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# Temporal variation of nitrate and phosphate transport in headwater catchments: the hydrological controls and landuse alteration

**T.-Y. Lee[1], J.-C. Huang[1], S.-J. Kao[2,3], and C.-P. Tung[4]**

[1]Department of Geography, National Taiwan University, Taipei, Taiwan
[2]Research Center of Environmental Changes, Academia Sinica, Taipei, Taiwan
[3]State Key Laboratory of Marine Environmental Science, Xiamen University, Xiamen, China
[4]Department of Bioenvironmental Systems Engineering, National Taiwan University, Taipei, Taiwan

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Correspondence to: J.-C. Huang (riverhuang@ntu.edu.tw)

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## Abstract

Oceania Rivers are hotspots of high DIN (dissolved inorganic nitrogen) and DIP (dissolved inorganic phosphorus) transport. However, the effects of hydrologic controls and land use alternation on the temporal variations of DIN and DIP are rarely documented. In this study, we monitored the nitrate and phosphate concentrations from three headwater catchments with different cultivation gradients at a 3-day interval. This sampling scheme was supplemented with a 3-h interval monitoring during typhoon periods. The results showed that the DIN and DIP yields in the pristine, moderately cultivated, and intensively cultivated watersheds were 7.52/0.31, 31.17/0.30, and 40.96/0.52 $\mathrm{kg\,ha^{-1}\,yr^{-1}}$, respectively. The high DIN yields are comparable to the intensively and extensively disturbed large rivers around the world. These N yields may be due to a high level of nitrogen deposition, rainfall-runoff, and fertilizer application. The importance of event sampling was indicated by the contribution of the three typhoons to the annual DIN and DIP fluxes, which were 30 % and 60 %, respectively. Both DIN and DIP fluxes significantly increased as the cultivation gradient increased. The DIN and DIP ratio varied from 54 to 230 depending on the decrease of the cultivation gradient. This value is higher than the global mean of $\sim 18$. Thus, we speculate that nitrogen saturation occurs in the headwater catchments of Oceania Rivers. The results obtained provide fundamental clues of DIN and DIP yield of Oceania Rivers, which are helpful in understanding the impact of human disturbance on headwater watersheds.

## 1 Introduction

The global biogeochemical cycles of nitrogen and phosphorus have been altered due to the increasing demand of food and energy caused by increasing human activities (Galloway and Cowling, 2002; Seitzinger et al., 2010). In the past five decades, the rate at which biologically available nitrogen (N) enters the terrestrial biosphere has doubled. The increase in the rate stems from human disturbances, such as fertilizer production, fossil fuel combustion, cultivation, and livestock industry (Galloway et al., 2004). The background Phosphorus (P) from weathering also doubled due to mining and to the use of rock phosphate as fertilizer, detergent additives, animal feed supplements, and other technical uses (Bennett et al., 2001; USGS, 2008). The worldwide eutrophication in freshwater and coastal marine ecosystems is due to the increase of DIN and DIP (Turner et al., 2003; Duan et al., 2007; Conley et al., 2009), which causes hypoxia, harmful algal blooms, and losses in fishery production in aquatic ecosystems (Lu et al., 2011; Billen and Garnier, 2007; Diaz and Rosenberg, 2008; Howarth et al., 1996; Rabalais, 2002). Moreover, the imbalanced emission of N and P that causes a change in the riverine N : P ratio has been deteriorating the ecosystem (Howarth et al., 1996; Elser et al., 2009), that is, the impact on phytoplankton production ratios and associated shifts of phytoplankton species in aquatic ecosystems (Justic et al., 1995; Rabalais et al., 1996).

Oceania Rivers accounts for 4.5 % of the total land surface area on earth and exports up to 12 % of the global water discharge. Thus, these rivers have important functions in global biogeochemical cycles (Milliman et al., 1999). Studies (Seitzinger et al., 2005, 2010) have demonstrated that Oceania Rivers are significant sources of global DIN and DIP export. Moreover, tropical cyclone invasions, which induce spiky stream discharge, may be the dominant driver for nutrient exports. The episodic injection of abundant nutrients also may disturb the ecosystem in the in-stream and coastal areas. Bouwman et al. (2005) have estimated that the riverine N flux in Oceania will increase to over 10 % in the next three decades. Many studies have focused on large rivers (Meybeck, 1982; Caraco and Cole, 1999; Smith et al., 2003), but only a few studies have investigated the nutrient fluxes in Oceania Rivers. The difficulty in studying Oceania headwater catchments is attributed to quick water level surge and landslides, which obstruct traffic and sampling.

In this paper, we investigated the DIN and DIP fluxes for headwater catchments for two years (2007–2008). The nitrate and phosphate concentration from three headwater catchments represented the pristine, moderately cultivated, and intensively cultivated watershed, respectively. These catchments were monitored at a 3-day interval, and were supplemented by typhoon sampling at a 3-h interval. The main goals of this study are (a) to describe the behavior of nitrate and phosphate in different hydrological and land use conditions; (b) to illustrate the overall pattern of temporal variations of nutrient fluxes over a 12-month period and its significance to typhoons; and (c) to highlight the contribution of Oceania Rivers in global biogeochemical cycles.

## 2 Study site

The Chichiawan Watershed located in Central Taiwan has a drainage area of 105 km$^2$ and elevations ranging from 1131 to 3882 m a.s.l. This Creek consists of three major tributaries, namely, Gaoshan (area = 21 km$^2$), Yikawan (area = 53 km$^2$), and Yusheng Creeks (area = 31 km$^2$). The Gaoshan and Yikawan Creeks are the only habitat for the Formosan Landlocked Salmon (*Oncorhynchus masou formosanus*) (Tung et al., 2006; Lee et al., 2011). In this study, the high-frequency water sampling sites were established in these three neighboring catchments, which represent the pristine (Gaoshan Creek), moderately cultivated (Yikawan Creek), and intensively cultivated (Yusheng Creek) watersheds, respectively (Fig. 1). Three precipitation gauges maintained by the Taiwan Power Company are located in this area. The annual precipitation is 2462 mm, and 75 % of the concentrates are from the wet season (May to Oct), which are mostly due to typhoons. Two hydrologic gauges that measure the hourly stream discharge are in Chichiawan and Yusheng Creeks (Fig. 1). The discharge for pristine watershed was derived from that of the Chichiawan Creek based on area proportion. The average daily discharge for the Chichiawan and Yusheng Creeks are 7.94 and 2.41 m$^3$ s$^{-1}$, respectively. During the wet season, the average daily discharges are 11.80 and 4.07 m$^3$ s$^{-1}$, respectively. The mean daily air temperature is 15.8 °C with an average of 4 °C in January and 23 °C in July.

The study watersheds represent the typical landscape in mountainous regions (i.e. small proportion of agricultural activities located along the riparian zone) where some of the residents earn their living by growing vegetables and fruits (Huang et al., 2012). The land use pattern and the landscape characteristics for each catchment are in shown in Fig. 1 and Table 1. The natural forest, mixed forest, and secondary forest are the main land use types, and are patched by grass, bare land, orchard, active farm, and inactive farm. The three adjacent creeks have a similar environmental background with varying cultivation gradients. These creeks are good experimental sites in revealing the relationship between nutrient export and land use combination.

## 3 Materials and methods

### 3.1 Water quality and discharge data

Biweekly water samples from the three sites, usually taken on Tuesdays and Fridays from 2007 to 2008, were analyzed for temporal variations. Samples were also obtained during typhoon events in 2007 to supplement in the understanding of the influences of flash flood. The event samples were taken in a 3-h interval after typhoon warnings were announced by the central weather bureau. The sampling was sustained until the water level dropped to the pre-typhoon level. In 2007, four typhoons brought relatively large amounts of rainfall in the study site, and our group obtained samples from the three typhoons. These typhoons were Pabuk, Sepat, and Krosa, which made landfall in Taiwan during 8/6 to 8/8, 8/16 to 8/19, and 10/4 to 10/7, respectively.

Water samples obtained from the streams were immediately filtered through GF/F filters (0.7 mm). The filtrates were quick-frozen in liquid nitrogen for $NO_3$ and $PO_4$ analysis. Nitrate content was determined by Ion Chromatography (IC) using a Dionex ICS-1500 instrument as described by Welch et al. (1996) with a detection limit of 0.01 $mg\,l^{-1}$. The concentration of nitrite and ammonium were below the detection limit. Hence, nitrates are the dominant species of dissolved inorganic nitrogen. $PO_4$, which is a representative of dissolved inorganic phosphorus, was measured via a custom-made flow injection analyzer with a 10 cm detection cell. The detection limit was 0.002 mg $\mathrm{l}^{-1}$ (Parson, 1984).

### 3.2 Flux calculation

The flux is the total amount of export elements from a watershed within a given period. The elemental concentrations measured in the stream were transformed into flux by multiplying the corresponding discharge to obtain the elemental mass load. Flux estimations are often essential in deriving the flux within a given period when there are limited samples. This estimation is performed when continuous measurement (i.e. daily) of the elemental concentration and discharge is not possible. The flow-weighted method, which considers hydrological controls on element concentration, was performed to calculate the flux on non-typhoon days because typhoon discharge could change the C-Q relation during the non-typhoon period. However, the close C-Q relationship observed during the typhoon period makes the rating curve method suitable, particularly when the samples cover the higher-discharge spectrum (Kao and Liu, 2001; Kao et al., 2004; 2005; Kao and Milliman, 2008; Lee et al., 2009).

The formula for the flow-weight method is shown below.

$$\text{Load} = K_1 \frac{\sum_{i=1}^{n} C_i Q_i}{\sum_{i=1}^{n} Q_i} \times Q_\mathrm{t} \tag{1}$$

where $K_1$ is the conversion factor used to calculate Load (kg) for a specific period (in this case, month). $C_i$ (mg $\mathrm{l}^{-1}$) is the nutrient concentration of $i$th sample in a month. $Q_i$($\mathrm{m}^3\,\mathrm{s}^{-1}$) is the daily discharge on the day while the $i$th sample is taken. $Q_\mathrm{t}$ ($\mathrm{m}^3$) is the total monthly discharge, and $n$ represents the total number of samples in a month.

The rating curve method presumes that a power function (i.e. $F = aQ^b$) exists between the observed nutrient flux ($F$) and discharge ($Q$). The coefficients of power function, *a* and *b*, in Eq. (2), can be derived from the observed nutrient fluxes and the water discharge rates by the log-linear least-square method. In this study, 3-h-interval samples are used to construct the power-function relation, which is further applied on the entire event period to estimate the total event load.

$$\text{Load} = K_2 \sum_{j=1}^{T} F_j = K_2 \sum_{j=1}^{T} aQ_j^b \tag{2}$$

where $K_2$ is also a conversion factor used to calculate Load (kg) for a specific period (in this case, event hours). $F_j$ ($\mathrm{g\,s^{-1}}$) is the hourly nutrient flux, which can be estimated by the hourly discharge rate $Q_j$ ($\mathrm{m^3\,s^{-1}}$) on the $j$th hour. $T$ (h) is the total event hour.

## 4 Results

The air temperature, discharge, and nitrate concentration for the pristine, moderately cultivated, and intensively cultivated watershed are shown in Fig. 2. The annual air temperature moderately varied at a range of 0 °C to 20 °C. By contrast, the rainfall in the wet (between May to October) and dry seasons are distinct. The abrupt discharge changes in the wet season could be as much as three orders of magnitude, which is mostly attributed to typhoons and characterizes small mountainous rivers (Milliman and Kao, 2005; Kao and Milliman, 2008). The running average was applied on the concentration data for every five samples to illustrate the temporal changes and its relation to discharge changes.

### 4.1 Temporal variation of nitrate concentration

The nitrate concentration in the pristine catchment (Fig. 2b) varied between 0.0 ppm to 2.5 ppm. The higher concentration could be found in the wet season, which corresponds to the discharge. The discharge or rainfall-runoff process is a dominant factor that controls the nitrate concentration in this stream. The highest nitrate concentration was observed in the first rainstorm in 2007, followed by a decreasing nitrate concentration until the end of the dry season. Studies have noted the influence of the first flash flood on nitrate export after the accumulation of nitrogen in the soil and watershed in the dry season (Creed et al., 1996; Creed and Band, 1998; Poor and McDonnell, 2007). Most of the flushable nitrate was flushed out during the first rainstorm, but the nitrate storage remained sufficient. Afterwards, the nitrate storage was gradually restored. At the onset of the dry season, the weaker carrying capacity of the flow could not wash out the nitrate, which began to accumulate in the watershed storage. In the beginning of 2008 as shown in Fig. 2b, the nitrogen storage was apparently accumulated and afterwards, the nitrate concentration began its annual cycles. The nitrate concentration measured in rivers reflects the compromise between the nitrogen supply within the watershed and the carrying capacity of the rainfall-runoff. The surface and subsurface flow through different nitrogen storages, which influences the stream nitrate concentration (Mulholland and Hill, 1997; Katsuyama et al., 2001; Poor and McDonnell, 2007) and complicates the determination of nitrogen sources.

The nitrate concentration in the moderately cultivated watersheds (Fig. 2c) was higher, which ranges from 0.8 ppm to ∼ 10 ppm, due to human disturbance (i.e. fertilization). The application of irregular fertilizer disarranged the correlation between the nitrate concentration and the discharge in this watershed. However, the influence of the first flood remained apparent. The flushing nitrate could be found at the onset of a rising hydrograph. Unlike in the pristine watershed (Fig. 2b), the overall nitrate concentration during the flood period was below the concentration for the antecedent regular samples (Fig. 2c). For the intensively cultivated watershed (Fig. 2d), the nitrate concentration was as high as 10 ppm (criterion for drinking water quality) and had a slightly decreasing trend. The long-term decline of nitrate concentration may be attributed to the forbidden cultivation since 2005 for preserving the landlocked salmon habitat. The human disturbance effect on nitrate concentrations may linger for several decades, even if the agricultural activities have been ceased.

## 4.2 Temporal variation of phosphate concentration

The running average for the phosphate concentration also corresponded well to the discharge pattern (Fig. 3). The phosphate concentrations have insignificant seasonality. The temperature did not significantly affect the phosphate concentration compared with large rivers (Smith et al., 2003). The mean phosphate concentrations of the three catchments were around 0.02 ppm. Human disturbances did not seem to elevate the phosphate concentration during the normal condition (non-flood period). The phosphate concentrations were comparable to the mean concentration among the three catchments. However, the increasing phosphate concentration accompanied the increase of discharge, as shown in the hydrologic controls on the enhancement of phosphate concentration (Sharpley and Menzel, 1987; Correll et al., 1999). Phosphate is a highly particulate-associated constituent as show in Fig. 4. The sediments that are eroded from the hill slope or are being re-suspended from the riverbed caused the attached phosphate to be released into the river. Therefore, the peak discharge and peak phosphate concentration were almost simultaneous. In a year, the phosphate concentration reached its highest value during typhoon events due to a greater supply of sediments from surface soil erosion and landslides. These episodic events are important in carrying nutrient inputs, particularly phosphate, to the river ecosystem (Green and Finlay, 2010). The scattered phosphate concentration is from the occasional input from either soil erosion or landslides. Notably, the increase of agricultural area would elevate the phosphate concentration significantly during the typhoon events.

## 4.3 Hydrological controls

The relationship between nitrate, phosphate concentrations and water discharge rate is illustrated in Fig. 5. For nitrate, the concentration was diluted in the flood period. However, the phosphate concentration was enhanced by the increase of discharge. The nitrate-discharge relationship of the intensively cultivated watershed in the low-flow period was not clear (Fig. 5a-3), which is possibly due to the timing of fertilizer applications

(Poor and McDonnell, 2007). On the other hand, the relationship between phosphate concentration and water discharge rate remained positively correlated regardless of high and low flows (right panels of Fig. 5), which indicates additional phosphate input while water discharge increases. One possible interpretation of this phenomenon is that the source area of the phosphate is proportional to the variable source area where the runoff washes the surface to the stream during rainstorm events. From those concentration and discharge plots, the nutrient transport is element dependent and controlled by discharge. Meanwhile, the plots also revealed the sampling work cover the whole discharge spectrum as possible which may influence the flux calculation substantially.

## 5 Discussion

### 5.1 Flux of nitrate-N and phosphate-P

The temporal variations of DIN and DIP export are illustrated in Fig. 6, which shows the monthly flux and the significance of event flow. The three typhoons in 2007 had 220, 522, and 660 mm of rainfall, which accounted for 35 % (7 %, 17 %, and 21 %, respectively) of the annual amount (3,128 mm) in only 3.5 % of the time within a year. The distinct water export in the time frame is a typical characteristic for Oceania Rivers. For nitrate export, around 32 % of the annual nitrogen export (36 %, 15 %, and 44 % for the pristine, moderately cultivated, and intensively cultivated watershed, respectively, in Table 2) was also transported during such a short period. Although the nitrate concentration was diluted during the typhoons, an increase of the discharge by three orders of magnitude compensated the dilution effect and eventually transported more nitrogen compared with the low-flow period. Meanwhile, the nitrate fluxes among the three events were directly proportional to the discharge magnitude. It may imply either the nitrogen storage in the watershed is sufficient to afford frequent flooding or the recovery of nitrogen is fast. For phosphorus export, approximately 54 % of the annual phosphorus loads (around 42 %, 40 %, and 81 % for the pristine, moderately cultivated, and intensively cultivated watershed, respectively, Table 2) were flushed out during the typhoons. During the typhoons the increase of the discharge and phosphate concentration by three and two orders of magnitude, respectively, substantially enhanced phosphorus export (Correll et al., 1999). Facing the increasing rainstorms in terms of frequency and intensity due to climate change (Tu et al., 2009), the alteration of nutrient export and the consequent effects on coastal environment deserve more attentions.

## 5.2 Yield of nitrate-N and phosphate-P

Except for the concentration, the nutrient fluxes were converted into the yield to illustrate the emission rate of DIN and DIP per unit area for comparison. The DIN yield varied from 41 $\text{kg ha}^{-1}\text{yr}^{-1}$ to 7.5 $\text{kg ha}^{-1}\text{yr}^{-1}$ from the intensively cultivated to the pristine watershed. This result reflects the cultivation gradient (Table 2). The DIN yield in the pristine watershed is comparable to that of the moderately cultivated watersheds around the world (Huang et al., 2012). A study (Caraco and Cole, 1999) has shown that only three of the 35 large rivers in the world had an $NO_3$-N yield of more than 7.0 $\text{kg ha}^{-1}\text{yr}^{-1}$. High nitrogen yields were also noticed in China (Lu et al., 2011). Such high yield may be partially attributed to air pollution (e.g. industrial and vehicle emission), which results in abundant DIN input (Lin et al., 2000; Fang et al., 2008).

For the phosphate yield, the exported amounts of phosphorus to streams of the three watersheds were 0.31, 0.30, and 0.52 $\text{kg ha}^{-1}\text{yr}^{-1}$, respectively (Table 2). These values were also larger than most tributaries of Changjiang River (Lu et al., 2011). However, if the contributions from the typhoons were removed, our phosphorus yields would be comparable to the Changjiang tributaries Frequent cyclone invasions (Greeen and Finlay, 2010) and fragile geology are responsible for the high riverine DIP yield of Oceania Rivers.

### 5.3 N : P ratio

DIN and DIP loading from land to ocean is tightly coupled with a constant loading ratio of about 18 : 1, even though DIN and DIP follow a substantially different biogeochemical cycle (Smith et al., 2003). However, our study showed that the ratio of DIN to DIP loading could vary from 54, 230, and 174 for the pristine, moderately cultivated, and intensively cultivated watershed, respectively (Table 2). Human disturbances elevated the N : P ratio due to nitrogenous fertilizer. The increased N : P ratio in the relatively pristine catchment indicates the excess nitrogen obtained from either atmospheric deposition (long-range transport) or rock weathering. Biogeochemical cycles in this region are characterized by the following: high atmospheric input (21 $\mathrm{kg\,N\,ha^{-1}\,yr^{-1}}$ to 34 $\mathrm{kg\,N\,ha^{-1}\,yr^{-1}}$ including wet and dry deposition, Huang et al., 2012), high geologic input (10 $\mathrm{kg\,N\,ha^{-1}\,yr^{-1}}$ to 20 $\mathrm{kg\,N\,ha^{-1}\,yr^{-1}}$, Huang et al., 2012), high DIN yield, and high N : P ratio. These phenomena imply that the catchment is likely nitrogen saturated. However, this inference could be further confirmed by analyzing the N : P ratio in plant foliage (Tessier and Raynal, 2003) or by understanding the nitrogen fluxes among storages. Previous studies showed the rates of nitrogen mineralization, nitrification (Owen et al., 2010), retention (Fang et al., 2008), and gaseous N losses (Koba et al., 2012) are important for nitrogen dynamics and cycling; however those processes remain unclear in Taiwan.

The monthly variations of N : P ratios are illustrated in Fig. 7. The N : P ratios fluctuate up to two orders of magnitude, which illustrates seasonal variability. The N : P ratios are higher in summer and lower in winter. The seasonal variations indicate that nitrogen is higher in summer while phosphorus remains unchanged. In addition, hydrological forcing (e.g. floods) causes a sharp drop in the N : P ratio. This drop may result from the dilution of DIN and the increase of DIP. Floods (strong pulse and injection with high erosion energy and sediment) usually wash the channel and thoroughly transport the nutrient. However, the sequential monthly N : P ratio immediately recovered, which implies that the intrinsic nutrient storage within the catchment is large and responds quickly to changes. The rapid return of nutrient status is important in aiding lotic ecosystem recovery.

## 5.4 Conceptual model for nitrate and phosphate transport

The N : P ratio versus DIP concentration are plotted in Fig. 8 to reveal the effect of hydrologic controls and the influence of agricultural activity. Besides, the N : P ratios versus discharges also showed in Fig. 8b, c, d for the three catchments, respectively. The N : P ratio increased from 20 to 10 000 with decreasing DIP concentration from 3.0 µM to 0.01 µM. The increase in agricultural activity causes a more significant DIN increase than DIP. Meanwhile, the variations of N : P ratios were magnified with the increase of cultivation. The change of N : P ratios vs phosphate concentrations in the three catchments were similar. In dry season, the N : P ratios were moderate as the annual average. During wet season, the nitrate concentration increases lead the high N : P ratios, but the phosphate concentration is relatively low. For flood periods, the abundant washed-out phosphorus reduce the N : P ratios significantly. The increase of phosphorus leads the low N : P ratios also could be found in previous studies (Saun et al., 2006; Green et al., 2007).

In this study, a conceptual model is proposed to illustrate the relationship between flow pathways and $NO_3$/$PO_4$ transport in different hydrological conditions (Fig. 9). During the dry period, only leachable nitrate and phosphate within the soil column can be leached out by the base flow (Fig. 9a). The nitrate and phosphate concentrations are similar to the annual average. During small rainstorms or prior to large rainstorms, the surface runoff gradually dominated the stream discharge and in this condition. However, the surface flow had abundant nitrate and fewer phosphate (e.g. limited erosion energy) elevating the N : P ratios significantly (Fig. 9b). During the flood periods, most nitrates depleted the surface runoff, which were mixed with abundant particle-associated phosphate is flushed to stream. Consequently, the N : P ratios in the river were significantly diluted (Fig. 9c). The present study demonstrated the role of rainstorm in driving the low N : P ratio surface runoff and high N : P subsurface flow to the stream. The transition from high N : P in dry to low N : P in wet conditions were accompanied by extremely high N : P ratios in between. The hydrological controls and land use alternation magnified the temporal variations of nitrate and phosphate transport in Oceania Rivers. Our results provide insights into the influences of discharge variation and land use pattern on DIN/DIP transport. The study does not only aid in estimating fluxes accurately, but also aids in assessing the effect of land use alternation.

## 6 Conclusions

This study investigated the temporal variation of nitrate and phosphate concentration in three headwater catchments from Taiwan. We found that the DIN concentrations have a distinct seasonality, but the DIP concentrations have indistinct seasonality. Rainstorms enhanced DIP concentrations, which are highly correlated to the total suspended matter. However, the nitrate concentration showed a dilution effect during rainstorms. Human disturbances considerably elevated the DIN, and subtly affected the DIP. The DIN and DIP yields for the pristine, moderately cultivated, and intensively cultivated watersheds were 7.52/0.31, 31.17/0.30, and 40.96/0.52 $\mathrm{kg\,ha^{-1}\,yr^{-1}}$, respectively. The three typhoons contributed as much as 30 % to 60 % of the annual DIN and DIP fluxes. Hence, the study highlighted the importance of typhoon sampling in estimating the nutrient export. The ratio of DIN to DIP yield varies from 230 to 54 with the decrease of cultivation gradient. This value was higher than the global mean of 18. The high N : P ratio was attributed to the high DIN yields due to abundant inputs (e.g. nitrogen deposition, geologic N input, and fertilizer application) because the DIP yields are comparable to other watersheds around the world. Such high ratios supplemented by the DIN yield in the base flow and the N : P ratios in plant tissues indicated that the headwater catchments in Oceania Rivers were likely nitrogen saturated. As for the hydrological controls, the role of rainstorm in driving the low N : P ratio surface runoff and high N : P subsurface flow to the stream was also demonstrated. The results provided fundamental clues of DIN and DIP yield for Oceania Rivers. This study would be helpful in understanding the impact of human disturbance on headwater watersheds.

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**Table 1.** Basic landscape characteristics and landuse patterns in the pristine, moderately-cultivated, and intensively-cultivated watershed.

| Landscape characteristics | Drainag area (km$^2$) | Slope (deg.) | Elevation (m) | Max. flow length (km) |
|---|---|---|---|---|
| Pristine | 21.05 | 74.4 | 2577 | 10.8 |
| Moderately-cultivated | 74.03 | 71.4 | 2581 | 17.09 |
| Intensively-cultivated | 30.92 | 56.8 | 2182 | 15.48 |

| Landuses | Natural forest | Mixed forest | Secondary forest | Grass | Bare land | Orchard | Active farm | Inactive farm |
|---|---|---|---|---|---|---|---|---|
| unit | % | % | % | % | % | % | % | % |
| Prisitne | 45.8 | 22.5 | 19.7 | 9.6 | 2.2 | 0.1 | 0 | 0 |
| Moderately-cultivated | 47.4 | 15.9 | 21.8 | 9.7 | 2 | 1.7 | 1 | 0 |
| Intensively-cultivated | 2.6 | 23.5 | 62.9 | 0.8 | 1.9 | 5.2 | 0 | 3.7 |

**Table 2.** Variation of water quality (discharge, nitrate, and phosphate) on regular and event days; nitrogen and phosphorus yield and contributions from 3 events in the pristine, moderately-cultivated, and intensively-cultivated watershed. Water quality data in 2007 were used for calculation.

| Regular days | Pristine | Moderately-cultivated | Intensively-cultivated |
|---|---|---|---|
| Discharge (cms) | 2.43 (2.14)* | 9.15 (2.14) | 2.71 (3.71) |
| Nitrate (ppm) | 0.71 (0.42) | 3.87 (0.21) | 7.72 (0.42) |
| Phosphate (ppm) | 0.02 (0.35) | 0.02 (0.29) | 0.02 (0.81) |
| Nitrate (µM) | 11.5 | 62.4 | 125 |
| Phosphate (µM) | 0.21 | 0.21 | 0.21 |
| N : P ratio | 54 | 296 | 591 |
| Events | | | |
| Nitrate (ppm) | 1.44 (0.36) | 2.43 (0.3) | 6.69 (0.19) |
| Phosphate (ppm) | 0.04 (0.24) | 0.03 (0.22) | 0.1 (0.54) |
| Nitrate (µM) | 22.5 | 38.0 | 105 |
| Phosphate (µM) | 0.42 | 0.32 | 1.05 |
| N : P ratio | 53 | 120 | 99 |
| Nutrient yield | | | |
| $NO_3$-N (kg ha$^{-1}$ yr$^{-1}$) | 7.52 | 31.17 | 40.96 |
| $PO_4$-P (kg ha$^{-1}$ yr$^{-1}$) | 0.31 | 0.30 | 0.52 |
| $NO_3$-N (mol ha$^{-1}$ yr$^{-1}$) | 537 | 2226 | 2925 |
| $PO_4$-P (mol ha$^{-1}$ yr$^{-1}$) | 10 | 9.7 | 17 |
| $NO_3$-N : $PO_4$-P | 54 | 230 | 174 |
| Events contribution | | | |
| $NO_3$-N (%) | 35.87 | 15.12 | 44.08 |
| $PO_4$-P (%) | 42.38 | 40.25 | 81.3 |

[*] Values in parentheses represent coefficients of variation.

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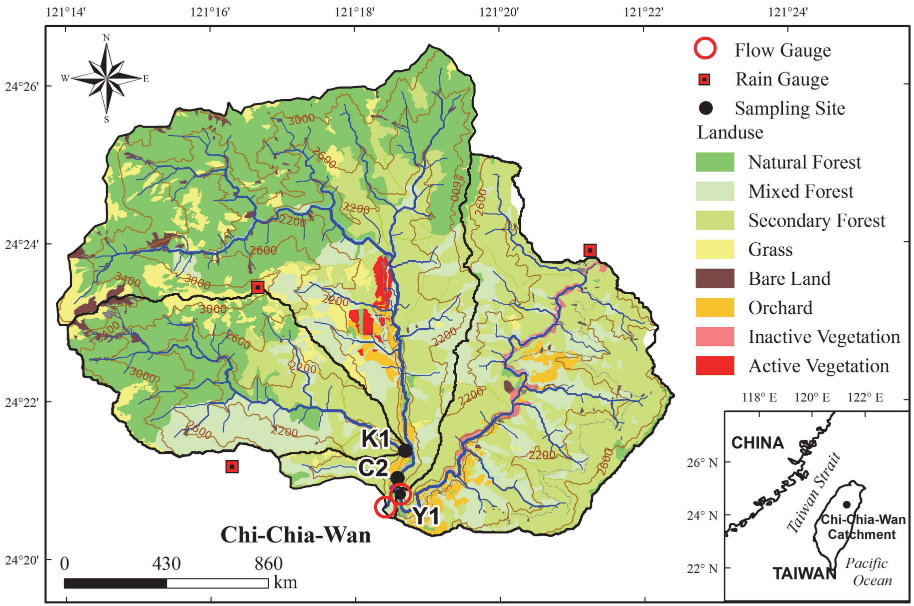

**Fig. 1.** The landscape of the study watershed, including sampling sites, rainfall gauges, discharge gauges and landuse patterns. The study watershed was divided into three sub-catchments representing pristine, moderately-cultivated, and intensively-cultivated watersheds.

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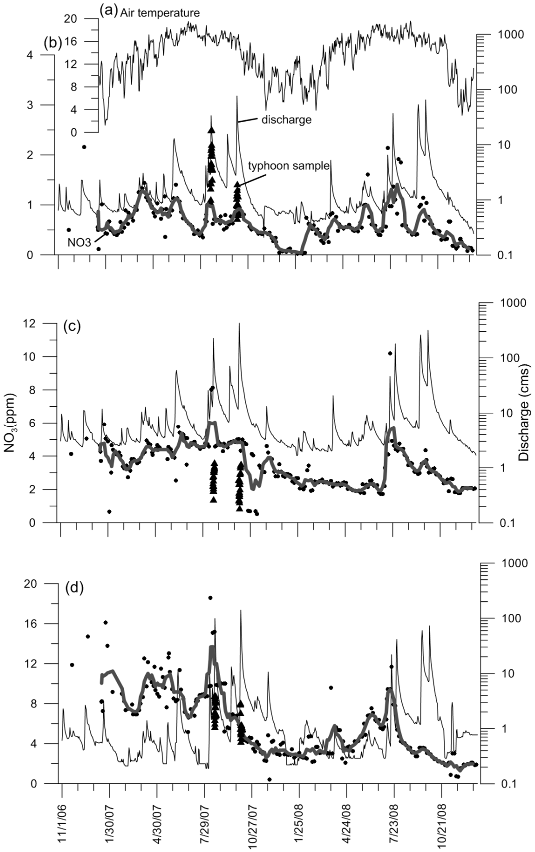

**Fig. 2.** The monitored **(a)** air temperature, discharge, and nitrate concentration in the **(b)** pristine, **(c)** moderately-cultivated and **(d)** intensively-cultivated watersheds. Nitrate concentrations were monitored during typhoon and non-typhoon period. The running average of 5 adjacent nitrate concentrations was illustrated.

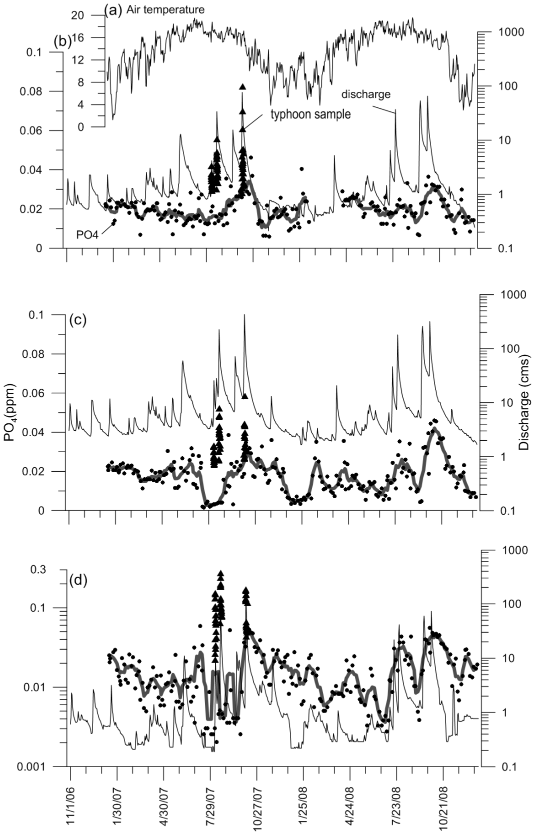

**Fig. 3.** The monitored **(a)** air temperature, discharge, and phosphate concentration in the **(b)** pristine, **(c)** moderately-cultivated and **(d)** intensively-cultivated watersheds. Phosphate concentrations were monitored during typhoon and non-typhoon period. The running average of 5 adjacent phosphate concentrations was illustrated.

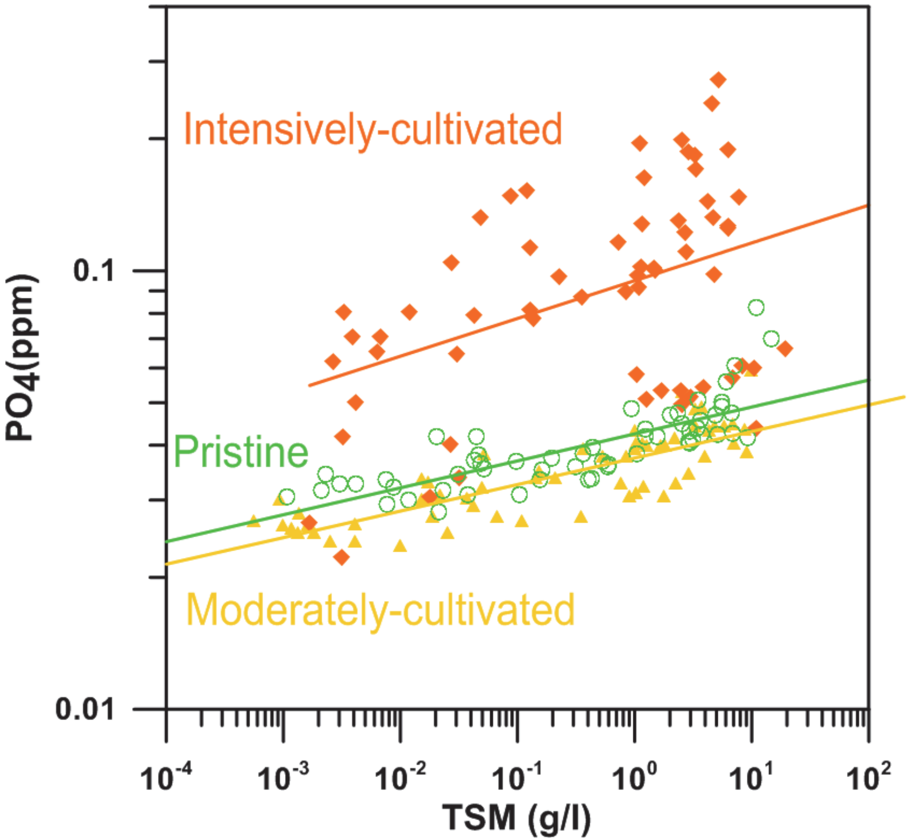

**Fig. 4.** The relationship between phosphate concentration against total suspended matter (TSM) in the pristine, moderately-cultivated and intensively-cultivated watersheds, respectively.

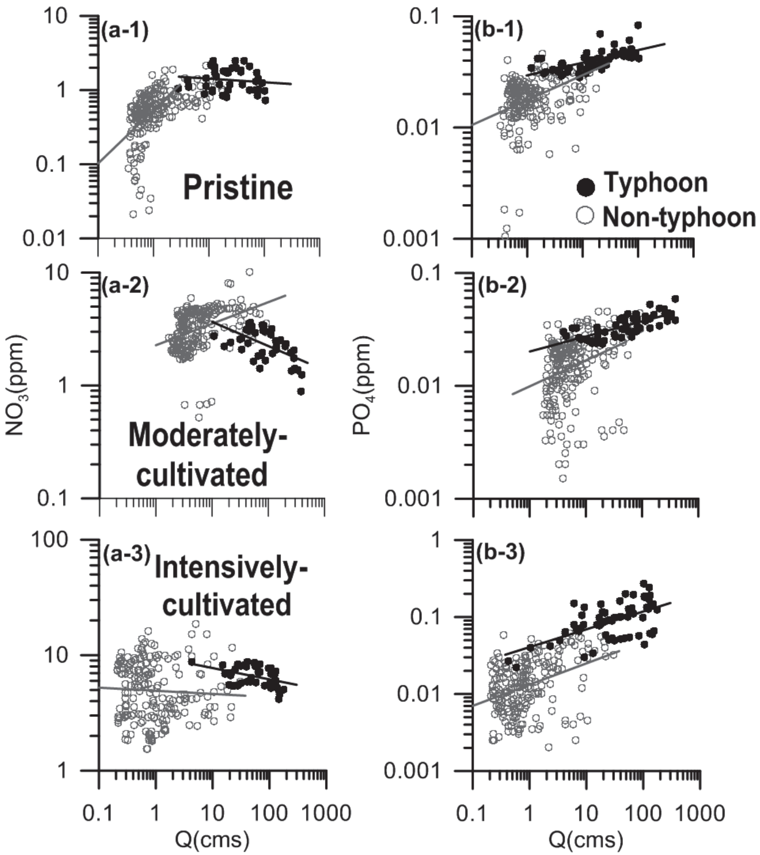

**Fig. 5.** The relation of **(a)** nitrate concentration and **(b)** phosphate concentration against discharge in the the pristine (-1), moderately-cultivated (-2) and intensively-cultivated watersheds (-3), respectively.

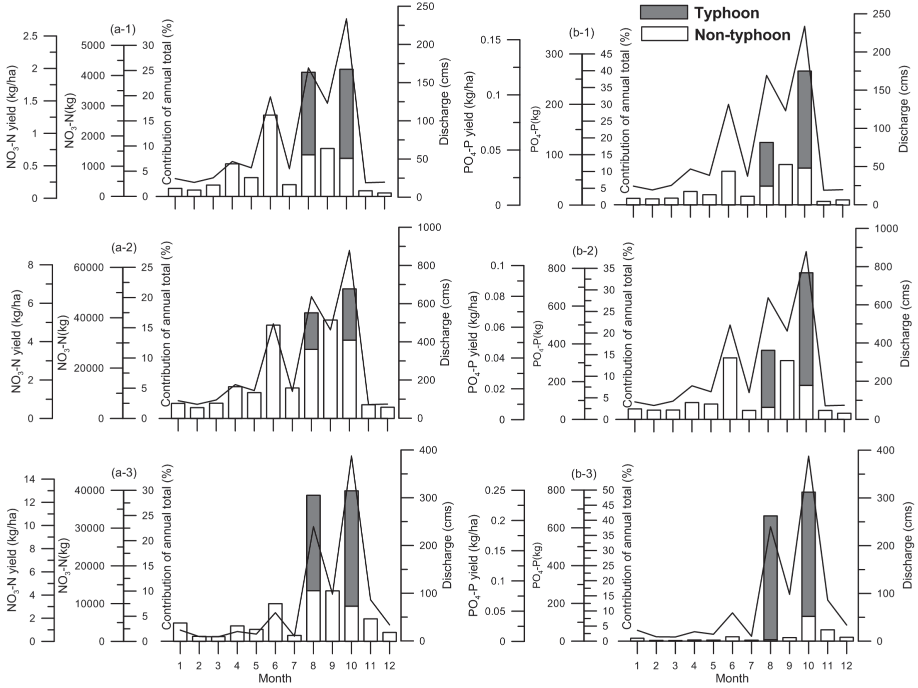

**Fig. 6.** The monthly distribution of **(a)** NO$_3$-N and **(b)** PO$_4$-P export/yield in the pristine (-1), moderately-cultivated (-2) and intensively-cultivated watersheds (-3), respectively. The contributions of typhoon and non-typhoon period to annual amount and monthly discharge are also illustrated.

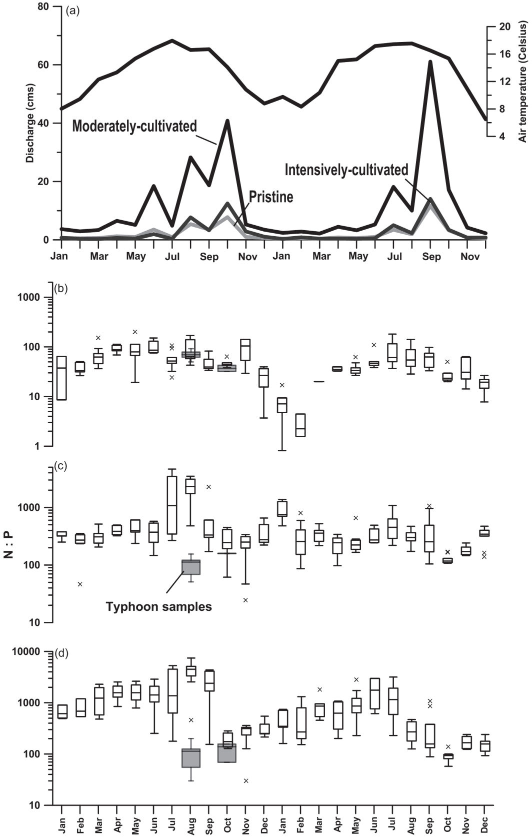

**Fig. 7.** The monthly distribution of **(a)** air temperature, discharge, and N : P ratio in the **(b)** pristine, **(c)** moderately-cultivated, and **(d)** intensively-cultivated watershed. Typhoon samples are highlighted separately.

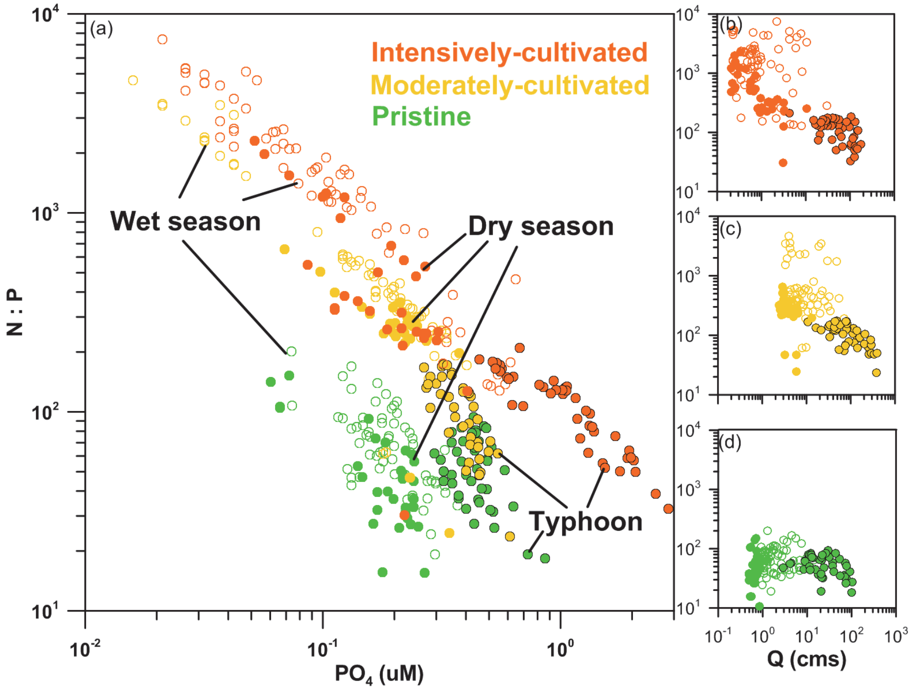

**Fig. 8. (a)** The distribution of N : P ratio variation against phosphate concentrations under different hydrologic controls and cultivation levels. The relationship between N : P ratio versus discharge for the **(b)** pristine, **(c)** moderately-cultivated, and **(d)** intensively-cultivated watersheds. The solid circle, hollow circle, and solid circle with black edge represent the concentrations in dry season, wet season, and typhoon period, respectively.

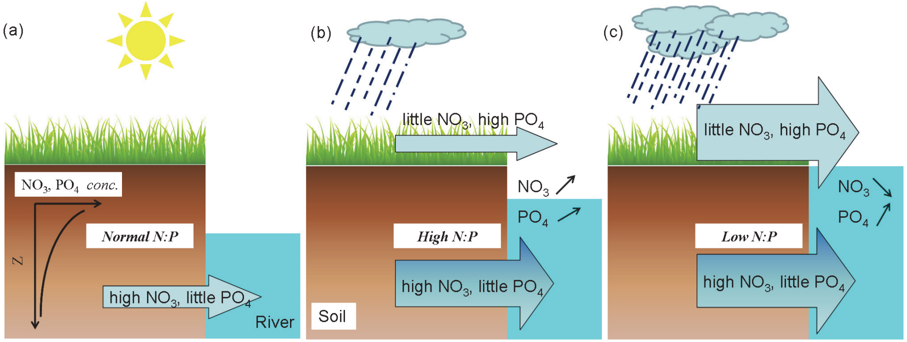

**Fig. 9.** The schematic diagram of estimated flow pathway during **(a)** recession, **(b)** pre-rainstorm, and **(c)** high-flow period. The array size represents the runoff amount. The increase or decrease of concentration was marked.