

# EFFECTS OF SUBSTITUTION OF MINERAL NITROGEN WITH ORGANIC AMENDMENTS ON NITROGEN LOSS FROM SLOPING CROPLAND OF PURPLE SOIL

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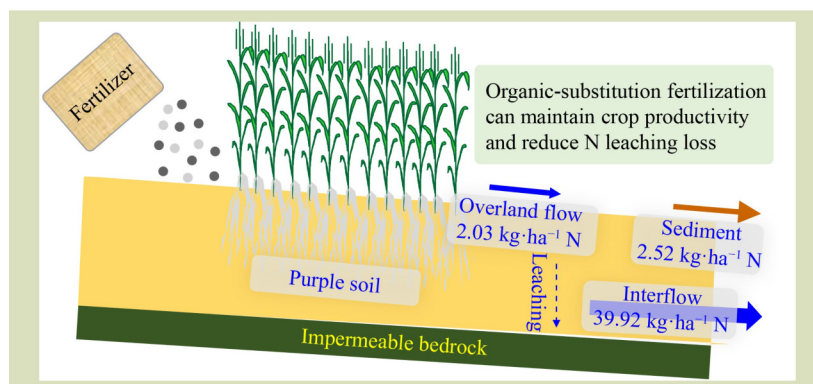
## KEYWORDS

improved fertilization regime, interflow, nitrogen forms, nitrogen leaching, purple soil, sloping cropland

## HIGHLIGHTS

- Interflow acts as the dominant pathway for N loss loadings.
- The purple soil region is a hot spot of nitrate leaching in China.
- Mineral N substitution with organic amendments can be recommended as optimal practices for cropland N management.

## GRAPHICAL ABSTRACT



## ABSTRACT

Nitrogen loss from purple soil can lead to large negative impacts to the environment considering the wide distribution of this soil type in the upper reaches of the Yangtze River. Therefore, nitrogen loss patterns from sloping cropland of purple soil in the Sichuan Basin with the following fertilization regimes were studied in a wheat-maize rotation system: 100% organic fertilizer (OM), using pig manure to replace 30% of mineral N (OMNPK) and crop residue to replace 15% of the mineral N (CRNPK) plus standard mineral fertilization (NPK) and no fertilizer control. The cumulative hydrological N loss could be as high as 45 kg·ha<sup>-1</sup> N. The interflow accounted for up to 90% of the total N loss followed by sediment and overland flow losses. The high N loss via interflow found in this study highlighting that sloping cropland of purple soil may be one of the hot spots of N leaching. Compared to the NPK regime, organic substitution regimes (i.e., OM, OMNPK and CRNPK) decreased total hydrological N loss loadings by 30%–68%. In addition, they can maintain annual crop yields and decrease yield-scaled total hydrological N losses by 18%–71%. In conclusion, long-term substitution of mineral N with organic amendments can maintain high crop productivity and reduce environmental N loss loadings, and thereby recommended as good N management practices to

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minimize the risk of agricultural non-point source pollution in the purple soil region of China.

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## 1 INTRODUCTION

Nitrogen is one of the most important limiting nutrients for crop yield and quality; the yields of grain crops can be increased by 55%–57% by applying N fertilizer<sup>[1]</sup>. The quantity of mineral N fertilizers input in China is increasing gradually and it was 2.2-fold higher in 2018 in comparison with that in 1980, which made a great contribution to national yield increase<sup>[2]</sup>. However, the over use of mineral N fertilizer induced accumulation of reactive N in environment, which was regarded as an important cause of environment problems such as N imbalance and agricultural non-point source pollution<sup>[3–5]</sup>. China launched a campaign called “zero increase of mineral fertilizers until 2020” in response to negative environmental impacts owing to excessive use of mineral fertilizers. In practice, it is an effective way to decrease the use of mineral N, increase the N use efficiency (NUE) and increase the sustainability of agriculture through substitution of mineral N with organic fertilizers or amendments.

The substitution of mineral N with organic amendments has received more attention and application over recent years. Radwan et al.<sup>[6]</sup> found that the substitution of mineral fertilizer with organic fertilizer can increase the microbial biomass of rhizosphere, increase crop growth and yield. Agbede et al.<sup>[7]</sup> also found that the substitution of mineral fertilizer with organic amendments can significantly ameliorate soil property. The field study conducted in north-western Germany indicated that the substitution of mineral fertilizer with organic fertilizer decreased soil N leaching by 50%<sup>[8]</sup>. Many related studies in China have shown that using organic N to replace its mineral N form can increase crop N uptake and NUE while maintain high crop yield<sup>[9–12]</sup>. The study of Han et al.<sup>[13]</sup> showed that replacing mineral N with organic materials can reduce the concentration of total N in runoff significantly. Zhang et al.<sup>[14]</sup> also found that the substitution of mineral fertilizer with organic fertilizer can significantly increase soil fertility while decrease the N loss from cropland. The study of Ning et al.<sup>[15]</sup> indicated that mineral fertilizer replacing with organic fertilizer would significantly accelerate crop growth, reduce excessive N accumulation at soil profile and then decrease the risk of N loss. However, most of those experiments were short-term fertilization experiments (< 3 years), but soil properties under the short time application of organic fertilizers are too unstable to reliably reveal patterns of nitrogen cycling. Also, the N returned from organic fertilizers was not incorporated into

application rates and nitrogen application levels were not consistent among most of those studies. For these reasons, the agronomic and environmental effects of the substitution of mineral fertilizer with organic amendments still need further estimation.

The Sichuan Basin is a major agriculture region in the upper reaches of Yangtze River with purple soil widely distributed (~160,000 km<sup>2</sup>). Purple soil is a Regosol developed from purple sandy and shale rock, characterized by coarse structure, high permeability, developed interflow<sup>[16]</sup> and severe N losses. It is also an important region of agricultural non-point source pollution in the upper reaches of Yangtze River<sup>[17–19]</sup>. The main contributors of the N-based non-point source pollution include N loss via overland flow, sediment and interflow<sup>[16]</sup>. Xie et al.<sup>[20]</sup> found that replacing 50% of the mineral N with organic N can increase N uptake and apparent NUE. Wang et al.<sup>[21]</sup> found that combined application of organic-inorganic fertilization can increase crop yield and decrease N losses from purple soil. In addition, the study of Xu et al.<sup>[22]</sup> indicated that replacement of mineral fertilizer with organic fertilizer can decrease N losses from sloping cropland with purple soil. These studies supported that using organic fertilizer to replace mineral fertilizer may contribute to reducing N loss from purple soil, however, most of those results were based on control of N loss from overland runoff without any investigation on impacts of N loss through interflow. In addition, available data have not elucidated the mechanisms underlying how organic fertilization could reduce N losses from purple soil. The agronomic and environmental effects under the substitution of mineral fertilizer with organic amendments should be further studied. Therefore, based on a long-term fertilization system, this study intended to use treatments of the substitution of mineral fertilizer with organic amendments to examine the impacts on crop productivities, N loss forms, pathways and fluxes so as to evaluate the agronomic and environmental effects to highlight improved cropland N management practices on purple soil.

## 2 MATERIALS & METHODS

### 2.1 Site description

The study site was located at the Yanting Agro-Ecological

Station of Purplish Soil (31°16' N, 105°27' E, 460 m above sea level, Sichuan Province, China), which belongs to Chinese Ecosystem Research Network. The study site has a moderate subtropical monsoon climate, with an annual average air temperature of 17.3 °C, the extreme low and high temperature were −5.1 °C and 40 °C, respectively; The precipitation is uneven with mean annual precipitation of 836 mm. The experimental soil is a calcareous purple soil developed on purplish rock of Jurassic formation, which is classified as Eutric Regosols (FAO soil taxonomy) and Pup-Orthic-Entisols (Chinese soil taxonomy). The topsoil (0–10 cm) physicochemical properties were: pH 8.2; clay, silt and sand of 22.3%, 34.6% and 43.1%, respectively; content of soil organic matter, total nitrogen (TN), total phosphorus and total potassium of 8.75, 0.81, 0.84 and 19.0 g·kg<sup>−1</sup>, respectively; available N, P, K of 42.3, 9.02 and 86.4 mg·kg<sup>−1</sup>, respectively; and soil bulk density of 1.34 g·cm<sup>−3</sup>. Local regular cropping is a winter wheat (*Triticum aestivum*)-summer maize (*Zea mays*) rotation system.

## 2.2 Experimental design

### 2.2.1 Experimental layout

The experimental site was in a long-term fertilization system of purple soil with slope gradient of 6.5° at the Yanting Agro-Ecological Station of Purplish Soil, Chinese Academy of Sciences. Individual plots were 8 m × 4 m with soil depth of 60 cm. The experimental plots were constructed in 2001 according to reference<sup>[16]</sup>. The border of each plot is sealed with concrete and has an independent drainage system. The plots function as free-drained lysimeters (Fig. 1). The overland runoff passes the confluence grooves and collecting grooves then conflux into the measuring tanks as standard runoff plot.

The interflow monitoring is set up at the soil-rock interface of lithomorphous soil<sup>[16]</sup>. The interflow runoff can be considered as the leaching water of purple soil. The collecting groove of the interflow was constructed at 60 cm below the soil surface, to conflux interflow runoff into the measuring tank<sup>[16]</sup>.

### 2.2.2 Fertilization regimes

This study was conducted in a randomized block design based on a long-term fertilization system (since 2003) including five treatments and three replicates under a winter wheat-summer maize rotation system. The experimented treatments were: (1) no fertilizer (CK); (2) standard mineral nitrogen, phosphorus and potassium fertilizer (designated as NPK); (3) fresh pig slurry as organic manure at 100% N equivalent application rate to mineral N in NPK (designated as OM, 100% organic substitution); (4) organic manure at N equivalent to 30% of mineral N fertilizer in combination with NPK (designated as OMNPK, 30% organic substitution); and (5) crop residues at N equivalent to 15% of mineral N fertilizer in combination with NPK (designated as CRNPK, 15% organic substitution). Detailed application of mineral fertilizers can be found in previous study<sup>[16]</sup>. The fresh pig slurry applied as organic manure was collected from the pig farm nearby, and had a TN of 15–16 mg·kg<sup>−1</sup>, total carbon of 338–350 mg·kg<sup>−1</sup>, and an average C:N ratio of 22:1. Crop residues were collected from a nearby field, with the same fertilization rate as the NPK treatment, were cut into small pieces, and had TN of 5.6–9.2 mg·kg<sup>−1</sup>, total carbon of 415–429 mg·kg<sup>−1</sup>, and a C:N ratio of 45:1 to 77:1. Organic manure and crop residues were uniformly spread onto the soil surface by hand and immediately incorporated into the soil to about 10 cm deep before sowing.

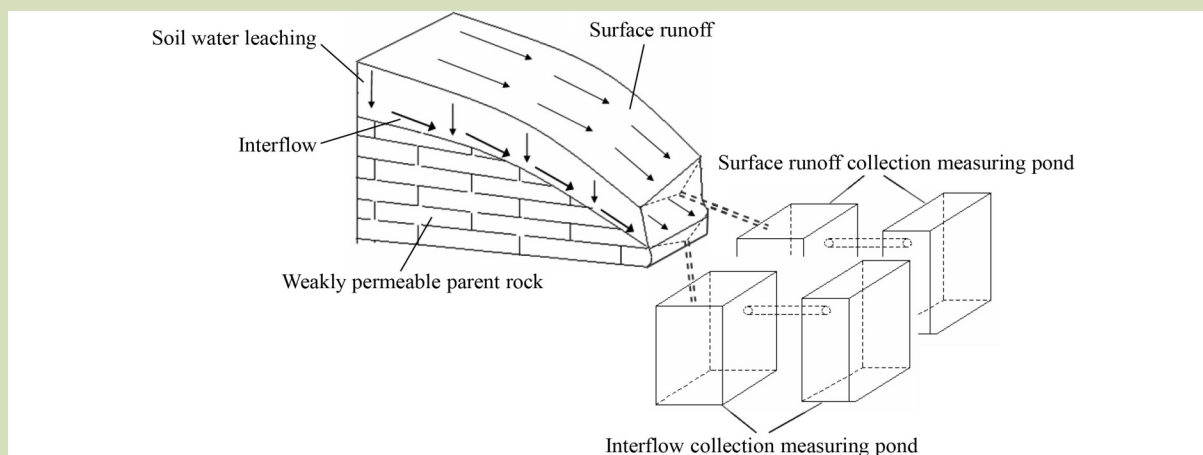


Fig. 1 Schematic of the free-drained lysimeters used in this study.

## 2.3 Field sampling and measurements

### 2.3.1 Crop biomass and grain yield

Crop biomass and yield were measured in triplicates from all experimental plots in a harvest area of 0.25 m<sup>2</sup> for wheat and 1 m<sup>2</sup> for maize. The shoots and roots were combined for biomass determination. The grains, shoots and roots were oven drying at 70 °C for 48 h for determination of their dry weight equivalent then ground to pass through 0.5 mm sieve for analysis of TN.

### 2.3.2 Monitoring of overland flow, interflow and sediment yield

The daily precipitation and temperature during the wheat and maize growing periods were collected from a nearby meteorological station (100 m far from the experimental site). Before collecting the water and sediment samples, the water level in each measuring tank was measured at four different positions. Overland flow, interflow water and water-sediment mixed samples were collected in the corresponding cleaned polyethylene bottles of 500 mL (Fig. 1) and water was taken from different ponds after each precipitation event when no water flowed. All water and sediment samples were fully mixed in the responsible ponds before sampling to ensure homogeneity.

## 2.4 Chemical analysis

### 2.4.1 Nitrogen content of crop and sediment

TN content in grain, shoot and root was determined by an elemental analyzer (Model, Vario El/micro cube, Germany). The TN content of sediment was digested as soil total nitrogen analysis<sup>[21]</sup>.

### 2.4.2 Nitrogen forms determination

Sub-samples of water were unfiltered or immediately filtered by 0.45 µm membrane, stored at 4 °C and analyzed within 48 h. The unfiltered sub-samples were used to determine the concentrations of TN and the filtered sub-samples for total dissolved nitrogen (TDN), NH<sub>4</sub><sup>+</sup>-N and NO<sub>3</sub><sup>-</sup>-N using a continuous flow auto-analyzer (model AA3, Bran + Luebbe, Norderstedt, Germany).

## 2.5 Data calculation and statistical analysis

### 2.5.1 Runoff discharge and sediment yield calculation

Runoff discharge (W) of overland flow and interflow from

different plots was calculated based on the equation:

$$W = \sum_{i=1}^n H_i \quad (1)$$

where, W (mm) is the cumulative runoff discharge of overland flow and interflow from different plots under the corresponding treatments, and H (mm) is runoff discharge of overland flow and interflow calculated from water level in each measuring pond.

The sediment yield of each treatment was calculated based on the equation:

$$S = \sum_{i=1}^n E_i \quad (2)$$

where, S (g·m<sup>-2</sup>) is the annual cumulative sediment loss from each treatment and E is all monitored sediment yield in each treatment (g·m<sup>-2</sup>) in each rain event.

### 2.5.2 Content of nitrogen form calculation

Dissolved organic nitrogen (DON) was calculated as TDN minus NH<sub>4</sub><sup>+</sup>-N plus NO<sub>3</sub><sup>-</sup>-N. Also, the particulate N, referred to herein as PN was calculated as TN minus TDN according to Zhou et al.<sup>[18]</sup>.

### 2.5.3 Nitrogen loss fluxes calculation

Total N, DON, NH<sub>4</sub><sup>+</sup>-N, NO<sub>3</sub><sup>-</sup>-N and PN loss flux was calculated based on the equation:

$$F = \frac{\sum_{i=1}^n C_i Q_i}{100 \times A} \quad (3)$$

where, F (kg·ha<sup>-1</sup>) is N loss flux from the sloping cropland of purple soil, C (mg·L<sup>-1</sup>) is the N concentration of the runoff, Q is overland and interflow runoff discharge in each runoff event, i indicates numbers of observed runoff event, A (m<sup>2</sup>) is the area of experimental plot, and 100 is the transformation coefficient.

### 2.5.4 Calculation of yield-scaled N loss coefficient

Yield-scaled N loss coefficient was calculated based on the equation:

$$L = \frac{B}{G} \quad (4)$$

where, L (kg·ha<sup>-1</sup>·Mg<sup>-1</sup>) is the yield-scaled N loss coefficient of each fertilization treatment, B (kg·ha<sup>-1</sup>) is the total N loss from each fertilization treatment, and G (Mg) is the crop yield of each fertilization treatment.

### 2.5.5 Statistical analysis

The effects of organic amendment treatments and year on crop

productivity, simultaneous overland flow and interflow N losses fluxes were examined by two-way analysis of variance in IBM SPSS Statistics 20 (IBM, Armonk, NY, USA). Significant differences in the mean of estimated parameters among treatments were verified by the least significant difference test at  $P < 0.05$  while significant differences between the year and between organic amendments treatments, and their interactions by Student's  $t$ -test at  $P < 0.05$ . Data for the three replicates are given as mean values and standard error. The graphical data presentations were prepared using SigmaPlot (version 12.5, Systat Software Inc. San Jose, CA, USA) and Excel (version 16.62, Microsoft Inc.).

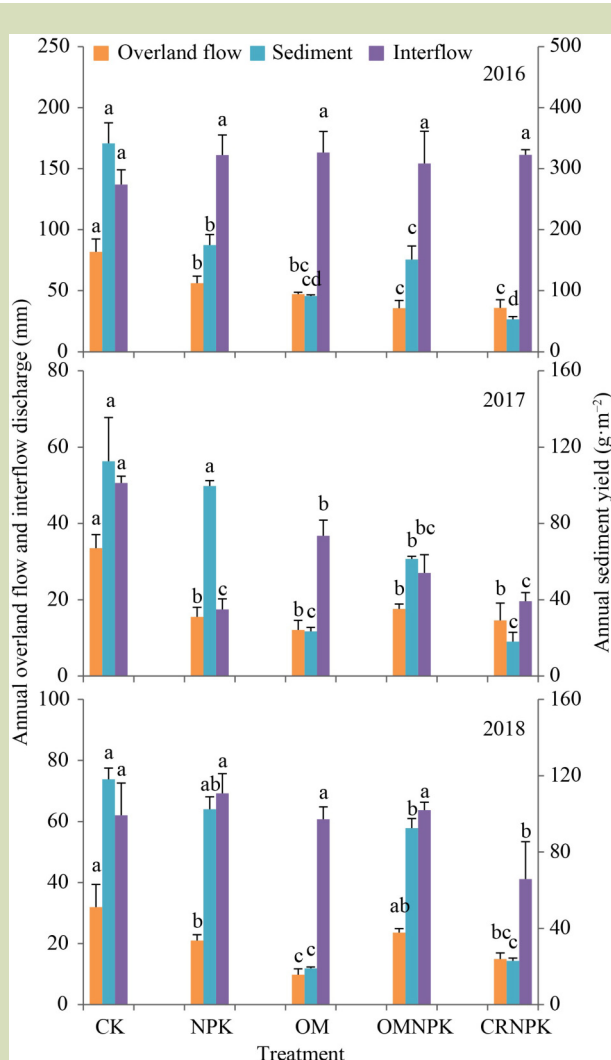
### 3 RESULTS

#### 3.1 Precipitation, overland flow, interflow discharges and sediment yield

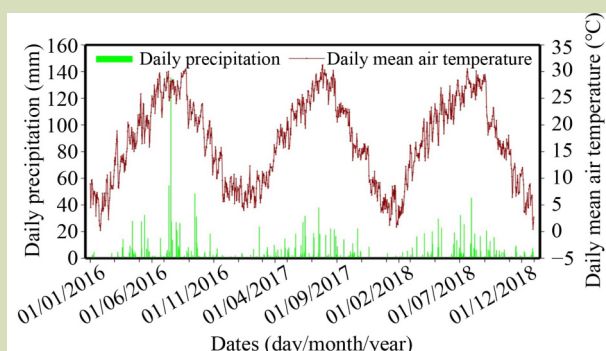
During the three experimental years, the annual precipitation was 803, 612 and 658 mm in 2016, 2017 and 2018, respectively (Fig. 2). During the study period, we observed 21 runoff events, and the highest precipitation (120 mm) occurred on 25 July 2016. No runoff event was observed during wheat season. The mean annual temperature during experimental period was 17.3 °C for the three years with the lowest of 5.7 °C in January and the highest of 28.1 °C in August (Fig. 2).

Significant differences were observed between the annual average overland flow and interflow between the organic amendment treatments (Fig. 3). The annual average discharges via overland flow were 51.4, 18.7 and 20.2 mm in 2016, 2017 and 2018, respectively, while the annual average interflow was 155.4, 30.3 and 59.3 mm in 2016, 2017 and 2018, respectively (Fig. 3). Based on the annual average, the discharge of interflow

was three to four times higher than that of overland flow across the three observation years. The overland flow discharges of OM, NPK, OMNPK and CRNPK accounted for 25.3%, 31.8%, 21.8% and 14.2% of the total discharges across the three years of experimental period, respectively (Fig. 4). The highest mean annual cumulative runoff discharges were observed under CK treatment with the lowest crop cover (Fig. 4). Compared to the

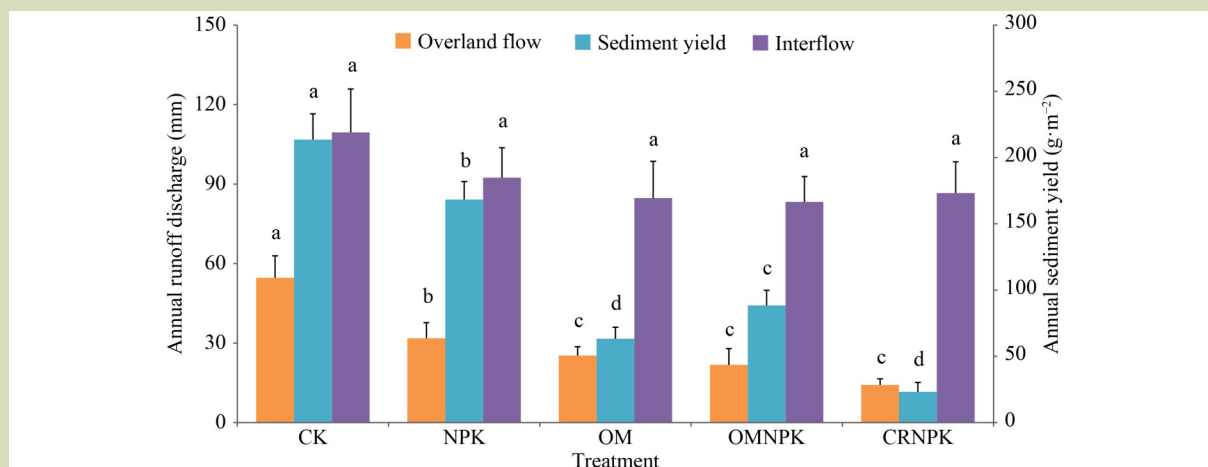


**Fig. 3** Average annual runoff discharges of overland flow and interflow from five fertilization regimes over the experimental period of 2016–2018. Vertical bars indicate the standard error of the three spatial replicates. Means with the same letter are not significantly different at  $P < 0.05$  within each measure: mean annual overland flow and interflow. CK: control with no fertilizer; NPK: standard application of chemical fertilizers; OM: pig manure with equivalent nitrogen as NPK treatment; OMNPK: using pig manure to replace 30% of the mineral nitrogen; CRNPK: using crop residue to replace 15% of the mineral nitrogen.



**Fig. 2** Daily precipitation (mm) and mean air temperature (°C) during the experimental period of 2016–2018.





**Fig. 4** Mean annual cumulative discharge of overland flow, interflow and sediment yield under five fertilization regimes on sloping cropland of purple soil over period of 2016–2018. Vertical bars indicate the standard error of the three spatial replicates. Means with the same letter are not significantly different at  $P < 0.05$  within each measure: mean annual cumulative discharges of overland flow and interflow and sediment yield, respectively. CK: control with no fertilizer; NPK: standard application of chemical fertilizers; OM: pig manure with equivalent nitrogen as NPK treatment; OMNPK: using pig manure to replace 30% of the mineral nitrogen; CRNPK: using crop residue to replace 15% of the mineral nitrogen.

NPK regime, organic substitution treatments (OM and CRNPK) significantly decreased the overland flow by 20.4% and 55.4%, respectively while the interflow was at the same level (Fig. 4). The mean annual cumulative sediment yield over period of 2016–2018 followed by the order of CK > NPK > OMNPK > OM > CRNPK. Sediment yield of organic substitution treatments (OM, OMNPK and CRNPK) decreased by 62.4%, 47.4% and 86.2%, respectively, compared to the NPK regime (Fig. 4).

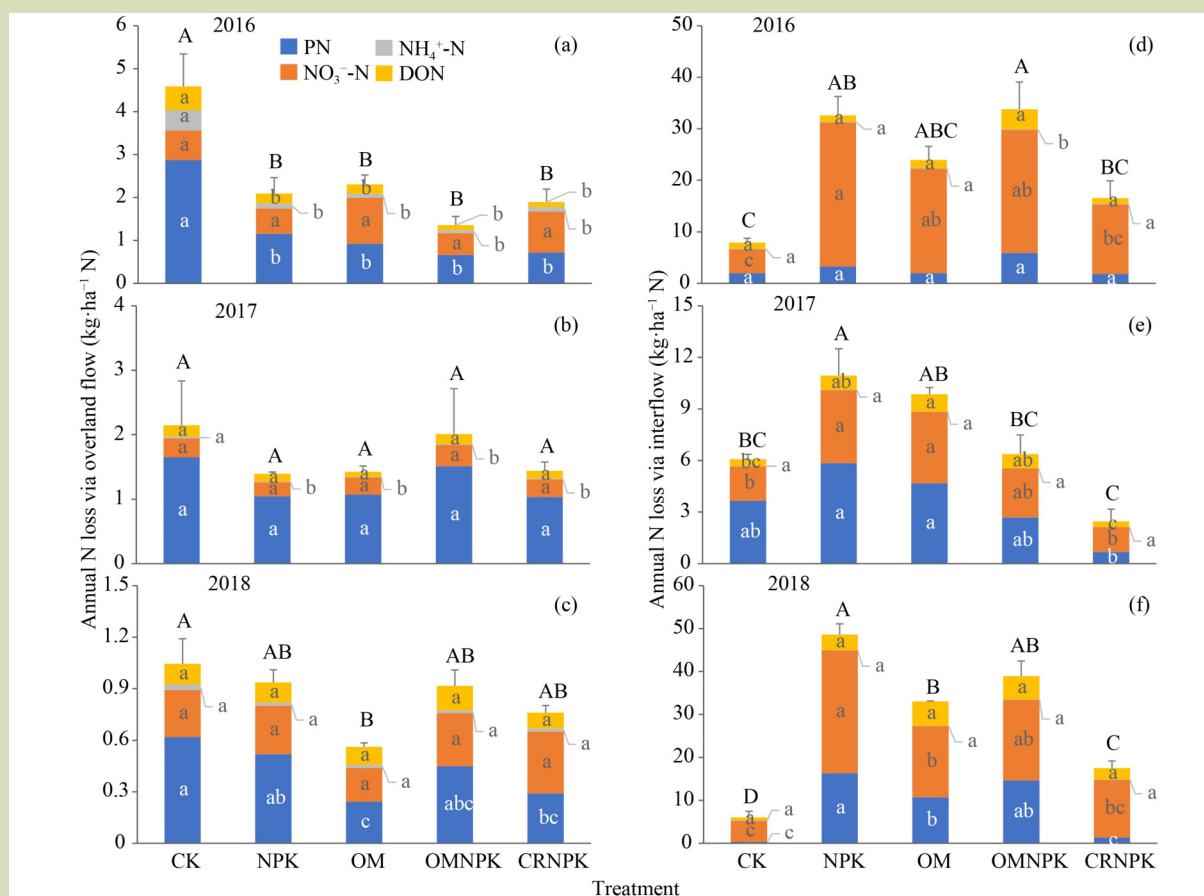
### 3.2 Nitrogen loss forms and fluxes via overland flow, interflow and sediment

The average annual nitrogen loss loadings of the five fertilization regimes for TN, PN,  $\text{NH}_4^+\text{-N}$ ,  $\text{NO}_3^-\text{-N}$  and DON ranged in 0.56–4.58, 0.24–2.87, 0.01–0.47, 0.19–1.07, and 0.08–0.55  $\text{kg}\cdot\text{ha}^{-1}$  N, respectively for overland flow. While those for interflow ranged in 2.45–48.6, 0.34–16.3, 0.01–0.14, 1.45–28.6, and 0.31–5.64  $\text{kg}\cdot\text{ha}^{-1}$  N, respectively (Fig. 5). The annual N loss loadings of  $\text{NH}_4^+\text{-N}$ ,  $\text{NO}_3^-\text{-N}$ , PN, and DON accounting about 4.2%, 26.6%, 59.3% and 9.9% via overland flow and about 0.4%, 63.6%, 25.7% and 10.3% via interflow of the TN loss, respectively, across all years and treatments. The results showed that PN loss fluxes (59.3%) was dominant N forms loss via overland flow, while  $\text{NO}_3^-\text{-N}$  loss fluxes (63.6%) was the highest N forms loss via interflow (Fig. 5). The N forms loss followed the order of PN >  $\text{NO}_3^-\text{-N}$  > DON >  $\text{NH}_4^+\text{-N}$  via overland flow, and  $\text{NO}_3^-\text{-N}$  > PN > DON >  $\text{NH}_4^+\text{-N}$  via

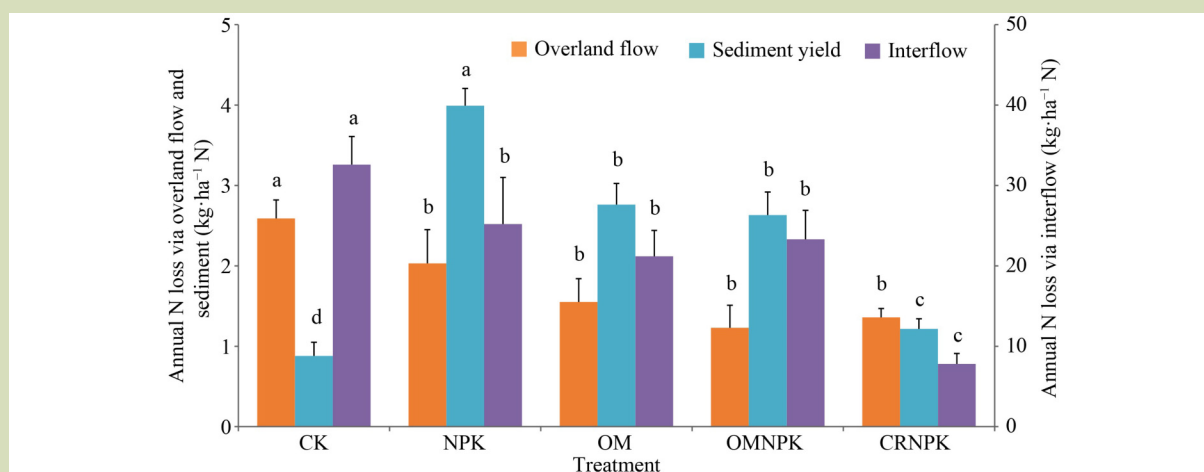
interflow. However, the annual cumulative TN loss loadings accounted for 7% via overland flow, 8% via sediment and 85% via interflow respectively, across all treatments (Fig. 6). The annual cumulative TN loss followed the order of NPK > OM > OMNPK > CRNPK > CK. The cumulative TN loss from organic substitution regimes (OM, OMNPK and CRNPK) reduced by 29.6%, 32.8% and 67.8%, respectively, compared to the NPK regime (Fig. 6).

### 3.3 Crop biomass, grain yield and yield-scaled N loss coefficient

Average annual biomass of winter wheat and summer maize was 2.14–5.91 and 2.65–6.38  $\text{Mg}\cdot\text{ha}^{-1}$ , and the corresponding peak biomass was observed in OM (wheat) and CRNPK (maize) treatment. However, grain yields of organic substitution regimes (OM, OMNPK and CRNPK) had no significant difference from the NPK regime in both wheat and maize season (Table 1). The yield-scaled N loss is a useful parameter to estimate the agronomic and environmental effects based on unit yield. The yield-scaled N loss ranged from 1.67 to 5.82  $\text{kg}\cdot\text{ha}^{-1}\cdot\text{Mg}^{-1}$  N under different fertilization regimes. The NPK regime had the highest yield-scaled N loss coefficient, which was significantly higher than those of organic substitution fertilization regimes (OM, OMNPK and CRNPK) (Table 1). This indicated partial substitution of mineral N fertilizer by organic amendments (OM, OMNPK and CRNPK) could reduce the yield-scaled N loss by 47.4%, 17.9% and



**Fig. 5** Annual loss fluxes of N forms through overland flow (a–c) and interflow (d–f) from five fertilization regimes over the three experimental years (2016–2018). The vertical bars indicate the standard error of the three spatial replicates. Means with the same uppercase and lowercase letter are not significantly different at  $P < 0.05$  for annual total and forms of N losses, respectively, within each measure: overland flow and interflow.



**Fig. 6** Average annual cumulative TN loss fluxes through overland flow, sediment yield and interflow under five fertilization regimes on sloping cropland of purple soil. Vertical bars indicate the standard error of the three spatial replicates. Means with the same letter are not significantly different at  $P < 0.05$  within each measure: overland flow, sediment yield and interflow.

**Table 1** Average annual crop biomass, grain yield, cumulative TN loss and yield-based TN loss in the wheat-maize rotation systems under five fertilization regimes over a 3-year experimental period from 2016 to 2018

Treatment	Wheat season		Maize season		Wheat-maize rotation	
	Biomass (Mg·ha <sup>-1</sup> )	Grain yield (Mg·ha <sup>-1</sup> )	Biomass (Mg·ha <sup>-1</sup> )	Grain Yield (Mg·ha <sup>-1</sup> )	Cumulative TN loss (kg·ha <sup>-1</sup> N)	TN loss per unit yield (kg·ha <sup>-1</sup> ·Mg <sup>-1</sup> )
CK	2.14 ± 0.102c	0.91 ± 0.04b	2.65 ± 0.23b	1.84 ± 0.08b	13.39 ± 1.43c	4.87 ± 0.22b
NPK	4.03 ± 0.08b	2.92 ± 0.10a	5.80 ± 0.39a	4.72 ± 0.39a	44.83 ± 3.53a	5.82 ± 0.48a
OM	5.91 ± 0.046a	3.35 ± 0.07a	6.23 ± 0.22a	4.86 ± 0.20a	29.31 ± 2.32b	3.06 ± 0.16c
OMNPK	4.69 ± 0.32b	3.38 ± 0.17a	6.00 ± 0.21a	5.39 ± 0.12a	40.12 ± 2.39a	4.78 ± 0.37b
CRNPK	4.82 ± 0.16b	3.02 ± 0.12a	6.38 ± 0.45a	5.44 ± 0.29a	14.19 ± 1.62c	1.67 ± 0.13d
ANOVA						
Year (Y)	F values	66.5	46.4	20.1	15.1	7.08
	P values	<b>0.000</b>	<b>0.000</b>	<b>0.000</b>	<b>0.000</b>	0.0312
Treatment (T)	F values	40.5	53.6	18.7	15.0	23.0
	P values	<b>0.000</b>	<b>0.000</b>	<b>0.000</b>	<b>0.000</b>	<b>0.000</b>
Y x T	F values	1.82	3.82	2.20	2.14	1.72
	P values	0.113	<b>0.003</b>	0.057	0.063	0.135

Note: Different lowercase letters in the columns indicate significant differences among the fertilization treatments. The ANOVA indicates the impacts of treatment, year and their interactions.

71.4%, respectively, compared to the NPK regime. Effects of experimental period in year (Y), the fertilization regime treatments (T) and the interaction between (Y x T) on biomass yield, grain yield, TN loss and yield-scaled N loss were analyzed for significance difference as shown in Table 1. During wheat and maize season, significant effects of year were observed on biomass, yield, grain yield, annual cumulative TN loss and yield-scaled N loss. Significant interactions (Y x T) occurred in wheat grain yield. However, no significant effects were exerted by interaction of (Y x T) on wheat and maize biomass, annual cumulative TN loss and yield-scaled N loss (Table 1).

## 4 DISCUSSION

### 4.1 Forms and pathways of nitrogen loss

Regardless the overland flow pathway, TN loss loadings was much lower compared to the interflow. The average annual TN loss loadings via overland flow accounted for only 8% of total hydrological loss on average (Fig. 6). This is much lower than 9%–46% reported by Wang et al.<sup>[21]</sup> in sloping cropland of purple soil during maize growth stages. The N forms loss followed the order of PN > NO<sub>3</sub><sup>-</sup>-N > DON > NH<sub>4</sub><sup>+</sup>-N via overland flow, and NO<sub>3</sub><sup>-</sup>-N > PN > DON via interflow (Fig. 5). While particulate nitrogen (PN), rather than nitrate nitrogen (NO<sub>3</sub><sup>-</sup>-N), was the main nitrogen form in overland flow

(Fig. 5). Thus, sediment is another pathway contributed 5.5%–24.3% of annual cumulative TN loss loadings. Previous studies have indicated that PN is the main form of N loss via overland flow<sup>[18–22]</sup>. Interflow maybe the dominant pathway of TN loss accounted for 85% of annual cumulative TN loadings (Fig. 6). Wang et al.<sup>[21]</sup> reported TN loss loadings via interflow accounted for 51%–89% of total hydrological loss in south-western China and concluded that interflow was the main pathway of TN loss loadings. Several studies have demonstrated that the interflow is the dominant hydrological pathway for TN loss in sloping cropland of purple soils<sup>[16,18]</sup>. However, annual TN loss loadings are positively correlated with annual discharges in the interflow, indicating that annual discharges are a key positive regulating factor influencing annual TN loss loadings via the interflow.

### 4.2 Purple soil is a hot spot for nitrate leaching

NO<sub>3</sub><sup>-</sup>-N is the dominant N loss form in the interflow accounting for about 64% of TN loadings via interflow (Fig. 5). This could be partly ascribed to the intensified nitrification of purple soil<sup>[23]</sup>, which can easily transform ammonia to nitrate in a short period of time, then, nitrate may accumulate in the soil profile with huge quantity during the wheat season. Conversely, the unique soil-bedrock structure results in shallow soil layer (~60 cm), coarse texture and high permeability, leading to large leaching water conflux at



interface of soil-bedrock, which maybe relative impermeable, to form large amount of interflow water diffuse from the soil<sup>[24,25]</sup>. This hydrological process overlaps intensified nitrification in purple soil, thus contributes to high nitrate leaching loss. In our study, N leaching loss loading was up to 32.6 kg-ha<sup>-1</sup> N in NPK, accounting for 11.6% of total mineral N applied to soil. Nitrate leaching loss loadings from dryland soil on the North China Plain accounted for about 4.2% of mineral N applied<sup>[26]</sup>, while, N leaching from vegetable soil in Huaihe River accounted for 10.8% of applied N<sup>[25–35]</sup>. N leaching loading from sloping cropland of purple soil is much higher than that from croplands of other region in China. Meanwhile, shallow groundwater of the purple soil region is more susceptible to nitrate pollution because the interflow from purple soil is the main source of drinking water in rural area. Previous monitoring results showed that the nitrate concentration of shallow groundwater of the purple soil region had about 50% of monitoring site exceeded the threshold of drinking water set by WHO<sup>[29,30]</sup>. Also, nitrate loss via interflow can be 10 times higher than that via the overland flow. Therefore, interflow is a dominant pathway of N loss loadings from sloping cropland of purple soil, which also indicates this would be the major mechanism of non-point source pollution in the purple soil region. Due to non-point source pollution caused by N leaching and its threat to local drinking water, the purple soil region is a hot spot of nitrate leaching in China.

### 4.3 Key mechanisms of reducing N loss from purple soil through organic substitution

Replacing mineral N with organic amendments by 100%, 30% and 15% (OM, OMNPK and CRNPK) significantly reduced the N loss loadings (Fig. 6). Compared to the NPK regime, peak soil nitrate contents of organic substitution treatments (OM, OMNPK and CRNPK) was about 50% lower lasted for a short period after fertilization<sup>[29,30]</sup>. This could be partly ascribed to the substitution of mineral N with organic amendments by reducing soil nitrification through suppressing the activities of nitrification-related microbes<sup>[23]</sup>, thus decreased nitrate contents as the leaching substrate. Additionally, the substitution of mineral N with organic amendments significantly reduced interflow discharge (Fig. 3), the major pathway for N leaching loss, compared to the NPK regime. This indicated that organic N substitution can decrease N loss loadings through reducing not only soil accumulated substrate quantity but also runoff discharge at the same time. Organic substitution fertilization could increase or maintain crop yield (Table 1), this could be explained by whole nutrient supply with enzyme activities promoting due to organic amendments

of pig manure and crop residue. Thus, the structures and richness of microbial community maybe ameliorated to enhance capability of crop N uptake and increase NUE<sup>[31–33]</sup>. However, it takes a long time to form stable soil conditions to continuously support growing crops with organic amendments<sup>[34]</sup>. Some short-term studies found that replacing mineral fertilizer by organic fertilization reduced soil N loss<sup>[9–15]</sup> but the effects on crop yield were inconsistent, which implied that the short-term effects of organic amendments as substitution of mineral fertilizer are not stable. Agronomic and environmental effects of organic substitutions need to be confirmed by long-term experiments. Also, some of those studies did not take organic N from organic amendments into account<sup>[9,10]</sup>, which resulted in inconsistent N level and unreliable comparison of the yield among different fertilization treatments. In this study, organic N of organic amendments were determined and considered into total application rates in order to ensure all comparisons of different fertilization regimes were at the same N level. These fertilization experiments have been conducted continuously since 2003, thus, this long-term fertilization system enable us elucidate the agronomic and environmental effects of organic substitution. Previous studies focused on how organic fertilization control N loss by reducing overland runoff and sediment yield<sup>[35]</sup>, whereas, nitrogen loss via interflow was neglected. We found that conservation of overland runoff and sediment yield can only reduce less than 30% TN loss (Fig. 6). As interflow contributes more than 65% of TN loss loadings, neglecting of interflow (or leaching) loss of N maybe fail to control N loss from sloping cropland of purple soil. Organic substitution fertilization regimes succeeded in not only reducing N loss via overland runoff and sediment but also via interflow. Consequently, substitution of mineral N with organic amendments can balance crop N uptake and soil N loss. It can maintain high crop yield while significantly reduce N loss in comparison to standard mineral NPK fertilization. Organic substitution fertilization can be recommended as an effective way for recycling N resources and extension in practice of “zero increase of mineral fertilizer” in the purple soil region.

## 5 CONCLUSIONS

Annual cumulative total N loss loadings from sloping cropland of purple soil were high (up to 45 kg-ha<sup>-1</sup> N) during the winter wheat-summer maize rotation. Over 85% TN loss was contributed by interflow. Hydrological driving forces of interflow mediated N leaching loss as the dominant pathway of total N loss from sloping cropland of purple soil. The purple soil region is considered to be a hot spot of N leaching loss in

China due to its large loading quantity and negative environmental effects. The substitution of mineral N with organic amendments succeeded in not only maintaining crop productivity but also reducing N loss through balancing conflicts between soil nitrate accumulation and crop N uptake. Substitution of mineral N fertilizer with organic amendments

(OM, OMNPK and CRNPK) could significantly reduce the yield-scaled N loss in comparison to standard mineral NPK fertilization. Our results suggest that organic fertilizers can be recommended in an optimal N fertilizer management strategy and extension in practice of “zero increase” of mineral fertilizer in the purple soil region.

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### Compliance with ethics guidelines

Bo Zhu, Zhiyuan Yao, Dongni Hu, and Hamidou Bah declare that they have no conflicts of interest or financial conflicts to disclose. This article does not contain any studies with human or animal subjects performed by any of the authors.

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