Subsurface lateral flow from hillslope and its contribution to nitrate loading in the streams during typical storm events in an agricultural catchment

J. Tang¹,³, B. Zhang¹,², C. Gao⁴, and H. Zepp⁵

¹Key State Laboratory of Soil and Sustainable Agriculture, Institute of Soil Science, Chinese Academy of Sciences (CAS), Nanjing 210008, China
²Key Laboratory of Crop Nutrition and Nutrient Cycling of Ministry of Agriculture of China, Institute of Agricultural Resources and Regional Planning, Chinese Academy of Agricultural Sciences (CAAS), Beijing, 100081, China
³Institute of Mountain Hazards and Environment, Chinese Academy of Sciences (CAS), Chengdu, 610041, China
⁴Geographical Institute of Nanjing University, Nanjing 210093, China
⁵Geographical Institute of Ruhr University, 44780, Bochum, Germany
Abstract

Compared with overland flow from agricultural hillslopes, subsurface lateral flow is often overlooked partly due to monitoring difficulties and the lack of quantitative identification its role in nutrient delivery to surface water. The objectives of this study were to examine how subsurface lateral flow generates from hillslopes to streams and to quantify its contribution to nutrient loading in streams. Hillslope hydrology and stream hydrology were simultaneously monitored during two typical storms and subsurface flow was separated by chemical mixing model. Positive soil water potential at the soil depths from 0.60 to 1.50 m was observed at the middle course of the storm events, suggesting soil water was saturated following the storms and the drained after the end of the storms. The hydro-chemographs in the stream in a trench below a hillslope showed that suspended sediment, particulate N and P were dominant in the stream during the storms, while after the end of the rainstorms the nitrate concentration and electricity conductivity (EC) in the stream increased with time on the recession limbs of the hydrographs. Meanwhile, a rebound or delayed curve appeared on the recession limbs for several hours immediately after the end of rainstorms. All the synchronous data confirmed nitrate was delivered from the hillslope through subsurface lateral flow to the streams even after the end of rainstorms. A chemical mixing model based on EC and pH showed that the subsurface lateral flow during the rainstorm events accounted for 29% to 45% of the stream flow and about 86% of total \( \text{NO}_3^- \) N loss (or 26% of total N loss) from the peanut hillslope and for 5.7% to 7.3% of the stream flow about 69% of total \( \text{NO}_3^- \) N loss (or 28% of total N loss) from the catchment outlet. The results suggest that subsurface lateral flow generated within a shallow soil profile have to be paid more attention for controlling non-point source surface water pollution from intensive agricultural catchment.
1 Introduction

Non-point source of nutrient exports from agricultural fields to surface water and groundwater is concerned worldwide (USEPA, 1996). Agriculture in China, for example, consumes more than two thirds of the world’s total chemical fertilizers (Zhou et al., 2004). It is estimated that as much as 0.97 million tons of N is delivered from agriculture through the Yangtze River, Yellow River and Pearl River to the oceans (Duan et al., 2000). Excess nitrogen concentration in rivers and streams has been linked to the eutrophication of rivers, lakes and coastal waters in China (Huang et al., 1998; Duan et al., 2000; Zhang et al., 2004) and has been shown to have negative effects on human and ecosystem health (Wu et al., 1999). Most of nutrient losses occur during rainfall events and overland flow is generally considered as the most important hydrological pathway from agricultural lands (Edwards and Owens, 1991; Kwong et al., 2002; Zhu and Chen, 2002). Overland flow during several rainstorms can deliver more than half (Lowrence et al., 1984; Edwards, 1991) or even 90% (Nash, 1999) of total annual losses of soils and nutrient in agricultural catchment. However, controlling overland flow is often less effective than expected in improving surface water quality especially in agricultural catchment.

Subsurface lateral flow is movement of water through near surface soils, regolith and bedrock on hillslopes (Newman et al., 1998). Subsurface lateral flow is generally initiated when rainwater percolates through a soil profile, meets an impeding layer of soil or bedrock, forms saturated conditions and then is diverted laterally downslope (Luxmoore, 1991; Newman et al., 1998). Subsurface flow is considered as a major hydrological process in some forested headwater catchments (Cirmo and McDonnell, 1997; DeWalle et al., 1988; Burns et al., 2001; Inamdar and Mitchell, 2007), but a relatively slow process, linking to spatial pedogenetic variations of nutrient and pollutant (Schlichting and Schweikle, 1980). It has been overlooked in agricultural catchment compared with overland flow because of the difficulties in direct monitoring (Allaire et al., 2009). Soil tillage frequently alters soil structure in the surface soil and field
machinery operations may result in formation of impeding layers in the subsurface soil due to compaction (Horn and Smucker, 2005). Therefore, subsurface lateral flow in agricultural catchment can be a fast process and have more implication to surface water quality. For example, nitrogen leached and accumulated in subsurface soil that is ready for take-up during later crop growth period can be washed off earlier by subsurface lateral flow to groundwater or stream water (Garg et al., 2005). However, generation of subsurface lateral flow from agricultural hillslope and its direct contribution to surface water remains poorly understood in agricultural catchment.

Hillslopes are the fundamental unit of landscapes where agricultural practices are carried out (Lin et al., 2006). Subsurface lateral flow from hillslopes and its connectivity to stream flow have been studied by monitoring the dynamics of soil moisture profiles along slopes (Lin, 2006; McNamara et al., 2005) or trench flow below hillslope (Newman et al., 1998; Tromp-van Meerveld and McDonnell, 2006; van Verseveld et al., 2009) or both of them (Burke and Kasahara, 2010). The spatial variations of soil water content within soil profiles measured in these studies (Burke and Kasahara, 2010; Inamdar and Mitchell, 2007; Lin et al., 2006; Lin, 2006) indicated generation of subsurface lateral flow, but gave no hint how it was generated as soil water movement is normally driven by the difference in soil water potential rather than by soil water content. It can be improved by monitoring spatial variations of soil water potential. Single trench flow measurement showed more direct evidences of generation of subsurface flow, but the results often need careful interpretation as they may be affected by the characteristics of trenched cross-section and by saturated flow around the trenches (Tromp-van Meerveld et al., 2007) as well as by the representativeness of the trenched hillslopes and their connection to riparian zones within catchment (van Verseveld et al., 2009). Moreover, most of the trenched hillslope experiments often lack detailed hydro-biogeochemical data, which are needed for separating hydrological components by hydrograph separation and understanding of hydrological processes at the catchment scale (e.g. Hornberger et al., 1994; Boyer et al., 1997). Therefore, integrative study combining hillslope soil hydrology, trench stream hydrology and biogeochemistry...
may improve our understanding of generation of subsurface lateral flow from hillslope and its contribution to nutrient delivery to stream (Cras et al., 2007).

An agricultural catchment (46.2 ha) has been used for multi-scale study on hydrological processes in subtropical China (Zepp et al., 2005). This study catchment has mixed land uses of slope uplands and terraced paddy fields. The catchment has a unique feature that irrigation channels were trenched right below hillslopes. Thus, all the hillslope flows issue directly into the irrigation stream, without any riparian zone modulation. This feature made it possible to identify and quantify subsurface lateral flow from hillslopes to streams by simultaneously monitoring hillslope hydrology and stream hydrology during rainstorm events. The fundamental questions of this study were how subsurface lateral flow generated during storms from the cropped hillslopes and whether it was significantly in controlling nutrient export to stream water out of the intensive agricultural catchment. It was assumed that the stream flows at the cropped hillslope and catchment outlet corresponded to soil water movement from the hillslope and that the stream flow chemistry at the catchment outlet changed with subsurface lateral flow from the hillslope. The specific objectives were to simultaneously monitor soil water potential within soil profiles at different hillslope positions under two contrasting landuses and stream flow and flow chemistry in the streams below a cropped hillslope and at the catchment outlet during two typical rainstorm events, and to identify and quantify subsurface lateral flow from the cropped hillslope and its contribution to deliver nutrient loadings to the steams by hydrograph separation using mixing chemical modelling.

2 Materials and methods

2.1 Study site and catchment

The research Sunjia catchment is located approximately 4 km away from the Ecological Experimental Station of Red Soil, Chinese Academy of Sciences (28°15’ N, 116°55’ E),
in Yingtan, Jiangxi Province. It is representative of widespread geomorphology and land uses in the low hilly region in southeast China. The catchment has an area of 46.2 ha (Fig. 1). Elevations rang from 55 m on the hills to 44 m in the valleys and slopes are around 5 to 8%. The catchment has been intensively used for agriculture, with mixed land uses on slope uplands and terraced paddy fields. The slope uplands were cultivated for rain-fed peanut (Arachis hypogaea L.) crop (47.9%), agroforestry system consisting of peanut crop intercropped with mandarin orange (Citrus reticulate L.) tree (11.7%) and chestnut (Castanea mollissima L.) orchard (8.1%). The paddy fields (29.5%) were cultivated with double rice (Oriza sativa L.) cropping followed by winter fallow. The remaining lands (2.8%) were occupied by ponds and residence.

The research area has a typical subtropical moist climate, with a mean annual temperature of 17.7 °C, a maximum daily temperature of around 40 °C in summer and an annual average of 262 frost-free days. Annual rainfall is 1786 mm and potential evaporation is 1230 mm. About 50% of the annual rainfall falls between March and early July, during which period potential evaporation was lower than rainfall. Potential evaporation exceeds rainfall from late July to November, causing seasonal drought. Stream flow discharges in the catchment consequently exhibit strong seasonality, with high base flow during the irrigation period and ephemeral drying-up periods after irrigation stopped since October in the dry season (Tang et al., 2007, 2008).

The geology in the region consists of weakly weathered Cretaceous sandstone underlying deeply weathered Quaternary red clay, resulting in the formation of lateritic profiles on the hills: surficial clayey, sandy or their mixture deposits, ferruginized caprock and mottled zone, overlying weakly weathered sandstone. Sandy soils were exposed in some locations due to long-term soil erosion of clayey soils overlying. The soil depths on the hills are generally shallow (<3 m) and there is no deep ground water on the hillslopes as identified with radiation method (data not reported) and in the stream hydrographs (Tang et al., 2007, 2008).
2.2 Soil properties and hydrological monitoring data

Soil hydraulic properties have been documented by Jing (2004) and Jing et al. (2008) for the upland soils and by Sander and Gerke (2007) and Janssen and Lennartz (2008) for the paddy fields. The soil hydraulic properties along the hillslopes were reported anisotropic in the surface soil (0–0.10 m), with a greater hydraulic conductivity in the vertical direction than the along contour and along slope directions, and isotropic in the deep soil layer (1.0 to 1.5 m) among the three directions (Jing et al., 2008). The selected soil physical and hydraulic properties are presented in Table 1 for the hillslopes under peanut cropping system and chestnut orchard (Jing, 2004). The catchment was equipped in 2001 to monitor rainfall, irrigation water, well water, spring water, soil water, overland flow, stream flow and through-fall (Zepp et al., 2005; Tang et al., 2007, 2008).

With consideration of the multi-scale interactions of hydrological processes in relation to soil and nutrient transport, gauging and sampling stations were installed at different scales from points to hillslopes and catchment outlet (Fig. 1). Briefly, sets of tensiometers and suction cups were installed at the same elevation on the upper and lower slope positions on the peanut hillslope and at the upper, middle and lower slope positions on the chestnut hillslope. The tensiometers equipped with pressure transducers (26PCDFA6G, Honeywell, USA) were installed at the depths of 0.20, 0.40, 0.60, 0.85, and 1.50 m to measure soil water potential ($\Psi$). The pressure transducers, covering a range of $\pm 30.0 \text{ psi} \pm 206.84 \text{ kPa}$ and having a very fast response time ($<1 \text{ ms}$), were connected to a data-logger (DL2, Delta T, Lt., UK) to record the readings at 10-min interval. The suction cups were installed at the depths of 0.20, 0.40 and 0.85 m for soil water sampling. A suction of 100 kPa was applied for one week before each sampling day. Erosion plots, 5 m wide and 20 m long along the slope, were positioned at the upper and lower slope positions along the peanut slope, with the tensiometers lining in the middle of the erosion plots. Overland flow and sediments were conducted to a tipping bucket system following the design reported by Khan and Ong (1997) to automatically sample water, sediment and record tipping number using event data loggers.
(Onset Computer Corporation, USA) and then calculate overland flow and sediment load on event base.

Hydrological weirs were constructed at the catchment inlets (Stations No. 1, 2 and 3) and catchment outlet (Station No. 4) and in a stream within the catchment (Stations No. 5 and 6), which was an irrigation channel trenched right below a peanut cropping hillslope. The hydrological area of the peanut hillslope was delineated by geographical information system (GIS) software (Fig. 1) and it was about one tenth of total catchment area (4.8 ha). Water levels at the hydrological stations were measured at 10-min interval using water level transducers connected to data-loggers (Keller Company, Switzerland) and were converted into stream flow flux. Water sampling was carried out weekly simultaneously from all water sources including soil water and stream water from above mentioned sites, the well locating in the chestnut orchard, and the spring lying between Stations No. 5 and 6. The well water and spring water represented the subsurface soil water. Although the sites for soil water sampling were not located within the peanut hillslope, we assumed that soil water chemistry was similar under the same soil condition and cropping system.

In addition to the regular sampling, stream water was sampled at relative short intervals from 20 to 60 min during storm events. There were total 23 sampled rainfall events (8 in 2002, 6 in 2003, and 9 in 2004) and most of the events data were not completed due to the limitation of manual sampling in the dark conditions during night when rainfall peaks appeared. Two typical storm events are presented here because the datasets were available to compare the profiles of soil water potential on the hillslopes and the hydrographs of the streams below the peanut hillslope and at the catchment outlet. More importantly, the stream flow chemistry data sets covered the whole period during the period of rainstorms and several hours after the end of the rainstorms. The rainstorm on 14 May 2003 lasted for 1020 min, with the total amount of 178.5 mm and the maximum rainfall intensity within 30 min of 27 mm h⁻¹, while another rainstorm on 12 May 2004 lasted for 1320 min, with the total amount of 124.5 mm and the maximum rainfall intensity within 30 min of 14 mm h⁻¹. There were 68.5 mm and 53.5 mm rainfalls
within 5 days before the rain storms on 14 May 2003 and on 12 May 2004, respectively. The water samples were stored at about 4°C in laboratory of the experimental station before the chemical analysis of total nitrogen (TN), total phosphorus (TP), nitrate-nitrogen (NO$_3^-$-N) and ammonium-nitrogen (NH$_4^+$-N). TN and TP concentrations were measured before and after filtering through the filter paper of 0.45 µm pore size. TN and TP measured after the filtering were taken as total dissolved nitrogen (TDN) and total dissolved phosphorus (TDP), respectively. The difference between TN and TDN was referred to as particulate-N (PN) and between TP and TDP was referred to as particulate-P (PP). The water samples were digested with K$_2$S$_2$O$_8$-NaOH solution before TN and TDN measurement and with K$_2$S$_2$O$_4$ before TP and TDP measurement. TN and NO$_3^-$-N were determined by ultraviolet spectrophotometry. NH$_4^+$-N and TP were determined by colorimetry. Suspended sediment concentrations were measured by weighing after being filtered and dried. Electricity conductivity (EC) and pH in water samples were also measured using meters constructed by the Institute of Soil Science, Chinese Academy of Sciences (ISSCAS).

The sediment and chemical datasets were summarized for the period from 2001 to 2004. The statistics was given for soil water at the 0.85 m depth under peanut cropping system ($n = 55$), well water, spring water and irrigation water at Station No. 2 ($n = 150$) based on the regular sampling and for rainfall water ($n = 153$), overland flow ($n = 169$) under the different land uses and stream flow at the catchment outlet ($n = 121$) and within the subcatchment ($n = 121$) based on the intensive monitoring during storms. An analysis of variance (ANOVA) was performed to compare the nutrient concentrations from different water bodies using SPSS 11.5. The least significant difference (LSD) test was adopted to assess the significant differences at $P < 0.05$ or $P < 0.01$ among the water sources. The statistics would be used to compare with the previous study for the period from 2001 to 2003 (Tang et al., 2008) and to determine if the chemical properties such as pH and EC were distinct among the water sources all the time.
2.3 Separation of subsurface lateral flow from stream flow

The components of stream water were estimated by hydrograph separation using chemical mixing model (Raiswell, 1984; Hagedorn, 1999). Given that their distinction among the water sources from overland flow, irrigation water to soil water (Tang et al., 2008; Table 2) and their conservativity during the relative short periods of rainstorms, pH and EC were used to separate soil water component in stream flow by solving the following mass-balance equations:

\[ Q_c = Q_o + Q_i + Q_s \]  
\[ Q_c C_{1c} = Q_o C_{1o} + Q_i C_{1i} + Q_s C_{1s} \]  
\[ Q_c C_{2c} = Q_o C_{2o} + Q_i C_{2i} + Q_s C_{2s} \]

where \( Q \) is the stream flow and the subscripts \( c, o, i, s \) refer to stream flow, overland flow from the erosion plots, irrigation water and soil water, respectively; \( C_1 \) and \( C_2 \) are \( H^+ \) concentration and EC value measured during the two storm events on 14 May 2003 and 12 May 2004.

The uncertainty of the modeling was calculated following the method described by Genereux (1998).

\[ W_{fi} = \sqrt{\left( \frac{\partial f_i}{\partial x_1} (W_{x1})^2 + \left( \frac{\partial f_i}{\partial x_2} W_{x2} \right)^2 + ... + \left( \frac{\partial f_i}{\partial x_n} W_{xn} \right)^2 \right)} \]  

where \( W_{fi} \) is the uncertainty value for \( i \)-th flow component; \( W_{xi} \) is the analytical uncertainties of chemical constituents in different water sources; \( fi \) is the proportion of water source in total stream flow.

Although NO\(_3\)-N is commonly known to be non-conservative and subjected to biogeochemical transformations, it can also be assumed that NO\(_3\)-N is a conservative tracer during a relatively short storm period (Durand and Torres, 1996; Soulsby et al., 2003; Tiemeyer et al., 2008). Therefore, NO\(_3\)-N concentration in stream flow can be
predicted by summing every separated flow component multiplied with the measured concentration in each component’s source, respectively. The predicted NO$_3^-$-N concentration was then compared with observed the NO$_3^-$-N concentration to evaluate the applicability of chemical mixing model using the coefficient of determination ($R^2$) and the Nash-Sutcliffe model efficiency ($E$) (Nash and Sutcliffe, 1970).

### 2.4 Estimation of nitrogen loading with subsurface lateral flow

NO$_3^-$-N concentration from subsurface lateral flow was estimated by multiplying fraction of subsurface lateral flow estimated in time series with actual NO$_3^-$-N concentration in stream flow. Loadings of TN and NO$_3^-$-N in the streams from the peanut hillslope and the whole catchment were then calculated following Eq. (5).

$$L = \sum_{i=1}^{n} C_i \times Q_i \times \Delta t_i$$  \hspace{1cm} (5)

where $L$ is the TN or NO$_3^-$-N loads during a sampling period; $\Delta t_i$ is the time interval between each sampling; $C_i$ is the TN concentration or NO$_3^-$-N concentration in stream flow or estimated lateral flow at the $i$-th sampling time; $Q_i$ is the amount of measured stream flow or estimated subsurface lateral flow at the $i$-th sampling time.

### 3 Results

#### 3.1 Chemistry of different water sources

The differences of water chemistry were distinct ($P < 0.05$) among the water resources within the agricultural catchment during the period from 2001 to 2004 (Table 2), confirming the same trend as reported in our previous study from 2001 to 2003 (Tang et al., 2008). The regular sampling showed that water pH value was greater in the irrigation water than in the subsurface water (as indicated by the spring water between...
Stations No. 5 and 6, soil water from the peanut hillslope and well water in the chestnut orchard), while water EC was greater in the subsurface waters (soil water from the peanut hillslope and well water in the orchard) than in the irrigation water, but lowest in the spring water taken between Stations No. 5 and 6. The intensive sampling showed that compared with the rainfall water, overland flow increased pH and decreased EC while stream waters increased pH and EC and there were no significant differences in pH and EC among the stream waters during the rainfall. In both sampling strategies, NH\textsubscript{4}\textsuperscript{+}-N concentration was lower than 0.20 mg L\textsuperscript{-1} in all water sources except for the rainfall (0.57 ± 0.55 mg L\textsuperscript{-1}). In contrast, NO\textsubscript{3}\textsuperscript{-}-N concentration was significantly (P < 0.05) greatest in subsurface waters (soil water from the peanut hillslope and well water in the chestnut orchard), followed by the surface stream waters, and lowest in other water sources. There were no significant differences in NO\textsubscript{3}\textsuperscript{-}-N concentrations among the stream waters and also among rainfall, overland flow and irrigation water. NO\textsubscript{3}\textsuperscript{-}-N concentrations were higher in stream waters than in rainfall, irrigation water and overland flow. Suspended sediment and TP were detected only during storms, with higher concentrations in overland flow than stream flow (P < 0.05). Particulate P accounted for nearly 100% of TP.

3.2 Hillslope soil hydrology during storm events

The soil water potential responded rapidly to rainfall during the storms and the responses varied with slope position and land use for the two storm events (Figs. 2 and 3). The soil water potential was always negative at the 0.20 and 0.40 m depths irrespective of land uses and storm event. The soil water potential on 14 May 2003 became positive during rainfall, meaning saturated, at the 0.60 m and 1.5 m depths on the upper and lower slope under peanut cropping system (Fig. 2a), and then decreased after the end of rainfall. The decrease was quicker at the 0.20 and 0.40 m depths than at other layers and on the upper slope than on the lower slope, indicating a fast drainage along the slope. On the chestnut hillslope (Fig. 2b), the positive soil water potential appeared during the course of rainfall at the 0.85 and 1.50 m depths.
at the middle and lower slope positions and then decreased after the end of rainfall. The soil water potential at the 1.50 m depth on the lower slope position continued to increase for 110 or 120 min after the maximum rainfall intensity, reaching a peak at 7.6 kPa under the peanut cropping system and a peak at 11.6 kPa under the chestnut orchard. The peaks of positive soil water potential illustrated that the depth of perched soil water over the 1.50 m depth was 0.76 m and 1.17 m at the lower slope positions on the peanut hillslope and the chestnut hillslope, respectively.

The dynamics of soil water potential on 12 May 2004 (Fig. 3) also demonstrated the processes of soil water saturation and drainage along the slope. The soil water potential at the 1.50 m depth on the lower slope position continued to increase for 400 and 250 min after the maximum rainfall intensity, respectively on the peanut hillslope and chestnut hillslope, reaching the peaks. The peaks of soil water potential showed that the depth of perched soil water was 0.54 m at the 1.50 m depth at the lower slope position on the peanut hillslope (Fig. 3a) and 1.13 m and 1.35 m at the 1.50 m depth on the middle and lower positions on the chestnut hillslope (Fig. 3b).

3.3 Stream hydro-chemo-graphs during storm events

The hydrographs and chemographs during the two storm events are illustrated in Figs. 4 and 5. The peak flows at Stations No. 4, 5 and 6 were 70, 215 and 7751 L s\(^{-1}\) on 14 May 2003 (Fig. 4), and 161, 211 and 3936 L s\(^{-1}\) on 12 May 2004 (Fig. 5). The hydrographs at each gauging station showed different patterns on the rising limbs depending on the rainfall intensities of the two storm events and similar patterns on the recession limbs after the end of rainfall. The flow recession was delayed as compared with the flow rising and even reversed at all stations on both storm events except for at Stations No. 6 and 4 on 12 May 2004 (Fig. 4). The delayed or reversed recession indicated flushes from new water source, which could be only subsurface lateral flow as there was no overland flow and irrigation flow was stable before and after the end of rainfall (data from Station No. 3 were not shown here).
The stream chemical parameters can be categorized into three groups, particulate nutrients (PN and PP) and suspended sediment (SS), soluble nutrients ($\text{NO}_3^-$-N), and EC and pH. The chemographs in each chemical category showed similar patterns at all the gauging stations during the two storm events. The concentrations of N and P in all forms were higher in the stream below the peanut hillslope (Stations No. 5 and 6) than at the catchment outlet (Station No. 4) in each of the storms. The concentrations of PN and PP and SS increased with time during the rainfall on the rising limb of each hydrograph and reached their peaks prior to the peak stream flow and diminished immediately after the end of the rainfall. The peak PN and PP concentrations appeared at the greatest rainfall intensity or at the time when the stream flow started to increase at a greater rate and appeared earlier at Stations No. 5 and 6 than at Station No. 4. The time of peak particulate nutrient concentration was about 40 min prior to peak flow at Stations No. 5 and 6 and about 40 min behind the peak flow at Station No. 4. On 12 May 2004, the time was about 80 min and 100 min prior to the peak stream flows at Stations No. 5 and 6 and at Station No. 4, respectively. PN and PP accounted for $>90\%$ of TN and about 100\% of TP, and their concentration was significantly correlated with SS concentration and stream flow ($P < 0.05$ for both SS concentration and stream flow, $n = 11$ on 14 May 2003; $P < 0.01$ for SS concentration and $P < 0.05$ for stream flow, $n = 20$ on 12 May 2004).

No soluble P was detected in the streams and the soluble N was dominated by $\text{NO}_3^-$-N on both the storms. The $\text{NO}_3^-$-N concentration was relatively low during the rainfall, accounting for less than 10\% and 30\% of TN, respectively on 14 May 2003 and on 12 May 2004. After the end of rainfall, $\text{NO}_3^-$-N concentration increased as flow decreased, accounting for 60\% to 90\% of TN at the end of the observations. The proportion of $\text{NO}_3^-$-N in TN after the end of rainfall was greater in the stream below the peanut hillslope than at the catchment outlet. The starting time of the increase in $\text{NO}_3^-$-N concentration after the rainfall met well the decrease in soil water potential after peak at the 1.5 m depth on the lower slope positions of both hillslopes. EC and pH had little response to rainfall though they generally decreased during the rainfall, while after
the end of rainfall, EC increased with time and the magnitude of increase was larger in the stream below the peanut hillslope than at the catchment outlet. After the rainfall EC was very significantly correlated to NO$_3^-$-N ($P < 0.01$ for both the rainfall events).

### 3.4 Stream flow separation and NO$_3^-$-N export estimate

The water chemistry among the three water sources was distinct in H$^+$ and EC (Table 2) and the mixing diagrams of H$^+$ concentration and EC value illustrated in Figs. 6 and 7 showed general evolution patterns of stream chemistry on the two storm events. The stream chemistry at all the stations were similar to irrigation water at the beginning of the observation, and became more similar to the overland flow chemistry during the rainfall and then more similar to the soil water chemistry. The stream water was mostly similar to soil water in the lower stream (Station No. 6) than in the upper stream (Station No. 6) below the peanut hillslope and was least similar in the stream at the catchment outlet (Station No. 4).

By solving the chemical mixing model, the different components of stream flow were separated for the two rainstorms and their temporal dynamics at all the gauging stations are shown in Fig. 7 and the sums of the subsurface lateral flow contributing to the stream flow below the peanut slope and at the catchment outlet are shown in Table 3. The subsurface lateral flow component derived from soil water contributed to about 10% of stream flow before and after the end of rainfall and to about 50% of stream flow after the end of rainfall and the proportion was larger in the stream below the peanut hillslope (Station No. 6) than at the catchment outlet (Station No. 4). The total subsurface lateral flow accounted for 5.7% to 7.3% of total flow at Station No. 4 and for 29.0% to 44.8% at Station No. 6 and the uncertainty of the estimation varied from 6.4% to 46.7% (Table 3), being later at Station No. 4 than at Station No. 6.

The NO$_3^-$-N concentrations estimated by the mixing formula based on the separated flow components are compared with the observed NO$_3^-$-N concentration for both Stations No. 6 and 4 for the two storm events (Fig. 8). The agreement was better at Station
No. 6 ($R^2 = 0.76$ and 0.98) than at Station No. 4 ($R^2 = 0.17$ and 0.60). The estimated NO$_3^-$-N export through subsurface lateral flow accounted for about 86% of total NO$_3^-$-N export at Station No. 6 and for about 68% at Station No. 4 (Table 3).

4 Discussion

The study catchment provided a unique feature that the sources and transport mechanisms of nutrients in stream could be identified from point, hillslope to catchment scales. The geology and annual stream hydrology (Tang et al., 2007, 2008) demonstrated a negligible influence of groundwater within the catchment. Trenched irrigation channels right below cropped hillslope made it possible to compare simultaneously the hillslope soil hydrology to the stream responses unimpeded by riparian zone. Such in situ natural experimental design was also applied to study the hydrological controls on dissolved organic matter and N fluxes from hillslopes in a small forestry watershed (van Verseveld et al., 2009). This study underscored the importance of subsurface lateral flow from the cropped hillslopes in transporting nutrients to surface stream in intensive agricultural catchment in the low hilly region with red soils in subtropical China.

4.1 Generation of subsurface lateral flow from hillslopes

The hillslope soil hydrology and stream hydrochemistry proved our previous assumption that subsurface flow was generated within the study catchment and resulted in spatial and temporal variations of nutrients in different water sources (Tang et al., 2008). The spatial and temporal dynamics of soil water potential demonstrated soil water saturation and drainage process in the deep soil layers irrespective of land uses in both storm events (Figs. 2 and 3). Soil water potential was always negative in the surface soil (above 0.40 m depth) and became positive at the deep soil depths (from 0.60 to 1.50 m) particularly at the lower slope positions during the observation periods of the storm events. These results suggested that intensive rainfall penetrated into soil
through vertical preferential flow in the surface soil and saturated soil water perched over the deep soil layers. Similar result that soil water saturation occurred in upper soil layers earlier than in deep layers was observed in a forested shale hill catchment (Lin and Zhou, 2008). The rise in saturated soil water table over the 1.5 m soil layer after the end of rainfall did not result from a rise of ground water table as the tensiometers measurements were conducted far above the stream and pond water level. The periodic dry up of streams in drying seasons (Tang et al., 2007) also confirmed little influence of groundwater water table. In this catchment, soil hydraulic conductivity decreased with soil depth (Table 1). The estimated saturated hydraulic conductivity ranged from 1.98 to 3.60 m day$^{-1}$ in the surface soil (above 0.40 m), to 0.08 to 0.64 m day$^{-1}$ in the deep soil (from 0.60 to 1.50 m depth). The deep soil layer from 0.6 to 1.5 m depths was generally below the Bt horizons which had highest clay content and bulk density (Table 1). The shift in hydraulic conductivity with soil depth can often shift water flow from vertical to lateral direction (Lin, 2006). Hillslope scale hydraulic connectivity allowed the shift from vertical to lateral flow to happen at this scale, causing widespread lateral flow along the hillslope (McNamara et al., 2005).

Commonly observed subsurface lateral flow on steep, wet hillslopes is through discrete soil pipes or macropores, most prevalent at the soil bedrock interface or above impeding layers (Sidle and Noguchi, 2001; Uchida et al., 2005; Tromp-van Meerveld and McDonnell, 2006). The decrease in the perched water table over the 1.5 m depth demonstrated that “old water” might be propelled out of the soil layer (Petry et al., 2002), resulting in the generation of subsurface lateral flow through the impeding soil layers along the slopes. The drainage of perched soil water over the deep depth (0.6 to 1.5 m depth) at different slope positions indicated that both discrete and prevalent subsurface lateral flow generated from the gentle cropped hillslopes when they were very wet, then draining to the spring lying between Stations No. 5 and 6. The time lag of peak soil water potential at the 1.5 m behind the maximum rainfall intensity could be attributed to the residence time of saturated soil water within soil profile. The residence time of saturated soil water within soil profile depended on rainfall characteristics and soil
profile features. The time lag behind the maximum rainfall was longer (250 to 400 min vs. 100 to 120 min) on 12 May 2004 than on 14 May 2003 and was shorter (100 and 250 min vs. 120 and 400 min) on the chestnut hillslope than on the peanut hillslope. These suggested that saturated soil water could be retained longer within the soil profiles with more clay textured soil such as on the peanut hillslope during the long lasting, buy less intensive storm (Table 1). In addition, the depth of saturated soil water table over the 1.5 m depth at the lower slope position was greater (1.13 to 1.35 m vs. 0.54 to 0.76 m) on the chestnut hillslope than on the peanut chestnut hillslope suggested that the chestnut hillslope retained more water within the soil profile due to its deeper soil profile from Ap to Bt horizons and would generate faster subsurface lateral flow due to its courser texture than the peanut hillslope. Lin and Zhou (2008) also demonstrated that soil profile features such as soil horizon depths and landform positions influences on generation of subsurface lateral flow. The decrease in positive soil water potential after the end of rainfall (Figs. 2 and 3) corresponded well to the first break point on the delayed flow recession curves after the end of rainfall (Figs. 4 and 5). This confirmed that the subsurface lateral flow generated from the peanut hillslope contributed to the stream flows within and out of the catchment. The flush time lag behind the maximum rainfall intensity or peak flow can be attributed to the residence time of subsurface lateral flow moving from upper slope to down slope (Soulsby et al., 2003). Comparing with the time of maximum rainfall on 14 May 2003, the time lag of the flush on the recession curves e.g. at Stations No. 5 and 6 in Fig. 4 and that of the peak soil water potential at the 1.5 m depth on the lower slope positions (Figs. 2 and 3) was about the same, being around 100 minutes, indicating that there was no interference for subsurface lateral flow to directly discharge into the trenched channel below the peanut hillslope during the storm.

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4.2 Nutrient delivery pathways to the streams at the hillslope and catchment scales

This study catchment was very intensively used for cropping. According to regular sampling (Table 1) and the intensive sampling (Figs. 4 and 5), the concentrations of N were generally higher and the concentrations of P in streams were generally lower than most of those reported in the literature for agricultural (e.g. Jiang et al., 2010), forestry (e.g. van Verseveld et al., 2009) or pasture (Holtz, 2010) catchment. These can be attributed to high application rates of fertilizers ranging from 218 kg N ha$^{-1}$ a$^{-1}$ to 71 kg P ha$^{-1}$ a$^{-1}$ (Tang et al., 2008) and to the soil with high content of iron oxides ranging from 60 to 65 g kg$^{-1}$ (Zhang and Horn, 2001) in relation to phosphorus adsorption process. The hydrographs and the chemographs of particulate N and P and suspended sediment were similar during the two storms (Figs. 4 and 5), showing increased concentrations with increased rainfall intensity, with the peak concentration before the peak flow and rapid decreases after the end of rainfall. This relationship has been widely reported in the literature (Holz, 2010; Nadal-Romero et al., 2008; Williams, 1989) and various explanations for this relationship have been proposed (e.g. Steinheimer et al., 1998; Seeger et al., 2004; Holz, 2010). The dominance of particulate N and P in total N and P (over 90% and about 100%, respectively) suggested that overland flow controlled the delivery of particulate nutrients together with suspended sediments from the hillslope to the trench. The time of peak particulate nutrient concentration before peak flow below the hillslope indicated the flushing effects (Boyer et al., 1997). Overland flow after the maximum rainfall intensity could be less effective in mixing with soil, releasing and transporting particulate nutrients on the hillslope, but continued to issue into the stream from the upper area of the slope. The longer time of peak particulate concentration ahead of peak flow on 12 May 2004 than on 14 May 2003 was attributed to the long-lasting and low intensity rainfall characteristics on 12 May 2004. The two different storms had different characteristics. This resulted in a difference in peak flow at the catchment outlet at Station No. 4 (7751 vs. 3936 L s$^{-1}$),
but no difference in the peak stream flow below the peanut hillslope at Station No. 6 (215 vs. 211 L s\(^{-1}\)). This suggested that overland flow from the monitored hillslope (4.8 ha) was less influential on the discharge at the catchment outlet during the more intensive rainstorm on 14 May 2003 than another rainstorm on 12 May 2004 due to the mixed contribution from other hillslopes and paddy fields. The difference in particulate nutrient concentration between Station No. 4 and Stations No. 5 or 6 suggested that the concentration of particulate nutrients at the catchment outlet was influenced not only by the sedimentation process in the streams, but also by the addition of irrigation flow, which influences the availability and transport of particulate nutrients from hillslope sources.

The dynamics of NO\(_3^-\)-N concentration and flow were also similar during the two rainstorms at all stations (Figs. 4 and 5). The NO\(_3^-\)-N concentration did not response to rainfall and increased on the recession limbs of hydrographs after the end of rainfall (Figs. 4 and 5). Many studies have shown the negative relationship (e.g. Ocampo et al., 2006; Rusjan et al., 2008; Holtz, 2010), but more other studies have shown positive relationship (Rusjan et al., 2008; van Verseveld et al., 2009; Jiang et al., 2010). The dynamics of labile nutrient concentration is commonly contributed to “flushing” hypothesis (Anderson and Burt, 1982; Hornberger et al., 1994). The flushing mechanisms have been studied from hillslope slope to catchment scales (e.g. Ocampo et al., 2006; Weiler and McDonnell, 2006) and generally include hydrological controls, e.g. quantity of lateral flow from event water or groundwater, and biogeochemical controls, e.g. availability and quantity of labile nutrients in the pathways. Therefore, the relationship between NO\(_3^-\)-N concentration and flow varied, depending on catchment specifics such as weather pattern, geology, topography, land use, soil and riparian zone characteristics, and on the spatial scales and sampling frequency, which resulted in differences in various rainfall events, antecedent soil wetness and saturated areas within catchment.

The hillslope soil hydrology (Figs. 2 and 3) has shown that rain water preferentially passed by the surface soil during the rainfall and saturated deep soil and perched over the 1.5 m soil depth. The depth of the perched saturated soil water at the lower slope
position indicated that the whole soil profile below 0.15 to 0.37 m on the chestnut and below 0.74 to 1.00 m on the peanut hillslope were fully saturated. The near-surface soils have higher water conductivity (Table 1) and facilitate the generation of subsurface lateral flow (Bishop et al., 2004). As the hillslopes within the catchment were not interfered by ground water, water saturation of the deep soil needs intensive rainfall as such observed storm events with 125 to 178 mm of rainfall. Otherwise, such fast subsurface flow may not be observed. \( \text{NO}_3^- \)-N concentration generally decreases with increased soil depth, but it can be easily leached downwards to deep soils. However, \( \text{NO}_3^- \)-N is weakly sorbed and slowly transformed in the acid soil (Kemmitt, 2005) and it can be leached and accumulated at deep soil layers (Vazquez et al., 2006). Our previous study on this studied peanut hillslope (Wang et al., 2011) also showed that the average \( \text{NO}_3^- \)-N concentration in soil water was greater at the 0.85 m depth than at the 0.20 and 0.40 m depths on both upper and lower slope positions (4.3–7.6 vs. 0.6–2.3 mg L\(^{-1}\)) and was lower at all soil depths on the lower slope than on the upper slope (1.9 vs. 4.2 mg L\(^{-1}\)). Therefore, the low concentration in surface soil solution and the dilution effect of overland flow may explained the stable and low \( \text{NO}_3^- \)-N concentration in stream flow during the rainfall period when overland flow dominated. The same starting times of the increase in \( \text{NO}_3^- \)-N concentration and the decrease in soil water potential at the 1.5 m at the lower slope positions confirmed that subsurface lateral flow generated from the saturated soil water and propelled and displaced the nutrient enrich “old soil water” through soil pedon along the slope (Chandler and Bisogni, 1999; Hooper et al., 1990; Petry et al., 2002). This may result in an increase of \( \text{NO}_3^- \)-N concentration in the streams through the recessing limb of stream flow during the observation period. The relative low \( \text{NO}_3^- \)-N concentration (1.39 mg L\(^{-1}\)) in the spring water as compared with soil water and well water (Table 2) may be attributed possibly to denitrification process which may occur through the long slope.
4.3 Contribution of nutrient loadings through subsurface lateral flow

The four-year regular and intensive monitoring showed that the water sources of irrigation water, soil water and overland water were distinct in H\(^+\) concentration and EC (Table 2, Fig. 6). And these two parameters were successfully used to establish a chemical mixing model particularly as indicated by the measured and predicted NO\(_3^-\)-N concentration in the stream below the peanut hillslope (Fig. 8). There were a few studies using H\(^+\) concentration in chemical mixing model (Raiswell, 1984; Neal and Christophersen, 1989; Javie et al., 2001), most successfully for acidic catchment as the biogeochemical process is generally low (Raiswell, 1984; Neal and Christophersen, 1989) and for episodic high flow events in which variations in pH was associated with different hydrological pathways (Javie et al., 2001). The soils in this study catchment were acidic, with pH changing from 4.5 to 5.5 (Tang et al., 2006; Wang et al., 2011). The low organic matter concentration in soil (8.6 g C kg\(^{-1}\) within the 0.20 m depth and 2.4 g C kg\(^{-1}\) below the 0.20 m depth, unpublished data) suggested negligible biogeochemical processes within the catchment. EC value was scarcely reported in chemical mixing model, but some studies have successfully used NO\(_3^-\)-N concentration in chemical mixing model (Soulsby et al., 2003; Tiemeyer et al., 2008). NO\(_3^-\)-N is known to be subjected to biogeochemical transformations and non-conservative for a long run, but it is still reasonable to use NO\(_3^-\)-N as an assumed conservative tracer during relatively short storm period (Durand and Torres, 1996). Because there was significant correlation between EC value and NO\(_3^-\)-N concentration (\(P < 0.01\)) and it is easier to measure EC value than NO\(_3^-\)-N concentration, which implies that EC can be measured instead of NO\(_3^-\)-N concentration using chemical mixing model to predict NO\(_3^-\)-N load exported from agricultural catchments. The mixing model using H\(^+\) and EC value gave reasonable goodness between the predicted and observed NO\(_3^-\)-N concentrations particularly at the hillslope scale (Station No. 6) (Fig. 8). The uncertainty was larger at the catchment scale than at the hillslope scale, suggesting an interference of other water source at the catchment outlet during the storms. This may be overland flow or subsurface...
flow generated from the paddy field, which may contain less NO$_3^-$-N concentration than that from the hillslopes. Lateral subsurface flow through paddy bunds was identified using dye tracing and measuring infiltration through the bunds (Janssen and Lennartz, 2009).

Few studies have attempted to estimate subsurface lateral flow from hillslopes in agricultural catchments. Using hydrograph separation, Soulsby et al. (2003) reported that subsurface lateral flow accounted for 10% to 52% of total stream during storm from a grazing catchment in Scotland, which had widely spread and well-drained alluvium and gravels within soil. Wang et al. (2011) applied two-dimensional modeling based on long-term monitored dynamics of soil water potential along the slopes and demonstrated that the subsurface lateral flow from the peanut hillslope as described here accounted for 35% to 42% of annual rainfall and exported 45 to 64 kg N ha$^{-1}$ a$^{-1}$ out of soil profile into the stream, which was larger than total N from the overland flow (6 to 6.9 kg ha$^{-1}$ a$^{-1}$). The chemical mixing model in this study demonstrated that the subsurface lateral flow accounted for 29% to 45% of total flow in the stream below the studied peanut hillslope and for 5.7% to 7.3% of the total catchment outflow (Table 3). Although this study demonstrated that overland flow was still the may pathway for particulate N and P export during the rainfall periods, it is clear that subsurface flow was the dominant pathway for NO$_3^-$-N export (Table 3). The subsurface lateral flow exported 1.5 to 2.4 kg N ha$^{-1}$ of NO$_3^-$-N from the hillslope during the observed storm events. Such heavy events with daily rainfall over 100 mm occurred 4 to 8 times a year in the region. The lower proportion of subsurface lateral flow and lower export of NO$_3$-N from the catchment outlet can be explained by contribution of other water sources which contained lower low concentration of NO$_3$-N or by denitrification in the stream flow running from hillslopes to the catchment outlet.

Nitrogen pollution had been paid a great attention in terms of downstream eutrophication (Duan et al., 2000). Many studies have demonstrated the importance of controlling soil erosion (e.g. Palma et al., 2007) and restoring riparian wetland (e.g. Song et al., 2010) to intercept nutrients before they reach the streams. This study has highlighted
the significance of controlling subsurface lateral flow from hillslope in agricultural catchment. Excess N fertilizers can be transformed into NO$_3^-$-N and leached into deep soil (Vazquez et al., 2006). If NO$_3^-$-N in the deep soil can not be promptly used by plants due to limited root depth, it will be intercepted by subsurface lateral flow and transported from the upland to streams (Steinheimer et al., 1998; Royer et al., 2006), which will result in a larger scale impact of water quality issue on the environment. Many best management practices with attempts to control soil and water erosion can be effective in controlling the flush of nutrients mainly in particulate forms on the rising limbs of stream flow, but may not be effective in controlling the flush of soluble nutrients on the recession limbs of stream flow. Therefore, new strategies have to be considered to reduce NO$_3^-$N leaching and accumulation in deep soil and subsurface flow. These strategies may be carried out by optimization of timing and dose of chemical fertilization to reduce N leaching or by adopting deep-root crops as in agroforestry system or buffering strips to intercept subsurface lateral flow and leached N (Song et al., 2010; Nair, 2011).

5 Conclusions

The monitored hillslope soil hydrology and stream hydrochemographs in combination underscored the importance of subsurface lateral flow in transporting N from gentle hillslope to surface waters in agricultural catchment in the subtropical climate. The typical intensive storm events with rainfall from 120 to 175 mm made the hillslopes saturated over the deep impermeable soil layers through vertical preferential flow in the surface soil. The saturated soil water table rose to near-surface soil with high conductivity at the lower slope position, resulting in a breakthrough of subsurface lateral flow. In addition, the stream flow below the hillslope corresponded quickly to the decrease in positive soil water potential at the 1.5 m depth on the lower position. These gave direct evidences of generation of subsurface lateral flow after the end of rainfalls. The positive correlation between particulate N and P concentrations and stream flow during the rainfall and the
negative correlation between labile nitrate concentration and stream flow after the end of rainfall indicated that the overland flow was the dominant pathway during the rainfall and the subsurface lateral flow was the dominant pathway after the rainfall. The negative relationship between nitrate concentration and stream flow after the rainfall also suggested that the subsurface flow expelled nitrate from the deep soil. The chemical mixing model based on EC and H$^+$ showed that the subsurface lateral flow during the rainstorm events accounted for 29% to 45% of the stream flow and about 86% of total NO$_3^-$-N loss (or 26% of total N loss) from the peanut hillslope and for 5.7% to 7.3% of the stream flow about 69% of total NO$_3^-$-N loss (or 28% of total N loss) at the catchment outlet. This implies that best management practices controlling non-point source pollution from agricultural catchment have to be effective in controlling overland flow, but also in controlling nutrient leaching and subsurface lateral flow.

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References


Table 1. Soil texture and saturated hydraulic conductivity \( (K_s) \) estimated from the soil water retention curves by soil horizon and slope position under the land uses of peanut cropping and chestnut orchard.

<table>
<thead>
<tr>
<th>Land use</th>
<th>Slope position</th>
<th>Soil horizon(^1)</th>
<th>Soil depth m</th>
<th>Clay g kg(^{-1})</th>
<th>Silt g kg(^{-1})</th>
<th>Sand g kg(^{-1})</th>
<th>Bulk Density Mg m(^{-3})</th>
<th>( K_s ) m d(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Peanut cropping</td>
<td>Upper slope</td>
<td>Ap 0–0.25</td>
<td>354</td>
<td>240</td>
<td>406</td>
<td>1.23</td>
<td>2.40</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>AB 0.25–0.50</td>
<td>368</td>
<td>259</td>
<td>373</td>
<td>1.43</td>
<td>0.64</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Bt 0.50–1.00</td>
<td>423</td>
<td>232</td>
<td>345</td>
<td>1.51</td>
<td>0.30</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>BCv 1.00–1.30</td>
<td>450</td>
<td>150</td>
<td>400</td>
<td>1.51</td>
<td>0.30</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Lower slope</td>
<td>Ap 0–0.25</td>
<td>252</td>
<td>208</td>
<td>540</td>
<td>1.38</td>
<td>1.98</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Bt1 0.25–0.50</td>
<td>410</td>
<td>90</td>
<td>500</td>
<td>1.51</td>
<td>0.70</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Bt2 0.50–0.90</td>
<td>354</td>
<td>146</td>
<td>500</td>
<td>1.51</td>
<td>0.70</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Bt3 0.90–1.30</td>
<td>275</td>
<td>145</td>
<td>580</td>
<td>1.55</td>
<td>0.26</td>
<td></td>
</tr>
<tr>
<td>Chestnut forest</td>
<td>Upper slope</td>
<td>Ap 0–0.20</td>
<td>171</td>
<td>131</td>
<td>698</td>
<td>1.48</td>
<td>2.80</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Bt1 0.20–0.50</td>
<td>284</td>
<td>182</td>
<td>534</td>
<td>1.66</td>
<td>0.40</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Bt2 0.50–0.70</td>
<td>390</td>
<td>189</td>
<td>421</td>
<td>1.67</td>
<td>0.11</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>BCv 0.70–1.45</td>
<td>346</td>
<td>193</td>
<td>461</td>
<td>1.67</td>
<td>0.11</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Middle slope</td>
<td>Ap 0–0.20</td>
<td>200</td>
<td>122</td>
<td>678</td>
<td>1.59</td>
<td>3.60</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Bt1 0.20–0.50</td>
<td>374</td>
<td>123</td>
<td>503</td>
<td>1.64</td>
<td>0.40</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Bt2 0.50–0.80</td>
<td>296</td>
<td>186</td>
<td>518</td>
<td>1.60</td>
<td>0.40</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>BCv 0.80–1.40</td>
<td>312</td>
<td>148</td>
<td>540</td>
<td>1.60</td>
<td>0.40</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Lower slope</td>
<td>Ap 0–0.20</td>
<td>169</td>
<td>200</td>
<td>631</td>
<td>1.58</td>
<td>3.02</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Bt1 0.20–0.90</td>
<td>235</td>
<td>251</td>
<td>514</td>
<td>1.46</td>
<td>0.40</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Bt2 0.90–1.30</td>
<td>298</td>
<td>199</td>
<td>503</td>
<td>1.46</td>
<td>0.40</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>BCv 1.30–1.80</td>
<td>292</td>
<td>185</td>
<td>523</td>
<td>1.50</td>
<td>0.08</td>
<td></td>
</tr>
</tbody>
</table>

1 The small letters for soil horizons are: p: plough layer, t: accumulation of silicate clay, and v: plinthic.
2 Clay: <0.002 mm, Silt: 0.002–0.05 mm, Sand: >0.05 mm.
Table 2. Averages, with their standard deviations in parentheses, of chemical properties and suspended sediment concentration (SS) in different water sources following weekly sampling and intensive sampling during rainstorms during the period from 2001 to 2004.

<table>
<thead>
<tr>
<th>Water sources</th>
<th>Sampling strategy</th>
<th>Averages</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>pH</td>
<td>EC µS m⁻¹</td>
</tr>
<tr>
<td>Soil water at 0.85 m depth on the peanut hillslope (n = 55)</td>
<td>5.55 c↑</td>
<td>2.0 a</td>
</tr>
<tr>
<td></td>
<td>(0.49)</td>
<td>(0.43)</td>
</tr>
<tr>
<td>Well water on the chestnut orchard (n = 150)</td>
<td>4.86 e</td>
<td>1.06 b</td>
</tr>
<tr>
<td></td>
<td>(0.51)</td>
<td>(0.30)</td>
</tr>
<tr>
<td>Spring water between Stations No. 5 and 6 (n = 150)</td>
<td>5.53 c</td>
<td>0.26 e</td>
</tr>
<tr>
<td>Irrigation water at the catchment inlet (n = 150)</td>
<td>6.95 a</td>
<td>0.48 c</td>
</tr>
<tr>
<td></td>
<td>(0.70)</td>
<td>(0.15)</td>
</tr>
<tr>
<td>Overland flow from erosion plots on the peanut hillslope (n = 169)</td>
<td>5.50 c</td>
<td>0.15 f</td>
</tr>
<tr>
<td>Rainfall water (n = 153)</td>
<td>5.26 d</td>
<td>0.26 e</td>
</tr>
<tr>
<td></td>
<td>(0.72)</td>
<td>(0.20)</td>
</tr>
<tr>
<td>Stream water at Station No. 4 (catchment outlet) (n = 121)</td>
<td>6.22 b</td>
<td>0.38 d</td>
</tr>
<tr>
<td></td>
<td>(0.39)</td>
<td>(0.10)</td>
</tr>
<tr>
<td>Stream water at Station No. 5 (n = 121)</td>
<td>5.94 b</td>
<td>0.42 cd</td>
</tr>
<tr>
<td></td>
<td>(0.42)</td>
<td>(0.17)</td>
</tr>
<tr>
<td>Stream water at Station No. 6 (n = 121)</td>
<td>5.87 b</td>
<td>0.41 cd</td>
</tr>
<tr>
<td></td>
<td>(0.47)</td>
<td>(0.14)</td>
</tr>
</tbody>
</table>

*: not detectable; †: the different letters in columns indicate significant difference at P < 0.05.
Table 3. Total outflow and percentage of subsurface lateral flow in total outflow estimated by mixing model, total N (TN) and total NO$_3^-$-N (TNN) export with overland flow (NN$_O$), irrigation flow (NN$_I$) and subsurface lateral flow (NN$_S$) estimated by mixing model during two storm events.

<table>
<thead>
<tr>
<th>Station</th>
<th>Total % of subsurface lateral flow in total outflow</th>
<th>Total outflow (m$^3$)</th>
<th>% of subsurface flow in total outflow</th>
<th>TN (kg ha$^{-1}$)</th>
<th>TNN (kg ha$^{-1}$)</th>
<th>% in TNN loss NN$_O$</th>
<th>NN$_I$</th>
<th>NN$_S$</th>
</tr>
</thead>
<tbody>
<tr>
<td>14 May 2003</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Station No. 6</td>
<td>2495</td>
<td>44.8 (21.4)</td>
<td>1.11</td>
<td>0.34</td>
<td>0.34</td>
<td>12.0</td>
<td>1.9</td>
<td>86.1</td>
</tr>
<tr>
<td>Station No. 4</td>
<td>79 865</td>
<td>7.3 (23.1)</td>
<td>5.41</td>
<td>1.51</td>
<td>1.51</td>
<td>24.7</td>
<td>5.3</td>
<td>70.0</td>
</tr>
<tr>
<td>12 May 2004</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Station No. 6</td>
<td>4187</td>
<td>29.0 (6.4)</td>
<td>1.61</td>
<td>0.48</td>
<td>0.48</td>
<td>10.6</td>
<td>3.1</td>
<td>86.3</td>
</tr>
<tr>
<td>Station No. 4</td>
<td>67 365</td>
<td>5.7 (46.7)</td>
<td>4.51</td>
<td>2.40</td>
<td>2.40</td>
<td>17.5</td>
<td>14.6</td>
<td>67.8</td>
</tr>
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</table>

Data in the brackets are the uncertainty of the data estimated by mixing model at the flow peak.
Fig. 1. Sketch of studied Sunjia catchment, showing the station positions at the irrigation inlets (Stations No. 1 and 2), irrigation outlet (Station No. 3), catchment outlet (Station No. 4), and the upper station (Station No. 5) and the lower station (Station No. 6) at the foot of the subcatchment (after Tang et al., 2008).
Fig. 2. Soil water potential over time for the 14 May 2003 storm at different soil depths within soil profile at different slope positions under the peanut cropping system (a) and the chestnut forest (b). Note: missing depth was due to malfunction of the tensiometers.
Fig. 3. Soil water potential over time for the 12 May 2004 storm at different soil depths within soil profile at different slope positions under the peanut cropping system (a) and the chestnut forest (b). Note: missing depths were due to malfunction of the tensiometers.
Fig. 4. Rainfall, discharge, total N (TN), NO$_3^-$-N, suspended sediment (SS), particulate N and P (PN and PP), electricity conductivity (EC) and pH in stream water at the catchment outlet (Station No. 4) (left), at the upper reach of the ditch (Station No. 5) (middle) and at the lower reach of the ditch (Station No. 6) (right) for the 14 May 2003 storm.
Fig. 5. Rainfall, discharge, total N (TN), NO$_3^-$-N, suspended sediment (SS), particulate N and P (PN and PP), electricity conductivity (EC) and pH in stream water at the catchment outlet (Station No. 4) (left), at the upper reach of the ditch (Station No. 5) (middle) and at the lower reach of the ditch (Station No. 6) (right) for the 12 May 2004 storm.
Fig. 6. Mixing diagrams showing stream water evolution indicated by $H^+$ and EC at the catchment outlet (Station No. 4) and at the subcatchment inlet (Station No. 5) and outlet (Station No. 6) for the 14 May 2003 (upper) and the 12 May 2004 (down) storms, with the arrows show the time sequence of water sampling.
Fig. 7. Observed and predicted NO$_3^-$-N concentrations by the mixing model using the two tracers, H$^+$, EC, at the subcatchment outlet (Station No. 6) and catchment outlet (Station No. 4) for the 14 May 2003 and 12 May 2004 storms.
Fig. 8. Precipitation and flows components at the catchment outlet (Station No. 4) and at the subcatchment inlet (Station No. 5) and outlet (Station No. 6) and the flow components such as soil water, irrigation and overland flow, predicted by mixing model for the storm events for the 14 May 2003 (upper) and 12 May 2004 (down) storms.