides present in the atmosphere are removed by rainfall and dry deposition [204].

Camargo et al. [205] reported that some algal species can cause toxicity to aquatic and terrestrial animals by synthesis of certain toxin such as anatoxins, microcystins, nodularins, brevetoxins, hemolysins and saxitoxins (Table 27) [205]. These toxins remain can inside the algal cells (intracellular toxins) or can be released into the water (extracellular toxins) during active algal growth or when cells lyse. These toxins are consumed by animals by direct exposure to water, drinking of water or injestion of algal cells from water.

# **Methods of Abatements**

### Animal waste treatment

In order to reduce the amount of nitrogen compound in animal

waste, manure is to be collected and treated in such a way as to make aerobic conditions prevail. Aerobic treatment will encourage the conversion of ammonium nitrogen into nitrate nitrogen through the process of nitrification. When the aerobic process is followed by anaerobic conditions, denitrification will be encouraged resulting in stripping out the elemental nitrogen to the atmosphere leaving the treated manure with a lower content of nitrate [141].

Another method is the ammonia removal from units holding animal wastewater. The ammonia release to the atmosphere is a function of the agitation. Aeration towers can be used to degasify animal waste. Because holding tanks are prevalent at animal production facilities, aeration systems can be used for ammonia release, where the amount of ammonia stripped from a solution is a function of the air flow rate, temperature, pH of the liquid, time and characteristics of waste water [206].

The ultimate utilization of animal manure will be land application. If nitrogen reduction is a goal in waste disposal, a rather wet schedule should be followed [207]. The applied waste water should contain some organic load so that a carbon substrate would be available for denitrifying bacteria. Once application of wastewater has begun on an area, it should be continued for as long as possible to ensure conversion of ammonia nitrogen to nitrate so that maximum reduction of nitrogen can be achieved by denitrification.

Proper storage and application of slurry and solid manure can help reduce emissions [208]. Rapid incorporation of slurry and solid manure into the soil is the simple way to reduce ammonia emission. Band spreading machineries such as trailing house and trailing shoe and sub-surface applicators reduces ammonia emissions by 30-40% compared with broadcast spreading. Shallow injection and deep injection can reduce ammonia emissions by 30-40% and 90%, respectively. The trailing house and subsurface applicators are shown in Figure 7 [208,209]. Some other additional methods of ammonia abatement are shown in Table 28 [208].

Slurry storage plays an important role in ammonia emission. Specifically made round covers fitted to above ground tanks and slurry lagoons can reduce ammonia emissions by up to 80%. In addition potentially cheaper covers such as LECA (light expanded clay aggregate) or UV stabilized plastic sheets provide significant reduction in ammonia emissions stored from pig slurry. The different emission

Toxins	Chemical Structure	Site and mode of action	Characteristic species
Anatoxin-a	Secondary amine alkaloid	Attacks nervous system by mimicking the action of acetylcholine and over stimulating muscle cells	Anabaena circinalis, Anabaena flos-aquae, Anabaena planctonica, Aphanizomenon flos-aquae
Anatoxin-a (s)	Organophosphate	Attacks nervous system by inhibiting acetyl-cholinesterase, and over stimulating muscle cells	Anabaena flos-aquae, Anabaena lemmermannii
Brevetoxins	Polycyclic ethers	Attacks nervous system by binding to sodium channels and disrupting nerve conduction	
Domoic acid	Tricarboxylic amino acid	Attacks nervous system by binding to kainate glutamate receptors, and causing depolarization of the neurons, with a subsequent increase in intracellular Ca <sup>2+</sup> . neuronal swelling, and cell death	
Hemolysins	Fatty acids	Target cells by altering membrane functions and causing cell lysis	Alexandrium monilatum, Gymnodinium aureolum, Karenia mikimotoi
Microcystins	Cyclic heptapeptides	Affects liver, hepatopancreas by shrinking the cytoskeleton, distorting cells and causing hepatic haemorrhages, and by inhibiting protein phosphatases, and causing tumor promotion	
Nodularins	Cyclic pentapeptides	Affects liver, hepatopancreas by shrinking the cytoskeleton, distorting cells and causing hepatic haemorrhages, and by inhibiting protein phosphatases, and causing tumor promotion	
Saxitoxins	Carbamate alkaloids	Attacks nervous system by blocking sodium channels and disrupting nerve conduction	Anabaena circinalis, Aphanizomenon flos-aquae, Alexandrium catenella, Alexandrium tamarense, Gymnodinium catenatum

Table 27: Impact of toxins from algae on aquatic and terrestrial animals [205].

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(a) Trailing house



Figure 7: Two types of applicators to reduce ammonia emissions [208,209].

control options for cattle and pig slurry storage is shown in Table 29 [208-210].

# Domestic waste treatment

The use of nitrification-denitrification as a method for eliminating

nitrogen contamination by waste water was examined by Mulbarger [211]. The process alternatives for the nitrification-denitrification process included: (a) substituting trickling filter for the high rate and/or nitrifying activates sludge systems, (b) adding inorganic or organic coagulants to primary clarifier to maximise solids removal and eliminate the high rate activated sludge systems and (c) utilizing anaerobic column or beds for denitrification. The whole process was carried out in a single, dual and three sludge systems. The author reported that an influent with 25.2 mg/L total nitrogen after treatment using the system produced an effluent with 5.4 mg/L total nitrogen (1.4 mg/L nitrate).

Strous et al. [212] studied the ammonium removal from concentrated waste streams with anaerobic ammonium oxidation (anammox) process. In this process, the ammonium was converted to dinitrogen gas with nitrite as the electron acceptor. The process is autotrophic and there was no need for COD addition to support denitrification. When the anammox process was preceded by a nitrification step, only a part of ammonium was nitrified and the anammox process combines the ammonium and nitrite to form dinitrogen gas. This reduced the oxygen demand and the biomass yield was very low. This approach reduces the total operation costs [213,214]. Strous et al. [212] studied the effects of sludge digestion effluent on waste streams in a fluidised bed reactor using anammox process. The whole process was carried out for 150 days at a pH of 8 and a temperature of 36°C. The results indicated that during 150 days of analysis, 82% of ammonium and 99% nitrite were removed in fluidized bed reactor. Dong et al. [215] studied the anaerobic digestion of poultry manure using anammox and denitrification processes. The results obtained from the study indicated that the anammox microorganisms developed at a very low rate and could not compete with the denitrifying bacteria for nitrite production.

Liao et al. [216] studied the removal of nitrogen from swine manure wastewaters by air (ammonia) stripping and aeration methods. The air stripping process took place in a stripping tower in which the wastewater was pumped in from the top which passed through the packing material and the air was blown from the opposite direction to release volatile ammonia in the air. The direct aeration involved pumped air directly into the reactor containing swine manure

Method	Mode of action	Disadvantages	
Reduce crude protein in livestock diet	Reduces amount of N excreted and hence potential for ammonia emission	More research needed	
Use extra straw for bedding cattle	Locks up ammonia	Research ongoing	
Modify design for livestock housing	Reduces time and area of slurry exposed to air	Mainly for pigs. Difficult to implement for existing houses	
Equip livestock houses with air scrubbers or filters	Removes ammonia from air ventilated from houses	Only for mechanical ventilated houses and it is very expensive	
Cover surface of store with straw plastic sheet, clay granules, oil etc.	Physical barrier to ammonia emission Can be unreliable. Granules or straw may block		
Additives (eg. Zeolites)	Physically locks up ammonia or form stable chemical compound Large quantities needed and not relia		
Dilute slurry with water	Speeds up infiltration into the soil Effectiveness varies with soil conditions. Increases slurry to be managed		
Add acid to slurry	Lowers pH and so ammonia stays in solution Hazardous and can release nitrous oxide		
Remove proportion of solids from slurry with a mechanical separating machine	a More free flowing liquid infiltrates into the soil more rapidly form the remaining solid material		
Irrigate with water after spreading slurry	Washes slurry into the soil Needs large amounts of water and may cause run off to waters		
Choose optimum time	Cool, humid weather discourages ammonia releases rain washes slurry into the soil Difficult to quantify effectiveness. May cause odour prol		
Match fertilizer type and use of crop need, soil and environmental conditions	Urea is one of fertilizers with highest ammonia emissions Requires more time on fertilizer planning		

Table 28: Additional methods for ammonia abatement [208].

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Methods	Emission reduction efficiency (%)	Applicability
Store with no cover or crust	0	
Tight lid, roof or tent structure	80	Concrete or steel tanks and silos. May not be suitable on existing storage tanks
Plastic sheeting (floating cover)	60	Small earth-banked lagoons
Allowing formation of natural crust by reducing mixing and manure input below the surface	40	Only for slurries with higher content of fibrous material. Not suitable on farms where it is necessary to mix and disturb the crust in order to spread slurry frequently. Crust may not form on pig manure in cool climates
Replacement of lagoon, etc. with covered tank or tall open tanks (depth >3 m)	30-60	Only new build and subject to any planning restrictions concerning taller structures
Storage bag	100	Available bag sites may limit use on larger livestock farms
Floating LECA balls (Hexa covers)	60	Not suitable for crusting manures
Plastic sheeting (floating cover)	60	Large earth blended lagoons and concrete or steel tanks. Management and other factors may limit use of this technique
Low technology floating covers (eg.: chopped straw, peat, bark)	40	Concrete or steel tanks and silos. Probably not practicable on large earth banked lagoons. Not suitable if materials likely cause slurry management problems

Table 29: Storage methods for the reduction of ammonia emission [210].

wastewater to release ammonia to the air. The results indicated that the air stripping method achieved 90% ammonia removal at a pH of 11.5 after 1 h of treatment and the aeration method achieved 90% removal at a pH of 11.5 after 150 h of treatment.

# **Crop production practice**

The use of nitrogen fertilizers is recommended to be at the optimum level required by the crop and soil type in order to eliminate addition of any excess. Land use practice and soil conservation methods that reduce the amount of erosion will consequently reduce the amount of organic nitrogen carried to the surface waters.

Flynn [217] recommended management strategies to improve the nitrogen use efficiency of crops, thereby reducing fertilizer requirements and associated greenhouse gas emissions. The author suggested that both environmental factors such as soil conditions and climate and management factors such as tillage play an important role in the amount of fertilizer to be applied. Appropriate nitrogen application rates are required to limit the buildup of nitrates in soil. Organic nitrogen sources such as animal manure, crop residues and nitrogen fixing crops can be used instead of synthetic fertilizer.

Tilman et al. [218] reported that nutrient use efficiency must be improved by better matching temporal and spatial nutrient supply with plant demand. Practices such as applying fertilizers during periods of greatest crop demand at or near the plant roots and smaller and frequent application of nutrients have the potential to reduce the nitrogen emissions and improving the yield and quality of the crops. This type of agriculture is called precision agriculture and it is currently carried out in large scale intensive farming which could be implemented on small level farming.

Multiple cropping systems such as using crop rotations or intercropping (two or more crops grown simultaneously) can help to improve pest control and increase nutrient and water use efficiency. Crops such as clover and other legumes can be in rotations to reduce fertilizer requirements by adding biologically fixed nitrogen into soils. Addition of post-harvest plants remains into the soil can increase the levels of soil organic matter and help in storing soil carbon. Agroforestry, in which growing trees can improve nutrient availability and efficiency and can reduce erosion in the soil [217,218].

Changing from fall nitrogen application to a spring application will reduce nitrous oxide emissions [219]. In Alberta cropping systems, between 30-50% nitrogen emissions have been reduced by changing fertilizer application methods. Increasing the acreage of minimum tillage also reduced the carbon di-oxide emissions from the soil and increased the carbon sequestration in soil. Naylor [220] reported that technologies such as drip irrigation can improve water use efficiency and decrease salinization in the soil. The sustainable growing of crops will require increased efficiency of nitrogen and water use along with ecologically based best management practices and effective use of pesticides.

# Conclusion

The natural cycle of nitrogen involves several biological and non-biological process including: mineralization, nitrification, denitrification, nitrogen fixation, microbial and plant uptake of nitrogen, ammonia volatilization, leaching of nitrite and nitrate and ammonia fixation. Nitrogen exists naturally in the environment and is constantly being converted from organic to an inorganic form and vice versa. Production of commercial fertilizer adds up to the natural source of nitrogen. The main source of nitrogen include: atmospheric precipitation, geological sources, agricultural land, livestock and poultry operations and urban waste. Agricultural emissions show a strong increase due to the application of fertilizer to agricultural soils, grazing of animals and spreading of animal manure. Emissions from agricultural practices and animal manure wastes are the major source of nitrogen pollution in surface and underground water. Soil erosion and runoff from fertilized land as well as domestic and industrial wastes contribute to the enrichment of lakes and streams with nutrients. Nitrates concentration exceeding certain limits in drinking water is toxic to animals and humans, especially infants. Nuisance of algal bloom and fish kills in lakes and rivers occurs due to eutrophication. Obnoxious colors and smells are developed as a result of organic matter decay and are destroying the natural beauty of the environment. The water born contaminants affect human health from both recreational use of contaminated surface water and from ingestion of contaminated drinking water derived from surface or ground water sources. The methods for abatement of nitrogen pollution must follow multi pathways. First, the source and amount of pollution must be detected and defined. Second, the possible ways to treat animal and domestic wastes should be carefully investigated. Third, better agricultural practices should be developed that include: proper storage and application of slurry and solid manure, rapid incorporation of slurry and solid manure into the soil, use of band spreading machineries such as trailing house and trailing shoe and sub-surface applicators, use of specifically made round covers fitted

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to above ground tanks and slurry lagoons, applying fertilizers during periods of greatest crop demand at or near the plant roots in smaller amounts with frequent applications, using multiple cropping systems such as using crop rotations or intercropping to increase the efficiency of nitrogen uses and changing current livestock production techniques.

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#### References

- Kotler DP, Thea DM, Heo M, Allison DB, Engelson ES, et al. (1999) Relative influences of sex, race, environment, and HIV infection on body composition in adults, Am J Clin Nutr 69: 432-439.
- UNEP (2008) Vital water graphics: An overview of the state of the world's fresh and Marine waters, 2nd edn. United Nations Environment Programme, Nairobi, Kenya.
- 3. Peavy HS, Rowe DR, Tchobanoglous G (1985) Environmental Engineering McGrawHill, New York, USA.
- Hammer MJ (2008) Water and wastewater technology. Upper Saddle River, New Jersey, USA.
- Wu RSS (1999) Eutrophication, water borne pathogens and xenobiotic compounds, Environmental risk and challenges. Marine Pollution Bulletin 39: 1-12.
- Smith VH, Joye SB, Howarth RW(2006) Eutrophication of freshwater and marine ecosystems. Limnol Oceanogr 51: 351-355.
- Mackenzie FT (1998) Our Changing Planet. An introduction to earth system science and global environmental change, Second Edition. Prentice Hall, Upper Saddle River, New Jersey, USA.
- Driscoll C, Whitall D, Aber J, Boyer E, Castro M, et al. (2003) Nitrogen Pollution in the Northeasterns United States: Sources, Effects and Management Options. Bioscience 53: 357-374.
- 9. Vitousek P, Aber J, Howarth R, Likens G, Matson P, et al. (1997) Human Alteration of the Global Nitrogen Cycle: Sources and Consequences. Ecol Appl 7: 737-750.
- Schimel JP, Bennett J (2004) Nitrogen mineralization: Challenges of a changing paradigm. Ecology 85: 591-602.
- Guggenberger G (2005) Humification and mineralization in Soils. In: Buscot F, Varma A (eds.) Microorganisms in soils: Roles in genesis and functions. Springer Berlin Heidelberg, New York, USA.
- O'Leary, M., G. Rehm, M. Schmitt. 2002. Understanding Nitrogen in Soils. University of Minnesota. Extension Service. P5.
- Rotz CA (2004) Management to reduce nitrogen losses in animal production. J Anim Sci 82 E-Suppl: E119-137.
- Parton W, Stewart J, Cole CV (1988) Dynamics of C, N, P and S in Grassland Soils: A Model. Biogeochemistry 5: 109-131.
- Anthonisen AC, Loehr RC, Prakasam TB, Srinath EG (1976) Inhibition of nitrification by ammonia and nitrous acid. J Water Pollut Control Fed 48: 835-852.
- Ward BB1 (2011) Measurement and distribution of nitrification rates in the oceans. Methods Enzymol 486: 307-323.
- Liu G Wang J (2012) Probing the stoichiometry of the nitrification process using the respirometric approach. Water Res 46: 5954-5962.
- Stark JM, Firestone MK (1995) Mechanisms for soil moisture effects on activity of nitrifying bacteria. Appl Environ Microbiol 61: 218-221.
- van der Heijden MG Bardgett RD, van Straalen NM (2008) The unseen majority: soil microbes as drivers of plant diversity and productivity in terrestrial ecosystems. Ecol Lett 11: 296-310.
- 20. Bonete MJ Martínez-Espinosa RM, Pire C, Zafrilla B, Richardson DJ (2008) Nitrogen metabolism in haloarchaea. Saline Systems 4: 9.
- 21. Knowles R (1982) Denitrification. Microbiol Rev 46: 43-70.
- 22. Tallec G, Garnier J, Billen G, Gousailles M (2008) Nitrous oxide emissions

from denitrifying activated sludge of urban wastewater treatment plants, under anoxia and low oxygenation. Bioresource Technol 99: 2200-2209.

- Kim SW, Miyahara M, Fushinobu S, Wakagi T, Shoun H (2010) Nitrous oxide emission from nitrifying activated sludge dependent on denitrification by ammonia-oxidizing bacteria. Bioresour Technol 101: 3958-3963.
- Wunderlin P Mohn J, Joss A, Emmenegger L, Siegrist H (2012) Mechanisms of N2O production in biological wastewater treatment under nitrifying and denitrifying conditions. Water Res 46: 1027-1037.
- 25. Alluisetti GE Almaraz AE, Amorebieta VT, Doctorovich F, Olabe JA (2004) Metal-catalyzed anaerobic disproportionation of hydroxylamine. Role of diazene and nitroxyl intermediates in the formation of N2, N2O, NO+, and NH3. J Am Chem Soc 126: 13432-13442.
- Robertson LA Kuenen JG (1990) Combined heterotrophic nitrification and aerobic denitrification in Thiosphaera pantotropha and other bacteria. Antonie Van Leeuwenhoek 57: 139-152.
- Kemp MJ, Dodds WK (2002) The influence of ammonium, nitrate and dissolved oxygen concentration on uptake nitrification and denitrification rates associated with prairie stream substrata. Limnology and Oceanography 47: 1380-1393.
- Postgate J (1998) Nitrogen fixation (3rd edn), Cambridge University Press, Cambridge, UK.
- 29. Kennedy IR, Choudhury ATMA, Kecskes ML (2004) Non symbiotic bacterial diazotrophs in crop farming systems: can their potential plant growth promotion be better exploited? Soil Biology and Biochemistry 36: 1229-1244.
- Kahindi JHP, Woomer P, George T, de Souza Moreira FM, Karanja NK, et al. (1997) Agricultural intensification, soil biodiversity and ecosystem function in the tropics: the role of nitrogen-fixing bacteria. Applied Soil Ecology 6: 55-76.
- Bohlool BB, JK Ladha, DP Garrity, T George (1992) Biological nitrogen fixation for sustainable agriculture: a perspective. Plant and Soil 141: 1-11.
- Orr CH, James A, Leifert C, Cooper JM, Cummings SP, et al. (2011) Diversity and activity of free-living nitrogen-fixing bacteria and total bacteria in organic and conventionally managed soils. Appl Environ Microbiol 77: 911-919.
- 33. Belnap J (2003) Factors influencing nitrogen fixation and nitrogen release in biological soil crusts. In: Belnap J, Lange OL (eds.), Biological soil crusts: structure, function and management. Ecological Studies. Springer-Verlag Berlin, Germany. 150: 241-261.
- Bürgmann H Widmer F, Von Sigler W, Zeyer J (2004) New molecular screening tools for analysis of free-living diazotrophs in soil. Appl Environ Microbiol 70: 240-247.
- Vitousek PM, Cassman K, Cleveland C, Crews T, Field CB, et al. (2002) Towards an ecological understanding of biological nitrogen fixation. Biogeochem 57/58: 1-45.
- Cleaveland CC, Townsend AR, Schimel DS, Fisher H, Howarth RW, et al. (1999) Global patterns of terrestrial biological nitrogen (N2) fixation in natural ecosystems. Global Biochemical Cycles 13: 623-645.
- Mylona P Pawlowski K, Bisseling T (1995) Symbiotic Nitrogen Fixation. Plant Cell 7: 869-885.
- Andrade SLA, Dickmanns A, Ficner R, Einsle O (2005) Expression, purification and crystallization of the ammonium transporter Amt-1 from Archaeoglobus fulgidus. Acta Crystallogr Sect F Struct Biol Cryst Commun F61: 861-863.
- Andrade SL Einsle O (2007) The Amt/Mep/Rh family of ammonium transport proteins. Mol Membr Biol 24: 357-365.
- Martínez-Espinosa RM Lledó B, Marhuenda-Egea FC, Bonete MJ (2007) The effect of ammonium on assimilatory nitrate reduction in the haloarchaeon Haloferax mediterranei. Extremophiles 11: 759-767.
- Crawford NM, Glass ADM (1998) Molecular and physiological aspects of nitrate uptake in plants. Trends in Plant Science Reviews 3: 389-395.
- Glass AD Britto DT, Kaiser BN, Kinghorn JR, Kronzucker HJ, et al. (2002) The regulation of nitrate and ammonium transport systems in plants. J Exp Bot 53: 855-864.
- Meyer C, Stitt M (2001) Nitrate reductase and signalling. In: Lea PJ, Morot-Gaudry JF (eds.) Plant Nitrogen, Springer, New York, USA, pp 37-59.
- Stitt M (1999) Nitrate regulation of metabolism and growth. Curr Opin Plant Biol 2: 178-186.

#### Page 23 of 26

- Lea PJ, Forde BG (1994) The use of mutants and transgenic plants to study amino acid metabolism. Plant, Cell and Environment 17: 541-556.
- 46. Masclaux-Daubresse C Daniel-Vedele F, Dechorgnat J, Chardon F, Gaufichon L, et al. (2010) Nitrogen uptake, assimilation and remobilization in plants: challenges for sustainable and productive agriculture. Ann Bot 105: 1141-1157.
- Suzuki A Knaff DB (2005) Glutamate synthase: structural, mechanistic and regulatory properties, and role in the amino acid metabolism. Photosynth Res 83: 191-217.
- Abrol Y, Raghuram N, Sachdev M (2007) Agricultural Nitrogen use & its Environmental Implications. I.K. International Publishing House, S-25, Uphaar Cinema Market, New Delhi; ISBN: 978-81-89866-33-4.
- 49. Kadlec R, Wallace S (2009) Treatment Wetlands. (2nd edn) CRC Press, Boca Raton, Florida, USA.
- Rengel Z (2003) Handbook of Soil Acidity. Marcel Dekker AG, Hutgasse, Basel, Switzerland.
- Agrifacts (2008) Ammonia volatilization from manure application. Practical Information for Alberta's Agriculture Industry. Soil Fertility Fact Sheet, Ag. Index No. 538-3. Alberta Agriculture and Rural Development, Edmonton, Alberta.
- 52. Meisinger JJ, Jokela WE (2000) Ammonia volatilization from dairy and poultry manure. Reproduced with permission from "Managing Nutrients and Pathogens from Animal Manure". Natural Resource, Agriculture and Engineering Service, Ithaca, New York, USA.
- Rochette P, Angers DA, Chantigny MH, Gasser MO, MacDonald JD, et al. (2013) NH3 volatilization, soil NH4<sup>+</sup> concentration and soil pH following subsurface banding of urea at increasing rates. Canadian Journal of Soil Science 93: 261-268.
- 54. du Preez CC, Burger RDT (1987) Effect of application methods on ammonia volatilization from soils in a controlled environment. South African Journal of Plant and Soil 4: 57-60.
- 55. Musa MM (1968) Nitrogen fertilizer transformations in the Sudan Geriza soil. Plant and Soil 28: 413-421.
- 56. Cai GD, Chen RE, White XH, Fan A, Pacholski ZL, et al. (2002) Gaseous nitrogen losses from urea applied to maize on a calcareous fluvo-aquic soil in the North China Plain. Australian Journal of Soil Research 40: 737-748.
- 57. Fenn LB, Matocha JE, Wu E (1980) A comparison of calcium carbonate precipitation and pH depression on calcium-reduced ammonia loss from surface-applied ammonia. Soil Science Society of America Journal 44: 1128-1131.
- Stumpe, JM, Vlek PLG, Lindsay WL (1984) Ammonia volatilization from urea and urea phosphates in calcareous soils. Soil Science Society of America Journal 48: 921-927.
- Fan XH, Song YS, Lin DX, Yang LZ, Zhou JM (2005) Ammonia volatilization losses from urea applied to wheat on a paddy soil in Taihu region, China. Pedosphere 15: 59-65.
- 60. Tian G Cai Z, Cao J, Li X (2001) Factors affecting ammonia volatilisation from a rice-wheat rotation system. Chemosphere 42: 123-129.
- Black AS, RR Sherlock, NP Smith (1987) Effect of timing of simulated rainfall on ammonia volatilization from urea, applied to soil of varying moisture content. Journal of Soil Science 38: 679-687.
- Watson CJ, Kilpatrick DJ (1991) The effect of urea pellet size and rate of application on ammonia volatilization and soil nitrogen dynamics. Fertilizer Res 28: 163-172.
- 63. Rimski-Korsakov H, Rubio G, Lavado RS (2012) Fate of nitrogen from fertilizers in field-grown maize. Nutrient Cycling in Agroecosystems 8: 253-263.
- 64. Rojas CAL, Bayer C, Fontoura SMV, Weber MA, Vieiro F (2012) Ammonia volatilization from urea as affected by tillage systems ad winter cover crops in the south central region of Parana. RevistaBrasileira de Ciência do Solo 36: 261-270.
- Sommer SG, Olesen JE (1991) Effects of dry matter content and temperature on ammonia loss from surface-applied cattle slurry. J Environ Qual 20: 679-683.
- Sommer SG, Hutchings NJ (2001) Ammonia emission from field applied manure and its reduction-invited paper. Eur J Agron 15: 1-15.

- Sommer SG, Jensen C(1994) Ammonia volatilization from urea and ammoniacal fertilizers surface applied to winter wheat and grassland. Fert Res 37: 85-92.
- Svensson L (1994) Ammonia volatilization following application of livestock manure to arable land. J Agr Eng Res 58: 241-260.
- 69. Thompson RB, Pain BF, Rees YJ (1990) Ammonia volatilization from cattle slurry following surface application to grassland. II. Influence of application rate, wind speed and applying slurry in narrow bands. Plant and Soil 125: 119-128.
- Misselbrook, TH, Smith KA, Johnson RA, Pain BF (2002) Slurry application techniques to reduce ammonia emissions: results of some UK field-scale experiments. Biosystems Engineering 81: 313-321.
- Smith KA, Jackson DR, Misselbrook TH, Pain BF, Johnson RA (2000) Reduction of ammonia emission by slurry application technique. Journal of Agriculture and Engineering Research 77(3): 277-287.
- Huijsmans JFM, Hol JMG, Vermeulen GD (2003) Effect of application method, manure characteristics, weather and field conditions on ammonia volatilization from manure applied to arable land. Atmospheric Environment 37: 3669-3680.
- Bussink DW, O Oenema (1998) Ammonia volatilization from dairy farming systems in temperature areas: a review. Nutrient Cycling in Agroecosystems 51: 19-33.
- 74. Nieder R, Benbi D (2008) Carbon and Nitrogen in the Terrestrial Environment. Springer. Dordrecht, South Holland, Netherlands.
- Carter M, Gregorich E (2008) Soil Sampling and Methods of Analysis. CRC Press, Boca Raton, Florida, USA.
- Prasad R, J Power (1997) Soil Fertility Management for Sustainable Agriculture, CRC Press LLC, Florida, USA.
- Smil V (2001) Enriching the Earth: Fritz Haber, Carl Bosch, and the transformation of world food production. Massachusetts Institute of Technology, Cambridge, Massachusetts, USA.
- EDGAR (2013) Nitrous Oxide. Emission Database for Global Atmospheric Research. Emission Database for Global Atmospheric Research. European Commission, London.
- EC (2013) Nitrogen oxide emission by source in Canada. Environment Canada, Quebec, Canada.
- 80. IPCC (2006) N<sub>2</sub>O Emissions from Managed Soils and CO2 Emissions from Lime and Urea Application. In: IPCC Guidelines for National Greenhouse Gas Inventories. Intergovernmental Panel for Climate Change (IPCC), Geneva, Switzerland. Agricultural, Forestry and Other Land Use 4: 11.1-11.54.
- Aneja V, Roelle P, Murray G, Southerland J, Erisman J, et al. (2001) Atmospheric Nitrogen Compounds II: Emissions, Transport, Transformation, Deposition and Assessment. Atmospheric Environment 35: 1903-1911.
- Chadwick M, Huryn A (2005) Response of Stream Mactoinvertebrate Production to Atmospheric Nitrogen Deposition and Channel Drying. American Society of Limnology and Ocenography 50: 228-236.
- 83. Cape JN, Kirika A, Rowland AP, Wilson DR, Jickells TD, et al. (2001) Organic nitrogen in precipitation: Real problem or sampling artefact? Optimizing Nitrogen Management in Food and Energy Production and Environmental Protection: Proceedings of the 2nd International Nitrogen Conference on Science and Policy. The Scientific World 1: 230-237.
- Cape JN, Anderson M, Rowland AP, Wilson D (2004) Organic nitrogen in precipitation across the United Kingdom. Water Air and Soil Pollution Focus 4: 25-35.
- Goldberg MC (1970) Source of nitrogen in water supplies. In: Agricultural Practice and Water Quality. Iowa State University Press, Iowa, USA.
- 86. IPCC (1992) Climate Change. In: Houghton JT, Callander BA, Varney SK (eds.) The Supplementary Report to the IPCC Scientific Assessment. Published for the Intergovernmental Panel for Climate Change (IPCC), Geneva, Switzerland. Cambridge University Press, Cambridge, UK.
- Mosier AR (1994) Nitrous oxide emissions from agricultural soils. Fertilizer Research 37: 191-200.
- Mosier AR., Duxbury JM, Freney JR, Heinemeyer O, Minami K, et al. (1996) Nitrous oxide emissions from agricultural fields: Assessment, measurement and mitigation. Plant and Soil 181: 95-108.
- Grosso S (2008) Estimating Agricultural Nitrous Oxide Emissions. EOS Transactions American Geophysical Union 89: 529-540.

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- Moiser A, Kroeze C, Nevison C, Oenema O, Seitzinger, et al. (1998) Closing the global N2O budget: nitrous oxide emissions through the agricultural nitrogen cycle. Nutrient Cycling in Agroecosystems, 52: 225-248.
- 91. World Bank (2013) Population Statistics, World Bank, Washington DC, USA.
- 92. EPA (1999) Nitrogen oxides (NOx), why and how they are controlled. Clean Air Technology Center (MD-12) Information Transfer and Program Integration Division, Office of Air Quality Planning and Standards, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina.
- Butcher SS, RJ Charlson, GH Orians, GV Wolfe (1992) Global biogeochemical cycles. Academic Press, New York, USA.
- Evans RD, Ehleringer JR (1994) Water and nitrogen dynamics in arid woodland. Oecologia 99: 233-242.
- 95. Noble IR (1995) Deserts in a changing climate: Impacts. In: Watson RT, Zinyowera MC, Moss RH (eds). Climate Change, Scientific-technical analyses of impacts, adaptations, and mitigation of climate change, The Intergovernmental Panel on Climate Change (IPCC) second assessment report, Geneva, Switzerland.
- 96. Ehleringer JR, Mooney HA, Rundel PW, Evans RD, Palms B, et al. (1992) Lack of nitrogen cycling in the Atacama Desert. Nature 359: 316-318.
- Holloway JM, Dahlgren RA, Hansen B, Casey WH (1998) Contribution of bedrock nitrogen to high nitrate concentrations in stream water. Nature 395: 785-788.
- Blatt H, Jones RL (1975) Proportions of exposed igneous, metamorphic, and sedimentary rocks. Geological Society of American Bulletin 86: 1085-1088.
- Morford SL Houlton BZ, Dahlgren RA (2011) Increased forest ecosystem carbon and nitrogen storage from nitrogen rich bedrock. Nature 477: 78-81.
- 100. Mulvaney RL, Khan SA, Ellsworth TR (2009) Synthetic nitrogen fertilizers deplete soil nitrogen: a global dilemma for sustainable cereal production. Journal of Environmental Quality 38: 2295-2314.
- 101.Kjaergaard T (1994) The Danish Revolution: An ecohistorical interpretation. Translated by D. Hohnen. Cambridge University Press, Cambridge, UK 1500-1800.
- 102. Galloway JN (1998) The global nitrogen cycle: changes and consequences. Environmental Pollution 1: 15-24.
- 103.FAO (2012) World stocks 2010. Food and Agricultural Organization, Rome, Italy.
- 104. World Resources Institute (2012) Fertilizer use (most recent) by country. World Resources Institute, Washington DC, USA.
- 105.Epoch (2011) Fertilizer Overuse Damage Agriculture and Environment in China.
- 106. Xing GX, Zhu JL (2000) An assessment of N loss from agricultural field to the environment in China. Nutrient Cycling in Agroecosystem 57: 67: 73.
- 107. Oomen, GJM, Lantinga EA, Goewie EA, Van der Hoek KW (1998) Mixed farming systems as a way towards a more efficient use of nitrogen in European Union agriculture, Environmental Pollution 51: 697-704.
- 108.USDA (2013) Fertilizer Use. United States Department of Agriculture, Washington DC, USA.
- 109. Baird J (1997) Nitrogen Management and Water Quality. Soil Facts. The North Carolina Agricultural Extension Service. North Carolina State University, Raleigh North Carolina. AG-439-2.
- 110. Byrnes BH (1990) Environmental Effects of N Fertilizer use- An Overview. Fertilizer Research 26: 209-215.
- Hooda PS Edwards AC, Anderson HA, Miller A (2000) A review of water quality concerns in livestock farming areas. Sci Total Environ 250: 143-167.
- 112. Bouman AF, G Van Drecht, KW Van der Hoek (2005) Global and regional surface nitrogen balances in intensive agricultural production systems for the period 1970-2030. Pedosphere 15: 137-155.
- 113. Iqbal MT (2006) Study on vertical and lateral leaching of nitrate from a wheat field in China. Turkish Journal of Agriculture and Forestry 30: 59-65.
- Platzer C (1999) Design recommendations for subsurface flow constructed wetlands for nitrification and denitrification, Water Science and Technology 40: 257-263.

- 115. Randall GW Mulla DJ (2001) Nitrate nitrogen in surface waters as influenced by climatic conditions and agricultural practices. J Environ Qual 30: 337-344.
- 116. Bolton EF, JW Aylesworth, FR Hore (1970) Nutrient losses through the drains under tree cropping systems and two fertility levels on a Brookston clay soil. Canadian Journal of Soil Science 50: 275-279.
- 117. Randall GW, Huggins DR, Russelle MP, Fuchs DJ, Nelson WW, Anderson JL (1997) Nitrate losses through subsurface tile drainage in conservation reserve program, alfalfa and row crop systems. Journal of Environmental Quality 26: 1240-1247.
- 118. USDA-FSA (2013) Conservation Reserve Program. United States Department of Agriculture-Farm Service Agency, Kansas City, Missouri, USA.
- 119. Kladivko EJ Frankenberger JR, Jaynes DB, Meek DW, Jenkinson BJ, et al. (2004) Nitrate leaching to subsurface drains as affected by drain spacing and changes in crop production system. J Environ Qual 33: 1803-1813.
- 120. Randall GW, Goss MJ (2008) Nitrate losses to surface water through subsurface tile drainage. In: Follett RF, Hatfield JL (eds.) Nitrogen in the environment: Sources, problems, and management. 2nd edn), Elsevier Science B.V., Amsterdam, Netherlands.
- 121.FAO (2013) FAOSTAT Database-Livestock Primary. Meat Consumption. Food and Agriculture Organization of the United Nation, Rome, Italy.
- 122.FAO (2013a) FAOSTAT Database-Live Animals. Food and Agriculture Organization of the United Nation, Rome, Italy.
- 123.Larsen J (2012) Meat consumption in China now double that in the United States. Earth Policy Institute, Washington DC, USA.
- 124. Statistics C (2012) Cattle Statistics. Statistics Canada, Ottawa, Ontario, Canada.
- 125. Hribar C (2010) Understanding concentrated animal feed operations and their impact on communities. National Association of Local Boards of Health, Bowling Green, Ohio, USA.
- 126.Sundrum A (2001) Organic live stock farming: A review. Livest Prod Sci 67: 207-215.
- 127. Phang J (2013) Concentrated animal feeding operations. Seton Hall University School of Law, Newark, New Jersey, USA.
- 128.Olson BM, Miller JJ, Rodvang SJ, Yanke LJ (2005) Soil and groundwater quality under a cattle feedlot in southern Alberta, Water Quality Research Journal of Canada, 40: 131-144.
- 129. Mackie RI Stroot PG, Varel VH (1998) Biochemical identification and biological origin of key odor components in livestock waste. J Anim Sci 76: 1331-1342.
- 130. Socolow RH1 (1999) Nitrogen management and the future of food: lessons from the management of energy and carbon. Proc Natl Acad Sci U S A 96: 6001-6008.
- 131.Burkholder J, Libra B, Weyer P, Heathcote S, Koplin D, et al. (2007) Impacts of waste from concentrated animal feeding operations on water quality. Environmental Health Perspectives 115: 308-312.
- 132. Sherman DG (2008) The untold costs of confined animal feeding operations. Union of Concerned Scientists (USC) Food Environment Program, Cambridge, Massachusetts, USA.
- 133.FAO (2013b) FAOSTAT Database-Livestock primary. Producing Animals/ Slaughtered (Head). Food and Agriculture Organization of the United Nation, Rome, Italy.
- 134.Kohn RA Dinneen MM, Russek-Cohen E (2005) Using blood urea nitrogen to predict nitrogen excretion and efficiency of nitrogen utilization in cattle, sheep, goats, horses, pigs, and rats. J Anim Sci 83: 879-889.
- Lopez G, Leeson S (1995) Nitrogen content of manure from older broiler breeders fed varying quantities of crude protein. Journal of Applied Poultry Research 4: 390-394.
- 136.Shannon JA (1938) The excretion of uric acid by the chicken. Journal of Cellular and Comparative Physiology 11: 135-148.
- 137.USDA (2013b) National Program 206: Manure and Byproduct utilization annual report. United States Department of Agriculture, Washington DC, USA.
- 138.Westerman PW, Huffman RL, Feng JS (1995) Swine-lagoon seepage in sandy soil. Trans Am Soc Agricult Engineers 38: 1749-1760.

Page 25 of 26

- 139. Stone KC, Hunt PG, Coffey SW, Matheny TA (1995) Water quality status of A USDA water quality demonstration project in the Eastern Coastal Plain. J Soil Water Conserv 50: 567-571.
- 140.Varel V (1997) Use of Urease Inhibitors to Control Nitrogen Loss from Livestock Waste. Bioresour Technol 62: 11-17.
- 141.Ndegwa PM, Hristov AN, Arogo J, Sheffield RE (2008) A review of ammonia emission mitigation techniques for concentrated animal feeding operations, Biosystems Engineering 100: 453-469.
- 142. Saint-Fort R, Raina RM, Prescott B (1995) Subsurface environmental quality under a cattle feedlot and adjacent cropfield. Journal of Environment Science and Health, Part A 30: 637-650.
- 143. Mahmoodabadi MR, Amini S, Khazaeepoul K (2010) Using animal manure for improving soil chemical properties under different leaching conditions. Middle East Journal of Scientific Research 5: 214-217.
- 144. Dikinya O, Mufwanzala N (2010) Chicken manure enhanced soil fertility and productivity: effects of application rates. Journal of Soil Science and Environmental Management 1: 46-54.
- 145. López-Mosquera ME Cabaleiro F, Sainz MJ, López-Fabal A, Carral E (2008) Fertilizing value of broiler litter: effects of drying and pelletizing. Bioresour Technol 99: 5626-5633.
- 146. Whalen JK, Chang C, Clayton GW, Carefoot JP (2000) Cattle manure amendments can increase the pH of acid soils. Soil Sci Soc Am J 64: 962-966.
- 147. Plaza C, Hernandez D, Garcia Gill JC, Polo A (2004) Microbial activity in pig slurry-amended soils under semiarid conditions. Soil Biology and Biochemistry 36: 1577-1585.
- 148.Naramabuye FX, Haynes RJ (2006a) Effect of organic amendments on soil pH and Al solubility and use of laboratory indices to predict their liming effect. Soil Science 177: 754-763.
- 149. Duruigbo CI, Obiefuna JC, Onweremadu EU (2007) Effects of poultry manure rates on soil activity in an Utisol. International Journal of Soil Science 2: 154-158.
- 150. Mokolobate MS, Haynes RJ (2002) Increases in pH and soluble salts influence the effect that additions of organic residues have on concentrations of exchangeable and soil solution aluminium. European Journal of Soil Science 53: 481-489.
- 151.Naramabuye FX, Haynes RJ (2006a) Effect of organic amendments on soil pH and Al solubility and use of laboratory indices to predict their liming effect. Soil Science 177: 754-763.
- 152. Tang Y, Zhang H, Schroder JL, Payton ME, Zhou D (2007) Animal manure reduces aluminum toxicity in an acid soil. Soil Science Society of America Journal 71: 1699-1707.
- 153. Ano AO, Ubochi CI (2007) Neutralization of soil acidity by animal manures: mechanism of reaction. African Journal of Biotechnology 6: 364-368.
- 154.Naramabuye FX, Haynes RJ (2007) The liming effect of five organic manures when incubated with an acid soil, Journal of Plant Nutrition and Soil Science 170: 615-622.
- 155. Whalen JK, Chang C, Clayton GW (2002) Cattle manure and lime amendments to improve crop production of acidic soils in northern Alberta. Canadian J Soil Sci 82: 227-238.
- 156. Loria ER, Sawyer JE (2005) Extractable soil phosphorus and inorganic nitrogen following application of raw and anaerobically digested swine manure. Agronomy Journal 97: 879-885.
- 157. Shen QR Shen ZG (2001) Effects of pig manure and wheat straw on growth of mung bean seedlings grown in aluminium toxicity soil. Bioresour Technol 76: 235-240.
- 158. Pescod M (1992) Wastewater Treatment and use in Agriculture FAO Irrigation and Drainage Paper No. 47. Wastewater Characteristics and Effluent Quality Parameters. FAO Corporate Document Repository, Food and Agriculture Organization of the United Nations, Rome, Italy.
- 159. Guyer PE (2010) An Introduction to Domestic Wastewater Treatment. Guyer Partners, El Macero, California, USA.
- 160.Metacalf, Eddy (2004) Wastewater Engineering: Treatment and Reuse (4thedn) McGraw Hill publication, New York, USA.

- 161.Wen D, Huai-en (2011) Analysis on Nitrogen Pollution Characteristics of Weihe River. Xian University, Xian, China.
- 162.Zhang X, Xia X, Yang Z (2007) Reasons of High Concentration Ammonium in Yello River, China. Environmental Simulation and Pollution Control, School of Environment, Beijing University, 28: 1437-41.
- 163. Galloway JN Townsend AR, Erisman JW, Bekunda M, Cai Z, et al. (2008) Transformation of the nitrogen cycle: recent trends, questions, and potential solutions. Science 320: 889-892.
- 164. Galloway JN, Dentener FJ, Capone DG, Boyer EW, Howarth RW, et al. (2004) Nitrogen Cycles: past, present and future. Biogeochemistry 70: 153-226.
- 165.ERFB (2005) River Pollution Case Study, Summary Report on Pollution of Tolka River Near Clonee, Co. Eastern Regional Fisheries Board, Dublin, Ireland.
- 166. Carpenter S, Caraco NF, Correll DL, Howarth RW, Sharpley AN, et al. (1998) Nonpoint pollution of surface waters with phosphorous and nitrogen. Issues in Ecology 3: 1-12.
- 167. Puckett L J (1994) Nonpoint and point sources of nitrogen in major watersheds of the United States, Water Resources Investigations Report, U. S. Geological Survey, Reston, Virginia, USA 94-4001: 1-12.
- 168. Rouse JD Bishop CA, Struger J (1999) Nitrogen pollution: an assessment of its threat to amphibian survival. Environ Health Perspect 107: 799-803.
- 169. Kean AJ, Harley RA, Littlejohn D, Kendall GA (2000) On road measurement of ammonia and other motor vehicle exhaust emissions. Environmental Science and Technology 34: 3535-3539.
- 170. Wetzel RG (1983) Limnology. Saunders College Publishing, Philadelphia, Pennsylvania, USA.
- Burkholder JM (2000) Eutrophication and oligotrophication. In: Levin S (ed.) Encyclopedia of Biodiversity, Academic Press, New York, USA, 2: 649-670.
- 172.Xiangcan J, Qiujin X, Changzhu H (2005) Current status and future tendency of lake eutrophication in China. Science in China Series C: Life Sciences 48: 948-954.
- 173. Vadeboncoeur Y, Jeppesen E, Zanden MJV, Schierup HH, et al. (2003) From Greenland to green lakes: cultural eutrophication and the loss of benthic pathway in lakes. Limnol Oceanogr 48: 1408-1418.
- Dugdale RC, Goering JJ (1967) Uptake of new and regenerated forms of nitrogen in primary productivity. Limnology and Oceanography 12: 196-206.
- 175. Glibert PM, Magnien R, Lomas MW, Alexander J, Fan C, et al. (2001) Harmful algal blooms in the Chesapeake and coastal bays of Maryland, USA: Comparison of 1997, 1998, and 1999 events. Estuaries 24: 875-883.
- 176. Fisher TR, Carlson PR Barber RT (1982) Carbon and nitrogen primary productivity in three North Carolina estuaries. Estuarine, Coastal, and Shelf Science 15: 621-644.
- 177. Mallin MA, Paerl HW, Rudek J, Bates PW (1993) Regulation of estuarine primary production by watershed rainfall and river flow. Marine Ecology Progress Series 93: 199-203.
- 178. National Research Council (2000) Glean Coastal Waters—Understanding and Reducing the Effects of Nutrient Pollution, National Academy Press Washington, DC, USA.
- 179. Wu RSS, Lam PKS, Mackay DW, Lau TC, Yam V, et al. (1994) Impact of marine fish farming on water quality and bottom sediment: A case study in the subtropical environment. Marine Environmental Research 38: 115-145.
- 180. Romdhane MS, Eilertsen HC, Yahia OKD, Yahia MND (1998) Toxic dinoflagellate blooms in Tunisian lagoons: Causes and consequences for aquaculture, In Reguera B, Balance J, Ferndez ML, Wyatt T (eds.), Harmful Algae. Xunta de Galicia and Intergovernmental Oceanographic Commission of United Nations Educational Scientific and Cultural Organization, Paris, France.
- 181.Zhang J (1994) Atmospheric wet depositions of nutrient elements: Correlations with harmful biological blooms in the Northwest Pacific coastal zones. Ambio 23: 464-468.
- 182. Hodgkiss IJ, Ho KC (1997) Are changes in N:P ratios in coastal waters the key to increased red tide blooms? Hydrobiologia 852: 141-147.
- 183. Hodgkiss IJ (2001) The N: P ratio revisited. In: Ho KC, ZD Wang (eds.)

Prevention and Management of Harmful Algal Blooms in the South China Sea., School of Science and Technology, The Open University of Hong Kong, Kowloon, Hongkong.

- 184. Takahashi M, Koike I, Iseki K, Bienfang PK, Hattori A (1982) Phytoplankton species responses to nutrient changes in experimental enclosures and coastal waters. In: Marine Mesocosms: Biological and Chemical Research in Experimental Ecosystems. Springer-Verlag, New York, USA.
- 185. Goldman JC (1993) Potential role of large oceanic diatoms in new primary production. Deep Sea Research Part I: Oceanographic Research Papers 40: 159-168.
- 186. Glibert PM Terlizzi DE (1999) Cooccurrence of elevated urea levels and dinoflagellate blooms in temperate estuarine aquaculture ponds. Appl Environ Microbiol 65: 5594-5596.
- 187. Glibert PM, O'neil JM (1999b) Dissolved organic nitrogen release and amino acid oxidase activity by Trichodesium spp., In: Charpy L, Larkum AWD (eds.) Marine Cyanobacteria. Bulletin de l'Instimte Oceanographique, Monaco Musee Oceanographique, Monaco. pp. 265-271.
- 188.Smith VH Tilman GD, Nekola JC (1999) Eutrophication: impacts of excess nutrient inputs on freshwater, marine, and terrestrial ecosystems. Environ Pollut 100: 179-196.
- 189.McGarrigle ML (1993) Aspects of river eutrophication in Ireland. Annals of Limnology 29: 355-364.
- 190. Miltner R.J, Rankin ET (1998) Primary nutrients and the biotic integrity of rivers and streams. Freshwater Biology 40: 145-158.
- Anderson DM, Glibert PM, Burkholder JM (2002) Harmful algal blooms and eutrophication: nutrient sources, composition and consequences. Estuaries 25: 704-726.
- 192. Duan H Ma R, Xu X, Kong F, Zhang S, et al. (2009) Two-decade reconstruction of algal blooms in China's Lake Taihu. Environ Sci Technol 43: 3522-3528.
- 193. Mackenthum KM (1969) The practice of water pollution biology. Federal Water Pollution Control Administration, Washington DC, USA.
- 194. Anderson DM Kulis DM, Sullivan JJ, Hall S (1990) Toxin composition variations in one isolate of the dinoflagellate Alexandrium fundyense. Toxicon 28: 885-893.
- 195. Boyer GL, JJ Sullivan, RJ Andersen, PJ Harrison, FJR Taylor (1987) Effects of nutrient limitation on toxin production and composition in the marine dinoflagellate Protogonnyaulax tamarensis. Marine Biology 96: 128-128.
- 196.Biggs BJF (2000) Eutrophication of streams and rivers: dissolved nutrientchlorophyll relationships for benthic algae. Journal of the North American Benthological Society 19: 17-31.
- 197.Webb J, Archer JR (1994) Pollution of soils and watercourses by wastes from livestock production systems. In: Dewi IA, Axford RFE, Marai IFM, Omed HM (eds) Pollution in Livestock Production Systems. CABI Publishing, Oxfordshire, UK.
- 198. Skinner JA, Lewis KA, Bardon KS, Tucker P, Catt JA, et al. (1997) An overview of the environmental impact of agriculture in the UK. Journal of Environmental Management 50: 111-128.
- 199. Mellon MC, Benbrook C, Benbrook KL (2001) Estimates of antimicrobial abuse in livestock. Union of Concerned Scientists, Cambridge, Massachusetts, USA.
- 200. WHO (1999) Human health aspects. In: Toxic cyanobacteria in water: a guide to their public health consequences, monitoring and management, World Health Organization, Geneva, Switzerland.
- 201. Carmichael WW Azevedo SM, An JS, Molica RJ, Jochimsen EM, et al. (2001) Human fatalities from cyanobacteria: chemical and biological evidence for cyanotoxins. Environ Health Perspect 109: 663-668.
- 202. Heldin RA (1971) Nitrate contamination of ground water in the Neepawa-Langruth area of Manitoba. Canadian Journal of Soil Science 51: 75-84.
- 203. Cornell SE, Jickells TD, Cape JN, Rowland AP, Duce RA (2003) Organic nitrogen deposition on land and coastal environments: a review methods and data. Atmospheric Environment 37: 2173-2191.

204. Raes F, Van Dingenen R, Vignati E, Wilson J, Putaud JP, et al. (2000) Formation and cycling of aerosols in the global troposphere. Atmospheric Environment 3 4215-4240.

Page 26 of 26

- 205. Camargo JA Alonso A (2006) Ecological and toxicological effects of inorganic nitrogen pollution in aquatic ecosystems: A global assessment. Environ Int 32: 831-849.
- 206. Koneswaran G Nierenberg D (2008) Global farm animal production and global warming: impacting and mitigating climate change. Environ Health Perspect 116: 578-582.
- 207.Koelliker JK, Miner JR (1970) Use of soil to treat anaerobic lagoon effluent renovations as a function of depth and application rate. Transactions of American Society of Agricultural Engineers 13: 496-499.
- 208. DEFRA (2002) Ammonia in the UK. Department for Environment Food & Rural Affairs. DEFRA Publications, London, UK.
- 209. Gay SW, Knowlton KF (2009) Ammonia emissions and animal agriculture. Virginia Cooperative Extension. Publication No. 442-110. Virginia Polytechnic Institute and State University, Blacksburg, Virginia, USA.
- 210. Oenema O, Velthof G, Klimont Z, Winiwarter W (2012) Emissions from agriculture and their control potentials. Thematic Strategy on Air Pollution Review (TSAP). International Institute for Applied Systems Analysis, Laxenburg, Austria.
- Mulbarger MC (1971) Nitrification and denitrification in activated sludge systems. Water Pollution Control Federation 43: 2059-2070.
- 212.Strous M, Gerven EV, Zheng P, Kuenen JG, Jetten MS (1997) Ammonium removal from concentrated waste streams with the anaerobic ammonium oxidation (anammox) process in different reactor configurations. Water Res 31: 1955-1962.
- Mulder A, van de Graaf AAA, Robertson LA, Kuenen JG (1995) Anaerobic ammonium oxidation discovered in a denitrifying fluidized bed reactor. FEMS Microbiology Ecology 16: 177-184.
- 214.Jetten MS Wagner M, Fuerst J, van Loosdrecht M, Kuenen G, et al. (2001) Microbiology and application of the anaerobic ammonium oxidation ('anammox') process. Curr Opin Biotechnol 12: 283-288.
- 215.Dong X Tollner EW (2003) Evaluation of Anammox and denitrification during anaerobic digestion of poultry manure. Bioresour Technol 86: 139-145.
- 216.Liao PH, Chen A, Lo KV (1995) Removal of nitrogen from swine manure wastewaters by ammonia stripping. Bioresource Technology 54: 17-20.
- 217. Flynn HC (2009) Agriculture and climate change: an agenda for negotiation in Copenhagen. The role of nutrient management in mitigation. International Food Policy Research Institute, Washington DC, USA.
- 218. Tilman D Cassman KG, Matson PA, Naylor R, Polasky S (2002) Agricultural sustainability and intensive production practices. Nature 418: 671-677.
- 219.AESAC (2000) Greenhouse gas emissions Alberta's cropping industry. Alberta Environmentally Sustainable Agriculture Council, Edmonton, Alberta.
- 220.Naylor RL (1996) Energy and resource constraints on intensive agricultural production, Annual Review of Energy and Environment 21: 99-123.