Research Article

Effect of Saturated Near Surface on Nitrate and Ammonia Nitrogen Losses in Surface Runoff at the Loess Soil Hillslope

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Water pollution from agricultural fields is a global problem and cause of eutrophication of surface waters. A laboratory study was designed to evaluate the effects of near-surface hydraulic gradients on NO_3–N and NH_4–N losses in surface runoff from soil boxes at 27% slope undersimulated rainfall of a loess soil hillslope. Experimental treatments included two near-surface hydraulic gradients (free drainage, FD; saturation, SA), three fertilizer application rates (control, no fertilizer input; low, 120 kg N ha^{-1}; high, 240 kg N ha^{-1}), and simulated rainfall of 100 mm h^{-1} was applied for 70 min. The results showed that saturated near-surface soil moisture had dramatic effects on NO_3–N and NH_4–N losses and water quality. Under the low fertilizer treatment, average NO_3–N concentrations in runoff water of SA averaged 2.2 times greater than that of FD, 1.6 times greater for NH_4–N. Under the high fertilizer treatment, NO_3–N concentrations in runoff water from SA averaged 5.7 times greater than that of FD, 4.3 times greater for NH_4–N. Nitrogen loss formed with NO_3–N is dominant during the event, but not NH_4–N. Under the SA condition, the total loss of NO_3–N from low fertilizer treatment was 34.2 to 42.3% of applied nitrogen, while under the FD treatment that was 3.9 to 6.9%. However, the total loss of NH_4–N was less than 1% of applied nitrogen. These results showed that saturated condition could make significant contribution to water quality problems.

1. Introduction

Water pollution is a major global problem that amounts for more than 14,000 deaths daily [1]. The national environmental statistic bulletin of China reported that total discharge amount of ammonia nitrogen was 127.0×10^4 t in waste water in 2008 [2]. In the most recent national report on water quality in the United States, 45 percent of assessed streammiles, 47 percent of assessed lake acres, and 32 percent of assessed bay and estuarine square miles were classified as polluted [3].

Phosphorous (P) and nitrogen (N) in runoff from agricultural fields are key components of nonpoint source pollution and can accelerate eutrophication of surface waters [4, 5]. Most mineral forms of nitrogen are quite soluble in water and may be easily lost from soils through leaching and volatilization. In most freshwater (lakes and streams), P is

the nutrient that can set off eutrophication, and N is the nutrient most likely to cause eutrophication for saltier waters (estuaries and costal areas) [6].

The transport of agricultural chemicals from the field to groundwater or to surface-water bodies is most commonly facilitated by water movement, and it is affected by rainfall characteristics, underlying surface conditions, and the properties of the soil solute. Hydrogeology, climate, and agricultural management practices can have important influences on the movement of water and chemicals [7, 8].

Spatially and temporally variations may affect the dominant erosion processes occurring on the hillslope. During rainfall events, different hydraulic gradients, especially due to seepage or drainage, at different locations on a hillslope profile may have a profound effect on the dominant erosion processes. Recent laboratory studies showed that near-surface hydraulic gradient had a profound effect in the

dominant erosion process and total sediment delivery [9, 10]. Gburek et al. [11, 12] studied results showed that most in-stream P came from soils within 60 m of the stream, and Zheng et al. [10] studied results showed that artesian seepage could make important contribution to water quality problems.

Nevertheless, interactions among hydrologic, surface runoff, sediment regimes and N & P losses, and how they are affected by changes in rainfall intensities have not been evaluated extensively in China [13–15]. Based on those studies, the purpose of this study was to examine nitrate and ammonia nitrogen loss of the loess soil in runoff under saturated soil that occurs at $100 \, mm \, h^{-1}$ rainfall intensity. Results of this study will further the understanding of how saturated soil water content impacts the losses of NO_3–N and NH_4–N in surface runoff of the loess soil at the hillslope of China.

2. Materials and Methods

2.1. Soil Sample Collection. The soil used in this study was a loess soil collected from the surface to a 40 cm depth at Ansai Country near Yan'an city, Shaanxi province, China. The collected soil was air dried and sieved through a 10-mm-opening sieve and stored in covered concrete floor until used in this experiment.

2.2. Soil Properties. The collected loess soil consists of 64.9% sand, 23.2%, clay and 11.9% silt. The soil contains 5.3 mg/kg organic matter, 0.4 g/kg total N, 0.6 g/kg total P, and 18.2 g/kg total K. The content of alkali-hydrolyzadle nitrogen is $32 \, mg \, kg^{-1}$, while the content of rapidly available phosphorus and potassium is $4 \, mg \, kg^{-1}$ and $114 \, mg \, kg^{-1}$, respectively. The water pH is 8.5 (water/soil ration is $5 : 1$) and the cation exchange capacity (CEC) is 6.01 cmol (+)/kg.

2.3. Experimental Setup. The study was conducted on three soil boxes that were 100 cm long, 50 cm wide, and 40 cm deep. Each soil box had 18 watering/drainage holes at the bottom. A water supply system was designed to supply water to the soil box from the bottom of the soil box to create the near-surface hydraulic gradient (Figure 1), especially the saturated condition, as described by Zheng et al. [10], and the free drainage condition was created by rainfall.

Two groups of rainfall simulation nozzles, each group with four nozzles, spaced 12 m apart, were used in this study. The nozzles were approximately 16 m above the soil surface. During the rainfall simulation, the nozzle pressure was kept at 2.5 kg/cm². This rainfall simulator could be set to any pre-selected rainfall intensities, ranging from 20 to $300 \, mm \, h^{-1}$, by programming the compounding of the nozzles [16].

Experimental treatments in this study included 2 near-surface hydraulic gradient treatments: saturated condition, and free drainage, and three fertilizer input treatments were subjected to the two soil moisture treatments: control (no fertilizer input, NF), low input (120 kg N ha⁻¹, LF), and high
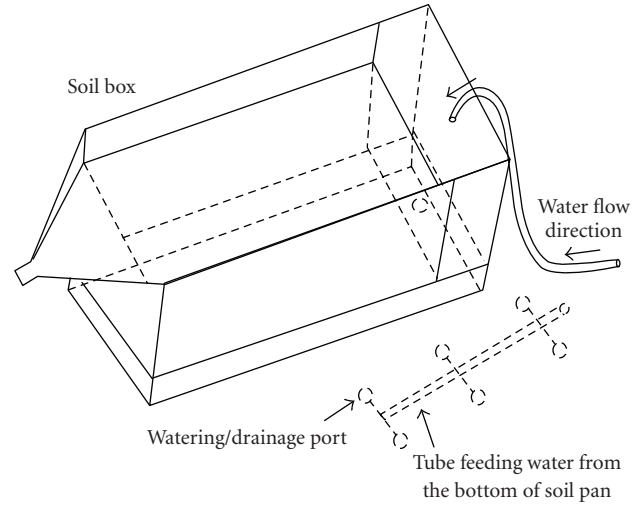

FIGURE 1: Experiment setup.

TABLE 1: List of experiment treatments.

Soil moisture treatment	Fertilizer treatment	Fertilizer inputs N Kg hm⁻²
Saturation (SA)	Control (NF)	0
	Low input (LF)	120
	High input (HF)	240
Free Drainage (FD)	NF	0
	LF	120
	HF	240

NF, no fertilizer input; LF, low fertilizer treatment/input (120 kg N ha⁻¹); HF, high fertilizer treatment/input (240 kg N ha⁻¹). FD, free drainage hydraulic gradient; SA, saturated hydraulic gradient.

input (240 kg N ha⁻¹, HF). The detailed experimental treatments appeared in Table 1. For each near-surface hydraulic gradient, three replicates were made for rainfall simulation.

2.4. Preparation of Soil Boxes. Each soil box was packed with a 5 cm layer of sand at the bottom and a 35 cm depth layer with the air-dried test soil. Moisture content of the test soil was determined prior to packing of the soil box to calculate the amount of soil needed to obtain a bulk density of 1.3 g cm⁻³. The moisture content of the air-dried test soil used for packing soil box ranged from 3% to 5% by weight. To ensure uniformity, the soil box was packed in individual 5 cm layers, and the upmost 5 cm soil was divided into 3 cm (below) and 2 cm (top), and the top 2 cm soil was thoroughly mixed with KNO_3 (AR) as designed [17].

For each layer of soil boxes, the weight of packaged wet soil was calculated by the following equation

$$W = \rho \times l \times w \times h \times \frac{1 + \theta}{100}, \quad (1)$$

where, W is the wet soil weight for packaging in kg, ρ is soil bulk density in 1.3 g cm⁻³, l is length of soil boxes in 100 cm,

w is width of soil boxes in 50 cm, h is deepness of each layer in soil boxes in cm, θ is soil moisture content in %.

After soil box preparation, to further avoid water-drop-induced splash and surface sealing, two layers of gauze were placed over the soil surface. This step was applied to obtain the correct hydraulic gradient, create a uniform surface soil moisture condition prior to the experiment, and reduce surface variability from preparation. After the water supplying, the soil box was covered with a plastic sheet and allowed to equilibrate under each hydraulic condition for 24 hrs.

2.5. Rainfall Experiments. After the water supplying, soil boxes were set to 15° (approximately 27%) slope steepness and subjected to the experimental hydraulic gradients. And a simulated rainstorm of 100 mm h^{-1} for 70 min was applied to all treatments based on the result of the basic erosive rainfall standard on the Loess Plateau is 5.8 mm/5 min [18, 19]. During rainfall simulation runs, runoff samples were collected every 6 min. During each event, the rainfall amount was measured at least twice with two hyetometers around soil boxes to calibrate the rainfall intensity.

Immediately after each run, runoff samples were weighted and set for 24 hrs. Water was stored in the plastic buckets in 100 ml and then was analyzed for the contents of NO_3^-–N and NH_4^+–N.

2.6. Calculation of Near-Surface Hydraulic Gradient. Soil moisture of the test soil was measured before packed into the soil boxes, preparing for calculating supply water volumes of each near-surface hydraulic gradient, and the volumes were calculated by (2) to control the used-water volumes and save excess water:

$$W_s = W \times 7 \times \frac{M - \theta}{(1 + \theta/100)/100},\qquad(2)$$

where, W_s is water volume of complementarities in kg, W is wet soil weight for packing in kg, 7 is the layers of soil packaged, M is near-surface hydraulic gradient to control in %, θ is soil moisture content of packing soil in %.

2.7. Analysis of NO_3^-–N and NH_4^{3+}–N in Surface Runoff Water. The collected surface runoff water was set for 24 hrs, centrifuged for 10 min with 8000 r/min by high speed refrigerated centrifuge (CR21G, Hitachi, Japan), and filtered to test the concentration of NO_3^-–N and NH_4^+–N, then all samples were determined by automated chemistry analyzer (Auto analyzer 3-AA3, Bran+Luebbe, Germany).

2.8. Calculation of NO_3–N and NH_4–N in Surface Runoff Water. For each simulated precipitation, NO_3–N or NH_4–N loss in surface runoff water for the event, L (mg), was calculated by [10]

$$L = \sum_{i=1}^{n} C_i R_i,\qquad(3)$$

where L is NO_3–N or NH_4–N loss in surface runoff water for the event at time increment i, mg; C_i is concentration in

surface runoff water at time i, mg/L; R_i is runoff volume at time i, L; n is the total number of collected samples.

For each run, the average NO_3–N or NH_4–N concentration in surface runoff water, C_n (mg/L), was calculated as [10]

$$C_n = \frac{L}{V},\qquad(4)$$

where, L is NO_3–N or NH_4–N loss, mg; and V is total runoff volume, L.

For each soil water content treatment under the same fertilizer treatment, the average NO_3–N or NH_4–N concentration in surface runoff water, C_m (mg/L), was calculated as [10]

$$Cm = \frac{\sum_{j=1}^{p} L_j}{\sum_{j=1}^{p} V_j},\qquad(5)$$

where, ρ is the number of replications in each soil water content treatment, $p = 3$, L_j is NO_3–N and NH_4–N loss for the event times j, mg, and V_j is total runoff volume, L.

2.9. Statistical Analysis. The LSD test was performed using SAS (SAS Institute Inc., Cary, NC, USA). Means of each NO_3–N and NH_4–H concentration and amount of loss resulting from different treatments were compared for significant difference ($P < .05$) using Duncan's procedure. In all statistical analyses, a probability level of .05 or less ($P \le .05$) was used for significance.

3. Results and Discussions

3.1. Concentration of NO_3–N and NH_4–N in Surface Runoff Water. The average concentrations of NO_3–N in surface runoff water were significantly greater than that of NH_4–N (Table 2). The average concentrations of NO_3–N and NH_4–N in surface runoff water of the FD treatments were less than 12.0 mg L^{-1} and 0.5 mg L^{-1}, respectively, regardless of the fertilizer treatments. When the near-surface hydraulic gradients shifted from FD to SA, concentrations of NO_3–N and NH_4–N in surface runoff water increased significantly.

For the control treatment, NO_3–N concentrations in runoff water of SA averaged 1.8 times grater than that of FD, but it was not statistically significantly difference. Under the low fertilizer treatment, NO_3–N concentrations in runoff water of SA averaged 2.2 times greater than that of FD. Under the high fertilizer treatment, NO_3–N concentrations in runoff water of SA averaged 5.7 times greater than that of FD. These results were similar to those reported by Zheng et al. [10]. Under the FD treatment, although NO_3–N concentrations in the runoff water of the low fertilizer treatment were numerically larger than that of the high fertilizer treatment, concentrations were not significantly different. This is probably the result of less water runoff and better infiltration into the soil.

Concentrations of NH_4–N in surface runoff water of SA were statistically lower than that of FD, those trends similar to NO_3–N concentrations in runoff water. For the control treatment, NH_4–N concentrations in runoff water of SA

TABLE 2: Means of nutrient concentration with runoff under different near-surface soil moisture conditions.

Treatment†	Concentration in surface runoff		Losses in surface runoff			
	NO_3^-–N	NH_4^+–N	NO_3^-–N	Loss as a percentage of N input	NH_4^+–N	Loss as a percentage of N input
	mg/L		kg ha^{-1}		kg ha^{-1}	
CFD	7.94c‡	0.45b	7.27d		0.42c	
CSA	14.14c	0.76a	21.11c		1.14b	
LFD	11.9c	0.46b	8.28d	6.9	0.32d	0.27
LSA	26.36b	0.73a	41.02b	34.2	1.14b	0.95
HFD	11.02c	0.17c	9.36d	3.9	0.15e	0.06
HSA	63.22a	0.73a	101.56a	42.3	1.18a	0.49

†C, control fertilizer treatment (no fertilizer input); L, low fertilizer treatment/input (120 kg N ha^{-1}); H, high fertilizer treatment/input (240 kg N ha^{-1}). FD, free drainage hydraulic gradient; SA, saturated hydraulic gradient.
‡Mean values with a fertilizer treatment followed by any identical letters are not statistically different at the 95% confidence level according to LSD tests.

averaged 1.7 times greater than that of FD. Under the low fertilizer treatment, NH_4–N concentrations in runoff water of SA averaged 1.6 times greater than that of FD. Under the high fertilizer treatment, NH_4–N concentrations in runoff water of SA averaged 4.3 times greater than that of FD.

Fertilizer application rates influenced NO_3–N concentrations under the saturation treatment, and the NH_4–N concentrations in surface runoff water under the FD treatment. Under the SA treatment, both the high and low fertilizer treatments resulted in significantly higher NO_3–N concentrations than that of the control, increasing by 347.1% and 139.8%, respectively. NH_4–N concentrations in the runoff water of the control input to low and high fertilizer treatment were not statistically different. Under the FD treatment, NH_4–N concentrations in runoff water from control input to low fertilizer input were not statistically different, but that of high fertilizer input was statistically smaller than that of control input and low fertilizer input. It is an interesting question for the results as described above, and no research results could explain the reason, because there were no fertilizers formed with NH_4–N to soil, and the whole conditions were similar between each soil box and each run, so it is necessary to have a deep research on that. Maybe the fertilizer application rate of KNO_3 was the key point for that, and NH_4–N loss with sediment was the other way for the results above because nutrients formed with NH_4–N in eroded sediment were enriched compared with topsoil [20, 21]. The results above indicated that denitrification had less effect on loss of NH_4–N in surface runoff water in SA treatment in this study.

3.2. NO_3–N and NH_4–N Losses. Average losses of NO_3–N and NH_4–N displayed similar trends as their concentrations (Table 2). Average NO_3–N and NH_4–N losses of the SA treatment were statistically significantly greater than that of FD. NO_3–N loss in the surface runoff water of CSA was 2.9 times greater than that of CFD. NO_3–N loss in the surface runoff water of LSA was 5.0 times greater than that of LFD. NO_3–N loss in the surface runoff water of HSA was 10.9 times greater than that of HFD. Compared to the CSA treatment, NO_3–N losses in surface runoff

water of the LSA and HSA treatment were 1.9 and 4.8 times greater, respectively. However, under the FD treatment, NO_3–N losses in the surface runoff water among control, low fertilizer, and high fertilizer input treatment were not significantly different.

Average NH_4–N loss in surface runoff water from CSA was 2.7 times greater than that of CFD. Under the low fertilizer treatment, average NH_4–N loss in surface runoff water of SA was 3.6 times greater than that of FD. Average NH_4–N loss in surface runoff water from HSA was 7.9 times greater than that of LFD. However, under the SA treatment, average NH_4–N losses of CSA and LSA were not statistically different, although it was statistically different from HSA to LSA and CSA. Under the FD treatment, average NH_4–N loss of control treatment was statistically greater than that of low and high fertilizer treatments, and it was 1.3 and 2.8 times greater, respectively. The change trend was similar to that as described on concentrations of the part of NO_3–N and NH_4–N in Surface Runoff Water in this study.

Under low and high fertilizer treatments, NO_3–N loss accounted from 3.9 to 42.3% of the applied N (Table 2). And NO_3–N loss as a percentage of N input of SA treatment was statistically greater than that of FD. However, NH_4–N loss accounted from 0.06 to 0.95% of the applied N, those were less than 1%.

These results showed that the saturated flow could make an important contribution to total chemical transport, which was similar to the results of P loss of Gburek and Sharpley studied in 1998 [11], and Zheng et al. [10]. However, it was opposite to the results of Fisher and Healy [8], which showed that the time of the year at which chemicals are applied may be important for chemical transport through the unsaturated zone. And the results of this study also showed that NO_3–N loss could be more important for contribution to nitrogen loss than that of NH_4–N.

3.3. Temporal Trends of NO_3–N and NH_4–N Concentrations. Under the FD treatment, the NO_3–N concentrations in runoff changed little as time progressed for all fertilizer treatments tested, and it was less pronounced than that
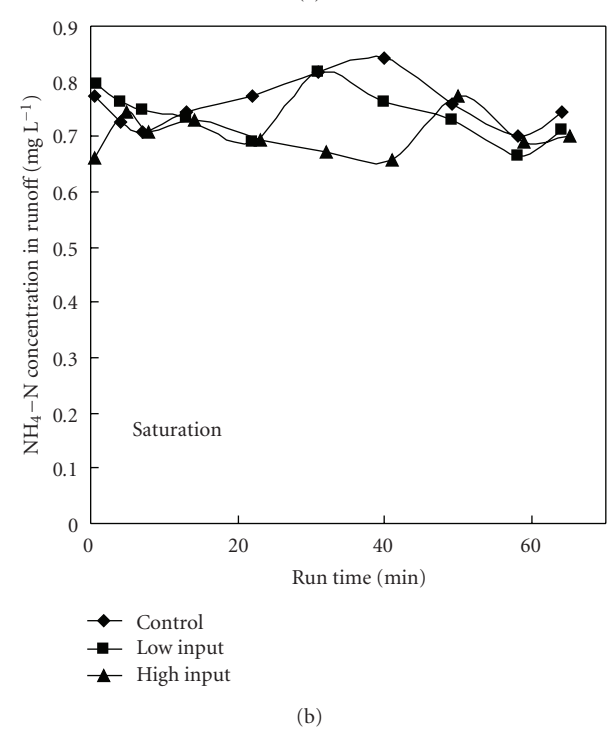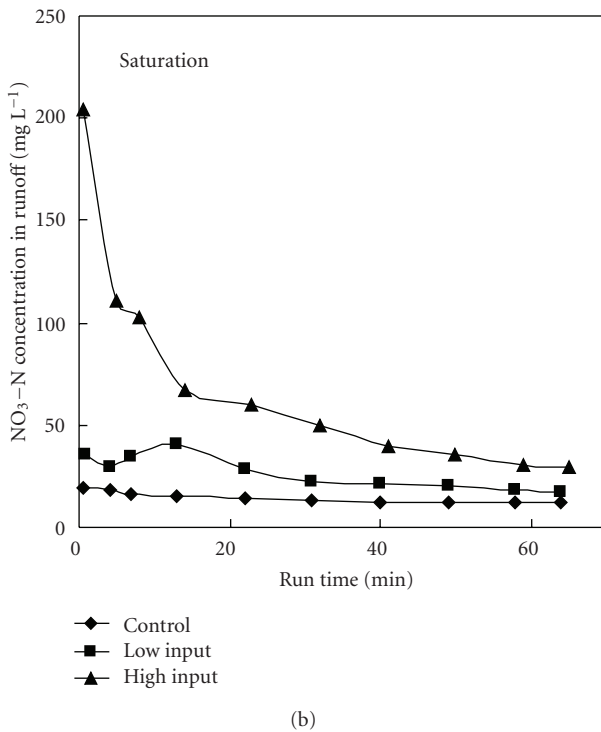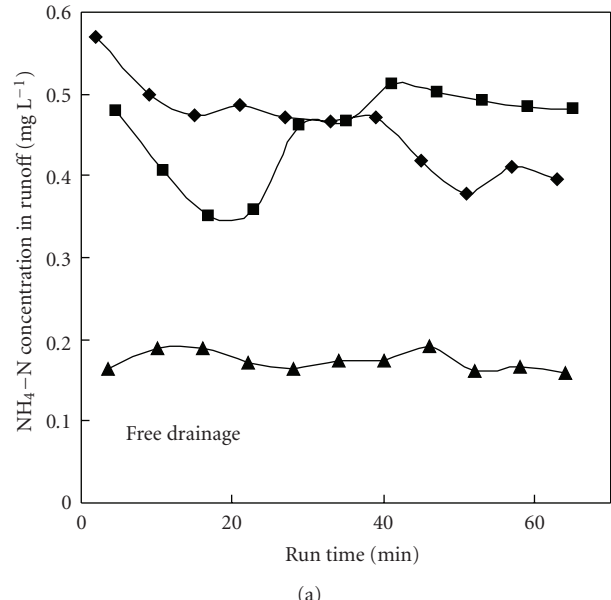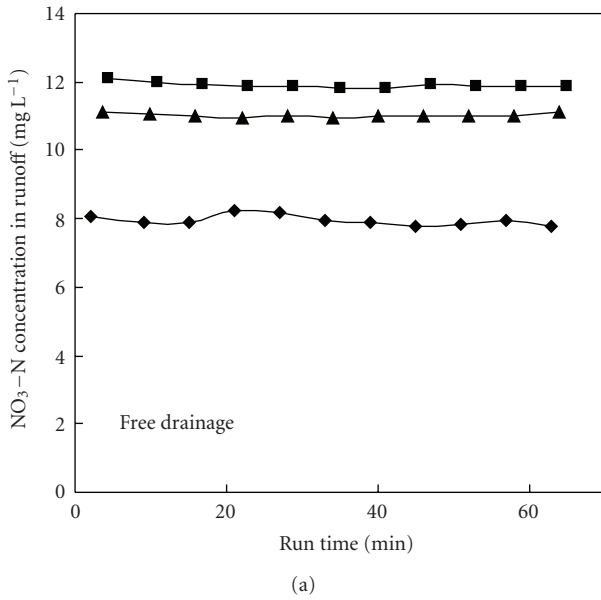
(a)

(b)

Figure 2: The NO_3–N concentration in runoff under different hydraulic gradients.

(a)

(b)

Figure 3: The NH_4–N concentration in runoff under different hydraulic gradients

of the SA treatments (Figure 2). And the trends of NO_3–N concentrations in runoff during the run were similar to the means of NO_3–N concentrations (Table 2). Under the SA treatment, although the temporal trend showed that NO_3–N concentrations in runoff were greatest in the initial runoff and decreased gradually during the run of high fertilizer input, NO_3–N concentrations of control and low fertilizer input treatments showed little change. And the total temporal trends of NO_3–N concentrations in surface runoff

were similar to the results of saturated condition of Zheng et al. [10].

Under the FD treatment, NH_4–N concentrations in runoff were greatest in the initial runoff and decreased gradually during the run of control treatment, while NH_4–N concentrations in runoff of the low fertilizer treatment were greatest in the initial runoff and decreased, then increased gradually (Figure 3). But the NH_4–N concentrations in runoff of high fertilizer treatment changed little. May be

those were influenced by runoff progress. Under the SA treatment, the NH_4–N concentrations in runoff changed little in waves with the entire three fertilizer application rate.

The results of this study indicated that a saturated condition event could cause a severe water quality problem, which is similar to the results reported on P loss by Gburek and Sharpley [11], and NO_3–N and P losses by Zheng et al. [10]. And in the saturated condition, compared to control treatment, the concentrations and amount of NH_4–N of low and high fertilizer treatment were similar; may be the fertilizer rates and denitrification have less effect on loss of NH_4–N in surface runoff water. While in free drainage condition, compared to topsoil, rapidly available P and NH_4–N in eroded sediment were enriched in the Loess Plateau of China [21], and artificial rainfall experiment results also showed that the amount of NH_4–N losses in surface runoff water increased with the fertilizer rate increasing [14]. So it would be necessary to study extensively on NH_4–N loss in surface runoff and sediment.

4. Conclusions

This paper presents a laboratory study of near-surface hydraulic gradient effects on losses of NO_3–N and NH_4–N in surface water under a simulated rainstorm. The results showed a significant increase of NO_3–N and NH_4–N transport or losses in surface runoff water under the saturated condition. These results demonstrate the importance of understanding watershed hydrology and its temporal patterns in predicting areas of high chemical loading potential and also showed that the saturated condition can cause greater chemical transport than that of the free drainage condition. The results show that NO_3–N losses in saturated condition could make a significant contribution to water quality problems.

The results of this study also showed that nitrogen loss formed with NO_3–N is dominant during the event, but not NH_4–N. However, under FD treatment, NH_4–N concentrations in runoff water from high fertilizer input were statistically smaller than those from control input and low fertilizer input without NH_4–N fertilizer input, and it also showed denitrification had less effect on loss of NH_4–N in surface runoff water in SA treatment. The trend of NH_4–N loss should be studied more and deeply in the future because of its toxicity to fish, and the rates of fertilizer formed with NH_4–N should be determined for agriculture during rain season.

Although many studies have been made to determine factors contributing to N loss, especially the effects of near-surface hydraulic gradient have been quantified. Incorporating the basic understanding of hydraulic factors and NH_4–N transport may contribute to control chemical transport to water and minimize water quality problems.

Acknowledgments

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