# Nitrogen export by surface runoff from a small agricultural watershed in southeast China: seasonal pattern and primary mechanism

**Nengwang Chen · Huasheng Hong**

**Abstract** The seasonal pattern and primary mechanism of nitrogen (N) export by surface runoff from the Wuchuan subwatershed (WCW), an agricultural upper watershed (1.88 km$^2$) located in southeast China, were investigated based on extensive streamwater measurements in 2004–2005 under subtropical climatic conditions. The results disclosed a highly variable but strong linkage between hydrological and anthropogenic controls and N export. N export via surface runoff presented a significant seasonal pattern caused by changes in rainfall and watershed N input. Approximately 75% of the annual N export (67 kg ha$^{-1}$) was flushed by those storm runoff mainly occurred during the wet season (March through September). The WCW dataset of N concentrations and loads during both baseflow and stormflow implied an interactive effects of anthropogenetic N input and hydrology conditions: N export was flush-driven in late spring, summer and autumn (wet season), but highly related with soil N in winter and early spring. Compared to undisturbed watersheds under similar rainfall conditions, WCW exported a considerable amount of N due to intensive fertilizer application (a mean of 690 kg N ha$^{-1}$ year$^{-1}$, commonly as surface applications). This work provides a first characterization of a small agricultural Chinese catchment under subtropical climates and its associated N export behavior.

**Keywords** Nitrogen export · Surface runoff · Seasonal pattern · Non-point source pollution

## Introduction

Significant amounts of nutrients enter streams and are transported downriver to estuarine and coastal marine systems (Seitzinger et al. 2005). This results in numerous negative ecological and toxicological impacts including drinking water degradation, acidification, eutrophication and adverse human health and economic effects (Vitousek et al. 1997; Galloway et al. 2004; Camargo and Alonso 2006). Nitrogen (N) is one of the most important nutrients in this respect, since the productivity of terrestrial and aquatic ecosystems are usually controlled by N availability (Vitousek et al. 2002). A variety of factors can influence the rate of N export from watersheds, including natural basin characteristics, hydrological and meteorological conditions, population growth, land use and management practices (Howarth et al. 1996; Biggs et al. 2004; Schaefer and Alber 2007; Sobota et al. 2009). Many studies suggest that the seasonality of precipitation and river flow are the primary factors affecting river nutrient concentration

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and load (Sigleo and Frick 2007; Rusjan et al. 2008). A worldwide analysis suggests that N exports from watersheds are highly variable, and that regional studies are more important than global-scale analyses (Boyer et al. 2006; Alvarez-Cobelas et al. 2008). Knowledge of watershed nutrient export in the subtropical climatic region of southern China is scarce, although limited studies have been conducted in central China (Gao et al. 2004; Yan et al. 2005; Tang et al. 2008).

In the Jiulong River watershed (JRW) and its estuarine region, located in southeast China, freshwater degradation and near-shore eutrophication have been increasingly critical since the mid-1980s (Chen et al. 1993; Hong et al. 1999). The N budget for the JRW indicates that fertilizer and animal feedstuffs (60% corn, 20% bean, 18% wheat and 2% other additives) contribute 88% of the total N input, of which about 14% is exported to the coastal sea by fluvial processes (Chen et al. 2008). This finding suggests that agricultural activities in the watershed substantially impact river–estuary–coastal water quality, and thus largely alter N biogeochemistry processes in this region. Based on studies of N sources and export from village-scale to mesoscale in the JRW (Cao et al. 2005, 2006; Chen et al. 2006, 2008), we further investigated the seasonal pattern and primary mechanism by which N was exported via surface runoff from an upstream subwatershed, in order to advance current understanding concerning the control of N export from watershed to estuary under subtropical climatic conditions. In this study, seasonal variation in streamwater N concentrations was observed throughout 2 years of monitoring. We tested the hypotheses that climate-related factors (i.e. rainfall and flow discharge) along with anthropogenic N inputs to the various land uses were the primary mechanism of N export by surface runoff. This is a first characterization of a small agricultural Chinese catchment under subtropical climates and its associated N export behavior.

## Materials and methods

### Description of study area

The Jiulong River is formed by the confluence of two major tributaries (the North River and West River)
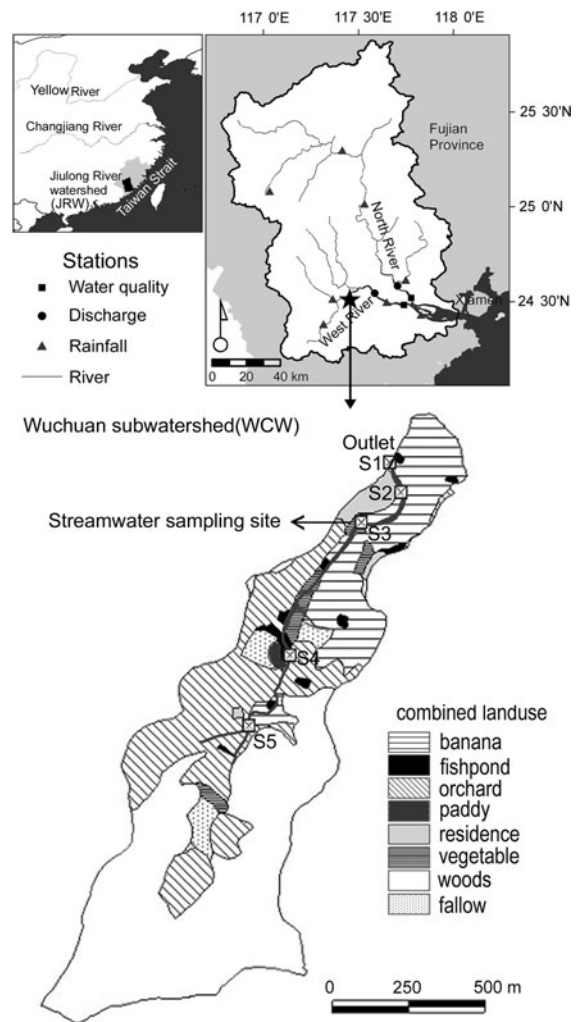


**Fig. 1** Map of the Jiulong River watershed and Wuchuan subwatershed

and discharges about 14 billion m$^3$ year$^{-1}$ of water into the Xiamen Sea through the Jiulong River Estuary (Fig. 1). The JRW is a mesoscale watershed (14,700 km$^2$) with a population of 3.4 million. Precipitation is strongly influenced by the monsoon system from May to November, especially the typhoon season between July and September (Ren et al. 2002). More than 300 hydropower dams/reservoirs have been installed along the river system. The watershed's topography is mostly hilly (about 77% has a slope greater than 15°) in upstream regions (altitude greater than 50 m), comprising 67% forest, 17.5% arable land, 3% residential land, 5% bare land, and 7.5% water (unsupervised classification based on

Landsat TM image). In the JRW, an increasing nutrient impact on water quality can most likely be attributed to discharges from intensive agricultural activities and animal feeding (Chen et al. 2008).

An investigation of N loss by surface runoff (both baseflow and stormflow) was conducted in the Wuchuan subwatershed (WCW), which has an area of 1.88 km$^2$. In the stream, there is a primary order tributary of the upper West River (Fig. 1). Total recorded rainfall in 2004 and 2005 was 1,408 and 1,891 mm, about 90% of which occurred between March and October. Daily mean temperature in 2004–2005 fluctuated from 4.3°C to 32.9°C with a mean value of 21.3°C. The subwatershed lies within an altitudinal range of 19–130 m; and the landform is characterized by undulating hills. Red earth and lateritic red earth are the main soil types in the catchment, and pH values ranged from 4.0 to 4.8 (a mean value of 4.5). According to a reploted 1:5,000 land use planning papery map provided by local government, land uses are digitized to a GIS layer and characterized as 40.2% orchard, 7.5% banana, 0.1% rice paddy, 0.5% vegetable, 0.5% fishpond, 1.5% residence, 42.7% woods, and 7% fallow (Fig. 1). Litchi, longan and citrus are the main fruits planted in the highlands, whereas bananas are mostly found in the valley bottom. An area-weighted mean application rate of 690 kg N ha$^{-1}$ is applied annually to the arable lands but this rate varies seasonally among the different crops (Fig. 2). For most crop land, surface application of fertilizers is used and the rates are high in spring. The predominant N fertilizers applied were urea, ammonium hydrocarbonate, and NPK compound fertilizers. The N budget of the
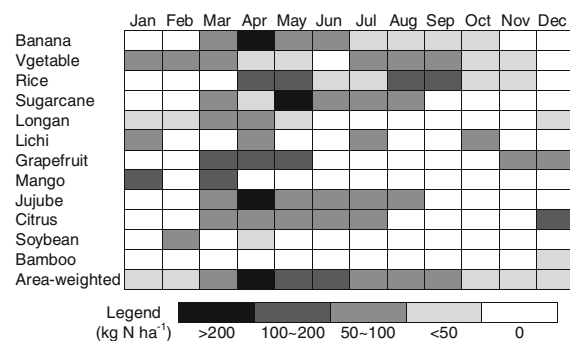
WCW shows that fertilizers account for 92.4% of the total N input (Chen et al. 2009).

### Field sampling and laboratory analysis

Water sampling and runoff monitoring were conducted in the WCW during storm events and during baseflow conditions (baseflow being defined as no appreciable rainfall over the previous 7 days and no significant change in water level). In 2004–2005, ten storm events were monitored at the outlet of the WCW, whereas baseflow was monitored monthly at the five sampling sites along the main stream (Fig. 1). The five sites were selected to reflect the effect of incremental increase in arable land area on water quality. We selected a forest margin site to try to determine natural background concentrations and loading, but there was no runoff under baseflow conditions. A flowmeter was installed to measure runoff during sampling, and flow was determined with flow velocity and cross area of channel. Stormflow water was sampled at 30 min to 4-h intervals, depending on rainfall duration and intensity. The first sample was collected when rainfall started, and the last sample after stream water fell to near pre-event levels. All water samples were collected in 500 ml clean polyethylene bottles that were rinsed with the stream water before sampling. Typically 8–15 water samples were manually collected for each storm event.

All samples were delivered to the laboratory within 24 h, and analyzed as soon as possible using standard spectrometric methods (State Environmental Protection Administration of the People's Republic of China [SEPA] 2002). Unfiltered aliquots and aliquots filtered through 0.45 μm Nuclepore membranes were analyzed. Total N (TN, unfiltered) and total dissolved N (TDN, filtered) were determined following oxidization with 1% potassium persulfate; nitrate N ($NO_3$-N) was analyzed using ion chromatography, and ammonium N ($NH_4$-N) using the indophenol blue method. Dissolved inorganic N (DIN) was calculated as the sum of $NH_4$-N and $NO_3$-N, while nitrite N was not separately considered since it was only a very small fraction. The detection limit was 0.05 mg l$^{-1}$ for TN, TDN and $NH_4$-N, and 0.08 mg l$^{-1}$ for $NO_3$-N (SEPA 2002). The data quality was monitored using inter-calibration, and the precision was estimated by repeated determinations of 10% of the samples and was better than 5%.



**Fig. 2** Application calendar of chemical N fertilizer in the Wuchuan subwatershed (modified from Cao et al. 2006)

Data analysis

Data preparation, calculation and statistical analyses were performed using Microsoft Office Excel and SPSS 11.0 (SPSS Inc.). In order to investigate the seasonal variation in N concentration and load, the growing (March through September wet season with high baseflow) and dormant (October through February dry season with low baseflow) periods of agricultural activity were defined. Seasonal differences in runoff variables were analyzed by performing one-way analysis of variance. Significantly different means were separated at the 0.05 probability level by the least significant difference test. Correlation between variables was analyzed using Pearson's correlation. Statistical analyses were carried out at a significance level of $a = 0.05$.

The amount of the N load was the integrated product of N concentration and water discharge over a specific time interval. Total runoff N in the WCW was summed as baseflow and storm runoff. The monthly baseflow N load was estimated by multiplying the measured concentration by the relevant flow (assuming that the baseflow was steady on the other days of a specific month). The total N load during each storm event was calculated as the overall product of interpolated concentrations and flows between sampling intervals. Then the net N exported by storm runoff was calculated by the baseflow load for the corresponding period from the total N load. To overcome missing measurements and to obtain the seasonal and annual N export, the validated AGNPS model (developed initially by Young et al. 1987) was used to calculate the N load during un-sampled storm events based on 2004 rainfall data and other associated parameters (Chen et al. 2006).

## Results

N concentration and load during baseflow

N concentrations at the outlet of the WCW (S1) during baseflow conditions exhibited a wide range of monthly variation in 2004–2005 (Fig. 3). Generally, baseflow TDN concentration was a little lower during the growing period (a mean of 3.47 mg l$^{-1}$) when compared with the dormant period (a mean of 4.64 mg l$^{-1}$) although there was no significant difference ($P > 0.05$). The highest concentrations of TN and TDN were observed in April and October 2004 (growing period) as well as in February 2005 (dormant period). Dissolved N was the dominant form in baseflow across the five WCW sites (Table 1). The TN, TDN and NH$_4$-N concentrations were generally elevated along the flow path from upstream (S5) to outlet (S1) with incremental increases of agricultural land (Fig. 4).

The monthly N load during baseflow fluctuated, showing a double peak (Fig. 5). N export was higher in the spring (i.e. April 2004 and May 2005) and autumn. In contrast, reduced baseflow and lower N concentrations resulted in the minimum N load in winter. The mean monthly loads of TN, TDN, NH$_4$-N and NO$_3$-N (as well as the recorded flow) were significantly ($P < 0.05$) higher during the growing

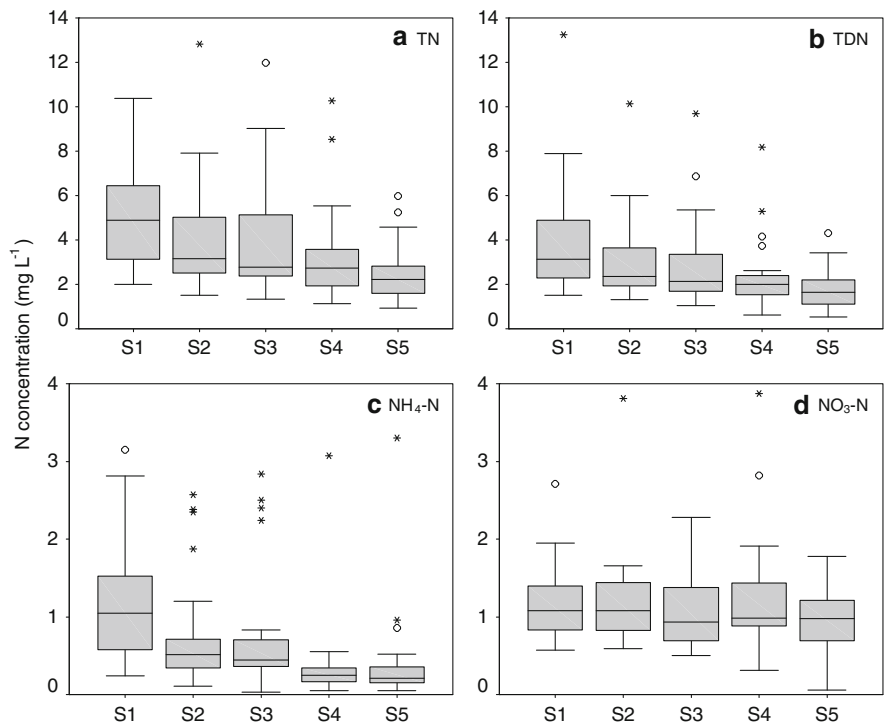Fig. 3 Time series of measured N concentrations under baseflow conditions at the outlet of the Wuchuan subwatershed (2004–2005)
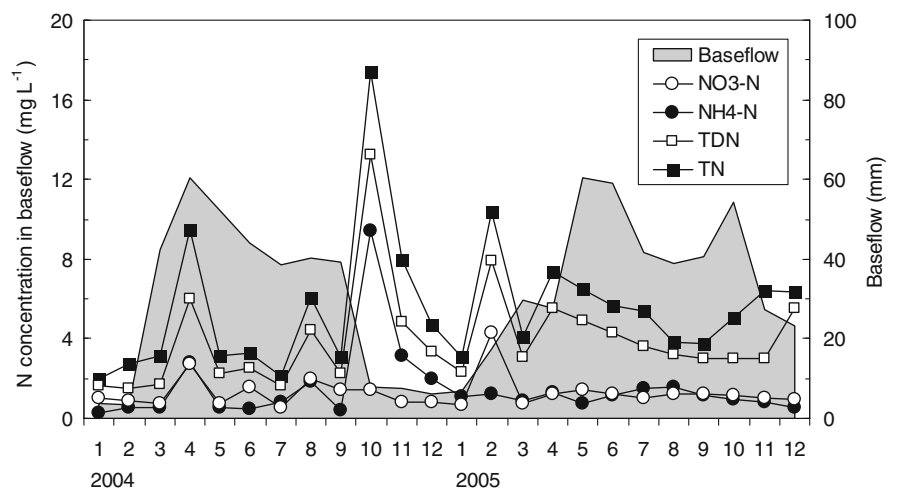
**Table 1** Species composition of N during baseflow in the Wuchuan subwatershed as their annual average percentages

| Sites | TDN/TN | PN/TN | NH$_4$–N/ TDN | NO$_3$–N/ TDN | DON/ TDN | DIN/ TDN | TDN/TN | PN/ TN | NH$_4$–N/ TDN | NO$_3$–N/ TDN | DON/ TDN | DIN/ TDN |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 2004 (%) | | | | | | 2005 (%) | | | | | |
| S1 | 69.7 | 30.3 | 40.2 | 40.9 | 18.8 | 81.3 | 72.9 | 27.1 | 29.7 | 32.4 | 38.2 | 61.8 |
| S2 | 74.3 | 25.7 | 31.8 | 47.1 | 21.3 | 78.8 | 76.0 | 24.0 | 20.5 | 47.8 | 31.8 | 68.3 |
| S3 | 76.7 | 23.3 | 29.4 | 46.8 | 23.9 | 76.1 | 71.9 | 28.1 | 24.3 | 45.3 | 30.7 | 69.3 |
| S4 | 70.6 | 29.4 | 23.0 | 54.5 | 22.8 | 77.2 | 77.3 | 22.7 | 12.5 | 60.7 | 26.8 | 73.3 |
| S5 | 70.5 | 29.5 | 23.8 | 45.6 | 30.7 | 69.3 | 77.2 | 22.8 | 12.9 | 68.6 | 18.5 | 81.5 |
| Mean | 72.4 | 27.6 | 29.6 | 47.0 | 23.5 | 76.5 | 75.1 | 24.9 | 20.0 | 51.0 | 29.2 | 70.8 |



**Fig. 4** Spatial variations of N concentrations during baseflow in the Wuchuan subwatershed (2004–2005). Five sampling sites, from the outlet of the subwatershed (*S1*) to the uppermost site of the stream (*S5*), were marked. Each box (*n* = 24 in all sites) encloses the 10th, 25th, 50th (median), 75th, and 90th percentiles of the concentrations; the *asterisks* and *circles* represent data whiskers and outliers, respectively



**Fig. 5** Monthly N load during baseflow in the Wuchuan subwatershed (2004–2005)
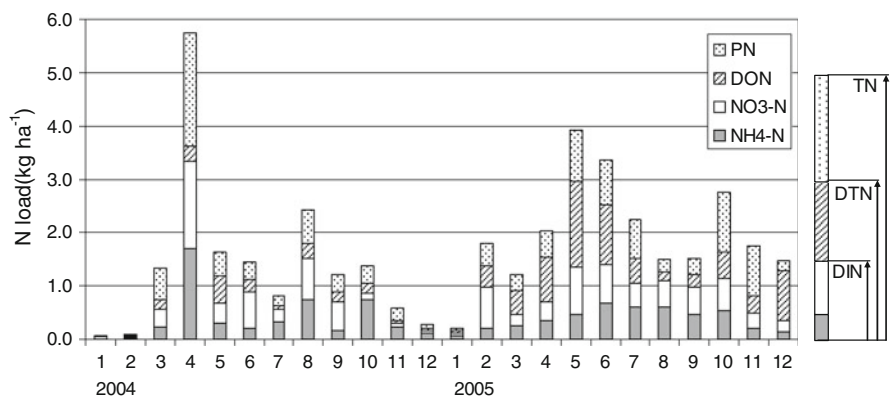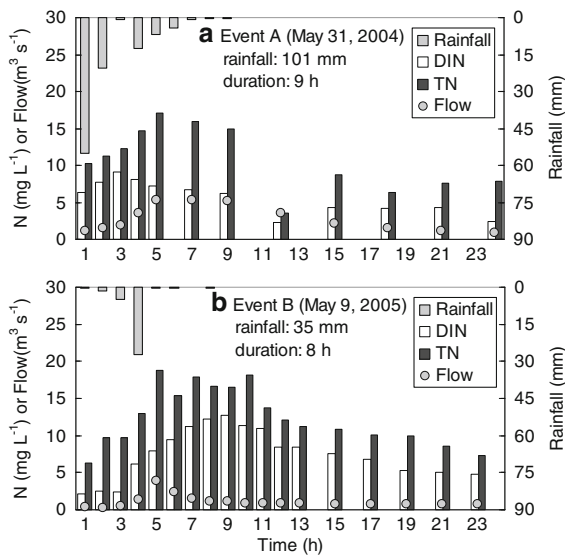
**Fig. 6** Time series of measured N concentrations in the stormflow of two typical storm events at the outlet of the Wuchuan subwatershed

period than the values in the dormant period. The baseflow of 2005 (normal year) was 23% higher than that of 2004 (dry year), and was accompanied by a 40% higher baseflow N load. Based on data for 2004–2005, mean monthly TN export in baseflow from the WCW was $2.0 \pm 1.6$ kg ha$^{-1}$ ($n = 16$) in the growing period, $0.26 \pm 0.24$ kg ha$^{-1}$ ($n = 8$) in the dormant period.

N concentration and load during stormflow

The time series of N concentrations during stormflow measured at the outlet (S1) of WCW during two typical storm events in May 2004 and May 2005 are compared in Fig. 6. For these two events, the peak concentrations of TN coincided with the rising rainfall and were accompanied by flow peaks, and they then declined after the rainfall ceased. The overall decrease of N concentrations on the falling hydrograph limbs was gradual, with different time intervals necessary for the concentrations to return to the pre-event baseflow levels. The time to peak for DIN (3 h after peak rainfall) was shorter than that for TN in event A (5 h after peak rainfall). In contrast, peak DIN in event B occurred after the hydrograph peak, hours after peak TN. Event B, with lower rainfall intensity, had a comparative continuance of high levels of N, dominated more by the dissolved

fraction than was the case in event A. In addition, the stronger, more intense rainfall of event A resulted in a large fluctuation of flow discharge compared with event B. Our results showed the N export pattern to be a function of individual storm characteristics. Thus, the N load during ten monitored storm events differed substantially, varying with rainfall amount and amongst the seasons (Table 2). Generally, high-intensity and longer duration rainfall caused greater N load, especially during spring events. The export ratio of TDN and/or DIN to TN was mostly greater than 60% except for some occasions with very high rainfall intensity (e.g., in event 2004/5/31, 9 h rainfall is 101.2 mm). Nitrate was dominant in stormflow-induced loss and accounted for about 50–75% of the DIN load among the ten storm events. Statistical analysis of the ten storm events showed that event-based loads (kg) of TN, TDN, NH$_4$-N and NO$_3$-N were all significantly correlated with cumulative flow (mm) ($P < 0.005$).

N export during streamflow

Monthly N exports by surface runoff under baseflow conditions and during storm events are summarized in Table 3. There were positive relationships between the magnitudes of various components of N export and recorded rainfall, as well as measured stream flow ($P < 0.001$ for all cases). Seasonal variation for TN ranged from 0.08 to 1.38 kg ha$^{-1}$ in the dormant period to 2.07–19.03 kg ha$^{-1}$ in the growing period. Apparently, rainfall-induced discharge was a key driver of N loss and export as agricultural sources of non-point source pollution. Under the subtropical climatic condition of the WCW in 2004, storms (daily rainfall $\geq 25$ mm) occurred only on 19 days (5% of the year) but provided more than 70% of the annual rainfall. Controlled by typhoon systems, four extreme storm events (daily rainfall $\geq 50$ mm), which occurred on May 20, May 31, July 28 and September 21, 2004, occasioned the largest N loss. The peak value of N export was found in May and August 2004, corresponding to the high frequency and intensity of rainfall during those months. More than 80% of TN export occurred from May through September in 2004, driven by 76% of the recorded rainfall (and 76% of the measured streamflow).

To separate the contributions of baseflow and stormflow (from total streamflow) to N export, we use

**Table 2** N loads during ten monitored storm events in the Wuchuan subwatershed

| Storm events | Duration (h) | Rainfall (mm) | Flow (mm) | TN (kg) | TDN (kg) | NH$_4$-N (kg) | NO$_3$-N (kg) | TDN/TN | DIN/TN |
|---|---|---|---|---|---|---|---|---|---|
| 2004/03/01 | 17 | 38.9 | 3.2 | 68 | 63 | 21 | 41 | 0.93 | 0.91 |
| 2004/04/03 | 5 | 15.1 | 1.6 | 23 | 13 | 7 | 5 | 0.57 | 0.52 |
| 2004/04/07 | 12 | 36.1 | 5.0 | 49 | 42 | 15 | 19 | 0.86 | 0.69 |
| 2004/04/17 | 9 | 35.6 | 5.7 | 386 | 278 | 135 | 135 | 0.72 | 0.70 |
| 2004/05/08 | 10 | 35.1 | 6.1 | 300 | 252 | 108 | 120 | 0.84 | 0.76 |
| 2004/05/19 | 19 | 58.2 | 15.3 | 1,035 | 947 | 252 | 602 | 0.91 | 0.83 |
| 2004/05/31 | 9 | 101.2 | 52.9 | 2,117 | 1,101 | 337 | 657 | 0.52 | 0.47 |
| 2004/07/04 | 9 | 20.7 | 4.4 | 30 | 22 | 5 | 16 | 0.73 | 0.70 |
| 2004/07/07 | 10 | 31.3 | 12.7 | 575 | 483 | 194 | 239 | 0.84 | 0.75 |
| 2005/05/09 | 8 | 34.8 | 8.0 | 531 | 467 | 175 | 171 | 0.88 | 0.65 |

**Table 3** Total streamflow N exports from the Wuchuan subwatershed (2004)

| Month | Season | Rainfall (mm) | Flow | TN | TDN | NH$_4$-N | NO$_3$-N | TDN/TN | DIN/TN | DIN/TDN | N load of baseflow to stormflow |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | (kg N ha$^{-1}$) | | | | | | | |
| January | D/D | 19.1 | 3.8 | 0.08 | 0.06 | 0.01 | 0.04 | 0.82 | 0.62 | 0.75 | 100:0 |
| February | D/D | 61.4 | 5.7 | 0.32 | 0.29 | 0.09 | 0.17 | 0.90 | 0.80 | 0.90 | 29:71 |
| March | G/W | 96.3 | 77.0 | 2.07 | 1.43 | 0.48 | 0.76 | 0.69 | 0.60 | 0.86 | 64:36 |
| April | G/W | 123.4 | 96.9 | 7.76 | 5.21 | 2.38 | 2.32 | 0.67 | 0.61 | 0.90 | 74:26 |
| May | G/W | 263.1 | 179.2 | 19.03 | 15.86 | 4.45 | 7.39 | 0.83 | 0.62 | 0.75 | 10:90 |
| June | G/W | 95.4 | 69.8 | 5.53 | 4.51 | 1.06 | 2.64 | 0.81 | 0.67 | 0.82 | 26:74 |
| July | G/W | 221.0 | 120.9 | 9.30 | 7.50 | 1.72 | 5.18 | 0.81 | 0.74 | 0.92 | 10:90 |
| August | G/W | 274.8 | 157.7 | 13.07 | 10.61 | 3.28 | 5.42 | 0.81 | 0.67 | 0.82 | 19:81 |
| September | G/W | 213.6 | 106.0 | 7.68 | 6.26 | 1.71 | 3.37 | 0.82 | 0.66 | 0.81 | 16:84 |
| October | D/D | 2.8 | 8.0 | 1.38 | 1.05 | 0.75 | 0.11 | 0.76 | 0.62 | 0.82 | 100:0 |
| November | D/D | 13.2 | 7.4 | 0.59 | 0.36 | 0.23 | 0.06 | 0.61 | 0.50 | 0.82 | 100:0 |
| December | D/D | 23.9 | 6.2 | 0.29 | 0.21 | 0.12 | 0.05 | 0.71 | 0.60 | 0.84 | 100:0 |
| Mean | | | | | | | | 0.79 | 0.65 | 0.82 | 25:75 |
| Total | | 1,408 | 838.6 | 67.10 | 53.34 | 16.27 | 27.52 | | | | |

G/W indicates the growing season and wet season (March through September), D/D indicates the dormant season and dry season (October through February)

the baseflow:stormflow ratio (Table 3). Stormflow contributed more than 70% of the total annual export; it dominated monthly export except in early spring (i.e. March and April) and during the dry season (October through January) when rainfall was slight. In these months, N was mostly exported as baseflow. There was a high frequency of showers with a considerable volume of rainfall in the March–April period, but the low daily rainfall (<25 mm) in combination with low intensity actually produced comparatively low stormflow N export. N exports in the dormant period and early spring were driven by

baseflow. On the other hand, the overall share of stormflow-driven N export in 2004 was 75%, approximately 85% during the May–September growing (i.e., wet) season.

Dissolved forms dominated N export. Average ratios of TDN to TN, DIN to TN, and DIN to TDN were 0.79, 0.65 and 0.82 (Table 3). However, ratios of TDN to TN (>0.80), and DIN to TN (>0.60) were generally higher in May through September, consistent with the larger share of stormflow N export in this rainy growing period. The DIN/TDN ratio varied randomly among seasons although it was greater than

0.75 for all months in 2004. $NO_3$-N comprised more than 50% of TDN export. As a nutrient readily assimilated by plant–microbe system, nitrate loss becomes a critical issue regarding sustainable agriculture and the maintenance of a healthy ecosystem.

## Discussion

### Anthropogenic controls on N export

Agriculturally dominated areas are usually regarded as a source non-point N pollution, caused by greater N inputs in the form of chemical fertilizers and manure (Austin et al. 2006; Chen et al. 2008), Various studies have shown that river N concentrations and loads are strongly correlated with watershed N input (Howarth et al. 2006; Duan et al. 2007; Sobota et al. 2009). In the WCW, a purely agricultural catchment, and the JRW, with a less than 20% urban population, agricultural activities have become the dominant anthropogenic contribution to N export via surface runoff and its eventual delivery to coastal region. The maximum N application rate in April (Fig. 2) stimulated leaching of chemical solutes to the groundwater, consequently reflected in the rising N concentration in the baseflow (Fig. 3). The highest N concentrations coincided with the low flows of late autumn, followed by a rapid decline during the dormant period before recovery in the next growing period (Fig. 3). The temporal patterns of N concentrations under baseflow conditions were presumably correlated with the soil N pool and the hydrological state of the groundwater through which N was mobilized to the stream. Additionally, the enriched N concentrations downstream (Fig. 4) implied human influences on the water quality which can be ascribed to the incremental increases in agricultural land and associated N inputs. Since the $NO_3$-N concentration was consistent but relatively low, we argued that nitrate reflected the equilibrium between stream mineralization, nitrification and denitrification and did not originate from field drainage. The mean flow-weighted N load in storm runoff in the WCW is six times higher than a forest subwatershed under similar rainfall conditions in the upstream of the JRW (Chen et al. 2008), further indicating human disturbance of the N export.

### Hydrological effect on stream N

This study demonstrated the importance of hydrology in regulating the temporal distribution of N within a stream, especially in a small watershed reflecting strong connections between hydrological and biogeochemical processes. These connections have also been suggested by other studies (Caraco and Cole 2001; Inamdar et al. 2004; Weiler and McDonnell 2006; Rusjan et al. 2008; Lohse et al. 2009). A conceptual explanation of the mechanism responsible for a commonly observed peak in solute concentration on the rising limb of hydrographs was proposed by Hornberger et al. (1994) (referred to as the "Flushing Hypothesis"). The increase of N concentration is attributed to the rapid displacement of pre-event water from soil reservoirs with higher N concentrations. Dilution then leads to lower N concentrations as the proportion of new-event water increases during the later phase of the hydrograph. Hydrological effect on stream N may different among storm events. In the event B, high N occurred long after the hydrograph peak had passed, partially due to the days since previous rainfall (>25 mm) are longer (38 days) than that in event A (11 days).

The biogeochemical behavior of various N components differed among various storm events, and this was ascribed to discrepancies in the antecedent conditions of the soil, as well as rainfall intensity and duration. For example, an extreme storm promoted soil detachment in the upper layers resulting in large concentrations of suspended particulate N with lower fraction of DIN (Fig. 6). In contrast, light rainfall resulted in more dissolved N passing through the soil and subsequently entering the stream by subsurface runoff. Peak N concentrations in storm events were positively correlated with the days since previous rainfall and with rainfall intensity (Fig. 7), suggesting that rainfall-induced runoff was a key factor for the flushing effect of N by storm water, especially in the spring seeding season with high soil N content related to intensive use of fertilizer. On the other hand, N loads under baseflow conditions, being a product of N concentrations and flow discharge, did not respond well to the seasonal pattern of N concentrations, whereas the relationship was significantly positive ($P < 0.01$) between N load and baseflow discharge.

**Fig. 7** Relationships between peak TN concentrations in storm events and (**a**) the pre-rainfall interval ($n = 10$); (**b**) the rainfall intensity ($n = 9$, with the exception of the extreme storm which occurred on May 31, 2004)
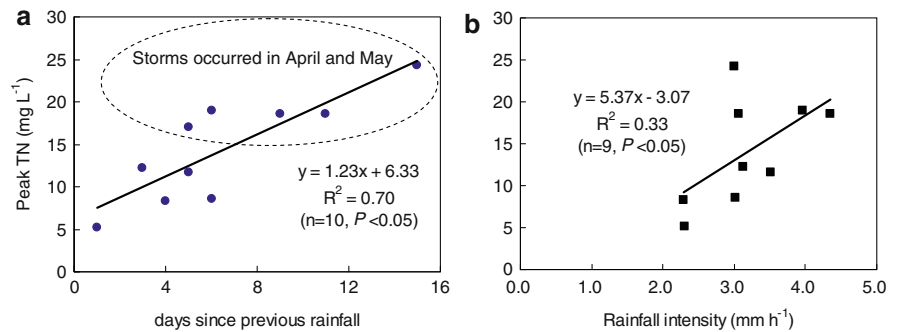
**Seasonal pattern and the primary mechanism of N loss**

In our results, N export via surface runoff presented a significant seasonal pattern caused by changes in rainfall and watershed N input. The primary mechanism of N loss in the WCW was flush-driven in late spring, summer and autumn (wet season) but highly related with soil N in winter and early spring. The WCW dataset of N concentrations and loads during baseflow and stormflow implied an interactive effects of anthropogenetic N input and hydrology conditions. Anthropogenic disturbance from agricultural activities such as intensive fertilization was presumably the primary contributor of non-point N pollution in this area. From the hydrological point of view, rainfall-induced runoff in the wet season was the key factor in flushing N from agricultural fields to the stream, especially during the N-saturated growing period. A similar study of nitrate export from a forested watershed (42 km$^2$) suggests that the role of specific hydrological events on nitrate mobilization is as important as the size of the accumulated nitrate pool available for mobilization (Rusjan et al. 2008).

**N export and retention**

The stream N concentrations (up to 15 mg l$^{-1}$) and the export in the WCW (67.10 kg ha$^{-1}$) and the JRW (17.78 kg ha$^{-1}$, see Chen et al. 2008) were generally higher than watersheds in the eastern United States and California (Boyer et al. 2002; Pieterse et al. 2003; Sobota et al. 2009). This is consistent with the fact that fertilizer contributes more anthropogenic N inputs to the JRW than to other regions (Chen et al. 2008). However, it is interesting that our watersheds export less of their N inputs (about 22% and 14% for

the WCW and the JRW, respectively, see Chen et al. 2009) compared to an average of 20–45% in large rivers in the northeastern United States and Europe (Howarth et al. 1996; Boyer et al. 2002; Van Breemen et al. 2002; Howarth et al. 2006) under temperate climates. We could argue that there may be considerable N deposits to the sediments (in this case, more than 300 reservoirs/dams in the JRW; and many fishponds in the WCW). Additionally, high rates of biological activity and an environment favorable to microbial denitrification, should result in a further decrease in N output via surface runoff. SWAT modeling work on the Huron and Raisin watersheds in southeastern Michigan indicates that impoundments have a substantial effect on riverine nutrient export (Bosch 2008), and David et al. (2006) show that a reservoir in Illinois removed 58% of the NO$_3$ passing through it over the 23-year period of record. Other studies addressing watershed N dynamics have shown that temperature and hydrology are important factors influencing watershed N retention and removal (Howarth et al. 2006; Schaefer and Alber 2007; Sobota et al. 2009).

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