Nitrogen Loss Assessment and Environmental Consequences in the Loess Soil of China

Yanan Tong
Department of Forest Ecology
Umeå

Doctoral thesis
Swedish University of Agricultural Sciences
Umeå 2003

Acta Universitatis Agriculturae Sueciae
Silvestria 284

ISSN 1401-6230
ISBN 91-576-6518-4

Printed by: SLU, Grafiska Enheten, Umeå, Sweden, 2003

Abstract

Tong, Y.A. 2003. Nitrogen Loss Assessment and Environmental Consequences in the Loess Soil of China. Doctor's dissertation.
ISSN 1401-6230, ISBN 91-576-6518-4

Attention is focused on fertilizer nitrogen loss and the environmental consequences in Shaanxi Province in loess region of China, including N losses to the atmosphere via ammonia volatilization, nitrification and denitrification, N losses to groundwater by leaching, and crop uptake by roots. Three soils were selected, Entisol, Anthrosol and Luvisol from north, central and south Shaanxi, respectively. Nitrification and NH_4^+ fixation were measured using a closed chamber method in the laboratory. Denitrification was tested in the laboratory with intact soil cores, C_2H_2 inhibition techniques. N_2O emission was assessed via *in situ* measurement of N_2O in the soil profile and at the soil surface in field experiments. Fertilizer use and crop yields obtained by the farmers were investigated on a large scale in Shaanxi Province.

Transformation of fertilizer NH_4^+ to NO_3^- was within nine days in the Entisol and Anthrosols, but it took 40 days in Luvisol due to NH_4^+ fixation by clay minerals. In the pot experiment open to the wind and sunshine with different water content, applied N fertilizer recovery was 74.2% for the Luvisol and 61.3% for the Entisol. Nitrogen recovery increased with increasing soil clay content. Large amount of nitrate was accumulated at 200-400 cm depth in the soil profile and accounted for 362-543, 144-677 and 165-569 kg N ha^{-1} in terrace and bottom land in north Shaanxi, terrace land in Guanzhong and south Shaanxi, respectively. N_2O measurements also showed that N_2O spatial variation in the profile could be ranked as, 10 cm < 30 cm < 150 cm < 90 cm < 60 cm. Temporal variation was correlated with rainfall or irrigation. An investigation showed that soil fertility in the Guanzhong area is high, but yield has not increased with increasing N fertilizer application during the last five years. over-application of N fertilizer was very common in the Guanzhong area and ranged from 100 to 382 kg N ha^{-1} for wheat and from 106 to 530 kg N ha^{-1} for maize. The results of the experiments indicate that the N fertilizer recovery efficiency is about 30% and the consequences of N losses are seriously threatening the environment by leaching to the groundwater and by denitrification to the atmosphere.

Keywords: Nitrate leaching, nitrification, denitrification, water pollution, N_2O emission, N fertilizer use efficiency, loess soil

Author's address: *present address*: Tong Yanan, Department of Forest Ecology, Swedish University of Agricultural Sciences, SE-901 83 Umea, Sweden. Tong. Yanan@sek.slu.se
Permanent address: Tong Yanan, College of Resource and Environment, Northwest Sci-Tech University of Agriculture and Forestry, 712100, Shaanxi, Yangling, P.R. of China. tongyanan@nwsuaf.edu.cn

Typical landscape in loess soil area: a) north Shaanxi and b) Guanzhong (strip-fragmented ownership where one farmer applied too much nitrogen fertilizer and got wheat lodging)

Contents

Appendix

Papers I - V

This thesis is based on the studies reported in the following papers, which will be referred to by the corresponding Roman numerals:

I. Tong, Y.A., O. Emteryd, D.Q. Lu & H. Grip. 1997. Effect of organic manure and chemical fertilizer on nitrogen uptake and nitrate leaching in a Eum-orthic anthrosol profile. *Nutrient Cycling in Agroecosystems*. 48(3): 225-229.

II. Tong, Y.A., O. Emteryd, H. Grip & D.Q. Lu. Nitrification, Ammonium fixation, and Nitrogen recovery in two Chinese soils. *Pedosphere*. (Submitted, 2003).

III. Lu, D.Q., Y.A. Tong, B.H. Sun & O. Emteryd. 1998. Effects of nitrogen fertilizer use on environmental pollution. *Plant Nutrition and Fertilizer Sciences*. 4(1): 8-15. (Translated from Chinese).

IV. Liang, D.L., Y.A. Tong, O. Emteryd & S.X. Li. 2002. *In situ* measurements of N_2O emissions from a loess soil profile. *Acta Pedologica Sinica*. 39(6): 802-809. (Translated from Chinese).

V. Emteryd, O., Y.A. Tong, D.L. Liang, T. Magnusson & H. Grip. Heavy nitrogen fertilizer application and losses in the loess soils areas of China. (Manuscript).

Paper I, III and IV are reproduced by permission of the journals concerned

Introduction

Nitrogen (N) is commonly the most limiting nutrient for plant growth. Therefore addition of nitrogen fertilizer in crop production normally gives large yield increase. Among the major nutrients, nitrogen has the greatest propensity to exist in gaseous state that could not be directly used by higher plants. To meet the demand by plants, mineral nitrogen fertilizer is applied in the nitrate (NO_3^-) and ammonium (NH_4^+) forms. Nitrate, as an anion is not attracted by negatively charged soil particles and is thus subject to leaching and water transport or it can be reduced to gaseous form and lost to the atmosphere. Nitrogen in the NH_4^+ form is attracted by soil particles where they can be exchanged by other cations. Ammonium is subject to ammonia (NH_3) volatilization and to fixation both by clays and soil organic matter or it can be transformed to nitrate. Nitrogen shortages, therefore, often limit plant productivity, but if in excess plant demand, both the gaseous and soluble phases of nitrogen lead to environmental pollution (Paul &Clark, 1989).

When NH_4^+ is applied to soils, it can be transformed into ammonia gas (NH_3) that can be lost from the soil and returned to the atmosphere. Ammonia volatilization most likely takes place when soils are moist and warm and the source of fertilizer is on or near the soil surface, especially if soils pH is greater than 8 (Killpack & Buchholz, 1993). Nitrification converts NH_4^+ via NO_2^- to NO_3^-. Percolation of infiltrating water causes movement of NO_3^- from the upper soil profile to deeper soil layers and to groundwater. Nitrate leaching is likely to take place in a coarse textured soil with precipitation and irrigation exceeding evaporation (Canter, 1997). In the lack of oxygen under anoxic conditions micro-organisms can use nitrous oxides as electron acceptors and reduce NO_3^- to NO_2^- and then to gaseous NO, N_2O and N_2, which are commonly lost to the atmosphere. This process is known as denitrification (Paul &Clark, 1989; Zhu *et al*., 1997).

Ammonia volatilization, nitrate leaching and denitrification are the main N loss pathsways in soil-plant system and also are the most important part in the N cycle in agriculture (*Fig*.1). Nitrogen loss by NH_3 volatilization lowers N use efficiency in agricultural soils. Volatilization losses could be as large as 55% of any added urea (Al-Kanani *et al*., 1990). When urea was broadcast to maize field 30% of the applied N was lost by ammonia volatilization (Cai, 1997) and the volatilization was 17% when urea was broadcast to a cabbage field, but it was only 11% when the urea was incorporated with the soil (Xi *et al*., 1987). Tong *et al*. (1994) found in a laboratory experiment that less than 5% of the N added was converted into NH_3 in a closed incubation box, where the NH_3 in the ventilated air was trapped and analysed.

Agronomists usually define nitrate leaching loss as nitrogen moving out of the crop rooting zone, while environmentalists emphasizes its entering into a water body (Zhu & Chen, 2002). In any cases, it reduces the N use efficiency and increases pollution of the environment. Regularly applications of organic amendments, for instance, cattle slurry, have a high potential for nitrate leaching (Ritter *et al*., 1990; Kristensen *et al*., 1994; Van Delden *et al*., 2003). Trindade *et* *al.* (1997) found with 170-220 kg N ha^{-1} of N fertilizer and regular cattle slurry applications of 263-474 kg N ha^{-1} that annual nitrate leaching losses ranged from 154 to 338 kg N ha^{-1}. Roelcke *et al.* (2000) found in one 0-250 cm profile in south part of the Loess Plateau in China, however, up to 400 kg NO_3-N ha^{-1} accumulated, more than 200 kg of which were in 140-250 cm depth. In the United States there is each year 3.6 billion kg more nitrogen available in farm fields than can be used by the growing crops (NRC, 1993). This excess nitrogen has to go somewhere, and much of it ends up in groundwater and surface waters used as drinking water supplies (Hallberg, 1986, NRC, 1993, NRDC, 1994). In a survey of groundwater nitrate contents conducted by Zhang *et al.* (1996) in the provinces of Beijing, Tianjing, Hebei, Shandong and Shanxi in China about 46% of 600 groundwater samples exceeding the WHO (1993) limit for nitrate in drinking water of 11.3 mg L^{-1}, with the highest nitrate concentration reaching 500 mg L^{-1}. A serious problem is when nitrate contaminated groundwater is used by infants as drinking water. Following consumption by an infant, the NO_3^- becomes reduced to NO_2^-, which in turn irreversibly reduces the blood hemoglobin to methemoglobin. Death results from oxygen deficiency. The disease is known as methemoglobinaemia or blue-baby syndrome (Simon, 1964).

Since denitrification not only leads to loss of N from the soil-plant system, but also to economical loss and environmental pollution, extensive research has been done on this aspect of N cycling. Denitrification can be a major source of atmospheric nitrous oxide (N_2O) (Mahmood *et al.*, 1998), which, besides acting as a greenhouse gas (Watson *et al.*, 1990), is implicated in destruction of the stratospheric ozone (Crutzen, 1981) that absorbs ultraviolet radiation in spectral windows not covered by other gases. Nitrous oxide contributes a few percent to the overall greenhouse warming (Crutzen, 1976; Liu *et al.*, 1976; Eichner, 1990; Albritton *et al.*, 1995). The concentration of nitrous oxide in the atmosphere is currently increasing at the rate of two- to three per mille per year. The contribution by agriculture to the present anthropogenic N_2O emission is estimated to account for 33% of the total (Christensen *et al.*, 1996; Freibauer & Kaltschmit, 2001).

China's nitrogen fertilizer consumption became the highest in the world in 1985 and further strongly increased in the 1990s (FAOSTAT, 1999) (*Fig.* 2). Zhu *et al.* (1997) estimated that the loss of fertilizer N from cropland was 60% for flooded rice and 45% for upland crops. They suggested that 50% of the fertilizer N in whole China was lost from the plant-soil system in 1980s. Due to the high pressure of the population, most of the scientists in China were focused on how to increase grain yield by fertilizer application strategy, only a few people realized environmental pollution from N fertilization until end of 1990s. Li and Xiao (1992) reviewed the effect of fertilizer application on soil fertility in loess region area, and used 77 published papers as references, but none of them related to nitrate leaching and denitrification. In the book Nitrogen in Soils of China (Zhu *et al.*, 1997) with 338 pages, there is no chapter related to nitrate leaching. In chapter 11, Fate and Management of Fertilizer Nitrogen in Agro-ecosystems, it is stated that "leaching was found to be insignificant in most cases, except in soils with high percolation rate". But over-application of N fertilizer is common in China. An investigation conducted in Shandong province (Ma, 1999) showed

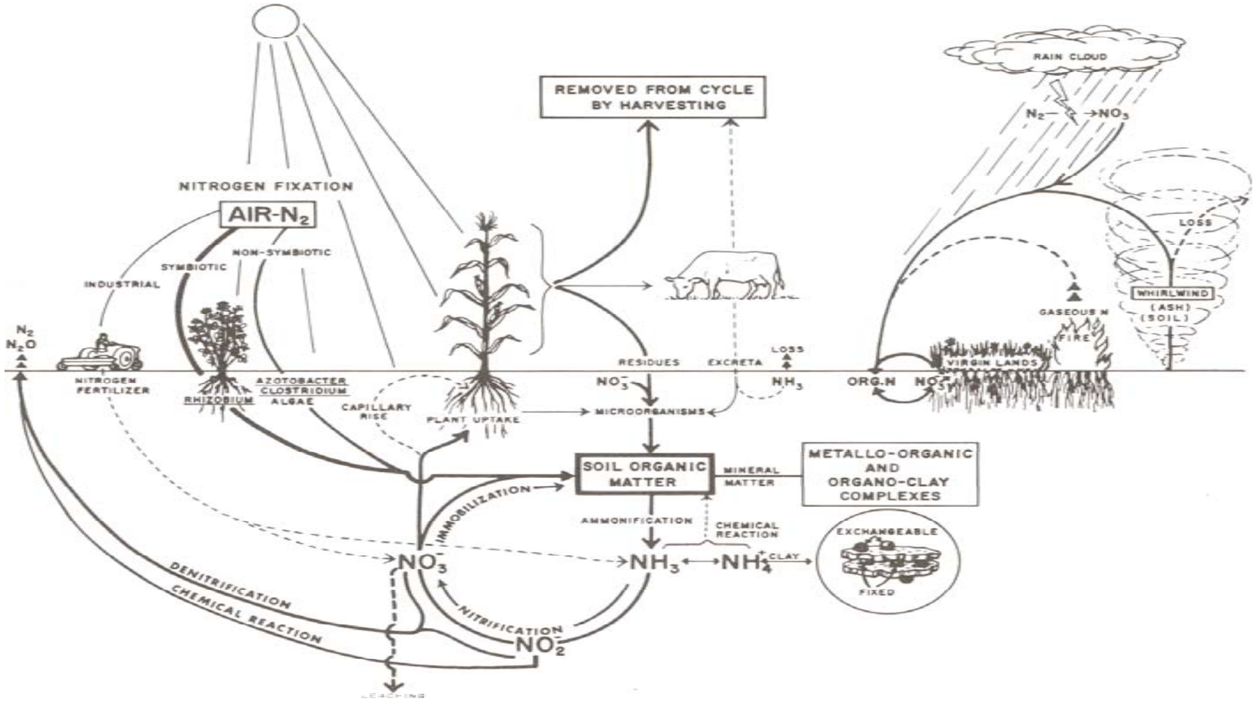

Fig. 1. Nitrogen cycle in soil. (From Stevenson, 1982; Paul & Clark, 1988)

that the average nitrogen fertilization rate in 957 fields was 280 kg N ha^{-1} for winter wheat and 208 kg N ha^{-1}for summer maize. In 147 protected vegetable fields the rate to one crop was 1700 kg N ha^{-1} while that in 217 apple orchards was 848 kg N ha^{-1}. In Shaanxi Province Liu *et al.* (2002) found in 606 orchards that the fertilizer application was 300-1200 kg N ha^{-1} yr^{-1}, the highest reaching 2075 kg N ha^{-1} yr^{-1}. According to Zhu *et al.* (1997), N loss could be 50% of applied fertilizer N, and the other 50% must be somewhere in the environment.

Objectives

When the present work started in 1993 there were to my knowledge no results reported on what happened with fertilizer nitrogen in excess of plant uptake in the loess soil area in China. The reasons to conduct the present work were therefore;

- To assess nitrification and ammonium fixation by clay mineral in loess soil
- To assess the nitrogen loss by ammonia volatilization, nitrate leaching and denitrífication and environmental pollution
- To assess the present situation of nitrogen fertilizer application and it's recommendation in Shaanxi Province

The detailed objectives for each attached paper are listed as following:

I. To determine the long time effect of combined application of organic manure and chemical fertilizer N and P on plant uptake and nitrate accumulation in the soil profile (**Paper I**)

II. To quantify nitrification rate, ammonium fixation and fertilizer nitrogen recovery when fertilizer was applied in different ways (**Paper II**)

III. To define the regional distribution of nitrate accumulation in soil profiles and contamination of groundwater and surface water and suggest ways to increase N fertilizer use efficiency and reduce losses (**Paper III**)

IV. To determine temporal and spatial variation of N_2O concentration under wheat-maize rotation and factors limiting N_2O production (**Paper IV**)

V. To estimate the fertilizer N recovery and try to find the ways of N losses from the aerobic soils. To evaluate amount of N fertilizer used by farmers and recommend proper amounts and fertilization techniques (**Paper V**).

A complete nitrogen budget for Chinese cropland should consider inputs as **chemical fertilizer**, **organic manure**, minerilization, biological nitrogen fixation, dry deposition, wet deposition from precipitation and irrigation and nitrogen in seeds; and outputs including **N uptake by crops removed from the field, ammonia volatilization, gaseous denitrification losses, leaching** and runoff. Changes in organic and **inorganic storages** in the soil should also be accounted for. The items with bold will be considered in this thesis.

Background

Nitrogen fertilizer use and the problem in China

In 2001, nitrogen fertilizer consumption amounted to over 24 Mt in China, equivalent to 60% of the total agricultural nutrient inputs. The average nitrogen application rate per crop was 155 kg N ha^{-1}, compared to around 60 kg N ha^{-1} on a world average (FAOSTAT, 2002). The rate of nitrogen fertilizer application in China varies widely among regions and crops because of uneven economic development, leading to both shortage of nitrogen fertilizer and excessive use. The annual nitrogen fertilizer application rate surpasses 400 kg per ha of arable land in Shanghai, Beijing, Jiangsu, Fujian provinces in 2001, where double-cropping even triple-cropping systems are conducted. But it was below 100 kg N per ha sown area in interior provinces such as Gansu, Heilongjiang, Qinghai and Tibet, where there is only one harvest annually (CCAY, 2001).

Over the past 20 years, increasing nitrogen fertilizer applications in China have played an important role in the development of agricultural production. However, the positive effect of increasing nitrogen fertilizer on yield has decreased recently. For the period 1949 to 2000 there was a strong correlation (r = 0.9) between yearly total yield and the yearly amount of N fertilizer applied, but if the period is split into five 10-year periods, the slope of the regression has decreased significantly during the last 20 years, since mineral nitrogen fertilizer consumption in China increased 3-4 fold, while the cereal yield only increased by 60% (Fig. 2) (Hong, 1997; Liu, 2001). Now, the nitrogen fertilizer use efficiency is only 30-40% or less and decreases with increasing fertilizer rate (CAAS, 1994).

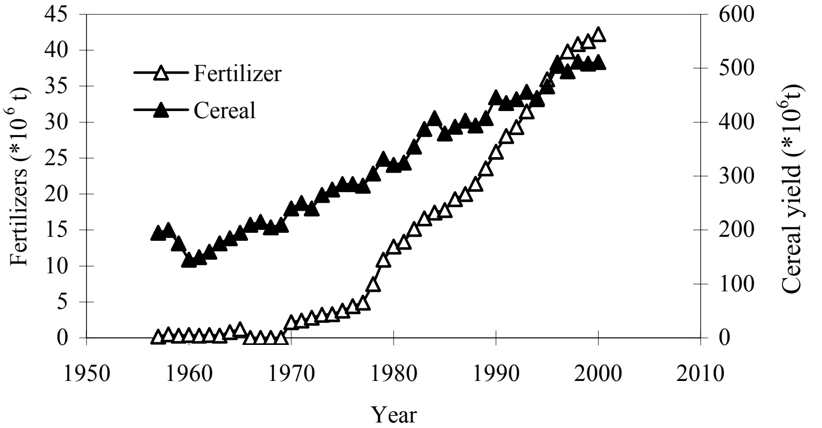

Fig. 2. Total mineral fertilizer (N + P + K) use out of which 60% is N and cereal yield in China (From Liu, 2001).

Unbalanced fertilizer application is another problem, and there are several kinds of imbalance phenomena in China (CAAS, 1994). First, fertilizer supply has a regional imbalance. Heavy fertilizer application first took place in east China and also in some areas in west China, where economic development has been rapid in recent decades, but in the remote provinces such as Qinghai and Tibet, N applied was in shortage. The second unbalance was in the different crops, especially for vegetable land or fruit gardens (so-called “cash crops”) from which the farmers can get more profit, and where 5 to 10 times more fertilizer may be used than necessary (Cheng *et al*., 1997; Gao, 1997). The third source of imbalance is inherent to some types of fertilizer used by farmers that are supplied by the government and other agents (Xing, 1999). Frequently, farmers have been unable to find potash or certain microelements in the market. The fourth source of imbalance is that farmers lack knowledge. The farmers do not know what and how to apply the fertilizer, what the crop needs, what nutrients are deficient in the soil or optimal amounts of fertilizer to apply. So, education and information to the farmers will be an important task for the future.

Xia *et al*. (2002) reported that nitrogen concentration in the Yellow River from non-point sources showed an accelerated trend of increase in the mainstream and tributaries in the years 1980, 1990, 1997 and 1999, and the cause of this trend was an increase in N fertilizer applications in the Yellow River system. “Red tides” have increased in frequency from 3-4 times to 4-6 times a year around coastal seas of China. The amount of the greenhouse gas N_2O released from agricultural land in China is estimated to be more than 10% of that from all farmland on the globe, as noted many times both within China and abroad (Cai *et al*., 1991). More serious problems are foreseen for the coming 30 years when the population will increase further. To meet the population needs for agricultural products and increases in living standards, the rate of N fertilizer will continue to grow. A huge challenge in the future will be to increase the N fertilizer use efficiency and to reduce the associated environmental pollution.

Nitrogen fertilizer use in the world

The heavy application of N fertilizer in China started in the later part of the 1970’s. In the middle of the 1980’s, the total amount of N fertilizer applied was greater than in the western countries. The N, P, K consumption in 1995 in China accounted for 41.4% of global use, USA only applied 23.4% and Canada 2.9%; China’s shares of the global production and consumption of N fertilizer were 33.3% and 45.8%, while USA’s shares were 24.9% and 21.6, and Canada’s were 7.0% and 3.1%, respectively. So, the N fertilizer production and consumption in China is much greater than that of other countries, and in addition12.5% of the N fertilizer used in China is imported from other countries (Xue, 1998; FAOSTAT, 1999).

Nitrogen should be used wisely, but it is not being used in this way in China at the moment, or even in the western countries. Application of large amounts of mineral nitrogen fertilizer started in the 1950’s in developed countries, resulting in the eutrophication of water in rivers, lakes and coastal seas. After the 1970’s, in developed countries such as the USA, Sweden, and Canada, the application of mineral nitrogen fertilizer was reduced. A survey was done for maize fields in Nebraska in US by Supalla *et al*. (1995) and who reported that N applications in the 1960s and 1970s ranged from 250 to 300 kg ha^{-1}, while early 1990s, as a result of educational programs and regulations, most applications have declined to 150 to 180 kg ha^{-1}, although 20% of the producers continue to apply more than is recommended. In the USA, in 1995 the unit rates of N fertilizer application were 143 kg N ha^{-1} for maize, 75 kg N ha^{-1} for wheat, 127 kg N ha^{-1} for rice, and the average N application was 60 kg N ha^{-1} (FAOSTAT, 1999). The N fertilizer rate in China averaged 155 kg N ha^{-1} in 1999: 2-3 times more than that applied in Sweden and the USA. The application rates of N fertilizer for wheat, maize and rice crops in China were 150, 225 and 120-140 kg N ha^{-1}, respectively (Xing, 1999). However, the yield of wheat in China was only half the figure in Sweden. The maize yield in China was 1/3 less than that in USA, but there was no difference in the rice yield between China and the USA (FAOSTAT, 2002). Thus, it can be seen that over-application of N fertilizer is common in China, but the yield is lower than in other countries, so the N fertilizer use efficiency must also be lower.

Balanced fertilizer applications and recommendations in China

Fertilization is balanced when macro- and micro- elements are available to the plants in physiologically optimal proportions, added in the fertilizer or readily available in the soil. Research on balanced fertilizer application techniques started in the early 1980’s in China, and since the end of the 1980’s, these techniques have been extended to the farmers. A basic requirement for balanced fertilizer application is soil testing, but in most cases at the county and township level, the laboratories and instruments do not function well. It is difficult to test the soil of every family’s land, so recommendations for fertilizer applications must be rather general.

Soil testing is the most common method used in places where laboratories are available. The principle is simple; the amount of fertilizer is applied according to the plants’ needs for a certain yield minus the amount already available according to the soil test, adjusted by fertilizer use efficiency. Due to lack of laboratories and the cost for soil testing this mode of extension has not been popular in China’s countryside. Field fertilizer experiments have been done with different amounts of N, P and K fertilizer. The data obtained from such field experiments are used to derive regression equations from which maximum and optimum amounts of fertilizer are calculated to develop recommendations for fertilizer regimes.

Phosphorus (P) application technique was extended and popular to utilize in China’s agriculture in early 1980s. Until the end of 1990s, soil P accumulation resulted in an increase in soil available level. It was generally even more than needed (Lu, 1997). Extension of potassium (K) application technique started first in south China in mid 1990s. Generally, the soil was rich in K in north China. Total K and available K are 1.5-2.6% and 75-180 mg kg^{-1}, respectively (ISS, 1986). The available K content in the soil has declined during the latest decades and K fertilizer was first available for cash crops such as apple trees and hot pepper (He *et al.*, 1999). It is now at a critical level for the cereal crops, but K application techniques are not well extended in north China, especially for loess soil area and the farmers have not yet accepted to apply K.

Nitrification and denitrification

The nitrification and denitrification processes can be summarized as follows.

$$NH_4^+ \xrightarrow{1} NO_2^- \xrightarrow{2} NO_3^- \xrightarrow{3} NO_2^- \xrightarrow{4} NO \xrightarrow{5} N_2O \xrightarrow{6} N_2$$

The first and second steps represent the nitrification process that occurs in the presence of nitrifying bacteria under aerobic conditions. The product is NO_3^- with a negative charge, which is not absorbed by the normally negatively charged soil particles, but will follow percolating water and pollute groundwater. The third to sixth steps are called denitrification. Here, nitrate and nitrite reductase are involved under anaerobic conditions. Biochemical, chemical, enzymatic and microbial/ physiological factors influence every step of nitrification and denitrification, and N_2O and N_2 could be emitted at any point and lost to the atmosphere (Zhu *et al.*, 1997). Thus, N_2O emissions from agricultural land, especially after heavy N fertilizer application, cannot be ignored.

Soil pH, moisture and soil texture are important factors affecting nitrification. Within the pH range 3.4-8.6, nitrification activity is positively correlated with pH (Sahrawat, 1982). In a study by Katyal *et al.* (1988), little or no nitrification took place in soil with pH 4.6-5.1, nitrification was slow in soils with pH 5.8-6.0, and active nitrification occurred in soils with pH 6.4-8.3. Soil moisture is another factor that influences nitrification in soil. The optimum moisture content for nitrification in soil is 50-70% of the maximum water-holding capacity (Li, 1997). Soil texture affects soil aeration and water permeability, as Li *et al.* (1986) showed there was a marked negative correlation between nitrification rate and clay content (<0.001 mm). If plants do not take up the NO_3^- produced during nitrification, it may leach down to the groundwater or denitrification may occur.

Denitrification could take place in many circumstances, even in a generally well-aerated soil, if the soil has an aggregate structure. Inside the aggregates anaerobic micro sites may be formed where denitrification can take place. Greater rates of denitrification have been reported in fine-textured soils (Lund *et al.*, 1974; Chaterpaul *et al.*, 1980). Ryden & Lund (1980) found the production of gaseous N by denitrification to be highly dependent on soil moisture. The flux of nitrous oxide was highest when the soil moisture suction was 5-10 kPa, as measured by the acetylene blockage method (Ryden & Lund, 1980), while at 25 kPa the flux was much weaker. Denitrification can occur within the pH range 3.5-11.2, but in general, the rate of denitrification is often positively correlated with the pH value (Valera & Alexander, 1961). It has also been suggested that the optimum pH range for denitrification is 7-8 (Jiang *et al.*, 1989).

In China, Cai *et al.* (1985) observed that when ammonium bicarbonate and urea were applied to a rice field, N losses by denitrification amounted to 39% and 37% of the applied N, respectively. Zhu *et al.* (1989) estimated the apparent denitrification loss to be 33% of the applied N when ammonium bicarbonate and urea were applied to a calcareous paddy soil in Henan Province. At two sites, the variation in apparent denitrification loss was small (range 33-37%). Under conditions conducive to ammonia volatilization, denitrification losses may be less important. Cai *et al.* (1992) estimated N losses from urea applied to an acid paddy soil in Zhejiang Province via apparent denitrification losses to be 40.7% and 41% of the applied N, when urea was broad-cast into the floodwater or incorporated as a basal dressing, respectively. Thus, under the given conditions, denitrification was a much more important pathway for N losses than ammonia volatilization.

NH_3 volatilization and NH_4^+ fixation

Nitrogen loss by NH_3 volatilization and NH_4^+ fixation lowers nitrogen use efficiency in agricultural soils. Many factors such as soil pH, soil structure, temperature, wind, water content, fertilizer type and N application rate affect NH_3 volatilization (Fenn & Hosser, 1985; Ferguson & Kissel, 1986; Beyrouty *et al.*, 1988; Paul & Clark, 1988; Reynolds & Wolf, 1988). Ammonia volatilization has been strongly related to the initial soil water content (Ferguson & Kissel, 1986). Fenn & Escarzaga (1977) reported that NH_3 volatilization decreased when water content was higher than a critical value of 8% (weight basis). Fenn & Escarzaga (1976) found that NH_3 loss was negligible after urea application to the surface of a dry soil. Al-Kanani *et al.* (1991) observed a direct linear relationship between the amount of NH_3 volatilized and the original soil water content after a surface application of urea. Application methods, soil and fertilizer type can all affect ammonium volatilization losses (Harper & Catchepoole, 1983; Hargrov, 1987). About 90% of the total emission of ammonia in Germany is attributed to agricultural sources, mainly resulting from animal husbandry and to a minor degree from mineral fertilizer (Freibauer & Kaltschmit, 2001).

Drury & Beauchamp (1991) found that about half of the ^{15}N fixation with urea occurred within 6 hr of application and the amount of fixed ^{15}N peaked after 30 days. Fixed NH_4^+ was released when nitrification and immobilization depleted extractable NH_4^+, so the fixed NH_4^+ release rate was slower than the rate of fixation.

There have been several investigations into the role of NH_4^+ fixation in the reduction of N lost through NH_3 volatilization and NO_3^- leaching (Black & Waring, 1972). Since soil water and N supply are the two most important factors contributing to crop productivity, it is important to study the effect of water content on NH_4^+ fixation and N losses in China to improve the management of inputs and increase productivity.

Nitrous and nitric oxides

Agricultural fertilization increases the concentration of volatile NH_3 in soils, increases microbial processing of fixed N, and ultimately increases emissions of nitrogen gases from soils. Hargreaves *et al.* (1996) estimated annual emission of N_2O from an organic soil to be 23.5 kg N ha^{-1}. The gas can be produced during denitrification or nitrification in soils within a few days or weeks after N fertilizer application (Eichner, 1990; Schlesinger & Hartley, 1992). Liang *et al.* (2002b) measured N_2O emission from vegetable fields and estimated it to be up to 6.3 kg N_2O-N ha^{-1} y^{-1}. The maximum emission was at 150 kg N ha^{-1} fertilization rate.

Unlike nitrous oxide, which is non-reactive in the lower atmosphere, nitric oxide is highly reactive and therefore much shorter lived. Nitric oxide plays several critical roles in atmospheric chemistry, including catalysing the formation of photochemical (or brown) smog. Nitric oxide, along with other oxides of nitrogen, can be transformed in the atmosphere into nitric acid, which is one of the major components of acid rain (Vitosek *et al*., 1997). Matson *et al*. (1996) showed that a more knowledge-intensive agricultural system gave higher yields and was more profitable and, at the same time emitted less nitrogen oxides to the atmosphere than simply adding more fertilizer. Vitousek *et al.* (1997) conclude that the development and transfer of N-efficient technologies to developing regions is particularly important and should have high priority. There are still very few results of N_2O emission reported from loess area.

Nitrate leaching and accumulation in loess soil profiles

Nitrate (NO_3^-) leaching is one of the N loss processes of concern for both economic reasons and for its impact on groundwater quality (Trindade *et al*., 1997). Nitrate could be leached directly down to the groundwater if the water table is shallow, otherwise, it is accumulated in the soil profile and will later reach the groundwater. A number of investigations have been done on the nitrate leaching process and nitrate accumulation in soil profiles. Accumulated soil mineral N ranged from 111 to 694 kg ha^{-1} in the depth of 0-100 cm soil profile in rice-sweet pepper cropping system (Shrestha and Ladha, 1998), in fallow plots where mineral N was either maintained or increased, there was movement to the lower soil profile demonstrating NO_3^- leaching without a crop. Then, nitrogen-catch crop was used and maize captured 176 kg N ha^{-1} and indigo 194 kg N ha^{-1}. They suggestion to develop indigo plus maize N-catch crop rotations to decrease NO_3^- leaching and maximize N use efficiency in rice-sweet pepper cropping system. Similarly, Delgado *et al.* (2001) used Nitrate Leaching and Economic Analysis Package (NLEAP) model to simulate soil water as well as the transport of NO_3^- in the soil profile for potato-barley systems, and the results showed that barley served as a scavenger for the NO_3^- that was added with irrigation water and residual soil nitrate from the potato-growing period.

Due to the difficulty in predicting the slurry N availability, the amounts of fertilizer N applied frequently exceed the crop requirements leading to the accumulation of high levels of nitrate-N in the soil profile after crops harvested. This nitrate can be leached out of the soil profile during the winter period particularly if the soil is kept bare (Cameron & Haynes, 1986). But the winter crop, as a N-catch crop, removed important quantities of nitrate-N (83-116 kg N ha^{-1}) left in the soil after maize crop plus N released by mineralization during the winter period (Trindade *et al*., 1997).

Over-applications of N fertilizer in developed regions of China are very common, especially in areas under vegetables near the cities, and in orchards, where the rate of fertilization can be 3-5 times higher than the rate in croplands (Xing, 1999). The landscape in the central reach of the Yellow River is typically hilly and gullied, and there is serious soil erosion. There are about 70 million people living in the Loess Plateau area, and the population density in the Mizhi area, north

Shaanxi, reaches up to 200 persons km^{-2}. With this population pressure the farmers cultivate even the hilltops and slopes (Zhu, 1986; Emteryd *et al.*, 1998). The most important land is the river valley terrace land (stepped land) and river valley beach land (bottom land), which the farmers rely on to obtain enough food. Therefore, much more fertilizer is used on this land than elsewhere. An investigation conducted by Liu (2002) in 126 protected vegetable field in the Beijing area demonstrated that the mean nitrate accumulation reached 1230 kg N ha^{-1} in the 0-400 cm soil profile, 434 kg N ha^{-1} of which were located in a depth of 200-400 cm, thereby being unavailable to vegetable crops with their short growing period and shallow rooting zone. This usually causes nitrate pollution in shallow subsoil water in Beijing area (Ouyang *et al.*, 1996; Zhang *et al.*, 1996).

Optimal water usage was considered the next most important factor. The sandy Entisols in Mizhi, which have sand contents greater than 90%, low organic matter content, and lack of confining soil horizons provide favourable conditions for leaching of water as well as soluble nutrients. Because large amounts of mineral fertilizer are applied as part of the routine crop production practices in the bottomland, where the groundwater table is only at 4.5-5 m depth, soluble nutrients such as nitrate are easily leached down to the groundwater (Emteryd *et al.*, 1998). So, it was predicted that there was plenty of nitrate would be accumulated in soil profile and leached down to groundwater.

Nitrate contamination of groundwater and surface water

Environmental pollution is a serious problem globally and over-application of mineral nitrogen fertilizer in agricultural systems is one of the largest sources of pollution (Rejesus & Hornbaker, 1999). Nitrate is a form of nitrogen found in soil, water and plants. Most plants take up soil nitrogen in the form of ammonium and nitrate in order to satisfy their nitrogen nutrient requirements. Plants can also accumulate nitrate in leaves and stem tissue if the biochemical process in the plant that normally convert ammonium or nitrate into organic N are insufficiently active. Nitrate is also highly water-soluble and is not strongly held at soil surfaces. These chemical characteristics of nitrate make it susceptible to leaching down through the soil and into groundwater (Zhu *et al.*, 2000). Since groundwater is a major source of drinking water, the health effects of ingesting nitrate in drinking water are sources of concern when nitrate levels are high.

For decades, nitrate concentrations in many rivers and drinking water supplies showed a historic rise in nitrogen levels in the surface waters. For instance, nitrate concentrations in the Mississippi River have more than doubled since 1965 (Turner & Rabalais, 1991), nitrate concentrations have risen three- to ten-fold in major rivers of the northeastern US since the early 1900s, and the evidence suggests there has been a similar trend in many European rivers (Justic *et al.*, 1995).

In Germany and South Africa the nitrate concentration limit for drinking water is 4.4 mg NO_3-N L^{-1}, more than twice as strict as the US standard of 10 mg NO_3-N L^{-1} (Kross *et al.*, 1995). The European Economic Community has established a nitrate health guideline of 5.6 mg NO_3-N L^{-1}, and the WHO one of 11.3 mg NO_3-N

L^{-1} (WHO, 1993). Unlike virtually all other contaminant standards, the 10 mg NO_3-N L^{-1} drinking water standard for nitrate contains no safety factor. For this reason, American scientists have suggested to Congress that it should immediately establish a new drinking water standard for nitrate of 5 mg NO_3-N L^{-1} (Cook *et al*., 1996).

Agriculture is the primary source of nitrate contamination. Farmers will, and must, continue to use nitrogen fertilizer. They do not, however, have to overuse it. Each year, there is 3.6 billion kg more nitrogen available in farm fields than can be used by the crops growing in the US (NRC, 1993). This excess nitrogen has to go somewhere, and much of it ends up in drinking water supplies (Hallberg, 1986, NRC, 1993, NRDC, 1994). In the four years from 1991 through 1994, Iowa farmers used 16% less fertilizer per unit area of maize than farmers in other Maize Belt states, and yet obtained the same maize yield (Hallberg, 1995).

In China, current agricultural practices have a high potential for non-point source pollution of groundwater, and nitrate contamination in groundwater was found in the 1970's. Chinese people took it as fertile water, with a nitrate concentration of 30-200 mg NO_3-N L^{-1} around the old villages. They used it for irrigation and could increase their yields by 5 to 15%. People regarded it as a wonderful kind of water for irrigation (Qian, 1985). They never thought it would be harmful to human health. Later on, in the 1980's, people knew that it was not good to drink water with high nitrate concentrations, but as yet there is still no standard limit for nitrate concentration in drinking water at a national level. So, the people, especially farmers, use water with high amounts of nitrate as normal drinking water (Emteryd *et al*., 1998).

Nitrogen management to minimize N loss and increase N fertilizer use efficiency

All measures that increase crop yield and minimize N loss can also increase the N fertilizer use efficiency. The application rates, timing, methods of both N fertilization and irrigation are important management tools that determine and control the fate and behaviour of N in soil-plant systems. Li and Yost (2000) used management oriented modeling (MOM) and showed that irrigation management and N fertilization are inextricably linked when considering possible leaching to groundwater and plant utilization. Rejesus and Hornbaker (1999) pointed out that nitrogen fertilizer application from agriculture is likely the largest contributor to non-point source nitrate pollution in the United States. To use site-specific management precision technology for N fertilizer application has great potential in reducing the mean and variability of nitrate pollution in a catchment while at the same time improving profitability of producers (Rejesus & Hornbaker, 1999). The practices recommended to minimize nitrate pollution at agricultural sites include:

- Source recycling and balanced fertilization, returning straw and maize stalks to the soil where they came from, and balancing applications of the macro- and micro- elements (Supalla *et al*., 1995).
- Testing soil or plant samples, and recommended proper amounts of nitrogen fertilizer for specific crop and soil conditions (Barbarick, 1996).

- Split application of nitrogen fertilizer over the growing season - dividing the total amount of nitrogen fertilizer to be applied to the plants into 2 to 3 separate amounts and applying these smaller amounts at different times during the growing season depending on plant development (Barbarick, 1996; Li and Yost, 2000).
- Maintenance of a healthy crop or vegetative cover to act as a sink for nitrogen - healthy plants can remove large amounts of nitrogen from the soil for so-called "N-catch crop" growth. In addition, vegetative cover reduces soil erosion, which can deposit nutrients into surface waters (Trindade *et al.,* 1997).
- Avoidance of over-irrigation - application of excess irrigation water can increase nitrate leaching out of the root zone (Spalding *et al*., 2001).

Description of the research sites

All the research work was done in the Shaanxi Province, which has a total area of 206,000 km^2 and the population of 36 million people. The landscape and climate are divided into three ecological zones from north to south. The Loess Plateau in the north, the Guanzhong plain in the middle and the subtropical zone in the south (see map in Fig. 3). The soil types, and their physical and chemical properties are listed in Table 1.

The Loess Plateau area, which is the largest such area (0.6 million km^2) in the world, is located in the middle reaches of the Yellow River with an altitude varying between 900 and 1500 m. North part of the Shaanxi Province is located in the center of the Loess Plateau. It is a semi-arid area with a yearly precipitation of 350-500 mm and a potential evaporation of about 850 mm (Guo *et al*., 1992). The landscape is a hilly area with gullies formed by wind and water erosion, and it is planted with crops of maize, potato, millet and buckwheat (one crop per year) (Zhu, 1986). Because of high population pressure slops larger than 25 degrees still is cultivated even if the harvest is low. Most of the bottomland close to the rivers, is important food production areas. High amount of fertilizer is applied, especially N fertilizer and flooded irrigation is used for maize and vegetables.

Guanzhong is situated in central Shaanxi and the altitude varies between 320 and 800 m. The area is semi-humid with a yearly precipitation of 550-700 mm and a potential evaporation of 800-900 mm (Guo *et al*., 1992). Cumulative Penman potential evaporation (PE), precipitation (P) and irrigation (I) in Yangling during October 1994 to September 1995 are given in Fig. 4. During this year potential evaporation peaked in June (6.6 mm d^{-1}) and was lowest in December (-0.3 mm d^{-1}). The wettest month was July (106 mm) and the driest was December (6 mm). The mean temperature was 13.8^{o}C, the warmest month was July (27.5^{o}C) and the coldest as January (0.2^{o}C). Wheat and maize are normally grown in rotation and two crops are harvested per year. Guanzhong was an ancient and traditional agricultural area where irrigation is possible with water from channels and groundwater wells. Winter irrigation is common for winter wheat, normally as flooded irrigation with about 100 mm. During maize growing season in summer irrigation should be done 2-4 times with 80-100 mm each time (Guo *et al*., 1992). Organic manure is normally applied in autumn before sowing wheat. The natural border between Guanzhong and south Shaanxi is the high Qinling mountain range, with an altitude of 2000 to 3700 m. In the south, there are mostly paddy areas, a subtropical climate, and a yearly precipitation of 800 to 1000 mm and a potential evaporation of 800-850 mm (Guo *et al*., 1992). A wheat and rice rotation is the main crop system and two crops are harvested per year. The field is water covered

Table 1. *Soil physical and chemical properties of Entisol, Anthrosol and Luvisol topsoils in the three ecological zones of Shaanxi Province.*

Parameter	Unit	Entisol	Anthrosol	Luvisol
Location		North Shaanxi	Guanzhong	South Shaanxi
Organic Matter	g kg^{-1}	2.9	11.8	10.2
Total N	g kg^{-1}	0.2	0.8	0.1
Total P	g kg^{-1}	1.1	0.8	0.9
NH_4^+	mg kg^{-1}	8.2	2.3	3.7
NO_3^-	mg kg^{-1}	11.5	9.2	26.6
Free $CaCO_3$	g kg^{-1}	104.3	61.2	4.4
pH		8.3	8.1	7.1
CEC	cmol kg^{-1}	7.3	15.0	15.5
Water holding capacity	%	22.5	23	27.7
Density	g cm^{-3}	1.1	1.2	1.5
Particle size distribution				
Sand (2-0.02 mm)	%	68.9	27.5	18.7
Silt (0.02-0.002)	%	24.6	49.0	40.8
Clay (<0.002)	%	6.5	23.5	40.5

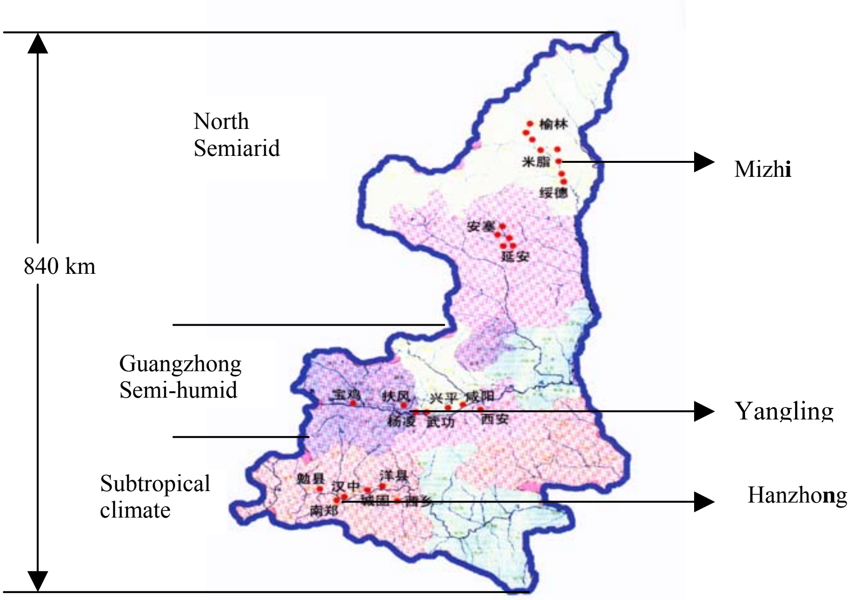

Fig.3. Map of Shaanxi Province in central China. Grey points denote investigated counties located in the southern, middle, and two northern areas, representing three general study areas.

during rice growing season from June to September and dry during wheat growing season from October to May.

Throughout the whole Shaanxi region, vegetables are planted around cities with and without use of greenhouses. Fruit trees are planted on 0.53 million ha and 0.33 million ha of that is planted with apple trees. 20000 ha of kiwi fruit are planted in Guanzhong and 66000 ha jujuba trees are planted in the northern part of Shaanxi. Green tea is planted in the mountain area of south Shaanxi.

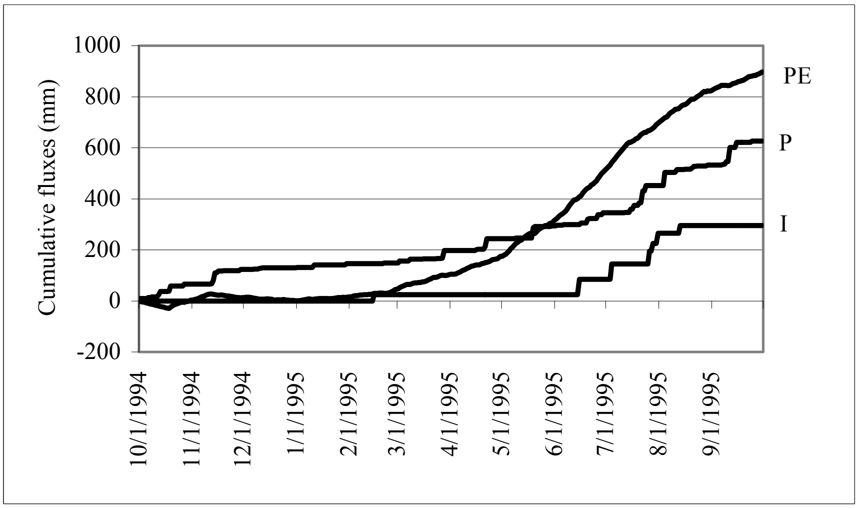

Fig. 4. Cumulative Penman potential evaporation (PE), precipitation (P) and irrigation (I) in Yangling during October 1994 to September 1995. The totals for the period were 897 (PE), 626 (P) and 295 (I) mm, respectively.

The research sites in these three ecological regions, and referred to in this thesis, are Mizhi (37°12’N & E110°48’) in north Shaanxi, which typifies the Loess Plateau area; Yangling (34°30’N, 108°02’E), typifying the agriculture and soil types in the Guanzhong area; and Hanzhong (32°58’N, 107°35’E), which typifies the paddy soil area in south Shaanxi.

In north Shaanxi, the dominant soil type is Entisol with high sand content and low content of clay and organic matter (Table 1). Soil profile has not developed and the loess is the parent material from the top to deep layers. The groundwater level is at about 4.5 to 20 m depth in terrace and bottomland; Anthrosol with moderate clay content and an organic matter content of 11.8 g kg^{-1} is mainly found at 0-20 cm depth in the Guanzhong area (Table 1). The soil profile is well developed with a top-layer of about 40-50 cm formed by prolonged tillage and application of farmyard manure. The subsoil depth is 40-60 cm and represents the original cinnamon soil profile, which is the ancient tillage layer. The clay content of the 80-140 cm layer is greater than 30%, and below this layer there is a Calcic horizon, approximately 40 cm deep and below that is the C-horizon, comprising the loess parent material (Guo *et al.*, 1992). The water table is at about 15-25 m depth in the Anthrosol area. The Luvisol is a paddy soil with high clay content in the top layer, and it is located in south Shaanxi (Table 1). Groundwater table is only 3-10 m depth.

China is one of the traditional organic agricultural countries, and Guanzhong was the cradle of Chinese agriculture. So organic manure used in Guanzhong has a long history, which formed 40-50 cm cover layer on the top of the Anthrosol. 20 years ago, such kind of organic manure was a mixture of swine slurry and loess soil with total N, P and K content of 0.3-0.94, 0,1-0.46 and 0.4-0.91%, respectively (CATESC, 1999). The nutrients content in organic manure was variable much dependent on how much soil was added to the slurry. Normally 60-85% of soil was added, so the local people call it loess soil movement. Nowadays, it is only swine or cow slurry applied, which results in much less transportation. 70-90% of the farmers applied organic manure to the bottomland in spring before sowing in north Shaanxi, 49% of the farmers applied organic manure to winter wheat but non to maize field in Guanzhong and 33% to rice field in south Shaanxi. Many farmers even use less and less organic manure because mineral fertilizers are more convenient to apply (the information from our investigation in 1997/1998).

Agriculture reforms in 1978 lead to a small-scale scattered farming systems, by which the land was separated to each family and 0.06-0.26 ha was assigned per capita in normal agricultural areas, which farmers rely on. So, sometimes it was difficult for us to find a piece of land with even soil fertility large enough to lay out experiments. Of course it is also a difficult life for the farmers to live on such small land area, especially in loess region of China.

Materials and methods

Nitrification, NH_4^+ fixation and ammonia volatilization determination

56 mg N kg^{-1} soil as Urea and NH_4HCO_3, were applied to Eum-orthic anthrosol from Yangling (**Paper V**); 142.5 g N kg^{-1} as NH_4HCO_3 and NH_4NO_3 were applied to Entisol from Mizhi and 285 g N kg^{-1} to Luvisol from Hanzhong (**Papers II**), the fertilizers were thoroughly mixed with 50 kg soil and loosely packed in a sealed airtight incubation box (Fig. 5). The temperature of the boxes was maintained at 17-22 ℃ for Luvisol and Entisol, 22-33 ℃ for Anthrosol. The soil moisture was maintained at 60% of water-holding capacity (WHC), corresponding to gravimetric water content of 19% in the Luvisol, 17% in the Eum-orthic anthrosol and 14% in the Entisol. Soil samples were removed for pH, NH_4^+ and NO_3^- determinations at different times to determine nitrification (**Papers II** & **V**). Ammonia volatilization and CO_2 were determined by extracting air with a pump from the box and volatilized NH_3 from the fertilizer was trapped in a solution of H_3BO_4 with an N indicator, which was titrated against a standard solution of HCl, CO_2 was trapped in a solution of KOH (Tong *et al*., 1994). Air let into the box was filtrated by a H_3BO_4 solution to trap NH_3 from the air, while at the same time, a box without soil as control treatment was used during the experiment.

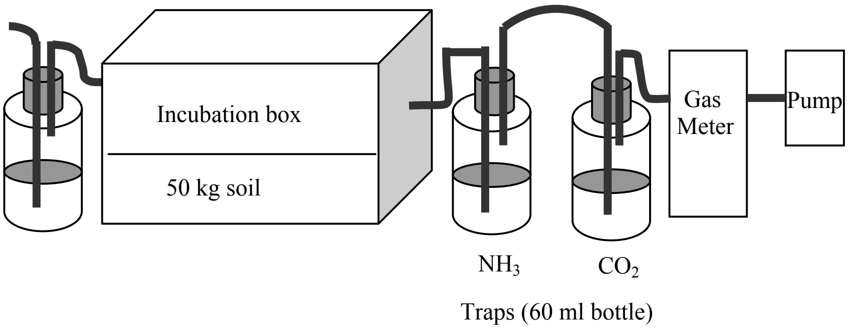

Fig. 5. Incubation box (length × width × height = 100 × 50 × 30 cm) used for determination of NH_3 volatilization, respiration, nitrification and NH_4^+ fixation (**Papers II** & **V**).

N_2O concentration in the soil profile and emission from the soil surface

N_2O concentration in the soil profile

This experiment was conducted at the National Monitoring Station on Loess Soil Fertility and Fertilizer Efficiency, Yangling. The last ten years before the experiment started the site was used as a 40 × 30 m control plot with wheat and maize growing in rotation with irrigation but without organic manure and mineral N fertilizer. There were two treatments in the experiment: a control without fertilization and another with fertilization. Fertilizer was applied to wheat, in the form of KNO_3, at the rate of 240 kg N ha^{-1}, when the wheat was in the elongation stage. For maize, 180 kg N ha^{-1}, in the form of KNO_3, was applied at the fifth leaf stage. The size of each plot was 20 m × 30 m, and three sampling sites were randomly distributed on each plot. According to the characteristics of the soil, permanent gas sampling probes (Magnusson, 1989) were installed at depths of 10, 30, 60, 90, and 150 cm down the soil profile. Soil gas samples were collected from the probes once a week, or more frequently after rain or irrigation, over a period of three years, from May 1999 until September 2001 (**Papers IV** & **V**).

The soil probes were made of PVC tubing (length, 24 cm; inner diameter, 6 mm; outer diameter, 8 mm). The tubes were perforated along the terminal 5 cm section and covered by a PTFE membrane. The PTFE membrane constitutes a waterproof layer, but it is permeable to gas molecules. A soft Viton tube with an inner diameter of 0.4 mm was connected to the end of the soil probe, and sealed with butyl rubber. The other end of the Viton tube was connected to a 3-way stopcock, above the soil surface. 2 ml gas samples were taken in plastic syringes, which were immediately sealed. Gas chromatographic analyses were done within a few hours (**Papers IV and V)**.

N_2O emissions from the soil surface

N_2O fluxes were measured using the closed chamber method (Mosier & Klemedtsson, 1994). Buckets of 16.5-liter volume were used for gas sampling and ten replicates were collected from each field. Gas samples were taken 0, 30 and 60 minutes from the time the buckets were placed upside down on the ground and gas analysis was performed within several hours of sample extraction. The gas samples were collected through a septum at the bottom of the bucket. The N_2O flux was calculated hourly as,

$$q = \frac{V(C_1 - C_0)^2}{At_1(2C_1 - C_2 - C_0)} \ln \frac{C_1 - C_0}{C_2 - C_1}$$

where q is the N_2O flux ($\mu g\ m^{-2}\ h^{-1}$) from the soil, V is the volume of the bucket (m^3), A is the area of soil covered (m^2), C_0 is the initial N_2O concentration in the chamber ($\mu g\ m^{-3}$), and C_1 and C_2 are the N_2O concentrations ($\mu g\ m^{-3}$) after times t_1 and t_2, where $t_2 = 2 \times t_1$ (h) (**Paper V**). The rate of concentration increase in the bucket must decrease with time (Hutchinson & Mosier, 1981), which was the case in this experiments.

N_2O gas analysis

The N_2O samples were analyzed using a Varian 3800 Gas chromatograph, equipped with a ^{63}Ni electron capture detector and a packed stainless steel column with N_2 carrier gas, flowing at a rate of 10 l/min. The temperatures of the column, injector and detector were maintained at 80, 120 and 350 °C, respectively. No significant differences in N_2O concentration were detected when the analysis was performed at any time within six hours of sample extraction.

Lay out of field experiments

The split plot latin square design was used in **Paper I** with organic manure as the main plot and NP as the split plot with three replicates. The experiments in **Papers III** and **V** were based on a completely random block design with different amount of N fertilizer under a base of PK application with three replicates. The field experiments were carried out in Mizhi, north Shaanxi, Guanzhong and south Shaanxi. Two catena transects were sampled in each of the three regions and in each transect three profiles were taken on each side of the river down to 400 cm depth in bottom land, slop and hilltop. Surface water and groundwater were sampled in three regions at regular distances along selected rivers and roads (**Paper III and V**).

Soil, water and plant samples analysis

A Flow Injection Analyzer (Tecator 5020) directly determined dissolved NH_4^+ and NO_3^-. NH_4^+ and NO_3^- in soil were extracted from fresh soil samples (fresh soil samples were kept in the refrigerator at below 5°C until the next day, if they could not be prepared during the sampling day) by 2 M KCl (soil:solution = 1:5), shaken for 30 min (Keeney & Nelson, 1982) and determined with a Flow Injection Analyzer (**Papers I, II, III** & **V**). Fixed NH_4^+ was determined by the Silva-Bremner method (Silva & Bremner, 1966; Bremner *et al.*, 1967) (**Paper II**). Total carbon and nitrogen contents in plant material were determined using a Perkin Elmer 2400 CHN Elemental Analyzer. C and N in the plant material were used to calibrate N uptake by plants, and to calculate biomass and yield production when the balance of N fertilizer was calculated (**Paper V**).

Measures to minimize N loss and increase N fertilizer use efficiency

Based on the results from a range of laboratory and field experiments, the farmers were given recommendation of fertilizer application with a double target of maintaining high yields while protecting environment. Specific techniques were used such as soil testing, proper timing of nitrogen application, balanced N fertilization with P, K, Zn and S. Application of organic manure, split and timing irrigation, information and education of the farmers.The demonstration villages were also used as control villages to estimate yield and nitrogen use rate for common farmers in Shaanxi.

Statistical analysis

Statistical analysis was done with the SPSS program (Version 10). Correlation coefficients between water content and fixed NH_4^+ rate were calculated in **Paper II**, the differences in ammonium fixation rates between different moisture contents were compared using Least Significant Difference (LSD) analysis (**Paper II**). Mean values of the N_2O concentrations from different depths of the soil profile were compared using Duncan's multiple-range test (**Paper IV**). Standard deviations were calculated for the mean values of nitrate accumulation in the soil profiles and N uptake by plants in the N balance calculations (**Paper V**). The differences in N balance between the treatments were compared using Least Significant Difference (LSD) analysis (**Paper V**).

Summary of results from Paper I - V

Paper I

Of primary concerns were the nitrate leakage to groundwater and the financial losses for the farmers. **Paper I** evaluated a 12-year old fertilizer experiment by soil sampling and subsequent soil analysis down to four meters depth, to measure the amount of nitrate stored in the profiles. The profiles contained 65 – 303 kg N ha^{-1} as NO_3-N at the date of sampling. The highest accumulation was found where no organic manure was applied. During the 12-year experiment the total nitrogen fertilizer application amounted to 1800 or 2880 kg N ha^{-1} and in addition 1800 or 3600 t ha^{-1} of organic manure was added. The total nitrogen uptake by the crops was 1600 (control) to 4056 (highest fertilizer rates) kg N ha^{-1}, and the apparent nitrogen recovery was 70,4 - 29.8%. The amount of nitrate accumulation in the 0-400 cm soil profile was positively related to the amount of N applied. High N application rates lead to low apparent N recoveries by crops and large NO_3-N accumulations in and losses from the soil profiles. Application of organic manure helped to reduce NO_3-N accumulation in the soil profile, but the total nitrate loss out of the profile may have been larger.

Paper II

The rate of NH_4^+ fixation was studied with NH_4HCO_3 in a Luvisol with water content of 8, 18 and 28%. No difference in the NH_4^+ fixation rate was found between the 8 and 18% soil moisture levels. However, at moisture levels of 18 and 28%, 1 h after fertilizer incorporation, the amount of NH_4^+ fixed was 51 or 66%, respectively. At these two moisture levels, after 2 h, 67 and 74% was fixed and after 48 h, 82 and 85% was fixed, respectively. No differences in nitrification rate were recorded for the Entisol when comparing the two fertilizers, NH_4HCO_3 and NH_4NO_3. In the Luvisol, the application of NH_4HCO_3 resulted in a gradual nitrification of fixed ammonia, followed by a slow release once all the free NH_4^+ had been exhausted. Laboratory nitrification studies were conducted over a longer time period, using different N fertilizers. These showed that almost all free NH_4^+ was nitrified within nine days in the Entisol, within three days in Anthrosol (**Paper V**), but took more than 40 days in the Luvisol (Fig. 6) because fixed NH_4^+ released slowly. An experiment with pots filled with 2 kg soil was carried out in a glass shelter open to wind and sunshine. N fertilizer was applied banded or incorporated under different water contents. N recovery was tested 26 days after fertilizer application. An average of 74.2% of the added N fertilizer was recovered 26 days after N fertilizer application to the Luvisol, while only 61.4% could be recovered from the Entisol. The results for the Luvisol showed lower nitrogen recovery as initial soil water content increased. The higher N recovery from the Luvisol at lower moisture levels could be explained by the faster rate of N removal from the available pool but it is difficult for the fixed NH_4^+ release when the soil water content is low. When the fertilizer was incorporated into the soil, the recovery of N was increased, compared with the banded treatment, by an average of 26.2% in the Luvisol and 11.2% in the Entisol.

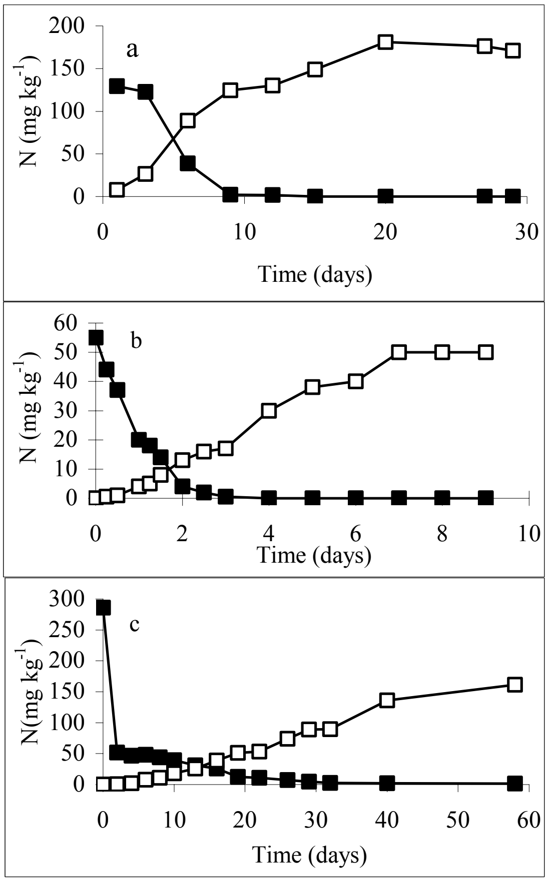

Fig. 6. Ammonium bicarbonate conversion to nitrate in incubation experiments with a: Entisol, b:Anthrosol and c: Luvisol.

■ NH_4-N; □ NO_3-N.

Paper III

Nitrate accumulation in the soil profile and in groundwater and surface waters in the different ecological zones of Shaanxi Province from north to south with different types of land utilization was surveyed and described. In the hilly and gullied area in north Shaanxi, nitrate leaching down to groundwater mainly took place from the bottomland, where large amounts of N fertilizer were applied and a flooding type of irrigation was utilized. There was no nitrate accumulation or leakage on top of the hills or slope land. Over-application of N fertilizer was common in Guanzhong. The amounts of accumulated nitrate in the soil profile at 0-400 cm depth were found to be 3414 and 1362 kg N ha^{-1} in orchard and vegetable land, respectively, which would be further leached down to deeper layers and finally down to the groundwater.

In a survey 93 well water samples were taken along either side of the roadway from Yuling to Suide (covering a distance of about 110 km) in north Shaanxi. Most of these wells were used as both drinking water and for irrigation. NO_3-N concentrations in the well water were >11.3, 5-11.3 and <5 mg N L^{-1} in 21.5%, 18.2% and 60.2% of the samples, respectively. In the Weibei dry plateau and the Guanzhong irrigation area 74 wells in 24 counties were investigated. Most of these were newly dug wells for irrigation, but some of them were near villages and used also as drinking water. The NO_3N concentration in these wells were >11.3, 5-11.3 and <5 mg N L^{-1} in 29.7%, 25.6%, and 44.6% of the samples, respectively. Thus, the nitrate concentration in groundwater was over the health limit for drinking water set by the WHO (1993) in 21.5% of investigated wells in north Shaanxi, and 29.7% in the Guanzhong area.

In 70 surface water samples, the NO_3-N concentration was >11.3, 5-11.3, and <5 mg N L^{-1} in 15.7%, 11.4% and 72.9% of the samples, respectively. At the same time, it was found that the NO_3-N concentration in water from the Yellow River in Shaanxi, the Wei river (a major tributary to the Yellow River) and a tributary to the Wei River near Xi'an city was 2.4, 8.2, and 16.6 mg N L^{-1}, respectively.

An experiment with N, NP and NPK started 1990 after a few years without any treatment. The experiment was first evaluated after a wheat-maize-wheat rotation period in which 517.5 kg N ha^{-1} had been applied. An inventory of NO_3-N in the soil profiles was then conducted. The amount of NO_3-N accumulated in 0-400 cm soil profiles was highly dependent on fertilizer composition (Fig. 7). If N fertilizer was applied in combination with P or P and K, the crop yield increased and the NO_3^- accumulated in the soil profile decreased from 272 to 116 and to 52 kg N ha^{-1} (Fig. 7).

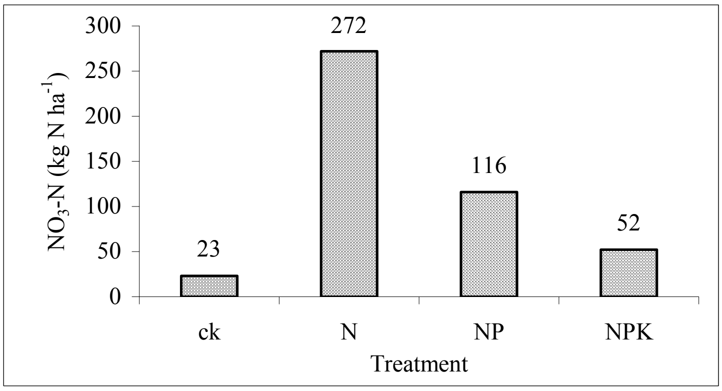

Fig. 7. NO_3-N accumulation in 0-400 cm soil profile with different fertilizer treatments (Data from **Paper III**, Fig. 6)

Paper IV

There have been few reports or papers describing the N lost by N_2O emission from loess soil. N_2O production in the loess soil profile and the factors affecting its production were investigated using field soil probes for *in situ* measurements and C_2H_2 inhibition soil cores.

There were significant spatial and temporal variations of the nitrous oxide in loess soil (Fig. 8). The temporal variation was correlated with the water supply (such as rainfall or irrigation events) and N_2O peaks occurred about three days after water events. The maximum N_2O concentration in the fertilized plot was 2.5 times higher than that in the plot where no fertilizer was applied. The range in concentration was 320 to 996 nl L^{-1} for the control plot (Fig. 8a) and 313 to 2476 nl L^{-1} for the fertilized plot (Fig. 8b). The spatial variation of N_2O concentration in the soil profile correlated with the clay content and moisture status. The concentration peaked at 60 or 90 cm depth in the soil profile, which shows that there was a production at these depths.

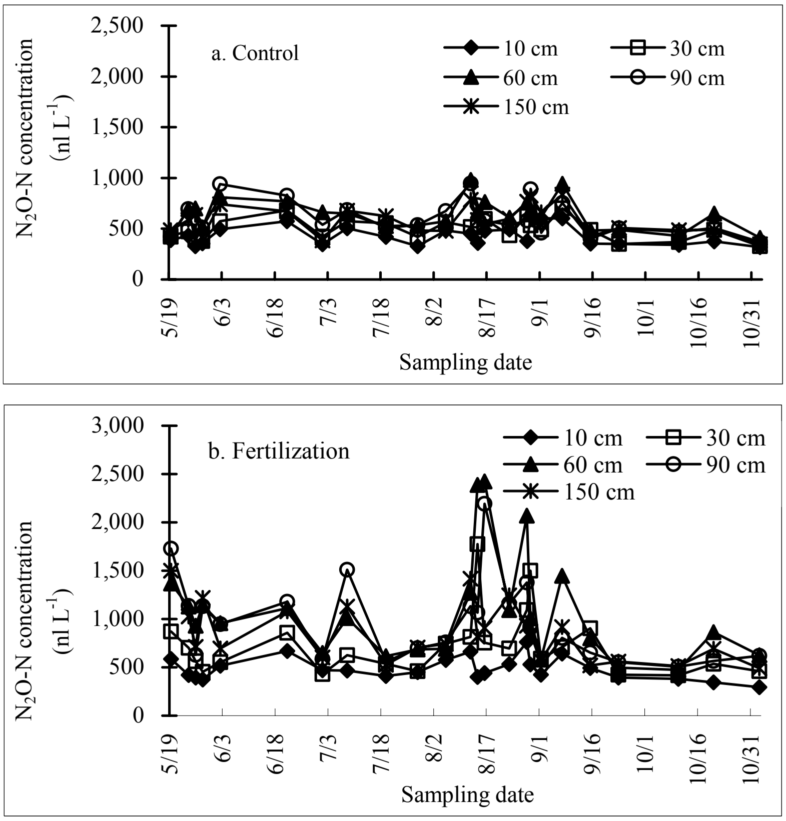

Fig. 8. Variation in N_2O concentration in the soil profiles during the period 19 May to 31 October 1999 in: a) the control plot and b) the fertilized plot.(Paper IV).

In the incubation experiment with C_2H_2 inhibition in 385 cm^3 intact soil samples from control soil N_2O flux was almost zero. Increasing the water content by 10% increased the flux to 546 ng d^{-1}. An addition of 300 µg NO_3-N did not change the flux during the first 16 h, but after 17 – 20 h the flux was 86.1 ng d^{-1}. Addition of 0.1 g carbon in the form of glucose to 100 g soil increased the N_2O flux up to 20.6 µg d^{-1}. Carbon and nitrate was added in water solution, which increased the water content by 5%, which may have influenced on the results. The conclusion from the incubation experiments was that NO_3^- was not limiting N_2O production in soil from the control plot, but carbon was the limiting factor controlling denitrification. When carbon was supplied, nitrate content and water became the limiting factors.

Paper V

In **Paper** V N uptake by crops, N storage, NO_3^- leaching and possible ways for nitrogen losses are quantified. In Guanzhong farmers apply N fertilizer at high rates, but grain yields do not increase with increased N application rates. The over-application of N fertilizers in Guanzhong area was estimated to 90,000 tons per year. There was no correlation between the amount of N fertilizer applied and the wheat and maize yields in several field fertilizer experiments in Guanzhong area conducted in 1997 and 1998. The crops did not use a large proportion of the N fertilizer, but it was readily transformed to nitrate, only to be lost later from the soil profile. In a balance calculation 119±54 kg N ha^{-1} yr^{-1} was lost from the upper 8 m of the soil profile (Fig. 9). A simple model calculation revealed that only 13 kg ha^{-1} y^{-1} passed the 2 m horizon and 5 kg ha^{-1} y^{-1} passed 8 m depth. The unaccounted amount must have been lost through other processes.

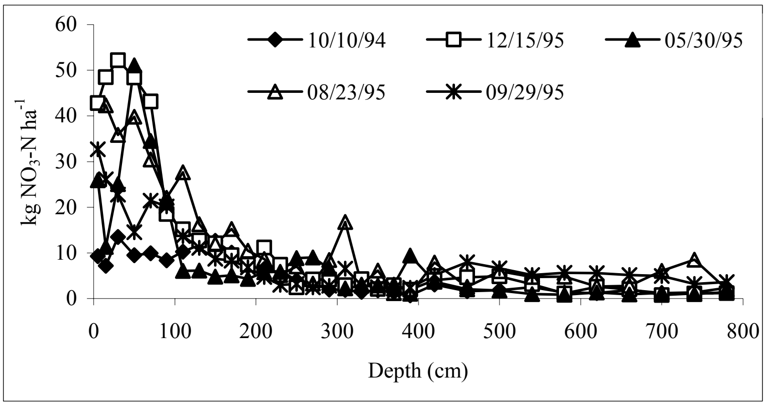

Fig. 9. The mean soil NO_3-N content per 20 cm depth in the soil profile at various times in the 1994-1995 growing season in field experiment 1.

Nitrate leaching did not account for all N loss from the 8-m soil profile (Fig. 10). Nitrogen gas as N_2O was determined from the soil profile and soil surface and indicated a possible way for nitrate losses through denitrification. The highest concentratins were measured at 60 and 90 cm depth, which shows a production here (Fig. 8). Fluxes from the soil surface were not statistically different from the two measurement methods, that is 10.3±8,3 and 15.2±3.8 µg m^{-2} h^{-1} for calculations from profile data and from *in situ* measurements at the soil surface. After reduction for bias sampling a yearly flux of 0.6 kg N_2O ha^{-1} was adopted. Most of N_2O losses appeared after irrigation and autumn rainfall. The highest net N_2O production in the soil profile was found at 2 – 20 cm depth and it then strongly decreased down in the profile. A net N_2O production does not imply a total production by denitrification because N_2O-N could be further reduced to N_2 gas. At present nothing is known about the proportion of N_2O that is reduced to N_2 deep in a loess profile, but from the NO_3^- leaching estimates a considerable amount of NO_3^- is lost above 8 m depth.

Previously, preventing ammonia volatilization and nitrate leaching into the groundwater were believed to be the main measures required to reduce N losses. Results in this paper, rather indicate that nitrogen is lost by a combination of leaching and denitrification. Farmers need to use less fertilizer and better timing to increase nitrogen-use efficiency and to increase profitability; which would also reduce greenhouse gas emissions.

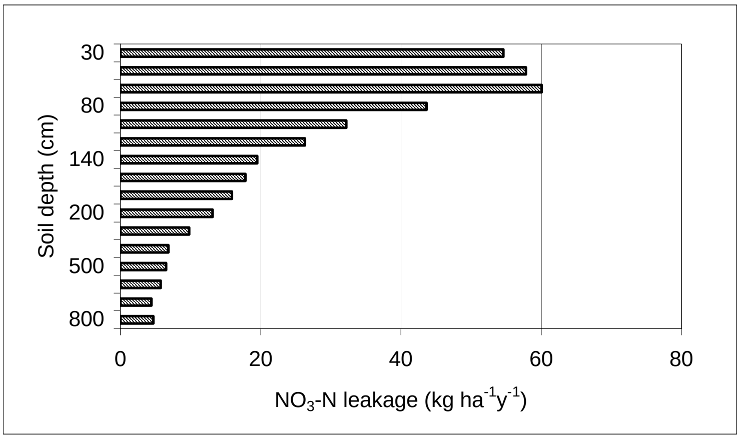

Fig. 10. Calculated NO_3-N leakage (kg ha^{-1} y^{-1}) out from different horizons during October 1994 to September 1995 for field experiment 1 in Yangling.

Discussion

The nitrification rate is high in high pH soils. Within the pH range 3.4-8.6, nitrification activity is positively correlated with pH (Sahrawat, 1982). An active nitrification takes place in soils with pH 6.4-8.3 (Katyal *et al.*, 1988). In Entisol (**Paper II**) and Anthrosol (**Paper V**) almost all added ammonium was transformed to nitrate within 9 days, but it took more than 40 days in the Luvisol because of the slow release of the fixed NH_4^+ when urea or ammonium bicarbonate was incorporated with the soils. Soil moisture and soil texture are also important factors affecting nitrification. The optimum moisture content for nitrification in soil is 50-70% of the maximum water-holding capacity (Li, 1997). Soil texture affects soil aeration and water permeability. Li *et al.* (1986) showed that there was a marked negative correlation between nitrification rate and clay content (<0.001 mm). The loess soil has a high pH (7.1 – 8.3, **Paper I**), in the experiment soil moisture was kept in 60% of field capacity, and consequently the nitrification rate was high. Because the clay content in Luvisol is higher than in Entisol and Anthrosol, the nitrification rate was much slower in Luvisol than in the other soil types. Due to high nitrification rate, NH_4^+ ions only exists in the soil for a short time, and the opportunity for NH_4^+ loss through NH_3 volatilization is small. But on the other hand the nitrate formed can easily leach down the soil profile away from the plant root system with percolating water.

Ammonium fixation rate was also high. One hour after fertilizer incorporation more than 50% was fixed in Luvisol, and after two days more than 80% was fixed. Increased water content increased NH_4^+ fixation rate (**Paper II**). When nitrification exhausted exchangeable or free NH_4^+ in Luvisol, the fixed ammonia was slowly released, which would limit N losses by NH_3 volatilization and NO_3^- leaching. As Drury & Beauchamp (1991) pointed out the fixed NH_4^+ pool appeared to act as a slow-release nitrogen reservoir. So, in agricultural soils, the release of fixed NH_4^+ from the clay minerals plays an important role in subsequent N supply to crops (Drury *et al.*, 1989). This was also verified by the pot experiment described below.

In the pot experiment (Paper II) the Luvisol showed high N recovery at low soil water content. This was in line with a large amount of fixed NH_4^+, which could be explained by the faster N removal rate from the available pool, but hampered release of fixed NH_4^+ when soil water content is low (Allison *et al.*, 1953; Mengel & Scherer, 1981). In the experiment 25.8% for Luvisol and 38.7% for Entisol was not recovered. There was no NO_3^- leaching during the experiment. Nitrogen immobilization, denitrification, NH_3 volatilization was not measured. NH_4^+ fixation was not measured for the Entisol,but the potential for N fixation was low in the Entisol due to the low clay content. Paul & Clark (1988) argued that denitrification is not significant at soil moisture contents of around 60% WHC or lower, but it increases at higher soil moisture contents. So denitrification could be carried out at the water content of 20-28%. Ammonia volatilization, however, is favored in soils with a high pH, because the equilibrium between the NH_4^+-ion and ammonia ($NH_{3(aq)}$) is shifted towards the gaseous form (Beyrouty *et al.*, 1988). This effect is quite pronounced at pH 9.0, where 35% is present as NH_3, while at pH 8.0 less than 5% of the total ammonium is in this form. The effect of the initial soil water content on NH_3 volatilization is significant (Fenn & Escarzaga, 1977; Al-Kanani *et al.*, 1991). But in the closed incubation box only less than 5% of the applied N was lost by ammonia volatilization (Tong *et al.*, 1994). There is still 6.5% clay content in Entisol, which could fix NH_4^+ and could contribute to the reasons for low N recovery in Entisol.

The incubation box was used to determine amounts of ammonia volatilized from applications of NH_4HCO_3 and urea fertilizer and the results are shown in Fig. 11 and 12, respectively. During the 20-day experiment, the absolute amount of ammonia volatilization was low: ammonia losses from NH_4HCO_3 in Eum-orthic anthrosol and Entisol were 331 and 533 mg NH_3-N m^{-2}, equivalent to 2.6% and 4.1% of the nitrogen applied, respectively. Ammonia losses from urea in Eum-orthic anthrosol and Entisol were 254 and 203 mg NH_3-N m^{-2}, respectively, equivalent to 2.0% and 1.6% of the nitrogen applied. In this experiment ammonia volatilization from NH_4HCO_3 was 1.8 times higher than that from urea. The ammonia volatilization from Etisol was 20% higher than that from Eum-orthic anthrosol (Tong *et al.*, 1994). The results from this experiment do not directly apply to field conditions, because the ventilation must have been lower than the free convection over a farm field. However, the decrease in volatilization rate (Fig. 11, 12) compares well with the depletion of the ammonium source reported in **Paper II**. Ferguson & Kissel (1986) found that ammonia volatilization to be strongly related to the initial soil water content. Ammonia is dissolved in soil water, but volatilization of ammonia can take place with evaporating soil water. In this experiment, the soil moisture was kept nearly constant and very little soil moisture was lost during the experiment, so little ammonia was lost. The time course of volatilization followed two different patterns. There was a large initial volatilization from NH_4HCO_3, which decreased rapidly with time when ammonium was nitrified (Fig. 11). In contrast, volatilization was initially low from urea, but increased to a peak after three to four days when all urea was hydrolyzed and the ammonium ion concentration peaked, after which the volatilization decreased as the ammonium was nitrified (Fig. 12).

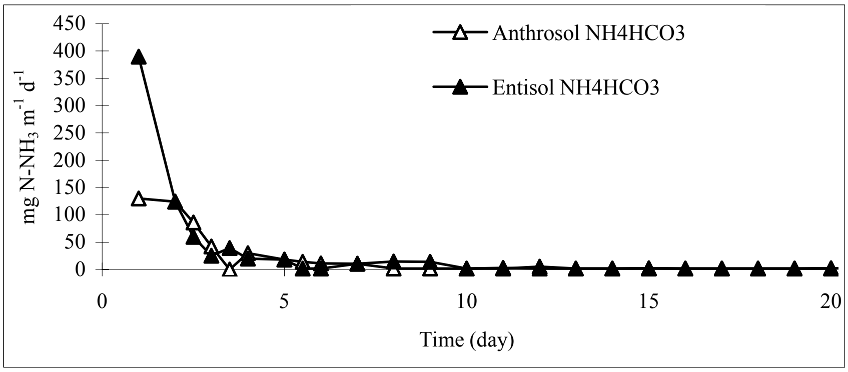

Fig. 11. Ammonia volatilization from NH_4NO_3 applied to Eum-orthic anthrosol and Entisol. (Redrawn from Tong *et al.*, 1994).

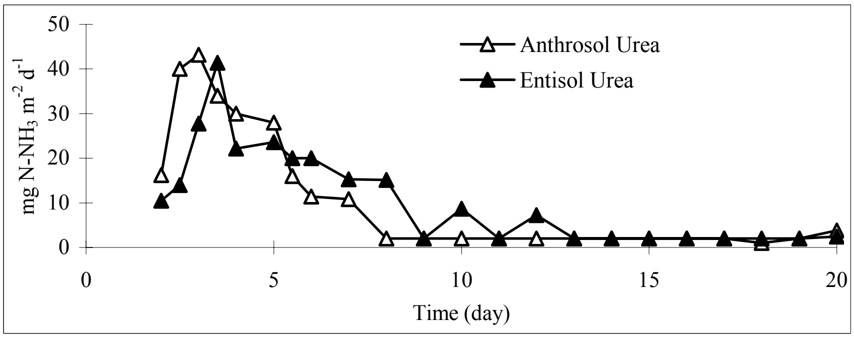

Fig.12. Ammonia volatilization from urea applied to Eum-orthic anthrosol and Entisol. (Redrawn from Tong *et al.*, 1994).

From ammonia volatilization measurements, the N loss from the pot experiment could not be explained. The conclusion was that unrecovered N could have been lost by denitrification, immobilization and ammonia volatilization for Luvisol and by ammonia volatilization, immobilization and NH_4^+ fixation for Entisol. A high NH_4^+ fixation rate could prevent N loss and increase N recovery.

Nitrate accumulation in the soil profiles in the different ecological zones of Shaanxi Province with different types of land utilization was large (**Paper III)**. In the hilly and gullied area in north Shaanxi, nitrate accumulation was mainly in the terrace- and bottomland. Here at 200 – 400 cm depth in the profiles, that is below the crop-rooting zone; about 540 and 360 kg N ha^{-1} was accumulated and would finally leach down to the groundwater. The main reason for the large amount of nitrate that was accumulated in the deep soil profiles in the terrace- and bottomland was that large amounts of N fertilizer were applied and a flooding type of irrigation was utilized on the sandy soil. The nitrate accumulation on top of the hills and on slope land was small. Over-application of N fertilizer was common in the high yield regions of Guanzhong. The amounts of accumulated nitrate in the soil profile at 200 - 400 cm depth were found to be about 1800 and 680 kg N ha^{-1} in orchard and vegetable land, respectively.

Nitrate accumulation and leaching in the soil profile were strongly related to the N fertilizer application rate. When the N fertilizer rate increased from 0, to 112.5, to 187.5 to 262.5 kg N ha^{-1}, the nitrate accumulated in the 0-400 cm profile increased from 114, to 212, to 237 to 331 kg N ha^{-1}, respectively (**Paper III**). This was also discussed in **Paper I**. When the N application rate increased from 0, to 150, to 240 kg N ha^{-1} y^{-1}, the nitrate accumulated in the 0-400 cm soil profile increased from 101, to 122 to 303 kg N ka^{-1} during a period of 12 years of wheat and maize rotation (**Paper I**). Fan *et al.* (2002) found also a similar result in a long term experiment (1984-1999) without irrigation in the south part of the Loess Plateau in Changwu County, Shaanxi Province (mean annual precipitation of 584 mm), the amounts of nitrate in 0-400 cm depth were 86, 116, 109, 405 and 550 kg ha^{-1}, when the respective annual nitrogen application rates were 0, 45, 90, 135, and 180 kg N ha^{-1}. The accumulated NO_3^- in the soil increased sharply when the annual N application rate exceeded 135 kg N ha^{-1}. Jaynes *et al.* (2001) found that when the N fertilizer rate increased from 67, to 135, to 202 kg N ha^{-1}, the nitrate losses in tile drainage water increased from 29, to 35 to 48 kg N ha^{-1}, respectively. Consequently the amount of nitrate leaching increased with increased N fertilizer application rate.

Balanced fertilization stimulates uptake of nutrients by plants and thus increase yield. It could also promote root growth and formation of a high-density root layer, which could prevent NO_3-N leaching. Unbalanced fertilization with too much N compared with P and K usually causes high nitrate accumulation in the soil (Fig. 7). A long term experiment (1980-1997) conducted in Henan Province (Sun *et al.* 2001) in a winter wheat - summer maize rotation resulted in accumulated amounts of nitrate in 0-100 cm profile of 152, 2990, 2123 and 1516 kg N ha^{-1} in the control (without N, P and K applied), the N treatment (120-180 kg N ha^{-1} per crop), the NP treatment (120 kg P_2O_5 ha^{-1} to every second crop) and the N-P-K treatment (120 kg K_2O ha^{-1} to every second crop), respectively. Obviously soil P and K is too low in the loess soil to support a yield of the size the nitrogen additions suggests. Application of P and K stimulated plant uptake of N and less nitrate accumulated in the soil profile.

Application of organic manure reduced the nitrate accumulation from 303 to 227 and to 181 kg N ha^{-1} in the 0-400 cm soil profile when the amount of organic manure applied increased from 0 to 75 t ha^{-1} y^{-1} and to 150 t ha^{-1} y^{-1}, respectively, after 12 years in an Eum-orthic anthrosol in the Guanzhong area (**Paper I**). The reason was probably that the organic matter content in loess soil is low (in the present experiment 11.8 g kg^{-1}) and some nutrients are in shortage due to the long-term cultivation. The water holding capacity and nutrients balance will improve when organic manure (traditionally it contains only 20–40% swine excreta mixed with soil) is applied to the soil. Cheng and Wen (1997) pointed out that the combined use of organic manure and N fertilizer could help to reduce the loss of fertilizer N and increase its availability. On loess soils in north-western China, in 14 out of 20 field experiments yield was significantly larger in the treatment with barnyard manure and fertilizer N applied in combination than in treatments with fertilizer N or barnyard manure applied alone. Mo and Qian (1981) reported that when 80 mg urea N kg^{-1} was applied in combination with 0.6% rice straw, residual urea N increased significantly and loss was greatly reduced. But Yoshida and Padre (1975) found that the plant uptake of fertilizer N was greatly decreased and the residual fertilizer N was greatly increased when 125 mg fertilizer N kg^{-1} was applied in combination with 0.5% rice straw. So Cheng and Wen (1997) concluded that the fate of manure N or fertilizer N in combined application might differ from when they are applied alone, depending on the type of manure, rate of application and the soil conditions. But in intensive dairy farming systems where organic N is added to the soil (Kristensen *et al*., 1994; Ritter *et al*., 1990), high N leaching losses occur. In Europe, regular application of slurry and N fertilizer cause annual nitrate leaching losses ranging from 154 to 338 kg N ha^{-1} (Trindade *et al*., 1997). There are few intensive dairy or swine farms in China, especially in the loess region and organic manure is always in deficiency. To improve the soil physical and chemical properties, increase yield or decrease the nitrogen loss, organic manure should sustainable be applied in increased amounts to the soil.

Nitrate leaching is also dependent on the amount of irrigation and soil physical properties. The crop roots are mainly distributed in the 0-40 cm layer of the soil profile. During the crop-growing season the amount of NO_3-N leaching away from the 0-40 cm layer was equivalent to 41%, 31% and 15% of the total amount of applied N fertilizer in Mizhi with sand soil (north Shaanxi), Yangling with silt clay loam and Hanzhong with a loam clay texture, respectively (**Paper III**). This indicated that the heavier the soil texture, the less amount of nitrate was leaching.

Nitrate in groundwater and surface water are to a varying extent associated with nitrate accumulation and leaching in soil profiles (**Paper III**). In the high-yield agricultural regions, which are subjected to over-application of N fertilizer and heavy flooding irrigation, and areas with significant inputs of industrial liquid waste and organic waste, were found to be the main areas affected by groundwater and surface water nitrate pollution. These conclusions agree with the results of Xia *et al*. (2002), who summarized a monitoring investigation of nitrogen contamination from the Yellow River upper basin to its lower basin in the years 1980, 1990, 1997 and 1999, finding that the nitrogen content of the river water increased significantly in the mainstream and the tributaries during this period. This change was ascribed an increase in wastewater discharge and N fertilizer applications in the Yellow River catchment.

Non-point source pollution from agriculture is becoming serious due to over-application of N fertilizer and continuously decreasing N fertilizer recovery rate by crops. The investigation (**Paper V**) of fertilizer use by farmers in Guanzhong area showed that farmers used 52 and 90 kg N ha^{-1} too much for wheat and maize, respectively. This surplus N will finally end up in the environment. Zhang *et al.* (1996) made a survey of groundwater nitrate concentrations in the provinces of Beijing, Tianjing, Hebei, Shandong and Shanxi and found about 46% of 600 groundwater samples that exceeded the FAO limit for nitrate in drinking water of 11.3 mg L^{-1}, with the highest nitrate concentration reaching 500 mg L^{-1}. Although the soil core sampling method is very suited for measuring the displacement of nitrate in the soil profile for crop production on upland soils, there is a shortage of practical methods for measuring the actual transition of nitrate into the groundwater and models are used to assess water percolation to be combined with concentration measurements to calculate nitrate fluxes (c.f. Paper V).

A group of western European countries defined a safe upper limit of annual manure application for preventing water pollution of 170 kg N ha^{-1} (Uunk, 1991; Archer & Marks, 1997), and stipulated that the residual mineral nitrogen content in the 0-90 cm soil layer after harvest should not exceed 45 kg N ha^{-1}. Upper limits as those mentioned above for Europe are not directly transferable to the Chinese situation due to different soil and climatic conditions, production and rotation systems, and yield levels. Still there are no regulations; legislations or rules related to agricultural fertilization or any evaluation made on which effect it might have on the environment in China.

Denitrification and N_2O emission from paddy soil has been extensively investigated (Cai *et al.*, 1985; 1991; 1992; Zhu *et al.*, 1989), and few on loess soil (Zhu *et al.*, 1997) in China. The studies reported in **Paper IV** and **V** are together with the work by Liang *et al.* (2002a and b) the first on upland loess soil. Liang *et al.* (2002b) found that when the N fertilizer rate increased from 75 kg N ha^{-1} to 150 kg N ha^{-1}, the N_2O flux increased from 3.1 kg ha^{-1} y^{-1} to 6.2 kg ha^{-1} y^{-1} on vegetable land in this area. This is consistent with the conclusions of Khalil *et al.* (2002) that the N_2O emissions from a maize-groundnut rotation mostly depended on the types and amounts of N fertilizers applied and water-filled pore space.

The N fertilizer use efficiency in **Paper I** was defined as the N recovery efficiency (fertilizer N uptake per unit applied N). Due to the N losses through ammonia volatilization (Tong *et al.*, 1994), nitrate leaching to groundwater and surface water (**Papers I & III**) and denitrification (**Papers IV & V**), N recovery efficiency is low; about 30% according to **Paper I**. Over-application of N fertilizer is common, and N recovery efficiency decreased as the rate of N fertilization increased. In **Paper I**, when the N fertilizer application rate increased from 75 to 120 kg N ha^{-1}, N recovery efficiency decreased from 70 to 65% when no organic manure was applied, and from 46 to 30% when 150 t ha^{-1} of organic manure was applied. An N application rate of 128 and 192 kg N ha^{-1} gave the same N fertilizer recovery efficiency. N fertilizer recovery efficiency could also be as high as 42-63% if the agricultural practices were in good conditions (Sigunga *et al.*, 2002). Sowers *et al.* (1994) found a N fertilizer recovery efficiency of 52.1% when 56 kg N ha^{-1} was applied to wheat field, while when 112 kg N ha^{-1} was applied it was only 29.3%. Thus, proper N application rate is critical to meet plant needs and improve N use efficiency.

Agricultural production coupled with low fertilizer recovery and high loss rates, and high pressure on the environment is a worldwide problem (Zheng *et al.*, 2002; Galloway & Cowling, 2002). Some developed countries with more arable land and lower population pressure solve these problems by improving fertilization techniques and by lowering their target yield in order to reduce the N application rate (Rehm & Schmitt, 1989). But in China, this latter way is hard to adopt because of the great pressure on grain production due to the shortage in per capital arable land. So China has to seek an optimum integration for obtaining both high grain yields and alleviating the pressures on the environment by improving the techniques of N fertilization management and searching for the corresponding theoretical foundation.

Measures to minimize N loss and increase N fertilizer use efficiency based on the results from a range of laboratory experiment, field trials, soil testing, investigation of farmers fertilizer application, nitrate contamination of groundwater and surface water, and techniques recommendation of fertilizer application to the farmers has been done with a double target of maintaining high yields while protecting the environment. Specific techniques is described as follow:

Soil tests could give a suggestion of optimum amount of fertilizer application to reduce the N fertilization rate and improve the environment. Soil samples were tested during the entire period of the wheat and maize growing stages to provide recommendations to the farmers in the demonstration villages. The amount of N fertilizer applied was reduced from 175 to 123 kg ha^{-1}, or by 30% of the amounts the farmers used outside the demonstration village, but the yield was the same as that obtained by other farmers during the experimental period (**Paper V**).

It was recommended that the N fertilizer application should be split, and the fertilizer applied on two or three occasions, according to the stage of plant growth and precipitation. For wheat, 40% of total fertilizer should be applied at the sowing time, 30% in the spring, and the remaining 30% should be added at the flowering stage if there is a wet or normal year. If it is a dry year, the yield will be lower, so the last 30% of the fertilizer should not then be used. For corn, 60% of the N fertilizer should be applied at 4-6 leaves stage and the remaining 40% before flowering stage.

Balanced fertilization is the best strategy to reduce N fertilizer rate and increase yield. The recommendation was to increase K fertilizer, keep certain amount of P, reduce N fertilizer and apply a certain amount of zinc and sulphur.

Apply organic manure and return wheat straw and corn stock to the soil were recommended to increase organic matter in the soil.

Due to the fast nitrification process, most of the N in soil is in the form of NO_3^-. Nitrate leaching in the Entisol and N_2O emission in the Eum-orthic anthrosols are much related to irrigation or precipitation. Less amount of water and split irrigation were recommended.

It is important to let the farmers know what and how to apply fertilizers and the consequences of the fertilization. Information and education of farmers should be given priority.

Conclusions

Because of its growing population and improving living standards with changing consumption patterns, China must try to realize a double target of environmental protection while maintaining high yields. In this study, found that over-application of N fertilizer was very common in the Guanzhong area and ranged from 100 to 382 kg N ha^{-1} for wheat and from 106 to 530 kg N ha^{-1} for maize. In the pot experiment open to the wind and sunshine with different water content, applied N fertilizer recovery was 74.2% for the Luvisol and 61.3% for the Entisol. Nitrogen recovery increased with increasing soil clay content. Transformation of fertilizer NH_4^+ to NO_3^- was within nine days in the Entisol and Eum-orthic anthrosols in north Shaanxi and the Guanzhong area, but it took 40 days in Luvisol from south Shaanxi due to NH_4^+ fixation by clay minerals. The nitrogen fertilizer recovery efficiency was estimated to be about 30% in Guanzhong and bottomland in north Shaanxi. Huge amounts of NO_3^- accumulated in 0-400 cm soil profile, 362-543, 144-677 and 165-569 kg N ha^{-1} in 200-400 cm depth were found in north Shaanxi, Guanzhong and sourth Shaanxi, respectively, which would be difficult for the crops to access. N_2O emission from fertilized plots was 2.5 times higher than that in the control plot, which was not expected in Guanzhong area earlier and could probably be higher from land where organic manure in combination with mineral N was used. The nitrogen losses were found to pose a serious threat to the environment by leaching to groundwater in three agri-ecological regions of whole Shaanxi province, and also by denitrification to the atmosphere in the Guanzhong area. Over-application of N fertilizer, unbalanced fertilization and heavy flooding type of irrigation were the main reasons causing the low N recovery efficiency and environmental pollution. Farmers could use techniques such as soil testing, fertilization timing, water management, and balanced fertilization to reduce N application rates, increase N fertilizer use efficiency and protect the environment.

Future studies

Nitrogen is the most important nutrient for plant growth since it is required to form proteins and nucleic acids. Nitrogen fertilizer is the most heavily used mineral fertilizer globally. Large numbers of agronomic scientists around the world are studying issues related to N nutrition. Nevertheless, the problems caused by N are very serious and widespread around the world. So, the study of nitrogen presented in this thesis is, for me, just a starting point. Investigations will be continued in the following fields:

In theory:

N behaviour in soil and plants;
N losses by ammonia volatilization, nitrate leaching and denitrification;
More detailed research on denitrification in Eum-orthic anthrosol, to obtain more precise and accurate quantification of N lost through denitrification;
N fertilizer and plant quality, especially of cash crops;
N and the environment: Nitrate leaching, N_2O emission, nitrate concentration limits in drinking water and vegetables.

In practice:

Develope better soil nutrient management regimes for the farmers;
Optimize fertilization amounts, and develope balanced fertilizer application recommendations for farmers;
Improving fertilizer application techniques to increase N fertilizer use efficiency;
Transferring knowledge to the farmers and training them.

References

Albritton, D.L., R.G. Derwent, I.S.A. Isaksen, M. Lal & D.J. Wuebbles. 1995. Trace gas radiative forcing indices. In: J.T. Houghton, L.G. Meira Filho, J. Bruce, H. Lee, B.A. Callander, E. Haites, N. Harris, & K. Maskell (Editors), *Climate change.* 1994: Radiative forcing of climate change. Cambridge University Press, Cambridge, England. pp. 209-231.

Al-Kanani, A., A.F. MacKenzie & N.N. Barthakur. 1991. Soil water and ammonia volatilization relationships with surface-applied nitrogen fertilizer solutions. *Soil Science Society of America Journal*. 55: 1761-1766.

Al-Kanani, T., A.F. MacKenzie & H. Blenkhorn. 1990. The influence of formula modifications and additives on ammonia losses from surface-applied urea-ammonium nitrate solutions. *Fertilizer Research*. 22: 49-59.

Allison, F.E., J.H. Doetsch & E.M. Roller. 1953. Availability of fixed ammonium in soils containing different clay minerals. *Soil Sci*. 75: 373-381.

Archer, J.R. & M.J. Marks. 1997. Control of nutrient losses to water from agriculture in Europe. *Proceedings of Fertilizer Society*. No 405.

Barbarick, K.A. 1996. Nitrogen sources and transformations. *Soil. Crop series*, No.0550. http://www.ext.colostate.edu/pubs/crops/00550.pdf

Beyrouty, C.A., L.E. Sommers & D.W. Nelson. 1988. Ammonia volatilization from surface-applied urea as affected by several phosphoro-amide compounds. *Soil Science Society of America Journal.* 52: 1173-1178.

Black, A.S. & S.A. Waring. 1972. Ammonium fixation and availability in some cereal producing soils in Queensland. *Australian Journal of Soil Research.* 10: 197-207.

Bremner, J.M., D. W. Nelson & J.A. Silva. 1967. Comparison and evaluation of methods of determining fixed ammonium in soils. *Soil Science Society of America Journal.* 31: 466-472.

Cai, G.X. 1997. Ammonia volatilization, in: Zhu, Z.L., Q.X. Wen & J. R. Freney. 1997. *Nitrogen in Soils of China*. Kluwer Academic Publishers. pp.193-213.

Cai, G.X., Y.C. Cao & N.C. Yang. 1991. Direct estimation of nitrogen gases emitted from flooded soils during denitrification of applied nitrogen. *Pedosphere*. 1(3): 241-251.

Cai, G.X., N.C. Yang, W.F. Lu, W. Chen, B.Q. Xia, X.Z. Wang & Z.L. Zhu. 1992. Gaseous loss of N from fertilizer applied to a paddy soil in south-eastern China. *Pedosphere*. 2: 209-217.

Cai, G.X., Z.L. Zhu, Z.W. Zhu, A.C. F. Trevitt, J.R. Freney & J.R. Simpson. 1985. Studies on N loss from ammonium bicarbonate and urea applied to flooded rice field. *Soils*. 17: 225-229.

Cameron, K.C., & R.J. Haynes. 1986. Retention and movement of nitrogen in soils. *In Mineral Nitrogen in the Plant-Soil System*. Ed. R.J. Haynes. Academic Press, London. Pp 166-241.

Canter, L.W. 1997. Illustration of nitrate pollution of groundwater, in: *Nitrates in Groundwater*. pp.39-72.

Chaterpaul, L., E.A. Paul & W. Calaco. 1980. Denitrification in Saskatchewan soils under field conditions. Abstracts of the 80th Annual Meeting, American Society of Microbiology, Miami Beach, Florida, May 11-16, 1980.

Cheng, J.Z., Q.X. Kang & C.X. Zhang. 1997. Research on the techniques of balance fertilizer application on vegetables. *Plant Nutrition and Fertilizer Sciences*. 3(4): 372-375.

Cheng, L.L. & Q.X. Wen. 1997. Transformation and management of manure nitrogen. In: *Nitrogen in Soils of China*. Zhu, Z.L., Q.X. Wen & J.R. Freney (ed.) pp 281-302. *Kluwer Academic Publishers.*

Chinese Academy of Agricultural Sciences (CAAS), Soil and fertilizer Institute ed. 1994. *China Fertilizer.* Shanghai Science and Technology Publisher. pp3-5.

Chinese Agricultural Techniques Extension and Service Center edit (CATESC). 1999. *Organic Manure Resource in China.* China Agriculture Publisher, pp.98.

Christensen, S., P. Ambus, J.R.M. Arah, H. Clayton, B. Galle, D.W.T. Griffith, K.J. Hargreaves, L. Klemedtsson, A-M. Lind, M. Maag, A. Scott, U. Skiba, K.A. Smith, M. Welling & F.G. Wienhold. 1996. Nitrous oxide emission from an agricultural field: Comparison between measurements by chamber and micrometeorological techniques. *Atmospheric Environment.*30: 4183-4190.

Committee of China Agriculture Yearbook (CCAY) edit. 2001. *China Agriculture Yearbook*. China Agriculture Publisher. Beijing, pp. 566-603.

Cook, M., A. Kenneth, B. Childress & R. Wiles. 1996. Nitrate Contamination of Drinking Water. Environmental Working Group. *Pouring It On:* 1436 U Street, NW, Suite 100, Washington, DC. 20009.

Crutzen, P.J. 1976. Upper limits on atmospheric ozone reductions following increased application of fixed nitrogen to the soil. *Geophys. Research Letter*. 3: 555-558.

Crutzen, P. J. 1981. Atmospheric chemical processes of the oxides of nitrogen, including nitrous oxide. In D*enitrification, Nitrification and Atmospheric Nitrous Oxide*. Ed. C.C. Delwiche. pp. 17-24. Wiley, New York.

Delgado, J.A., R.R. Riggenbach, R.T. Sparks, M.A. Dillon, L.M. Kawanabe &R.J. Ristau. 2001. Evaluation of nitrate-nitrogen transport in a potato-barley rotation. *Soil Science Society of America Journal.* 65:878-883.

Drury, C.F. & E.G. Beauchamp. 1991. Ammonium Fixation, Release, Nitrification and immobilization in a high-and low-fixing soil. *Soil Science Society of America Journal.*55: 125-129.

Drury, C.F., E.G. Beauchamp & L.J. Evans. 1989. Fixation and immobilization of recently applied $^{15}NH_4$ in selected Ontario and Quebec Soils. *Canada Journal of Soil Science*. 69: 391-400.

Eichner, M.J. 1990. Nitrous oxide emissions from fertilized soils: summary of the available data. *Journal of Environmental Quality.*19: 272-280.

Emteryd O., D.Q. Lu & N. Nykvist. 1998. Nitrate in soil profiles and nitrate pollution of drinking water in the loess region of China. *Ambio.* 27(6): 441-443.

Fan, J., M.D. Hao & T.H. Dang. 2002. Distribution and accumulation of NO3—N in soil profile of long-term located fertilizer experiment. *Soil and Environmental Sciences*. 9:23-26.

FAOSTAT. 1999. FAO Statistical Databases. Agriculture Data.

FAOSTAT. 2002. FAO Statistical Databases. Agriculture Data.

Fenn, L.B. & R. Escarzaga. 1976. Ammonia volatilization from surface applications of ammonium compounds on calcareous soils. V. Soil water content and methods of nitrogen application. *Soil Science Society of America Journal.* 40: 537-541.

Fenn, L.B. & R. Escarzaga. 1977. Ammonia volatilization from surface applications of ammonium compounds on calcareous soils . VI. Effects of initial soil water content and quantity of applied water. *Soil Science Society of America Journal.* 41: 358-363.

Fenn, L.B. & L.R. Hosser. 1985. Ammonia volatilization from ammonium forming nitrogen fertilizers. *Advances in Soil Science*. 1: 123-169.

Ferguson, R.B. & D.E. Kissel. 1986. Effects of soil drying on ammonia volatilization from surface-applied urea. *Soil Science Society of America Journal.* 50: 485-490.

Freibauer, A. & M. Kaltschmit. 2001. *Biogenic greenhouse gas emission from agriculture in Europe*. ISSN 0938-1228.

Galloway, J.N. & E.B. Cowling. 2002. Reactive nitrogen and the world: 200 years of change. *Ambio*. 31:64-71.

Gao, X.J. 1997. Evaluation of the situation about nitrate pollution on main type of vegetables around
Nanjing. *Rural Environment and Ecology*. 13(1): 59-61.

Guo, Z.Y., Z.L. Huang, L.X. Feng.1992. Loess soil. In: *Shaanxi Soil*. *Science press*. pp 91-110.

Hallberg, G. 1986. From hoes to herbicides: Agriculture and groundwater quality. *Journalof Soil Water Conservation*. 41: 357-364.

Hallberg, G. 1995. A progress review of Iowa's agricultural-energy-environmental initiatives: Nitrogen management in Iowa. *Technical Information.* Series 22. Iowa Department of Natural Resources. December.

Hargreaves, K.J., F.G. Wienhold, L. Klemedtsson, J.R.M. Arah, I.J. Beverlad, D. Fowler, B. Galle, D.W. T.Griffith, U. Skiba, K.A.Smith, M. Welling & G.W. Harris. 1996. Measurement of nitrous oxide emission from agricultural land using micrometeorological methods. *Atmosphere Environment*. 30: 1563-1571.

Hargrove, W.L., 1987. Comparison of a forced-draft technique to nitrogen-15 recovery for measuring
ammonia volatilization under field conditions. *Soil Science Society of America Journal.* 51: 124 -128.

Harper, L.A. & V.R. Catchepoole. 1983. Ammonia volatilization: Soil plant and microclimate effects on diurnal and seasonal fluctuations. *Agronomy Journal.* 75: 212-218.

Hong, F.Z. 1997. *China agricultural yearly book for 1996*, printed by the Agricultural Ministry of China.

Hutchinson, G.L. & A.R. Mosier. 1981. Improved soil cover method for field measurement of nitrous oxide fluxes. *Soil Science Society of America Journal*, 45: 311-316.

Institute of Soil Science (ISS). 1986. Map of soil potassium potential of China. Soruce: Academia Sinica. http://www.fao.org/landandwater/swlwpnr/reports/y_ea/china/Image_e/E205.htm

Jaynes, D. B., T.S. Colvin, D.L. Karlen, C.A. Cambardella & D.W. Meek. 2001. Nitrate loss in subsurface drainage as affected by nitrogen fertilizer rate. *Journal of Environmental Quality.* 30: 1305-1314.

Jiang, D.A., Y.D. Tang, Y.H. Ma, L. Zhou, Y.Y. Gong & Y.B. Chen. 1989. Effect of different conditions on denitrification in soil. *Environmental Science*. 10:13-19.

Justic, N., N.N. Rabalais, R.E. Turner & Q. Dortch. 1995. Changes in nutrient structure of river-dominated coastal waters: stoichiometric nutrient balance and its consequences. *Estuarine,Coastal and Shelf Science.* 40: 339-356.

Katyal, J.C., M.F. Cater and P.L.G. Vlek. 1988. Nitrification activity in submerged soil and its relation to denitrification loss. *Biology and fertility of soils.* 7: 16-22.

Keeney, D.R. & D.W. Nelson. 1982. Nitrogen- Inorganic forms. In: *Methods of Soil Analysis, Part 2. Chemical and Microbiological Properties*-Agronomy Monograph no. 9 (2nd Edition). pp 643-698.

Khalil, M.I., A.B. Rosenani, O. Van Cleemput, C.I. Fauziah & J. Shamshuddin. 2002. Nitrous oxide emissions from an ultisol of the humid tropics under maize-groundnut rotation. *Journal of Environmental Quality.* 31: 1071-1078.

Killpack, S.C. & D. Buchholz. 1993. Nitrogen in the Environment: *Ammonia Volatilization*, Water Quality Initiative publication. WQ257 — Reviewed October 1. http://muextension.missouri.edu/explore/envqual/wq0257.htm

Kristensen, S.P., J. Mathiasen, J. Lassen, H.B. Madsen & A. Reenberg. 1994. A comparison of the leachable inorganic nitrogen content in organic and conventional farming systems. *Acta Agricultural Scandinavica, Section B, Soil and Plant Science.* 44:19-27.

Kross, B.C., M.L. Olson, A. Ayebo & J.K. Johnson. 1995. Humans. In: *Soil Amendments*: Impacts on Biotic Systems. JE Rechcigl (ed). Ann Arbor: CRC Press, Inc. Chapter 6: 153-214.

Li, L.M. 1997. Nitrification. In: Zhu, Z.L., Q.X. Wen and J. R. Freney. 1997. *Nitrogen in Soils of China*. Kluwer Academic Publishers. pp. 117.

Li, L.M., Y.H. Pan, X.R. Zhou, Q.T. Wu and Z.G. Li. 1986. Nitrification and nitrogen loss in different soils. In: Soil Science Society of China (ed.), Current Progress in Soil Research in the P.R. of China. pp. 135-143. Jiangsu Science and Technology Publishing House, Nanjing.

Li, M.B, R.S. Yost. 2000. Management-oriented modeling: optimizing nitrogen management with artifical intelligence. *Agricultural Systems*. 65:1-27.

Li, S. X., L. Xiao. 1992. Raising soil fertility. In: Stewart, B.A. 1992. Advances in Soil Science. 18: 244-256.

Liang, D.L., Y.A. Tong, O. Emteryd & S.X. Li. 2002a. Effect of irrigation and rainfall on the N_2O losses in dryland. *Plant Nutrition and Fertilizer Sciences.* 8(3): 298-302.

Liang, D.L., Y.A. Tong, O. Emteryd & L.Y. Ma. 2002b. N_2O losses from vegetable fields after applying different amounts of NO_3-N. *Journal of Northwest Sci-Tech Univiversity. of Agriculture and Forestry*. 30(2): 73-77.

Liu, H.B. 2002. Effects of nitrogen fertilizer application on soil NO3—N accumulation and groundwater pollution in Beijing area. Ph.D thesis, Chinese Academy of Agricultural Sciences, Beijing, China.

Liu, H.J., X.T. Ju, Y.A. Tong, F.S. Zhang & J.L. Lu. 2002. The status and problems of fertilization of main fruit trees in Shaanxi Province, *Agricultural Research in the Arid Area*. 20: 38-44.

Liu, J. 2001. *China agricultural yearly book for 2000*, printed by the Agricultural Ministry of China.

Liu, S.C., R.J. Cicerone, T.M. Donahue & W.L. Chameides. 1976. Limitation of fertilizer induced ozone reduction by the long life-time of the reservoir of fixed nitrogen. *Geophy Research Letter*. 3: 157-160.

Lu, R.K. 1997. Phosphorus in China Agriculture. Soil Science Institute. Chinese Academy of Sciences. Content. Historical review on P application in China. file:///C:/Documents%20and%20Settings/toy/Local%20Settings/Temporary%20Internet%20Files/Content.IE5/8HAN0L6F/256,1,

Lund, L.J., D.C. Adriano & P.F. Pratt. 1974. Nitrate concentrations in deep soil cores as related to soil profile characteristics. *Journal of Environmental Quality.* 3: 78-82.

Ma, W.Q. 1999. Current status and evaluation of crop fertilization in Shandong Province. Ph.D thesis, *China Agricultural University*, Beijing, China.

Magnusson, T. 1989. A method for equilibration chamber sampling and gas chromatographic analysisof the soil atmosphere. *Plant Soil*. 120: 39-47.

Mahmood, T., K.A. Malik, S.R.A. Shamsi & M.I. Sajjad. 1998. Denitrification and total N losses from an irrigated sandy-clay loam under maize-wheat cropping system. *Plant soil*. 199: 239-250.

Matson, P.A., C.R. Billow, S.J. Hall & J. Zachariassen. 1996. Fertilization practices and soil variations control nitrogen oxide emissions from tropical sugar cane. *Journal of Geophysical Research*. 101: 18533-18545.

Mengel, K. & H.W. Scherer. 1981. Release of nonexchangeable (fixed) soil ammonium under field conditions during the growing season. *Soil Sci*. 131: 226-232.

Mo, S.X., & J.F. Qian. 1981. Uptake of nitrogen by rice plant from straw manure, urea and soil. In: ISSAS (ed.), Proc. of Symp. On Paddy soil. pp. 800-804. Science Press, Beijing.

Mosier, A.R. & L. Klemedtsson. 1994. *Methods of Soil Analysis, Part 2. Microbiological and Biochemical Properties.* SSSA Book Series, No 5, pp 1047-1062.

National Research Council (NRC), Board on Agriculture. 1993. *Soil and Water Quality: An Agenda For Agriculture*. National Academy Press. Washington, DC.

Natural Resources Defence Council (NRDC). 1994. *Think Before You Drink: 1992-93 Update*. Washington, DC.

Ouyang, X.H., Q.Q. Zhu & C. Zui. 1996. Studies on fertilization and control water pollution in water source protected area in Beijing. *Agro-environmental Protection*. 15:107-110.

Paul, E.A. & F.E. Clark. 1988. *Soil Microbiology and Biochemistry*. 1st Ed., Academic Press, San Diego. pp. 131-196.

of Environmental Quality. 31:782-796.

Qian, H. 1985. *Use and development of fertile water*. Shaanxi Publishing House of Science and Technology. pp. 21-39.

Rehm, G. & M. Schmitt. 1989. Setting realistic crop yield goals. University of Minnesota extension service. FS-03873-GO . http://www.extension.umn.edu/distribution/cropsystems/DC3873.html

Rejesus, R.M. & R.H. Hornbaker. 1999. Economic and environmental evaluation of alternative pollution-reducing nitrogen management practices in central Illinois. *Agriculture, Ecoststems and Environment.* 75:41-53.

Reynolds, C.M. & D.C. Wolf. 1988. Effects of field methods and soil cover on estimating ammonia loss from nitrogen-15- urea. *Soil Science Society of America Journal.* 52: 706-712.

Ritter, W.F., A.F.M. Chirnside & R.W. Scarborough. 1990. Soil nitrate profiles under irrigation on coastal plain soil. *Journal of Irrigation and Drainage Engineering.* 116:738-751.

Roelcke, M., R.M. Rees, S.X. Li, & J. Richter. 2000. Studies of the nitrogen cycle on the southern edge of the Chinese Loess Plateau. In: Laflen, J., C. Huang & J. Tian. (eds): *Proceeding of Conference Soil Erosion And Dryland Farming*. Xi'an, China, Sept. 1997. CRC Press, New York, Chapter 12, pp 103-119.

Ryden, J.C. & L.J. Lund. 1980. Nitrous oxide evolution from irrigated land. *Journal of Environmental Quality.* 9: 387-393.

Sahrawat, K.L. 1982. Nitrification in some tropical soils. *Plant Soil*. 65: 281-286.

Sattelmacher, P.G. 1962. Methemoglobinemia from nitrates in drinking water. *Schriftenreiche des Vererins fur Wasser.* Boden und Lufthygiene. No. 21.

Schlesinger, W.H. & A.E. Hartley. 1992. A global budget for atmospheric NH_3. *Biogeochemistry.* 15: 191-211.

Shrestha, R. & J. Ladha. 1998. Nitrate in groundwater and integration of nitrogen-catch crop in rice-sweet pepper cropping system. *Journal of Environmental Quality.* 62:1610-1619.

Sigunga, D.O., B.H. Janssen & O. Oenema. 2002. Effects of improved drainage and nitrogen source on yield, nutrient uptake and utilization efficiencies by maize (*Zea mays* L.) on Vertisols in sub-humid environments. *Nutrient Cycling in Agroecosystems*. 62: 263-275.

Silva, J.A. & J.M. Bremner. 1966. Determination and isotope-ratio analysis of different forms of nitrogen in soils. 5. Fixed ammonium. *Soil Science Society of America Journal.*30: 587-594.

Simon, B. 1964. Uber vorkommen, pathogenese, und moglichkeiten zur prophylaxe der durch nitrit verursachten methamoglobinamie. *Zeitschrift fur Kinderheilkunde.* 91: 124-138.

Sowers, K.E., W.L. Pan, B.C. Miller & J.L. Smith. 1994. Nitrogen use efficiency of split nitrogen applications in soft white winter wheat. *Agronomy Journal*. 86: 942-948.

Spalding, R.F., D.G. Watts, J.S. Schepers, M.E. Burbach, M.E. Exner, R.J. Poreda, & G.E. Martin. 2001. Controlling nitrate leaching in irrigated agriculture. *Journal of Environmental Quality.* 30:1184-1194.

Sun, K.G., X.B. Zhang, Z.Q. Wu, H.Y. Gong & L.G. Wang. 2001. Effect of long-term and different measures of fertilizer application on crop yield and accumulation of NO3—N in the profile of three major soils. *Acta Agriculture Boreali- occidentalis Sinica*. 16:105-109.

Supalla, R.J., R.A. Selley, S. Bredeweg, & D.G. Watts. 1995. Adoption of nitrogen and water management practices to improve water quality. *Journal Soil Water Conservation.* 50:77-82.

Tong, Y.A., W.X., Zhang, W.S. Han & O. Emteryd. 1994. Transformation of different types of fertilizer in Luvtisol and Entisol. *J. Soil Sci*. 25: 107-109.

Trindade, H., J. Coutinho, M.L. Van Beusichem, D. Scholefied & N. Moreira. 1997. Nitrate leaching from sandy loam soils under a double-cropping forage system estimated from suction-probe measurements. *Plant Soil*. 195: 247-256.

Turner, R. E. & N.N. Rabalais. 1991. Changes in Mississippi River water quality this century. *BioScience.* 41: 140-147.

Uunk, E.J.B. 1991. Eutrophication of surface water and the contribution of agriculture. *Proceeding of the Fertilizer Society*. No 303, 55 pp.

Valera, C.L. & M. Alexander. 1961. Nutrition and physiology of denitrifying bacteria. *Plant Soil*. 15:268-280.

Van Delden, A., J.J. Schroder, M.J. Kropff, C. Grashoff & R. Booij. 2003. Simulated potato yield, and crop and soil nitrogen dynamics under different organic nitrogen management strategies in the Netherlands. Agriculture, Ecosystems and Environment. 96:77-95.

Vitousek, P.M., J.D. Aber, R.W. Howarth, G.E. Likens, P.A. Matson, D.W. Schindler, W.H. chlesinger & D.G. Tilman. 1997. Human alteration of the global nitrogen cycle: Sources and consequences. *Ecological Applications.* 7: 737-750.

Watson, R.T., H. Rodhe, H. Oeschger & U. Siegenthaler. 1990. *Greenhouse gases and aerosols. In Climate change*: The IPCC Scientific Assessment. Eds. J. T. Houghton, G. S. Jenkins and J.J. Ephraums. Pp 1-40. Cambridge University Press, Cambridge.

WHO. 1993. *Guidelines for drinking-water quality.* Second edition, volume 1. World Health Organisation, Geneva, Switzerland. pp. 174.

Woodward, W. 1995. *Summary results: Soil nitrate tests for corn*: 1993 state surveys. USDA, Economic Research Service. Washington, DC.

Xia, X.H., J.S. Zhou & Z.F. Yang. 2002. Nitrogen contamination in the Yellow River basin of China. *Journal of Environmental Quality.* 31: 917-925.

Xing, W. 1999. Problems and measurements on the fertilizer utilization in China. *Soil Sciences in 21 century.* Ninth Conf. of Chinese Assoc. of Soil Sciences, Nan Jing, Jiang Su. pp. 39-42.

Xue, J.C. 1998. Situation and prospects of the fertilizer use in the world. *Plant Nutrition and Fertilizer Science.*, 4(4): 321-330.

Xi, Z.B., E. Humphreys, X.Z. Shi, J.R. Freney, W.X. Huang, Z. Yao & J.R. Simpson. 1987. Effect of application method on am´monia loss from urea applied to cabbages in the Shanghai district. *Acta Agriculture of Shanghai*. 3: 47-56.

Yoshida, T., & J.B.C. Padre. 1975. Effect of organic matter application and water regimes on transformation of fertilizer nitrogen in a Philippine soil. *Soil Science and Plant Nutrition*. 21:281-292.

Zhang, W.L., Z.X. Tian, N. Zhang & X.Q. Li. 1996. Nitrate pollution of groundwater in northern China. *Agriculture, Ecosystems and Environment. 59:223-231.*

Zheng, X.H., C.B. Fu, X.K. Xu, X.D. Yan, Y. Huang, S.H. Han, F. Hu & G.X. Chen. 2002. The Asian nitrogen cycle case study. *Ambio*. 31:79-87.

Zhu, J.G., Y. Han, G. Liu, Y.L. Zhang & X.H. Shao. 2000. Nitrogen in percolation water in paddy fields with a rice-wheat rotation. *Nutrient Cycling in Agroecosystems*. 57: 75-82.

Zhu, X. M. 1986. Land resource in the Loess Plateau of China, Science and Technology Publishing House of Shaanxi Province. 16202.150. pp1-2.

Zhu, Z.L., G.X. Cai, J.R. Simpson, S.L. Zhang, D.L. Chen, A.V. Jackson & J.R. Freney. 1989. Processes of nitrogen loss from fertilizers applied to flooded rice fields on a calcareous soil north-central China. Fertilizer Research. 18: 101-115.

Zhu, Z.L. & D.L. Chen. 2002. Nitrogen fertilizer use in China-Contributions to food production, impacts on the environment and best management strategies. *Nutrient Cycling in Agroecosystems*. 63:117-127.

Zhu, Z.L., G.X. Cai, J.R. Simpson, S.L. Zhang, D.L. Chen, A.V. Jackson & J.R. Freney. 1989. Precesses of nitrogen loss from fertilizer applied to flooded rice fields on a calcareous soil in noeth-central China. *Fertilizer Research*. 18: 101-115.

Zhu, Z.L., Q.X. Wen & J. R. Freney. 1997. *Nitrogen in Soils of China*. Kluwer Academic Publishers. pp. 113-192.

Acknowledgements

First of all, I would like to express my sincere gratitude to my supervisor Dr. Harald Grip, for bringing me to a new field and leading me through it, for his continuous scientific support and never-ending encouragement in academic endeavors. He guided me in the area of my major field and provided inspirational supervision and discussion, emphasizing the importance of clarifying my thinking, research direction and scientific writing. I am also greatly indebted to him for his patient reading of my manuscripts and for correcting my English. I am grateful also to Dr. Leif Klemedtsson, as a co-supervisor. He supported me during the N_2O analyses, providing suggestions, equipment and academic discussions. His wide knowledge stimulated me to study more in this field along the way.

I would like to especially thank Prof. Ove Emteryd for enlightening me on many aspects of laboratory and nitrogen behaviour. He has been helping me for 15 years and never stopped even for a moment. Every time I met difficulties and could not find the way, he always sent a boat and rowed me to the other shore. My grateful thanks are also extended to his wife Eva who took care of me in everyday matters, make me feeling at home in Umeå, and even teaching me how to dance, so now I am a good dancer. I am also very grateful to Claes and Pär, who took me around Stockholm and made me feel that I have friends around the world.

I am greatly indebted to Lars Lövdahl. He brought me to the new field of modeling, which has widened my knowledge and will be increasingly important in the future for the western part of China, where there is always drought stress. If I ask for help he never turns me down and can help me in virtually all cases, especially with computer questions. Many thanks to him and Anna-Lena, whose hospitality also makes me feels at home in Umeå. I thank him and his family for inviting me to dinner (and I really enjoyed picking mushrooms and blueberries in the forest to make jams together) and for making me feel almost a member of the family.

I am grateful to Tord Magnusson for his knowledge of soil physical parameters and soil gas sampling techniques, which were essential to the success of the N_2O study. I am also grateful to him, and his family, for always inviting me for dinner and for the wonderful Christmas time spent with them and their children 15 years ago. Many thanks to Per-Erik.Jansson for teaching me and helping me in the field of CoupModel simulation. Thanks also to Nils Nykvist, who started up our cooperative project 15 years ago, thus providing the possibility to meet my Swedish friends and continue with this exciting project up to the present day.

I would also like to thank Drs. Mats Nilsson, Anders Nordgren, Mikaell Ottosson Löfvenius, Reiner Giesler, Ulf Skyllberg and the staff in the Department of Forest Ecology.

Thanks are due, in addition, to our group members for their diverse kinds of support and discussions. They are Leif and Birgitta Olsson, Håkan and Elisabeth Wallmark, Bengt Andersson, Göte Moen, and Kerstin Johansson, who I thank for always taking care of me, for the great birthday cake from Håkan and Elisabeth,

and taking me skiing down a very steep slope; the fermented fish from Leif and Birgitta, a special delicious taste that I could never forget, and for showing me the very old instrument used by Birgitta's mother to produce nice looking clothes far away from Umea.

I would like to thank my colleagues and staff at the Soil and Fertilizer Institute. Prof. Lu Dianqing guided me from the time I graduated from the university to the present day, Assoc. Prof. Zhang Wenxiao, Zhang Shulan, Liang Dongli, Ma Linying, Fang Riyao, Gao Yimin, Zhao Hubing, are also thanked for their varied support. I am also grateful to Mr. Yang Xueyun and Sun Benhua, for their help, support and understanding.

Finally, I want to thank my dearest wife, Cheng Xiufang, for her love and care, and for doing all the household chores, as well as her tolerance and constant support. And my daughter, Tong Yu: she cannot do much to help in practice yet, but she always gives me hope for the future, which encourages me enormously. I deeply thank my brother and my sister-in-law for their care, encouragement, and parent-like support, great thanks also to my sisters, mother-in-law, and all the members of my family for their love, care and encouragement.