A tracer experiment and numerical simulation of potential nitrogen pollution from agricultural fertilization

LIHUA TANG[1,2], SICONG ZHANG[1,2] & XIUFEN SUN[1]

1 *Department of Hydraulic Engineering, Tsinghua University, Beijing 100084, China*
tanglh@tsinghua.edu.cn

2 *State Key Laboratory of Hydroscience and Engineering, Tsinghua University, Beijing 100084, China*

Abstract Agricultural non-point source pollution is probably the most significant anthropogenic source of nitrogen pollution for water bodies. The excessive fertilizers rushed into surface water bodies by runoff or leached into groundwater by percolation may cause eutrophication or groundwater pollution. It is usually difficult to estimate the non-point source pollution due to its random and distributed nature. In this paper, a winter wheat potted-planting experiment was carried out, and the fertilizer with added ^{15}N as the tracer was added to soil. By examining the nitrogen contents in soil and crop samples during the wheat growth period, the fate of fertilizer nitrogen was analysed, and the potential pollution fertilizer left in soil was estimated. In order to analyse the fertilization and irrigation effects on nitrogen losses, a one-dimensional model, LEACHM (Leaching Estimation And CHemistry Model), was adapted to simulate the nitrogen transport in the agricultural soil profile. The results showed that soil nitrate nitrogen increased significantly after wheat planting, which may result in a high probability of nitrogen losses by runoff or leaching, and therefore excessive fertilization and irrigation may increase nitrogen losses as well as cause a high risk of nitrogen pollution.

Key words tracing experiment; non-point source pollution; agricultural fertilization; LEACHM model

INTRODUCTION

The application of fertilizer has accelerated the increase of crop yields in modern agriculture in recent decades. It was reported that more than 25% of the increase of crop yields is due to the use of fertilizer in the world (Shen, 1992; Wu, 1994). However, the utilization efficiency of fertilizer is rather low. Zeng (1995) pointed out that in China, the utilization efficiency of nitrogen fertilizer was only 30–35%; for phosphorus fertilizer it was about 10–20%. Therefore in order to achieve high crop yields and productivities, large quantities of chemical fertilizers are being put into agricultural fields, and most of them are lost into the environment through runoff, leaching, denitrification, absorption, etc. Leaching of chemicals below the root zone may contaminate groundwater for irrigation or drinking purposes, while excess accumulation of chemical fertilizer in surface water bodies may cause eutrophication problems and even health problems, rendering the water unfit for drinking, recreation, industry, or other common functions. Agricultural non-point source pollution has become the main source of water pollution in many countries (Novotny, 1999; Walton, 2000; Tang, 2003).

Although various studies have proved that chemical fertilizers may cause water pollution, it is difficult to quantify how much pollutant would be discharged into nearby water systems, groundwater or the atmosphere, because of many factors affecting the pollution processes. These factors include the amount and time of fertilizer application, ploughing method, climate condition, topology, etc. (Tsiouris *et al.*, 2002). In general, mathematical simulation is a cheap method to study agricultural pollution. Many numerical models, including one-dimensional (1-D) and 2-D models, have been developed and applied in different areas. Some physically-based models, such as LEACHM, HYDRUS, SWAT, AGNPS, BASINS, can simulate the transport and transformation processes of nutrients and pesticides, considering decomposition, mineralization, crop uptake, etc. Experiments are another means of finding the temporal and spatial rules of fertilizer pollution. Isotope tracers, such as ^{15}N, are good choices for studying the fate of fertilizer in farmland. Many agricultural scientists and hydrologists have used isotopic analysis to understand the fate of agrochemicals; as well as to monitor water quality and hydrochemical behaviour on a catchment scale. Rückauf *et al.* (2004) used the ^{15}N tracer technique to investigate the effect of different soil moisture conditions on nitrate turnover and removal in degraded fen soils. Tetzlaff *et al.* (2007)

collected tracer data, and combined with GIS to understand the catchment's hydrochemical response and hydrological processes. Annable *et al.* (2007) used isotopes, ^{15}N, ^{13}C and ^{37}Cl, to analyse the common agrochemicals for identifying non-point source agricultural contaminants. However, the cost of isotopic experiments on a catchment scale is very expensive, so a pot planting experiment is often used to do some theoretical research.

Nitrogen is a vital nutrient for enhancing crop growth and is also a major pollutant of non-point source pollution (Mehdi & Madramootoo, 1999). Nitrate and ammonia nitrogen are two dominant forms due to their high solubility. The main factors affecting nitrogen transport and transformation in farmland include precipitation (irrigation) intensity, soil type, topography condition, fertilization, plant coverage (Qiao, 2002; Bandaranayake & Arshad, 2006). Among these factors, fertilization and irrigation are what can be effectively controlled by human beings. Therefore agricultural pollution control should be focused on the management of fertilization and irrigation.

In order to quantify the fertilizer pollution in agricultural fields, the aim of the study presented here was to investigate the potential loads of nitrogen after crop planting and fertilization. For this purpose a wheat-potted planting experiment was performed to study the nitrogen transportation and transformation processes during a crop growing period using the ^{15}N tracer technique. Also a 1-D numerical model, LEACHM (Leaching Estimation And CHemistry Model), was used to simulate the transport and losses of nitrogen in the soil profile and the effects of different fertilization and irrigation conditions on nitrogen losses were analysed.

MATERIAL AND METHODS

Experiment description

The experiment of winter wheat-potted planting was carried out from October 2005 to June 2006 at Tsinghua University campus. The experiment pots were made of PVC, about 30 cm in diameter, 40 cm in height, and there was a bottom outlet of 2 cm diameter for each one. The experimental soil, a brown aluvial soil, sandy loam, was obtained from agricultural field in the upper basin of Miyun Reservoir in Beijing. The soil dry density was measured as 1.387 g cm^{-3}. Other chemical contents of initial mixed soil were also measured by the Institute of Soil and Fertilizer in Beijing Academy of Agriculture and Forestry Science, as listed in Table 1.

There were three treatments, ^{15}N fertilizer (the abundance of ^{15}N was 10%), common fertilizer and no fertilizer, and each treatment had three replications. The fertilizer was ammonium sulphate, applied twice during the experiment, once before sowing and then at the wheat jointing stage. The quantities of fertilizer used was 7 g (about 206.2 N kg ha^{-1}), and irrigation amount was about 300 mm. Soil samplings were taken four times during the experiment. The nitrogen contents and ^{15}N abundances of samples were examined and analysed.

Model description

In order to predict the effects of fertilization and irrigation on nitrogen pollution, some scenarios with different fertilization and irrigation patterns were designed, and water and solute movement

Table 1 Initial contents of the experimental soil.

Soil layer (cm)	Total nitrogen (g kg^{-1})	Total phosphorus (g kg^{-1})	NH_4^--N (mg kg^{-1})	NO_3^--N (mg kg^{-1})	Organic matter (g kg^{-1})
Mixed soil	1.03	1.1	3.31	7.86	18.45
0~5	1.13	1.27	7.30	5.52	20.17
5~10	1.18	1.29	6.83	6.69	21.55
10~20	0.378	0.977	5.89	3.51	8.21
20~30	0.317	0.847	4.86	3.18	8.21

in soil were simulated by adopting a 1-D model, LEACHM (Leaching Estimation And Chemistry Model). This model was developed at Cornell University, USA (Hustson, 2003). The governing equation for water movement in soil is Richards equation, as in equation (1):

$$\frac{\partial \theta}{\partial t} = \frac{\partial}{\partial z}\left[k(\theta)\frac{\partial H}{\partial z} - U(z,t) \right] \tag{1}$$

where θ is volumetric water content (m^3 m^{-3}), H is hydraulic head (mm), K is hydraulic conductivity (mm day^{-1}), t is time (days), z is depth (mm), positive downwards; and U is a sink term, representing water lost per unit time by transpiration (day^{-1}).

Convection–dispersion equations (CDEs) are used in the model, as in equation (2), and the sink term of solute, sorption of solid phase, dispersion of volatile solute in gas phase are also considered.

$$\frac{\partial C_t}{\partial t} = -\frac{\partial J_s}{\partial z} \pm \phi \tag{2}$$

where C_t is the total solute concentration in all phases (liquid, gas, adsorbed) and Φ represents as yet unspecified sources or sinks of solute.

In order to obtain the soil characteristic and model parameters, such as grain-size distribution, initial water content, saturated hydraulic conductivity, breakthrough curve, etc. soil column experiments and some other laboratory tests were performed in combination with the pot planting experiment. Table 2 and Fig. 1 show some comparisons of simulated results and experiment examination, which indicate that the model simulation had a good agreement with the experiment. After model validation, three simulation scenarios were designed as below:

– Different fertilizer amount: by changing the additional fertilizer with 87.6 kg N ha^{-1}, 175.2 kg N ha^{-1} and 262.7 kg N ha^{-1};
– Different nitrogen content in base fertilizer: by changing the nitrogen content with 98 kg N ha^{-1}, 147 kg N ha^{-1} and 196 kg N ha^{-1} in base fertilizer;
– Different irrigation amount: by changing the irrigating water with 300 mm, 330 mm and 360 mm.

RESULTS AND DISCUSSION

Experimental results and analysis

By examining soil and crop samples, the nitrogen contents and distributions in the soil profile during the winter wheat growing period were obtained, and the spatial and temporal distribution of nitrogen in different forms was analysed. From these results the potential pollution loads in soil just before flood season could be estimated.

Table 2 Comparison of NH_4^--N and NO_3^--N between measured and simulated results (unit: mg kg^{-1}).

		Before fertilization		After fertilization	
	Soil layer (cm)	Measured	Simulated	Measured	Simulated
NH_4^--N	0–5	7.3	7.11	40.9	30
	5–10	6.83	7.17	21.7	20.8
	10–20	5.89	5.91	22	20.7
	20–30	4.86	5.39	16.3	22.5
NO_3^--N	0–5	5.52	7.4	101	78.7
	5–10	6.69	5.05	27.6	26.7
	10–20	3.51	3.53	11.9	13.4
	20–30	3.18	3.77	11.8	14.7

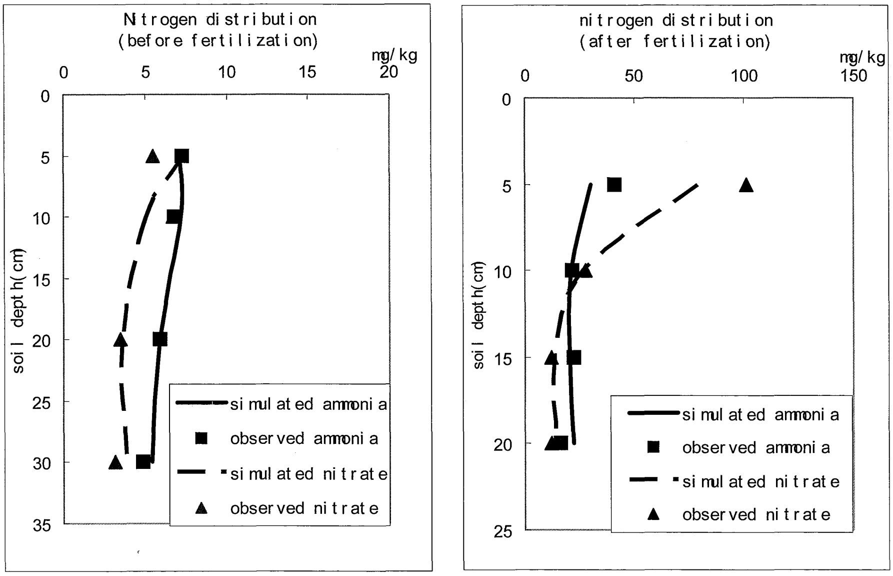

Fig. 1 Nitrogen distribution in soil profile (comparing between simulated and measured values).

Fate of fertilizer nitrogen

Assuming that ^{15}N and ^{14}N uptake by the crop keep a constant proportion, from the measured results of total nitrogen (i.e. TN) content and ^{15}N abundance in soil, the fate of fertilizer nitrogen was analysed. Table 3 shows the fertilizer nitrogen balance in this experiment. The averaged percentages of fertilizer left in soil after the planting period was about 87%; only 8.0–13.6% of fertilizer was taken up by crops. In this experiment there was no leaching because of limited irrigation, therefore the loss of fertilizer nitrogen in this case was by volatilization. Depending on the nitrogen balance analysis, the fertilizer nitrogen loss by volatilization was about 2.45%. For biological nitrogen in different parts of wheat at a mature stage, about 30% of nitrogen in wheat straw came from fertilizer, and in wheat head it was about 37%.

From this experiment it is known that the contribution of fertilizer nitrogen to seasonal crops is very low, and that the large part of fertilizer left in the soil may become potential pollution sources for surface water and groundwater. Because the nitrogen losses in runoff, flow and leaching were not considered in this experiment, the results only present the potential loads for agricultural water pollution.

The distribution of nitrogen in the soil profile

By sampling different layers of soil and examining the nitrogen contents, it is shown in Table 2 and Fig. 1 that both NH_4^--N and NO_3^--N in the soil profile have distributions that decrease with

Table 3 The fate of fertilizer nitrogen.

	Min value		Max value		Average value	
	(g)	(%)	(g)	(%)	(g)	(%)
Left in soil	1.285	86.561	1.292	87.046	1.289	86.803
Plant uptake	0.120	8.063	0.203	13.656	0.161	10.860
Loss	–	–	–	–	0.035*	2.337*
Sum	–	–	–	–	1.485	100

* The fertilizer loss was estimated by mass balance.

depths due to the root system activities and surface fertilization. Also it indicates that after fertilization, nitrogen change is more notable in the top 10 cm soil layer, which is generally the dominant layer for water and soil particles fully mixing under rainfall conditions. If surface runoff is generated, nitrogen in the top layer would be easily flushed into the water system. The model simulated results also had good agreement with measured values, as also shown in Fig. 1.

In general, the fertilizer nitrogen will be re-allocated in different ways after fertilization: some will be taken up by plants, some will be leached into groundwater, some will be washed into runoff, and some will remain in the soil. From the experiment results, it is clear that fertilization makes NO_3^--N increase quickly in the top layer, and then gradually be transported downwards. Due to nitrification and some other chemical reactions, at the end of the planting period the concentration of NO_3^--N in soil obviously increased. At the same time, because of the volatility and instability, the concentration of NH_4^--N and NO_2^--N experienced a small change, and the total nitrogen in the soil stayed at a similiar level to that before planting. The phenomenon implies that the organic nitrogen and hence soil fertility decreased, which may increase nitrogen pollution risk.

The transfer characteristics in different nitrogen forms

In general, the nitrogen in soil can be divided into organic and inorganic. The inorganic nitrogen has three major forms: NH_4^+-N, NO_3^--N and NO_2^--N. Each form can be transferred from one to another under microbal activities. Main chemical processes include decomposition and mineralization (from organic to inorganic), nitrification (NH_4^+-N > NO_2^--N > NO_3^--N) and denitrification (NO_3^--N > N_2O > N_2), and these processes are greatly affected by soil temperature and soil moisture.

In this experiment, some soil samples were taken from each pot and the nitrogen content tested (seen in Table 4). Figure 2 demonstrates the trends of nitrogen contents in soil during the planting period. The total nitrogen (TN) in soil after planting was nearly equal to the initial value; NH_4^+-N and NO_2^--N increased slightly (nitrite nitrogen is omitted in Fig. 2 because of its negligible quantity), while NO_3^--N obviously increased from 7.86 mg kg^{-1} to 66.2 mg kg^{-1} on average. The increase of inorganic nitrogen (which tended to be lost easily) and decreasing organic content may result in low soil productivity and high pollution risk. The possible reason for these changes might be the rising temperature and low soil water content in the main growth period from April to June. Under these conditions mineralization and nitrification actions in soil become stronger, and denitrification action is relatively weak. Therefore, at the end of a wheat planting period, also the beginning of the flood season, inorganic nitrogen concentration in the top soil will increase to a high value, which is easy to be desorbed from soil particles, and then to leach into groundwater by infiltration or to be flushed into surface water bodies by runoff.

Modelling results and analysis

Much previous research indicated that the amounts and patterns of fertilization and irrigation had significant effects on the loss of nitrogen in soil. In this paper the LEACHM model was applied to simulate these effects in an experiment. In such a 1-D vertical simulation, the surface runoff is forbidden, but leaching exists. The losses by leaching, transformation (it presents the nitrification action), and plant uptake are calculated and compared below.

Table 4 Averaged experimental results in different growing period.

Testing items	Total N (mg kg^{-1})	NH_4^--N (mg kg^{-1})	NO_3^--N (mg kg^{-1})	NO_2^--N (mg kg^{-1})
Before planting	1030	3.31	7.86	0.20
Before fertilization	1280	15.97	8.13	0.61
after fertilization(24h later)	1090	22.20	39.50	0.54
After harvesting	1020	12.83	66.20	0.41

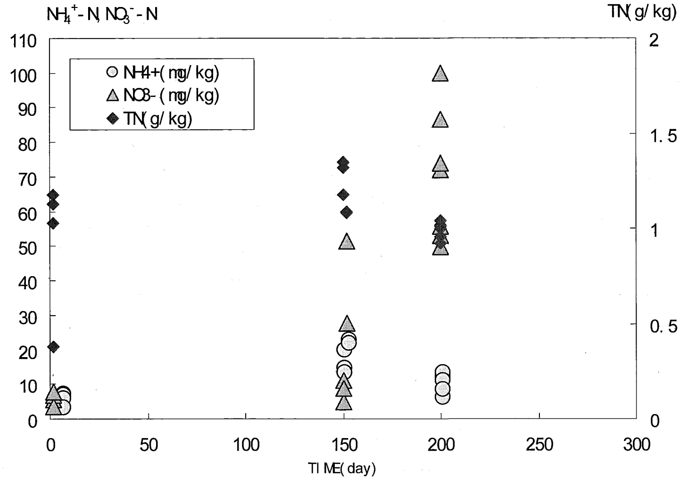

Fig. 2 Trends of nitrogen contents in soil during planting period.

Effects of fertilization level By changing levels of additional fertilizer to 87.6 kg N ha^{-1}, 175.2 kg N ha^{-1} and 262.7 kg N ha^{-1}, respectively, the changes of NH_4^--N and NO_3^--N in soil under different conditions are listed in Table 5. It is shown that both NH_4^--N and NO_3^--N losses by leaching increased by adding additional fertilizer. The amount of NO_3^--N leaching was more than NH_4^--N, which was also proved by other researchers (Qiao, 2004; Zhao, 2006). Losses by transformation of NH_4^--N also increased, while losses by plant uptake were little affected by fertilization when the common fertilization demand was met.

Effect of nitrogen content in base fertilizer The influence of the effect of nitrogen content in base fertilizer is shown in Table 6. Cases 1, 2, 3 represent the nitrogen content with 98 kg N ha^{-1}, 147 kg N ha^{-1} and 196 kg N ha^{-1}, respectively, in base fertilizer. It is indicated that increasing the nitrogen content in base fertilizer had a bigger influence on plant uptake of nitrogen, but fewer losses in drainage and via transformation occurred.

Effect of irrigation amount Irrigation has more notable influences on losses in drainage compared with fertilization. Cases 1, 2 and 3 represent irrigating with 300 mm, 330 mm and 360 mm water, respectively. In Table 7, the results imply that excess irrigation had little influence on plant nitrogen uptake, but caused more losses by drainage and by transformation. Some other studies also approved this conclusion (Tang, 2003). In this case the saving of irrigation water has a significant effect on environmental protection.

Table 5 The losses of NH_4^+-N and NO_3^--N in soil with different fertilization level.

	NH_4^+-N (kg ha^{-1})			NO_3^--N (kg ha^{-1})		
	Case 1	Case 2	Case 3	Case 1	Case 2	Case 3
leaching loss	9.7	11.7	14.2	27.2	28.5	33.6
transformation loss	46.7	53.2	64.8	0	0	0
plant uptake loss	5.4	5.4	5.4	3.5	3.5	3.5

Table 6 The losses of NH_4^+-N and NO_3^--N in soil with different nitrogen content in base fertilizer.

	NH_4^+-N (kg ha^{-1})			NO_3^--N (kg ha^{-1})		
	Case 1	Case 2	Case 3	Case 1	Case 2	Case 3
leaching loss	7.4	7.6	7.9	24.5	25.2	25.8
transformation loss	38.5	39.7	40.6	0	0	0
plant uptake loss	5.5	5.7	5.8	3.6	3.6	3.7

Table 7 the losses of NH_4^+-N and NO_3^--N in soil under different irrigation condition.

	NH_4^+-N (kg ha^{-1})			NO_3^--N (kg ha^{-1})		
	Case 1	Case 2	Case 3	Case 1	Case 2	Case 3
leaching loss	17.6	19.6	22.6	51.0	51.0	51.3
transformation loss	61.5	61.3	61.1	0	0	0
plant uptake loss	5.4	5.4	5.4	3.5	3.5	3.5

SUMMARY AND CONCLUSION

In this study, the tracing experiment shows that the fertilizer utilization ratio was very low, only <15% was taken up by wheat, about 2.35% lost by volatilization, and the majority, >80% of fertilizer applied, remained left in soil after the planting period. Under rainfall or irrigation conditions, the accumulated nitrogen in soil would become a potential source of pollution for groundwater and surface water bodies. Moreover, because chemical fertilizer was surface applied into the top 10 cm of the soil layer, the dominant layer for water and soil particles mixing fully under rainfall conditions, it might add the possibility of surface water pollution. Furthermore, the results indicated that inorganic nitrogen, especially nitrate nitrogen, increased after chemical fertilizer was applied onto farmland. The organic nitrogen content reduced, and resulted in a soil crust. This might also increase the risk of water and nutrient losses. Although the proportions in the different fates of fertilizer nitrogen will vary from the case concerned above, depending on fertilizer chemical content, soil moisture, soil temperature, etc. the risk of surface water and groundwater pollution in an agricultural area is higher than in a non-planting area.

From LEACHM model simulation results, it is shown that both excessive fertilization and irrigation increased nitrogen leaching and caused a greater threat to groundwater quality. Base fertilization had more effects on nitrogen plant uptake than additional fertilization, and consequently improving the fertilizer utilization efficiency and reducing nitrogen loss. Thereby water-saving irrigation and proper fertilization are effective practices of human control on water environmental pollution.

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