# OXIDIZED AND REDUCED NITROGEN IN THE ATMOSPHERE

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## Contents

UNESCO – EOLSS SAMPLE CHAPTERS

## Summary

Nitrogen plays a vital role in food production, and helps to feed the world's ever growing population. At the same time, considerable amounts of nitrogen are lost to the environment in the production of food and energy. This leads to an unbalance in the nitrogen cycle, which results in problems with human health and damage to ecosystems. An important component in the nitrogen cycle is the emission, transport and deposition of oxidized and reduced nitrogen. The emissions result from combustion processes, especially of fossil fuels, from industries and agriculture. Deposition of these forms of nitrogen result in acidification and eutrophication of terrestrial and aquatic ecosystems, algae blooms, effects on marine ecosystems and climate changes. In the past years measures have been taken to abate nitrogen emissions, especially $NO_x$. Europe has been successful in reducing the emissions of several nitrogenous pollutants over recent decades. This is reflected in concentrations and deposition rates that have decreased for several components. Emissions of nitrogen containing gases are estimated to have decreased in Europe by 8%, 30% and 9% for $N_2O$, $NO_x$ and $NH_3$, respectively, between 1990 and 2002. The main reductions are the result of a decrease in industrial and agricultural activities in the east of Europe as a result of the economic situation, measures in the transport sector, industry and agricultural sector, with only a small part of the reduction due to specific measures designed to reduce emissions. The reduction is significant, but far from the end goal for large areas in Europe in relation to different environmental problems. So far, much of the "nitrogen" policy has been aimed at a single nitrogen compound, which can shift the environmental problem to other compartments and in time. An integrated approach will lead to a more efficient and cost-effective policy.

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## 1. Introduction

The atmosphere contains almost 80% of nitrogen gas ($N_2$). In this form nitrogen is not relevant for environmental issues. Once nitrogen is in a reactive form, either reduced or oxidized, it has a very different role. In this form it is essential for life on earth. Proteins need nitrogen and therefore a certain amount of reactive nitrogen in the bio-chemical cycles is necessary. The global nitrogen cycle is being perturbed in many ways. Fossil fuel combustion, mineral fertilizers and livestock manure's all provide major sources of fixed reactive nitrogen ($N$). This leads to a cascade of effects as the $N$ is transported and transformed through the environment (e.g. Vitousek et. al., 1997; Mansfield et. al., 1998; Langan, 1999). The major man-made atmospheric oxidized and reduced forms of $N$ are nitric oxide, $NO$ and nitrogen dioxide, $NO_2$ and ammonia, $NH_3$. The other abundant atmospheric oxide of nitrogen, nitrous oxide, $N_2O$, which, although important as a greenhouse gas, does not participate actively in atmospheric chemical processes in the lower atmosphere. Emissions of oxidized and reduced nitrogen to the atmosphere result in impacts on human health through particle and ozone (nitrogen oxides) formation, visibility, crop loss, regional acidification and eutrophication, as well as global warming, while releases to land result in eutrophication of both fresh and coastal waters.

This chapter describes the emission processes of oxidized and reduced nitrogen and the major source categories. Furthermore, it gives estimates of the European and global nitrogen emissions. The losses in the atmosphere through chemical reactions and through deposition are discussed. The chapter ends with some conclusions.

## 2. Emissions

There are several processes that lead to emissions of oxidized or reduced nitrogen to the atmosphere. In general these are grouped according to source categories, which in turn are linked to target groups. This is done to support policy development and measures to reduce the emissions in order to limit its effects. In this chapter first the oxidized nitrogen sources will be described followed by a discussion on sources of reduced nitrogen components.

### 2.1. Oxidized Nitrogen

The primary emission of oxidized nitrogen is through the formation of nitrogen oxide ($NO$). The only other gas that can be directly emitted is nitrous oxide ($N_2O$). All other oxidized nitrogen compounds are formed through reactions in the atmosphere. Oxidized nitrogen has several sources, but is formed mainly at combustion processes where fuel $N$ is oxidized or atmospheric $N_2$ is oxidized at high temperatures. These processes are relevant for industries, traffic and energy production. Among the other sources of oxidized nitrogen, soils are most important. In this section first the combustion processes will be discussed followed by a description of the soil emissions.

#### 2.1.1. Oxidized Nitrogen Formed by Combustion Processes

$NO$ is known to be formed in a variety of ways (Dean and Bozzelli, 1999): i) "Thermal $NO$" (Zeldovich 1946) is primarily a consequence of high flame temperatures; ii) "Prompt $NO$" (Fenimore 1976) is generated in fuel-rich parts of flames; iii) the "$N_2O$ mechanism" (Wolfrum 1972; Malte and Pratt 1974) can be important in high-pressure flames; iv) "Fuel nitrogen" $NO$ (Fenimore 1976) results from converting nitrogen containing compounds in the fuel into $NO$; and v) the $NNH$ mechanism (Bozzelli and Dean 1995) is active in flame fronts where high atom concentrations appear. All but iv) convert atmospheric nitrogen into $NO$ and relate to all fuels, while pathway iv) pertains to flames of petroleum, coal, and biomass. The different pathways will be discussed below.

*Thermal, or Zeldovich,* $NO$

The principal elementary reactions here are:

$$O + N_2 \leftrightarrow NO + N \quad (1)$$

$$N + O_2 \leftrightarrow NO + O \quad (2)$$

$$N + OH \leftrightarrow NO + H \quad (3)$$

The first two reactions compose a chain sequence, so a small amount of atomic oxygen can produce large amounts of $NO$. The first one is rate limiting because of its high activation energy, about 320 kJ/mol. The Zeldovich mechanism is very sensitive to temperature not only because of the high activation energy of reaction (1), but also because the concentration of oxygen atoms in flames increases rapidly with increasing temperature.

*Prompt, or Fenimore,* $NO$

This is aptly called Prompt $NO$, because it is manifested by prompt, that is, rapid, production of $NO$ in a flame front. In a flame front, the concentration of hydrocarbon

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radicals is large, and $NO$ production is initiated by their reaction with $N_2$ to break the N-N bond. The most important such reaction is thought to be

$$CH + N_2 \leftrightarrow HCN + N \tag{4}$$

The product $N$ atom can form a $NO$ molecule via reactions (1) or (2), while the $HCN$ can lead to a second $NO$ molecule through a series of reactions.

*The* $N_2O$ *pathway*

Reaction (1) above is one pathway for reactions of oxygen atoms with molecular nitrogen. Another is intermediate formation of $N_2O$ by a "recombination reaction":

$$O + N_2 + M \leftrightarrow N_2O + M\,, \tag{5}$$

where the "collision partner" $M$ collectively represents all molecules present. The $N_2O$ formed in reaction (4) can then react to form $NO$ by

$$O + N_2O \leftrightarrow 2NO \tag{6}$$

and

$$H + N_2O \leftrightarrow NO + NH\,. \tag{7}$$

The thermo-molecular character of reaction (5) implies that it becomes more important at higher pressures.

*Fuel nitrogen*

It is frequently assumed that most fuel nitrogen is quickly converted to $HCN$ in names (Morley, 1980). The subsequent kinetics of $HCN$ is generally similar to those that apply to $HCN$ in forming Prompt $NO$. There is, however, evidence suggesting that the assumption of rapid conversion of fuel nitrogen to $HCN$ is not always valid (Mackie et al. 1990). It may eventually turn out that correct accounting for $NO$ formation from fuel nitrogen also requires including details of other N-containing species besides $HCN$.

*The* $NNH$ *mechanism*

Under combustion conditions, where the concentrations of atoms are high, that is, in flame fronts, the reaction:

$$O + NNH \leftrightarrow NO + NH \tag{8}$$

contributes significantly to $NO$ production. This mechanism requires participation of $H$ atoms to form $NNH$ from $N_2$ as well as $O$ atoms to react with $NNH$.

*Effects of temperature and pressure*

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The relative importance of the first three channels for $NO$ production in methane air flames has been addressed in a series of model calculations reported by Drake et al. (1990; 1991a; 1991b), and these can also be taken as representative of the situation for other fuels. For a 0.1 atm stoichiometric laminar premixed flame, their calculations indicated that the Fenimore mechanism was dominant. At these relatively low pressures, much of the Zeldovich $NO$ production could be traced to super-equilibrium oxygen atom concentrations. In a 20 atm stoichiometric methane air flame, the major contributor is equilibrium Zeldovich $NO$, but the higher pressure has increased the contribution of the $N_2O$ pathway to be comparable to that of Fenimore $NO$. In laminar diffusion flames at 1 atm, they concluded that Fenimore $NO$ was the dominant pathway, contributing more than two-thirds of the total $NO$, with the Zeldovich and $N_2O$ paths being comparably minor components.

These results illustrate the complexity of $NO$ production chemistry. Given the very high sensitivity to temperature of the Zeldovich route, use of different fuels (with different adiabatic flame temperatures) or considering a flame configuration with a different amount of heat loss dramatically affects the predicted amount of Zeldovich $NO$. Similarly, different fuels change the amount of CH produced in the flame front, thus affecting the amount of Fenimore $NO$ formed.

*NO reduction*

There are several reactions by which $NO$ can be converted to $N_2$ or to species that may subsequently be converted to $N_2$ during the combustion or post-combustion process. These include:

$$NO + CH_3 \leftrightarrow H_2CN + OH \qquad (9)$$

$$+ NH_2 \leftrightarrow N_2 + H_2O \qquad (10)$$

$$+ NH_2 \leftrightarrow NNH + OH \qquad (11)$$

$$+ NH \leftrightarrow N_2 + OH \qquad (12)$$

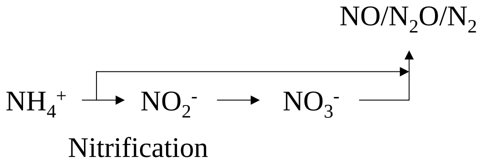
$$+ NH \leftrightarrow N_2O + H. \qquad (13)$$

The first can be important in "reburning", where additional fuel is added after the primary combustion stage (Bowman 1992). The second and third play central roles in post-combustion NO removal-Selective Non-Catalytic Reduction (SNCR)-processes such as Thermal De-$NO_x$, wherein ammonia is added in the post-combustion zone to reduce $NO_x$ emission levels in the exhaust gas (Lyon, 1975). The last two illustrate the complexity of the chemistry again: $N_2$ may be a direct product (Eq. (12)), or the initial product $N_2O$ can subsequently react either to reform $NO$ or to be converted to $N_2$.

### 2.1.2. Soil Emissions

UNESCO – EOLSS
SAMPLE CHAPTERS

Nitric oxide in soil is produced primarily by microbial nitrification (oxidation of ammonium to nitrate) and denitrification (the reduction of nitrate to gaseous forms of N ):



The release of NO from nitrification is generally considered as a leakage during the oxidation pathway and in well aerated soils this gaseous loss represents between 1 and 4% of the $NH_4$ oxidized (e.g. Fowler et. al., 1998). Similarly, NO occurs as an intermediate in the denitrification pathway, which has been shown by Remde et. al. (1989) to produce twice as much NO as nitrification. However, the anaerobic soil conditions required for denitrification limit rates of gaseous diffusion to the soil surface, and a substantial fraction of the NO produced is subsequently reduced further by denitrifiers to $N_2$ (Skiba et al., 1997). Thus nitrification processes are generally considered to be the major source of soil NO emissions. Rates of NO release from soil were shown to be regulated by three soil variables: soil temperature, soil N and gaseous diffusivity.

UNESCO – EOLSS SAMPLE CHAPTERS

The microbial oxidation of $NH_4$ in soil was shown to be strongly influenced by temperatures (Johansson and Granat, 1984). The positive relationship between soil temperature and NO emission does not, however, provide a unique or particularly reliable guide to emission fluxes. In very dry or very wet conditions for example, the influence of temperature may be strongly suppressed. The concentration of soil nitrogen has been widely shown to influence NO emission by both nitrification and denitrification. The supply of mineral fertilizer generally stimulates NO emission. The period of enhanced emission after fertilization varies with type of fertilizer, soil water content and temperature from a few days to 3 weeks. Measurements of NO emissions before and after fertilizer application have provided a means of quantifying the fractional loss of applied N . In a compilation of studies of NO emissions from grassland and arable fields, Skiba et al. (1997) showed that the NO emission represented between 0.003 and 11% of the applied N , with the individual values distributed log-normally about a geometric mean of 0.3%. By combining the temperature and soil N variables, a large data set for soil NO emission measurements can be fitted into a relatively simple linear regression model. Skiba et al. (1994) showed that in this way >60% of the variability in soil NO emissions for a variety of land use could be represented by:

$$\log\,(NO\ emission) = -3.23 + 1.01\ \log\ (soil\ NO_3) + 0.165\,(T_s)\,, \tag{14}$$

in which $T_s$ is the soil temperature at a depth of 5 cm.

The variability in NO emissions with soil water content is the consequence of two different processes. In very dry soils, the supply of substrates for microbial activity becomes the major limitation, whereas in wet soils, the rates of gaseous diffusion eventually limit the loss and the further reduction of $NO$ to $N_2$ becomes the major sink for $NO$. The most useful variable to characterize the effect of soil water on $NO$ emission is the so-called water filled pore space (WFPS). The emissions may either be increased or decreased with increasing soil moisture depending on the $NO$ productive pathway and gaseous diffusion in the soil. The optimum WFPS for $NO$ emission appears to be in the range 30-60% with a gradual decrease in emission at higher values as rates of diffusion become limiting (Fowler et al., 1998).

Nitric oxide is an intermediate in the microbial reduction of $NO_3$ and as such it is both a product and a reactant. In an atmosphere with large $NO$ concentrations, soil is a net sink for $NO$, while at low concentrations, soil is a net source. The ambient concentrations leading to a net soil-atmosphere exchange is known as the compensation point and has been shown by Johansson (1987).

## 2.2. Reduced Nitrogen

### 2.2.1. Emission Processes

Ammonia is a natural occurring gas in the atmosphere. The oceans, manure from wild animals and aging and rotting plants form the most important natural sources of $NH_3$ in the air. In the past, the highest concentrations were measured in cities, probably as the result of the presence of horses and other animals and because of the burning of coal, from which also $NH_3$ is emitted. Nowadays animal manure is considered as most important source for $NH_3$.

Volatilization of $NH_3$ from natural and anthropogenic sources depends on the chemical equilibrium and meteorological factors. With the exception of emissions from combustion processes, ammonia sources can be regarded as solutions containing $NH_4$ and/or $NH_3$, formed by biological mineralization of organic material, hydrolyses of urea, inorganic anthropogenic manure, or reactions in cells of living plants and/or animals or humans. These compounds are in equilibrium according to:

$$NH_3 + H_2O \overset{K_b}{\leftrightarrow} NH_4^+ + OH^- \qquad (15)$$

In which:

$$K_b = [NH_4^+]\,[OH^-] / [NH_3] \qquad (16)$$

The $NH_3/NH_4$ ratio strongly depends on the pH: at pH < 6 the ratio is zero and approaches one at pH > 10. The equilibrium also depends on the temperature of the solution; at increasing temperatures the equilibrium in Eq. (15) shifts to the left, so more emission of $NH_3$ to the atmosphere (or from the solution) and vice versa. Henry's law can determine the vapour pressure of $NH_3$ over the solution:

UNESCO – EOLSS SAMPLE CHAPTERS

$$p_s = R\,T\,[NH_3]/H \qquad (17)$$

In this equation $p_s$ is the $NH_3$ vapor pressure, $H$ is the Henry-constant and $[NH_3]$ the molar concentration of $NH_3$ in the solution. Eq. (16) and (17) show that the $NH_3$-vapour pressure (and also the emission) increases with increasing $NH_4$ concentration in the solution, pH and temperature.

The exchange between the source and the atmosphere can be described using of Fick's law:

$$F = k(p_s - p_a) \qquad (18)$$

in which $p_a$ represents the atmospheric partial pressure of $NH_3$ and k is the exchange coefficient, which is determined by the rate of diffusion and by meteorological conditions. Emission will take place if the air over a solution shows a positive pressure difference with the atmospheric pressure. The surface concentration at which the net flux is zero is called the compensation point. The atmospheric partial pressure can be higher than the $NH_3$ vapor pressure over a number of natural sources, having low compensation points, leading to emissions. However, even by very strong sources, the effect can vary between emission and deposition, depending on the concentration of $NH_3$ in the air and the daily variation therein. In areas with many anthropogenic sources the natural sources can be neglected, because the ambient concentrations are so high that the relatively small natural sources cannot emit according to Fick's law and probably deposition will occur. In this section a short overview of the most important sources of ammonia will be given.

### 2.2.2. Source Categories

$NH_3$ can be emitted from a large number of sources: application of nitrogen containing fertilizers, burning of coal, exhaust emissions of cars equipped with a three-way catalyst, natural processes in soil and plants, domestic sources, industry and animal manure (e.g. Buijsman et al., 1987).

*Animal manure*

Animal manure is by far the most important source of ammonia to the atmosphere. Animals bred for meat or milk produce manure, which is considered an anthropogenic source. The nitrogen cycle in manure is displayed in Figure 1. It shows where in the manure cycle ammonia emissions can take place. The amount of N in the manure is the starting point of $NH_3$ emission. $NH_3$ is emitted from the manure in animal housings, during storage or in the pasture and after application in the field. In soil ammonium can be fixed by clay minerals or it can be nitrified. Nitrification is the main loss process for ammonium, next to plant uptake. An other source of N is fertilizer, which follows the same route as manure. Plants can emit ammonia through their stomata following excess

UNESCO – EOLSS SAMPLE CHAPTERS

uptake from the atmosphere or soil. During senescence some of the plant N is emitted to the atmosphere. If the plants serve as food for animals, the N cycle closes.

The emission of ammonia from manure depends on many factors, such as food composition, type and age of the animals, the surroundings where the manure is produced, the manure treatment method in and outside and the method of manure application. These factors can be influenced by meteorological conditions. The emission can be determined theoretical or with measurements (Buijsman et al., 1987; Heij et al., 1991; Asman, 1992). The amount of N in manure is calculated and the ammonia emission is estimated using emission factors, a percentage if N in manure. Emission factors for each source are derived from measurements. The source categories we distinguish are: animal-housing systems, manure storage, application of manure and from grazed pastures.

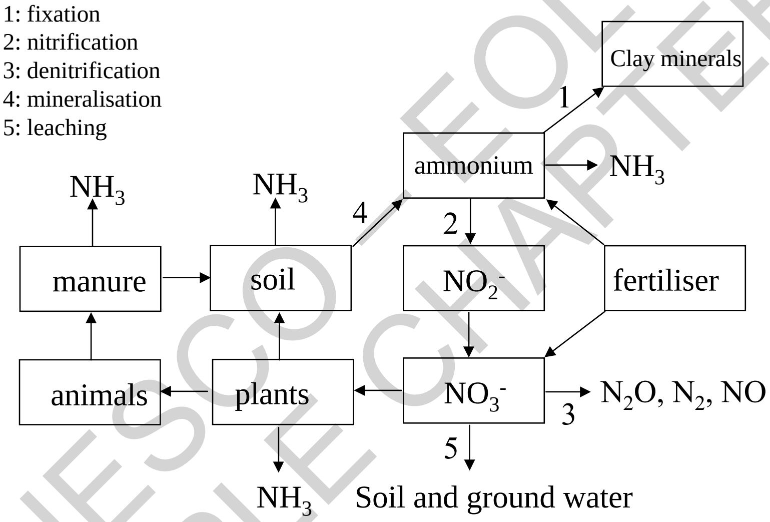


Figure 1: Nitrogen cycle at a farm

*Fertilizer*

During fertilizer production ammonia is emitted to the atmosphere. Therefore, fertilizer industries contribute to the total ammonia emissions. However, the highest contribution comes from application of the fertilizer in the field to increase crop yields. Different types of fertilizer are used, such as ammonium nitrate, ammonium sulphate, calcium nitrate, di-ammonium phosphate, ammonia solutions, etc. The emission depends on the same factors as with application of manure. Because of these different factors, the variation of the emission in space and time is very large. A typical value of 2% of the applied ammonium is taken as representative for the emission.

*Traffic*

Already in 1967 ammonia was measured in the exhaust emissions of an Oldsmobile V-8 (Harkins and Nicksic, 1967). The concentrations depended on the car speed and varied from 1 ppm during stationary conditions to 4 ppm at 40 mph and 6.5 ppm at 50 mph. The type of gasoline did not make a difference to the measured concentrations. Higher

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emissions are nowadays observed at cars equipped with three-way catalysts (Lies et al., 1986). Cars equipped with catalysts produced 60 mg $NH_3$ per mile, whereas diesels only produced 1 to 5 mg.

*Other categories*

Other anthropogenic categories include combustion of fossil fuel and biomass burning or gassification, the use of ammonia in housekeeping's, industry and wastewater treatment. Natural sources include emissions from stomata and senescence plants, when the ambient concentration is below the compensation point. Other sources include wild life manure and emissions from seas and oceans (Erisman et al., 1989).

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UNESCO – EOLSS SAMPLE CHAPTERS

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UNESCO – EOLSS
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## Biographical Sketches

**Jan Willem Erisman** has a technical chemistry education at the HTS ‘s Gravenhage. In 1985 he started working at the National Institute of Public Health and the Environment. During his 10 years appointment he developed as a senior (inter)national researcher in the area of the atmosphere - biosphere interactions and the relation between loads and levels of atmospheric pollutants and the ecosystem effect. In 1992 he finished his PhD on atmospheric deposition of acidifying components in the Netherlands. He coordinated several national and international projects. Furthermore, he participated in several research co-ordination groups and steering groups. Between 1997 and 2001 he was Head of the Department of Air Quality of the Energy Research Center of the Netherlands. Currently he is unit manager Biomass, Coal and Environmental Research at ECN, leading 60 scientists working in the field of Energy, specific biomass and coal technology and the Environment, Emission reduction technologies and technological assessments of clean and efficient use of fossil fuels.

Jan Willem Erisman has a great experience in atmosphere – biosphere research. Several field studies, monitoring studies, modeling studies, evaluations and assessments have been undertaken during the last 20 years. Furthermore, he participated in many studies related to acidification and eutrophication, both scientific as well as policy development and evaluation studies. Recently work has focused on nitrogen cycling in relation to ecosystem functioning and on the influence of natural stress and air pollution on forest health. Much experience has been gained in ammonia work: emissions, atmospheric processes, atmosphere – biosphere exchange, monitoring, policy development and implications and evaluation of abatement measures. He has been involved in studies on climate change, such as monitoring and evaluation of greenhouse gas emissions, the exchange of greenhouse gases between the atmosphere and biosphere and options to reduce greenhouse gas emissions, research on the relation between human health and particle matter exposure and on the influence of aerosols on the radiative balance.

**David Fowler** currently works for the Centre for Ecology & Hydrology at their Edinburgh research site near Penicuik. He is the Science Director of the Centre's Biogeochemistry research programme, involving nearly 100 scientists from across the UK. The Centre for Ecology & Hydrology is the UK's Centre of Excellence for research in the land and freshwater environmental sciences. David obtained a PhD entitled "Uptake of SO2 by crops and soil" from Nottingham University in 1976 and has worked for the Centre for Ecology & Hydrology since 1975. David's research career has included work on all the major gaseous atmospheric pollutants, including several greenhouse gases. He has also worked on the effects of pollutant gases on vegetation and soil and has been closely involved with the development of UK maps of the distribution of air pollutants. He chairs and sits on several international committees looking at air pollution within Europe. David has published over 300 scientific papers and book chapters. He was awarded an honorary professorship from the University of Nottingham in 1990 and elected a Follow of the Royal Society of Edinburgh in 1999 and a Fellow of the Royal Society of London in 2002.

UNESCO – EOLSS
SAMPLE CHAPTERS