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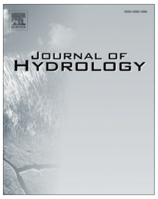

Coupled effects of biogeochemical and hydrological processes on C, N, and P export during extreme rainfall events in a purple soil watershed in southwestern China

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SUMMARY

As global warming and extreme weather events increase and intensify across the globe, it becomes ever more urgent to study and understand the effects of extreme rainfall events on carbon (C), nitrogen (N), and phosphorus (P) export from terrestrial to riverine ecosystems. There is still much to learn regarding C, N, and P non-point source discharge that results from extremely heavy rainfall as well as their effects on downstream ecosystems. This study aimed to shed light on C, N, and P biogeochemical and hydrological coupling processes. Long-term and short-term water composition monitoring research was carried out within a purple soil watershed in China's Sichuan Province. This study captured both base flow from long-term observations and dynamic runoff under extreme rainfall events that took place during the 2012 rainy season. Dissolved total nitrogen (DTN) was the largest percentage of total nitrogen (TN) in storm runoff. DTN exceeded particulate nitrogen (PN), which itself exceeded dissolved organic nitrogen (DON). Under site conditions, particulate phosphorus (PP) formed the largest constituent of total phosphorus (TP) followed by dissolved total phosphorus (DTP) and dissolved organic phosphorus (DOP). Furthermore, results showed that C, N, and P loads increased sharply in response to heavy rainfall. Although P abundance in purple soils is limited, it was nevertheless shown that C:N:P ratios measured during rainstorms corresponded much more closely to the Redfield ratio than to ratios measured in base flows. This adds to the evidence that suggests that increased storm runoff will increase eutrophication likelihood in ecosystems further downstream.

1. Introduction

As global climate changes intensify, extreme rainfall events will increase in magnitude. It is therefore reasonable to assume that ecologically deleterious effects will increase as a result. Excess nitrogen (N) and phosphorus (P) exports resulting from extreme rainfall events have an acute impact on water quality and soil environments, much more so than exports would during normal rainfall events (Liu, 1999). Carbon (C), N, and P export into aquatic ecosystems through rainstorms is governed by interactions between the hydrological cycle and a number of geochemical and biological processes that take place within terrestrial environments and riverine systems (Harris, 2001; Lapworth et al., 2013). Outcomes of such interactions greatly affect environmental conditions. It is not only the total nutrient load that results in forced change but also the nutrient composition of the load and the timing of the load in relation to seasonal timescales (Scanlon et al., 2004; McDowell and Wilcock, 2004; Stutter et al., 2008a; Gao et al., 2012). Although environmental scientists have studied these effects in some detail, it has been done in a rather piecemeal fashion. This study adds yet more details to the emerging picture.

C, N, and P cycles are inherently linked to water availability and hydrologic transport through overland flow and subsurface runoff (Manzoni and Porporato, 2011). These three key environmental nutrients may be exported in the form of dissolved inorganic chemicals, organic complexes, or in association with particulate materials (Ernstberger et al., 2004), all of which may produce differing effects on aquatic ecosystems. Understanding the composition and transport of C, N, and P in surface water flow is essential not only in practical terms, such as enabling quantitative constraint of riverine export flux, but also in theoretical terms, such

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as allowing for more nuanced models to simulate biogeochemical cycling processes and aquatic ecosystem functions (Sterner and Elser, 2002; Czamanski et al., 2011). Stutter et al. (2008a) reported that there is a strong first flush effect of sediments and dissolved nutrients in catchments during rainstorms, particularly those following periods of dry conditions. This first flush carries the greatest mass of C, N, and P enriched sediments while simultaneously mobilizing materials of C, N, and P content from riparian subsoil. Other important factors that regulate C, N, and P watershed export include physical geography, geology, land use, and the biogeochemical environment (Vink et al., 2007). Water quantity and flow path play an important role in determining how reactants are transported into catchments, transformed, and delivered to draining streams (Welter et al., 2005; Vink et al., 2007). Therefore, it can only be assumed that climate change, particularly as it affects the frequency and severity of rainstorms, will alter hydrological regimes while potentially altering the chemical composition of draining streams in areas effected (Stutter et al., 2008b).

Redfield (1934) reported that the C:N:P molar ratio is 106:16:1 for both phytoplankton and oceanic water bodies. This ratio is fundamental when modeling the basic biogeochemical patterns of marine ecosystems (Pujo-Pay et al., 2011). It is also important for studies related to C, N, and P export because a stoichiometric ratio closer to the Redfield ratio is a good indicator of the capacity of water to support higher trophic levels and eutrophication as a result (Vink et al., 2007). However, it is still unknown how rainfall mediates the export of different C:N:P ratios from terrestrial to riverine systems, especially under heavy rainstorm events, which is important in understanding the effects of rainfall on water quality and eutrophication. This study concentrated on changes related to C:N:P ratios in base flow and storm runoff in order to understand runoff biogeochemistry and its possible effects on downstream water bodies.

Despite notable differences between water bodies and biogeochemical cycles of terrestrial and riverine systems, similarities in their fundamental processes exist that shape their coupling and lead to common patterns across landscapes (Manzoni and Porporato, 2011). Hydrologic factors control biogeochemical processes from terrestrial to riverine systems by mediating C, N, and P exchange between different physical and chemical compartments. This would give rise to spatially heterogeneous biogeochemical dynamics that are also highly variable in time due to fluctuations in hydro-climatic drivers (Manzoni and Porporato, 2011). Although many reports have been published concerning C, N, and P nonpoint transport from watersheds, what remains unclear are C, N, and P exchange and coupling processes driven by rainfall, especially rainstorms. In this study, long-term and short-term dynamic monitoring on a purple soil watershed in southwestern China was carried out in order to understand the effects of extreme rainfall on different forms of C, N, and P export from watersheds as well as associated stoichiometric effects. Two related factors were also given consideration. They were: (1) to ascertain how C, N, P export from terrestrial to riverine systems would be affected by different scales of rainfall and watershed; and (2) to investigate changes in biogeochemical and hydrological coupling processes observed in storm runoff and how they would contrast to those observed in base flow.

2. Materials and methods

2.1. Study area

This study was carried out at the Yanting Agro-Ecological Experimental Station established in 1981 and supported by the Chinese Academy of Sciences (CAS). The station is located in the middle region of the Sichuan Basin (105°27′ E, 31°16′ N) (Fig. 1a). The watershed (referred to as “drainage divide” in the United States of America) selected for this study is representative of headwater watersheds of Jialing River, a first-order tributary of the Yangtze River. It is situated within the purple soil region of Sichuan Province where soil loss by runoff has been estimated to reach up to 36.34 kg km^{-2} during rainstorms (Gao et al., 2009, 2010). The parent nucleus in purple soil is prone to rapid physical efflorescence and vulnerable to slope wash. Consequently, the infiltration capacity of the soil is poor, and it exhibits weak resistance to causticity. Due to serious levels of soil erosion, increased C, N, and P export accelerates water quality deterioration in the Yangtze River and its tributaries (Zhu et al., 2009). The overall watershed drainage area is 18.62 km^2. Elevations in the region vary between 400 and 600 m (Fig. 1b). Four main land use types characterize this catchment: sloping croplands (42%), forestlands (36%), paddy fields (12%), and village residential areas (3.5%) (Zhu et al., 2009, 2012). The mountains that surround the watershed act as its boundary. Owing to this natural topography, runoff from each tributary catchment can converge and therefore export from a single outlet due to its lower elevation, making the watershed a good representation of a closed system.

The climate of the region can be characterized as seasonal, subtropical, and moist, with an average annual rainfall of 826 mm. The peak rainfall season occurs in summer. Historical climate records (maintained since 1950) show that rainstorms greater than 50 mm (measured over the duration of rainfall events) have occurred no more than four times during a period of a single year. Consequently, it is reasonable to classify rainfall events greater than 50 mm as extreme. The soil is locally referred to as purple soil and is classified as Pup-Orthic Entisol in Chinese Soil Taxonomy and Eutric Regosol in FAO Soil Classification (Gong, 1999). Measured soil parameters are as follows: pH, 8.1 ± 0.2; bulk density, 1.3 ± 0.03 g cm^{-3}; capillary porosity, 38.53 ± 1.10%; non-capillary porosity, 11.11 ± 2.00%; total N, 0.62 ± 0.7 g kg^{-1} (determined by the Semi-micrometheel of Kai’s Fixed Nitrogen method); available N, 103 ± 4.44 mg kg^{-1} (determined by the alkaline hydrolysis method); total P, 0.81 ± 0.3 g kg^{-1} (determined by the sulphic/perchloric acid digestion method); available P, 44.72 ± 5.91 mg kg^{-1} (determined by the 0.5 M sodium bicarbonate method); and organic matter, 7.8 ± 0.7 g kg^{-1} (determined by the potassium bichromate oxidation method). As it pertains to the watershed investigated, soil C:N:P molar ratios for cropland and forestland were 63:2:1 and 80:2:1, respectively (Wang and Zhu, 2011; Wang et al., 2012).

2.2. Runoff sampling

As Fig. 1 illustrates, the study selected two sub-watersheds (Fig 1c): a small-scale upstream watershed (Fig. 1d) and a macro-scale downstream watershed (Fig. 1e), situated at different elevations within the larger watershed. Both sub-watersheds are monitored by hydrological weirs. Several weirs were erected at inlets and outlets where they monitor runoff discharge. Samples were taken each month throughout most of the year and every 8–12 day interval during the summer and early autumn rainy season. This study was therefore able to obtain a good record of seasonal variation and annual baseflow.

For the purposes of this experiment, ISCO-6712 automatic sequential water samplers were installed at each hydrological weir and set manually to take samples at 1 min intervals when runoff from rainstorms began to flow and at 1 h intervals after flow rates stabilized. Monitoring during rainstorms was carried out from July to August 2012, during the summer rainy season. Rainfall data were obtained from the meteorological station at the Yanting

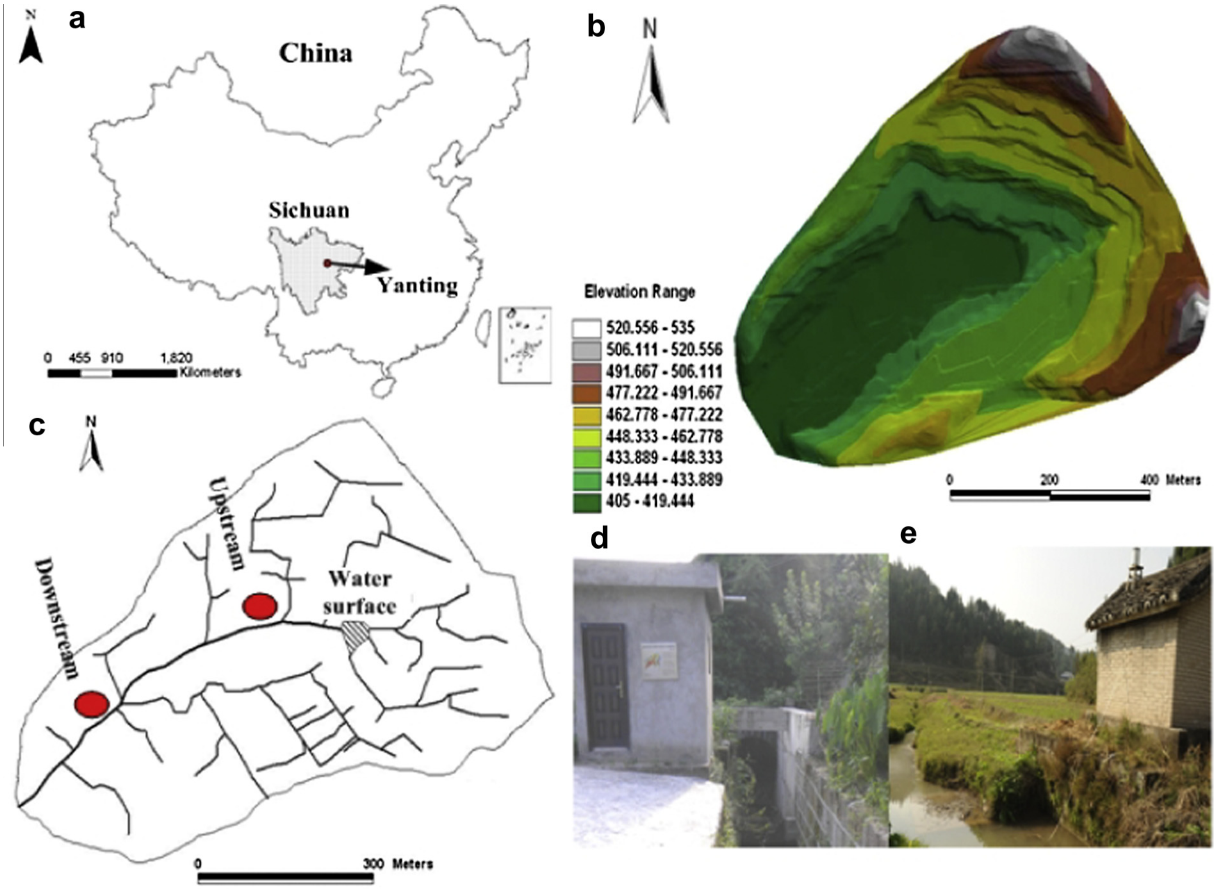

Fig. 1. Watershed location (a); elevation contour map (b); purple soil sub-watersheds (c) for upstream (d) and downstream (e).

Agro-Ecological Experimental Station. Collected samples were then analyzed in a laboratory as described in the following section.

2.3. Laboratory methods

Water samples were stored in a refrigerator at a low temperature (4 °C). Sediment was allowed to settle before being separated from water and dried in an air-forced oven to a constant weight at 105 °C for weighing purposes. Suspended sediment and water mixed sample filtrates were analyzed using AutoAnalyzer 3 (SEAL Analytical Ltd., Germany) for NO_3–N, NH_4–N, NO_2–N, and molybdate reactive P (PO_4–P) before again being analyzed for total dissolved N (DTN), total dissolved phosphorus (TDP), and dissolved organic carbon (DOC). Unfiltered samples were manually digested by a persulphate autoclave procedure that simultaneously digests N and P forms (Williams et al., 1995) before being analyzed for NO_3–N, NO_2–N, and PO_4–P.

Dissolved organic N (DON) was calculated using the formula:

$$\mathrm{DON} = \mathrm{DTN}-(\mathrm{NO_3}-\mathrm{N}+\mathrm{NH_4}-\mathrm{N}+\mathrm{NO_2}-\mathrm{N}),$$

and molybdate nonreactive P was calculated using the formula:

$$\mathrm{DOP} = \mathrm{DTP} - \mathrm{PO_4}-\mathrm{P}.$$

Associative particulate forms of N and P (particulate nitrogen, PN; particulate phosphorus, PP) were used as the digest value from unfiltered samples (PN = TN-TDN and PP = TP-DTP).

2.4. Flux calculations

Walling and Webb (1985) used an interpolation method (Formula (1)) to calculate seasonal and annual C, N, and P export loads from C, N, and P sample concentrations and monitored runoff data.

$$\text{Total load} = K\frac{\sum_{i=1}^{n} c_i Q_i}{\sum_{i=1}^{n} Q_i}\bar{Q}, \tag{1}$$

where K is a conversion factor for the measurement period; $\bar{Q}$ is mean seasonal discharge; C_i and Q_i are changes in concentrations and discharges for each month monitored, respectively; and n is the number of samples. This interpolation formula assumes that the concentration measured in a sample is representative of that found in streams between samplings and that the discharge calculated by the runoff coefficient represents the annual total. However, this method is admittedly inaccurate when used to calculate chemical behavior and runoff dynamics during a storm (Walling and Webb, 1985; Degens and Donohue, 2002).

This interpolation formula was therefore supplemented with the following formulas, as outlined by Ide et al. (2008). Rates of changes in discharge ($\mathrm{d}Q/\mathrm{d}t$) and load ($\mathrm{d}L/\mathrm{d}t$) were calculated as follows:

$$\frac{\mathrm{d}Q}{\mathrm{d}t} \cong \frac{Q_i - Q_{i-1}}{t_i - t_{i-1}}, \tag{2}$$

$$\frac{\mathrm{d}L}{\mathrm{d}t} \cong \frac{L_i - L_{i-1}}{t_i - t_{i-1}} = \frac{C_iQ_i - C_{i-1}Q_{i-1}}{t_i - t_{i-1}}, \tag{3}$$

where i is the order of the time series data; t_i is time (s); and L are the C, N, and P loads (mg L^{-1}). Using formulas (2) and (3), the total discharge and load for the entire rainstorm event was calculated as follows:

$$\text{Total runoff} = \int_0^1 q_t(t)\mathrm{d}t \approx \sum_{i=1}^{n-1} Q_i \Delta t_i = \sum_{i=1}^{n-1} \frac{q_i + q_{i+1}}{2} \tag{4}$$

$$\begin{aligned}\text{Total load} &= \int_0^1 c_t(t) \times q_t(t)\mathrm{d}t \approx \sum_{i=1}^{n-1} C_i Q_i \Delta t_i \\ &= \sum_{i=1}^{n-1} \Delta t_i \frac{c_i + c_{i+1}}{2} \times \frac{q_i + q_{i+1}}{2}\end{aligned} \tag{5}$$

where Q_i is the load (L s^{-1}), and q_i is the dynamic discharge during a rainstorm event (L s^{-1}).

The concentration of C, N, and P for each water sample was used to determine ratios of C:N, C:P, and N:P. C, N, and P stoichiometry was calculated as a molar ratio.

3. Results

3.1. Rainfall and hydrological variability

Fig. 2a illustrates measurements taken of three rainstorm events between July 2012 and August 2012: July 20, 19.8 mm rainfall; August 20, 59.4 mm rainfall; and August 30, 33.2 mm rainfall. A glance at Fig. 2b shows that rainfall increased with runoff velocity. Changes in runoff velocity were greatest for the 59.5 mm rainfall event. Rainstorms are associated with longer and bigger flow recessions and greater peak discharges (Fig. 2b and c).

3.2. Hydrochemical variability

3.2.1. Changes in DOC

As Fig. 3a shows, average variation in DOC concentrations between July and October was 2.49 ± 1.41 mg L^{-1} where concentrations varied from 1 to 3.3 mg L^{-1}. The downstream watershed showed greater changes in DOC concentrations. DOC concentration variability occurred rapidly during rainstorms, most notably in the upstream watershed. With increasing watershed scale and rainfall intensity, DOC concentrations increased sharply for rainstorm events, showing an average flux of 4.72 ± 3.30 mg L^{-1} (Fig. 3b). This was much higher than variations in DOC concentrations for base flow.

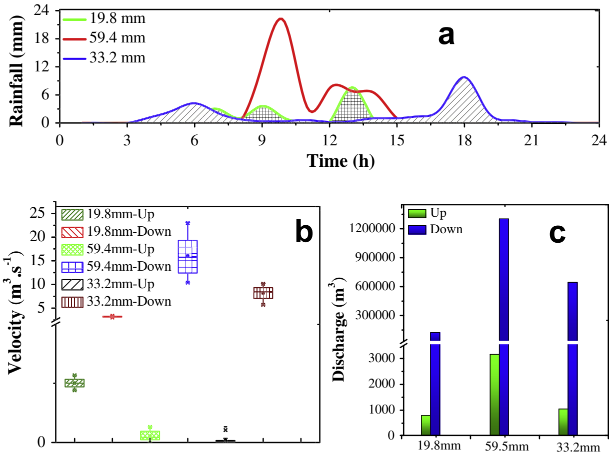

Fig. 2. Dynamics of rainfall intensity (a); velocity (b); and discharge (c) during storm events in Yanting watershed. *Note:* Up stands for upstream (Fig. 1d) and down stands for downstream (Fig. 1e) in the study watershed.

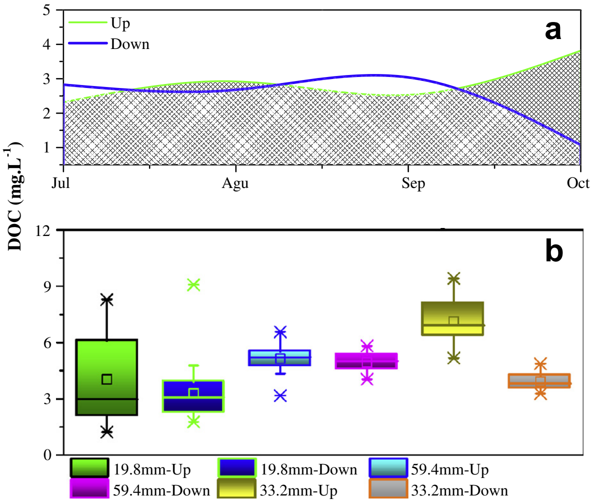

Fig. 3. Change of DOC concentrations for different watersheds under base flow conditions between July and October (a), and summary of DOC concentrations measured during storm events (b). *Note:* up stands for upstream (Fig. 1d) and down stands for downstream (Fig. 1e) in the study watershed.

3.2.2. Changes in N forms

As rainfall intensified, DTN exports gradually declined and PN exports significantly increased. The proportion of DTN to TN was significantly higher in base flow (Fig. 4). As watershed scale and rainfall increased, fluctuations in TN concentrations increased while PN release sharply increased (Fig. 5). NO_3–N was the dominant form of N found in water samples taken during the 19.8 mm rainfall event. This was also the case for base flow samples. NO_3–N and DTN concentrations sampled at these periods showed less variation than concentrations sampled during larger rainstorm events (Fig. 5). Because NH_4–N and NO_2–N formed such a small proportion of TN, variation in base flow NH_4–N and NO_2–N concentrations was below 1 mg L^{-1}. Measurements taken during the smaller rainstorm events also showed limited response to watershed storm flushing. In contrast, NO_3–N and DTN concentrations were relatively low during heavier rainfall events (59.4 mm and 33.2 mm, respectively). As NO_3–N concentrations declined, PN and DON became the dominant N flux constituents, particularly during mid-storm periods. Increasing rainfall intensity primarily led to TN concentration export, and the contribution of PN and DON to TN sharply increased during rainstorms.

3.2.3. Changes in P forms

Minimal PO_4–P and dissolved organic phosphorus (DOP) concentrations were found in baseflow, which showed a predominance of PP (Fig. 4). Concentrations of PP and dissolved total phosphorus (DTP) increased rapidly during rainstorm events. Concentrations of DOP and PO_4–P also increased during rainstorm events, most notably during the heaviest rainfall (59.4 mm) (Fig. 6). No regular variation in different P forms responding to rainfall intensity and watershed scale was observed. However, peak values of PP export concentrations were observed for rainstorm runoff. Storm events were observed to cause an increase in DOP concentrations, although the contribution of DOP to TP export remained small. Even though the proportion of DTP and PO_4–P varied during individual runoff events, concentrations of DTP and PO_4–P in TP were on average relatively consistent throughout rainstorm events.

3.3. C, N, and P concentrations in storm runoff

The weighted sum of C, nutrients (N and P), and discharge concentrations measured at each watershed during rainstorm events

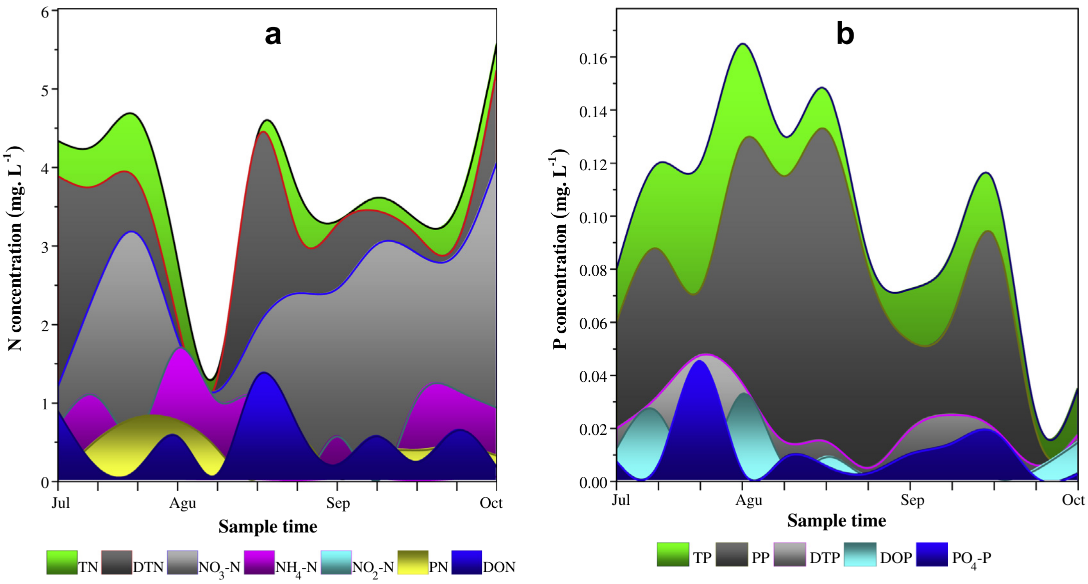

Fig. 4. Changes in N (a) and P (b) forms and concentrations in base flow from July to August 2012 in the Yanting watershed.

are provided in Table 1. Compared to values measured during lighter rainfall events (up to 19.8 mm), it can be seen that C, N, and P export showed exponential growth during extreme rainfall events. Increases in watershed scale and rainfall intensity gave rise to C, N, and P concentrations during rainstorm events. C and nutrient loads were affected by differences in runoff discharge. DTN was the dominant form of N in TN loads for rainstorm runoff, ranging between 50% and 84% of TN. DON and PN loads were smaller than DTN loads while PN loads were larger than DON loads. Thus, different forms of N export during rainstorm events followed the order: DTN > PN > DON. PP was the largest constituent of TP loads in rainstorm runoff, typically comprising 40% of TP. DON and DOP loads significantly increased during rainstorm events. The maximum DON value was 28% of TP and the maximum DOP value was 9.3% of TP. Concentrations of different forms of P in TP followed the order: PP > DTP > DOP.

4. Discussion

4.1. Biogeochemistry and hydrological coupling processes

It should be clear from the above results that large DOC and nutrient loads in rainstorm runoff lead to significant changes in regional water environments. Concentrations of C, N, and P in runoff respond rapidly to rainstorms and resulting soil erosion. Moreover, changes in DOC notably increase during rainstorms. This contrasts to base flow levels. What this suggests is that rainfall flushes organic matter out of surface soils and transports it to local watersheds (Vink et al., 2007). Hydrology impacts biogeochemical processes that also regulate C and nutrient export (BassiriRad et al., 1999; Belnap et al., 2005). Results also suggest that differences in stream chemistry can be correlated to the size of the catchment.

4.2. Nitrogen

Due to the N leaching effect caused by heavy rainfall (Gao et al., 2011, 2013a), DTN variation under extreme rainfall was significantly higher than seen under base flow. For this study, NO_3–N behavior in low intensity rainfall and base flow differed from that seen during extreme rainfall events. This could be characteristic of slower flushing of deeper soil water during conditions of light or no rainfall (Stutter et al., 2008a). During extreme rainfall events, PN sharply increased and NO_3–N initially decreased. This can be an effect of an increase in surface soil dislodged by rain, reducing overall NO_3–N proportions in TN. NH_4–N can either be absorbed or desorbed by rainfall driven soil erosion. Accordingly, NH_4–N export in storm runoff exhibited irregular changes. NO_2–N can be oxidized as it is either being transported to streams or in streams themselves. This can produce irregular changes (such as seen with NH_4–N). During mid-storm periods, PN and DON become the dominant constituents of N flux. This is what one would expect based on the report by Harris (2001) that suggested that N exports from forested headwater catchments were dominated by DON and PN.

4.3. Phosphorus

It is commonly believed that increased PP transport during rainfall may result from remobilization of accumulated fine, P enriched sediments that stem from field slope erosion. PO_4–P also increased in rainstorm runoff. It is likely that the concurrent release of PO_4–P was a product of PO_4–P desorbed from particles mobilized by rainstorm runoff (Stutter et al., 2008b). DOP transport during rainstorm events was significantly higher than in base flow. This observation has important implications for our understanding of P transformation in watersheds as well as the impact of P on riverine ecosystems. It may explain biological conversion of inorganic to organic P during stream processes. Edwards et al. (2000) showed that some PO_4–P is converted to DOP through biological activity. As Table 1 shows, equal contributions of particulate and dissolved P suggest that P transport involves both leaching and erosion. This implies that the management of headwater soil erosion, particularly during rainstorms, is necessary to protect downstream ecosystems. We can also take note that as watershed scales increase, so do sediment residence times, suggesting that even smaller bioavailability of P forms will produce an increasing eutrophication potential downstream (Hilton et al., 2006; Gao et al., 2012).

4.4. General observations

Manzoni and Porporato (2011) argued that hydrological and biogeochemical processes in streams are mediated by C and

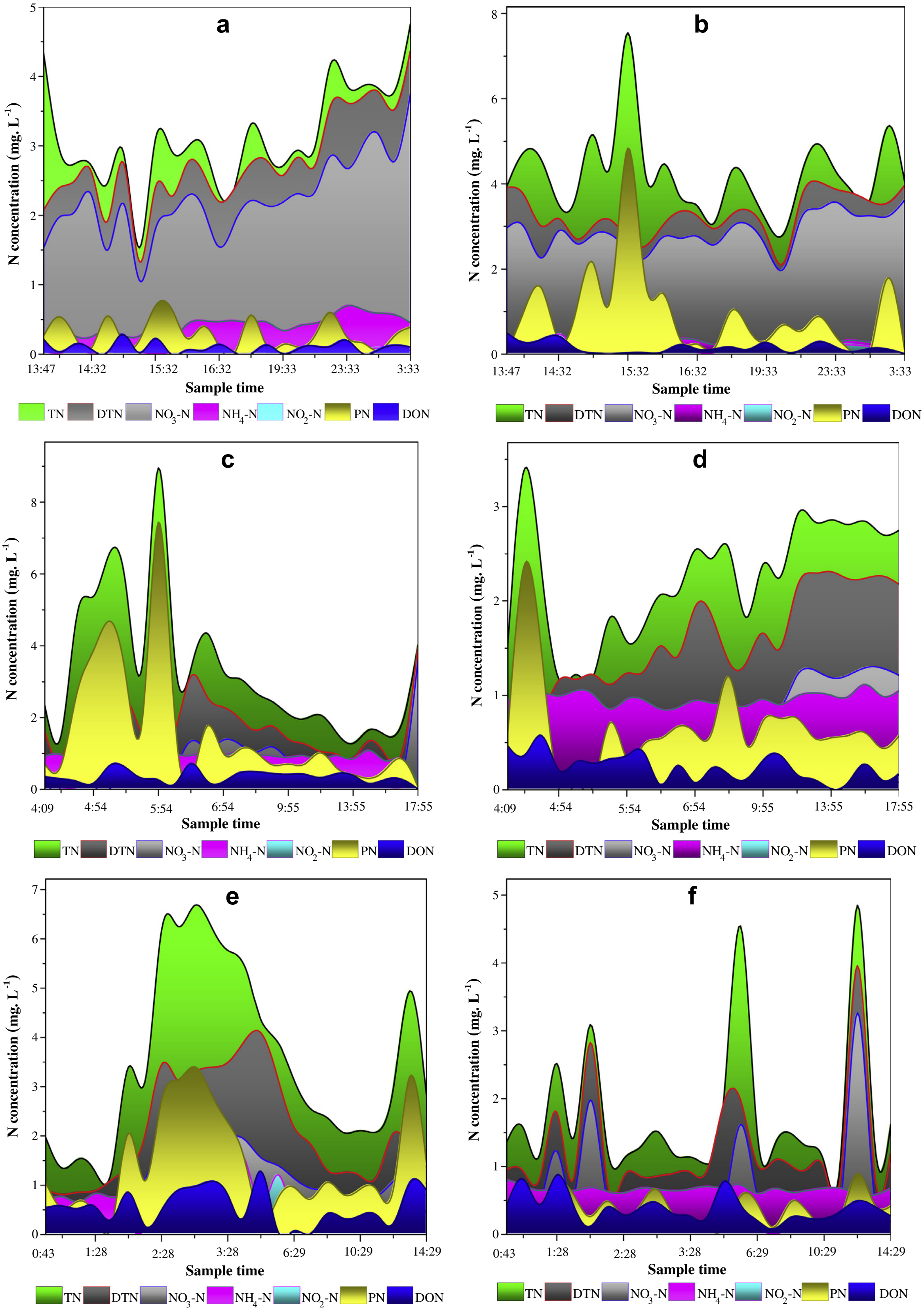

Fig. 5. Dynamics of N forms under different storm events. Effects of 19.8 mm rainfall for upstream (a) and downstream (b) watersheds. Effects of 59.4 mm for upstream (c) and downstream (d) watersheds. Effects of 33.2 mm rainfall for upstream (e), and downstream (f) watersheds.

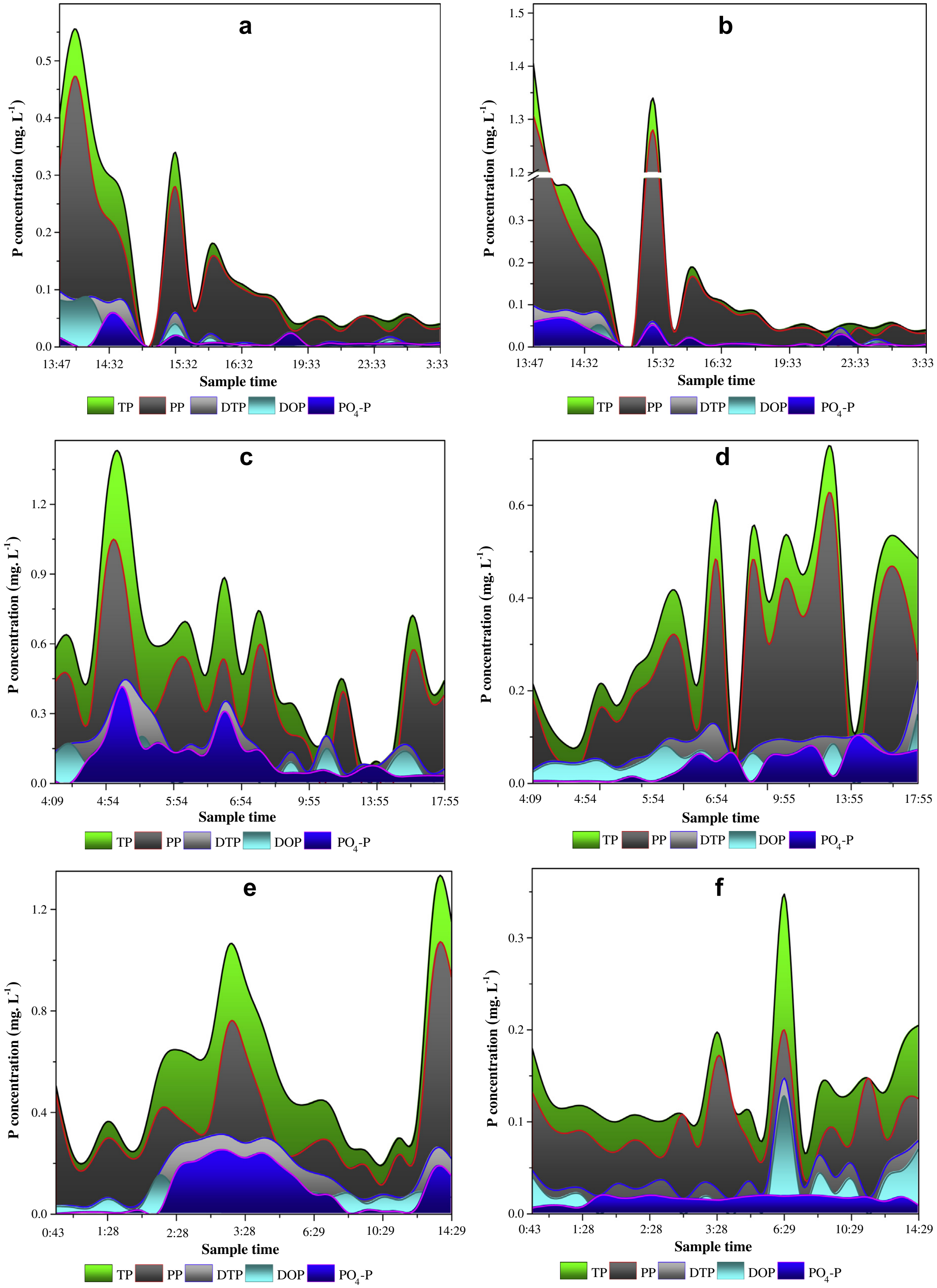

Fig. 6. Dynamics of P forms under different storm events. Effects of 19.8 mm rainfall for upstream (a) and downstream (b) watersheds. Effects of 59.4 mm for upstream (c) and downstream (d) watersheds. Effects of 33.2 mm rainfall for upstream (e), and downstream (f) watersheds.

Table 1
Total discharge, C, N and P budgets, and chemical ratios after storm events.

Type	Up	Down	Up	Down	Up	Down
Rainfall (mm)	19.8	19.8	59.4	59.4	33.2	33.2
Discharge (m^3)	745	1.14×10^5	3113	1.30×10^5	999	6.35×10^5
DOC (kg)	0.32×10^{-3}	0.39	1.66×10^{-2}	6.65	7.39×10^{-3}	2.61
TN (kg)	2.48×10^{-3}	0.48	9.8×10^{-3}	2.91	3.49×10^{-3}	1.11
DTN (kg)	2.06×10^{-3}	0.37	4.87×10^{-3}	2.06	2.08×10^{-3}	0.80
PN (kg)	2.8×10^{-4}	0.11	4.94×10^{-3}	0.85	1.41×10^{-3}	0.31
DON (kg)	6.95×10^{-4}	1.73×10^{-2}	1.06×10^{-3}	0.31	5.49×10^{-4}	0.24
TP (kg)	2.14×10^{-4}	5.15×10^{-2}	3.26×10^{-3}	0.84	1.06×10^{-3}	0.18
DTP (kg)	3.97×10^{-5}	6.23×10^{-3}	1.05×10^{-3}	0.19	3.16×10^{-4}	5.26×10^{-2}
PP (kg)	8.75×10^{-5}	2.26×10^{-2}	1.10×10^{-3}	0.33	3.73×10^{-4}	6.27×10^{-2}
DOP (kg)	1.28×10^{-5}	9.76×10^{-4}	1.89×10^{-4}	4.89×10^{-2}	6.39×10^{-5}	1.62×10^{-2}
DTN/TN (%)	83	77	50	71	60	72
DON/TN (%)	28	3.6	11	11	16	22
DOP/TP (%)	6.0	1.9	5.8	5.8	6.0	9.0
PP/TP (%)	41	44	34	39	35	35

Note: up is upstream (Fig. 1d) and down is downstream (Fig. 1e) in the study watershed.

nutrient exchanges that take place between organic and inorganic compounds. The present study suggests that C and N and C and P cycles are affected by water availability and hydrologic transport during rainstorm events (Fig. 7). C, N, and P exports exhibited significant correlation between heavy rainfall and increased export, with an R^2 coefficient generally above 0.9. This marked a shift between local control of biogeochemical processes under base flow and external control under rainstorm as reported by other studies (Saunders et al., 2006; Valett et al., 2008; Frost et al., 2009). Others have suggested that this phenomenon is an effect of repeated rainstorm events and soil drying-rewetting cycles that trigger pulses of biological activity in fast-responding microbial soil and nutrient pools (Turner and Haygarth, 2001; Austin et al., 2004; Schwinning and Sala, 2004). During such rainfall triggered pulses, generally dormant biological drivers become active. Therefore, biogeochemical dynamics of C, N, and P in base flow are qualitatively and quantitatively different from dynamics occurring after rainfall events, particularly concerning peak flow behavior under base flow and extreme rainfall events.

4.5. Stoichiometry

Ecosystem C, N, and P element ratios can affect resident organisms while organisms can also affect elemental C, N, and P composition by absorbing or releasing elements in ratios that differ from ambient. C, N, and P element ratios therefore determine the key characteristics of organisms and ecosystems (Michaels, 2003). Rainstorm runoff significantly changes the C:N ratio, in particular the DOC:DTN ratio, when compared to base flow (Fig. 8a). C:N ratios under base flow varied from 1 to 2 while C:N ratios in rainstorm runoff varied from 2 to 8 (Fig. 8a). The C:N ratio for rainstorm runoff more closely resembled the Redfield ratio. This is

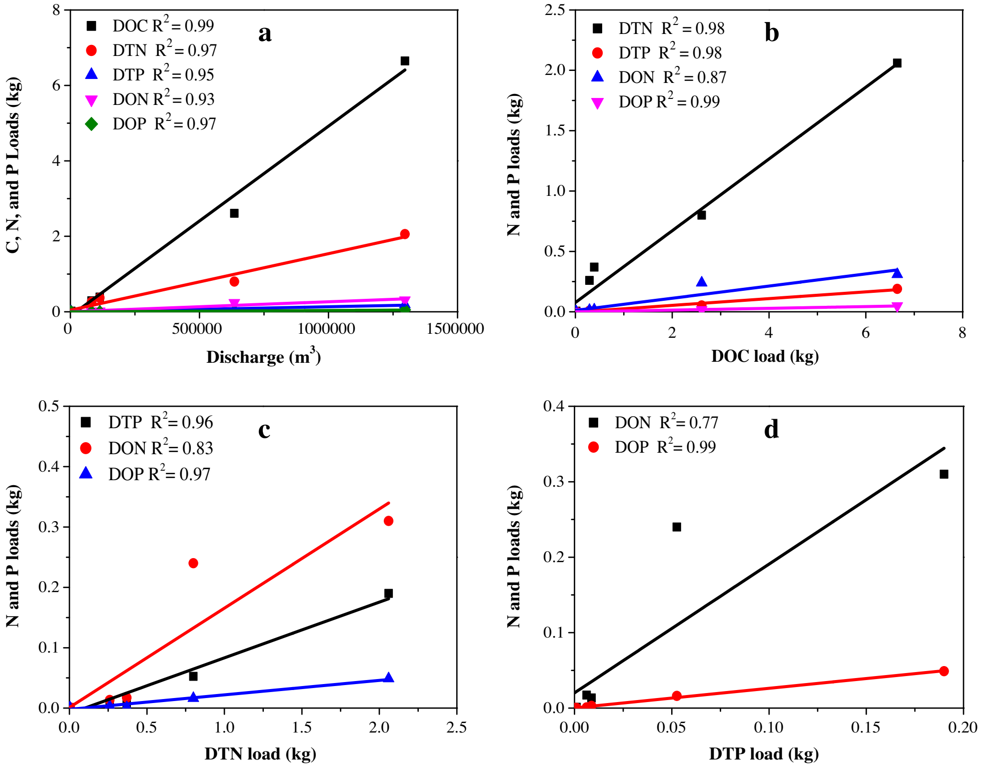

Fig. 7. Linear correlation of dissolved C, N, P and water discharge during storm events.

associated with how rainstorms temporarily increase N export and deplete N availability under base flow.

In contrast, changes in N:P ratios, in particular the DTN:DTP ratio, were far higher under base flow and low rainfall than under extreme rainfall. For example, N:P ratios under base flow and low rainfall fluctuated between 35 and 600 whereas N:P ratios in runoff under extreme rainfall fluctuated between 4 and 50 (Fig. 8b). This is explained by the fact that an increase in runoff triggers an increase in N leaching during extreme rainfall more than P losses due to erosion. Observed decreases in N:P ratios in streams could be attributable to the downward trend in N losses. This suggests that rainstorms occurring during the rainy season will alter nutrient stoichiometry, potentially leading to seasonal changes in nutrient availability in aquatic ecosystems.

Zou et al. (2006) suggested that seasonal changes in C:N ratios is primarily the result of DOM sources shifting from mostly terrestrial DOM during spring freshet to a mixed aqua-terrestrial DOM during the open-ice season to a microbial modified or reworked DOM under the ice during winter freeze. Sañudo-Wilhelmy et al. (2004) believed that C:N:P ratios are strongly affected by P partitioning into surface-adsorbed and intracellular P pools. When comparing cropland and forestland soil C:N:P molar ratios, the present study found that C:N:P ratios, especially during rainstorm events, were significantly higher in runoff than in soil. This phenomenon is the result of rainfall and runoff processes that lead to incidences of significant N transport, mainly in the form of NO_3^- release through runoff. N content therefore increases significantly in runoff. P can be absorbed by soil particulates and slowly desorbed during rainfall or runoff processes. Therefore, changes in N concentrations are more pronounced than changes in P concentrations in runoff. At the same time, DOC sorption–desorption competition with P (Kang et al., 2011) would also lead to less P release compared to N release during rainfall and runoff processes (Gao et al., 2013b).

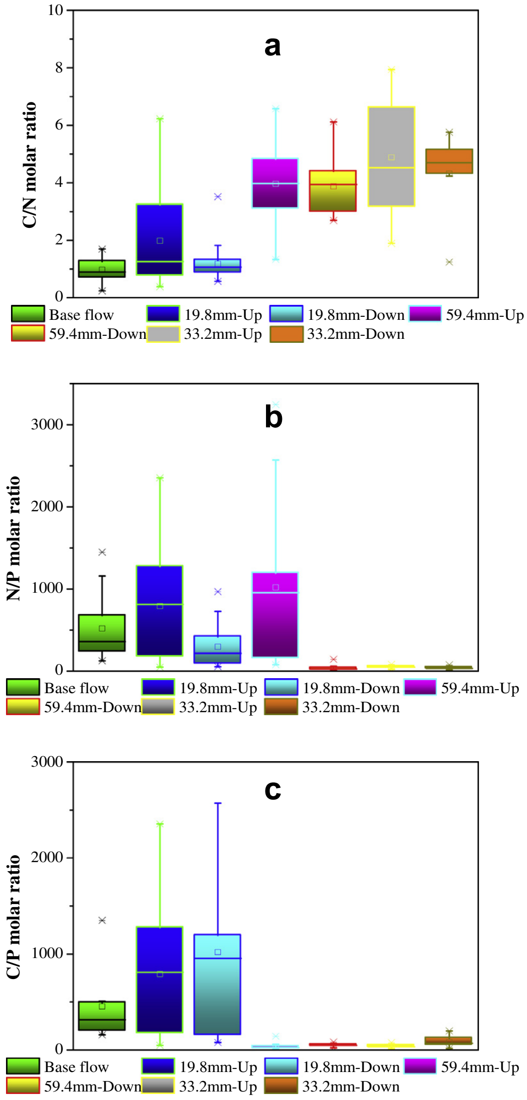

Fig. 8. Box plots showing changes in C:N (a), N:P (b) and C:P (c) ratios in storm runoff and base flow.

Optimal DTN:TDP ratios for freshwater autotrophs are between 10 and 17. Values lower or higher will limit growth (Santinelli et al., 2012). Edwards et al. (2000) indicated that N:P ratios between 80 and 170 for tributaries would mean that P is severely limited whenever NO_3–N is readily available. This suggests that the Yanting watershed selected for this study should be sensitive to the presence and bioavailability of DOP. Changes in C:P ratios for DOC:DTP paralleled changes in N:P ratios in rainstorm runoff (Fig. 8c). C:P ratios in base flow and runoff under low rainfall was significantly higher than the Redfield ratio, suggesting that P as a rule is limited in purple soil watersheds. Under rainstorm, however, significant P leaching and release were observed.

Undissolved nutrients that result from stoichiometric requirements of organisms decomposing particulates largely control the balance of C and organic nutrients in aquatic ecosystems (Elser et al., 2000; Cross et al., 2005). In the present study, C:N:P ratios measured during rainstorm events were much more closely related to the Redfield ratio than they were under base flow. This is perhaps to be expected as rainstorm runoff would enhance nutrient leaching and release in aquatic systems. This could therefore affect stoichiometry of decomposing material by causing preferential nutrient losses (Manzoni et al., 2010). In addition, rainstorm-induced changes in C:N:P stoichiometry and percentages of dissolved nutrients will also benefit certain algal species more than others, which could affect water quality and produce additional effects on downstream ecosystems.

4.6. Watershed management

The main pollution source for purple soil watersheds in southwestern China is through agricultural activity. Therefore, controlling agricultural non-point source pollution is crucial. As it pertains to reducing C, N, and P transport from terrestrial to riverine systems with the goal of protecting aquatic environments, effective temporal and spatial targeting based on pathway and time of delivery is required (Stutter et al., 2008a). Although attention has been focused on regulatory measures related to inorganic nutrients loss, agricultural N and P loads leaching into watersheds was dominated by organic and particulate forms in the present study. Reducing fertilizer application during the rainy season, increasing plant cover along ditches and catchments, and slowing down flow velocities by increasing ditch cambers and lengths may be more appropriate regulatory measures to reduce pollutant and sediment inflow into aquatic environments (Gao et al., 2012; Cao et al., 2009a,b). In addition, watershed managers should have a clear understanding of climate change impacts on nutrient transport. At the very least, they should have a better understanding that extreme short-term rainfall events or long-term changes in climatic conditions may potentially counteract measures adopted to decrease agricultural non-point pollution into aquatic ecosystems.

5. Conclusion

Comparisons between C, N, and P export under base flow and extreme rainfall events indicate that increases in rainfall intensity will raise C, N, and P concentrations and loads during rainstorms. DTN and PP were the dominant forms found in TN and TP loads measured in rainstorm runoff. Extreme rainfall events significantly enhanced C:N ratios in rainstorm runoff compared to base flow. Conversely, changes in N:P ratios, in particular the DTN:DTP ratio, were far more significant under base flow than under extreme rainfall runoff. Moreover, increased runoff under extreme rainfall events increases N leaching to a greater extent than it does erosional P losses. Changes in C:P ratios paralleled changes in N:P ratios in rainstorm runoff, but C:P ratios for base flow and runoff under low rainfall were significantly higher than the Redfield ratio, suggesting that P as a rule is limited in purple soil watersheds. Changes in C:N:P ratios suggest that rainstorm runoff will increase eutrophication in watersheds. Large quantities of dissolved and particulate nutrients will be transported from upstream to downstream ecosystems, which will drive increased phytoplankton productivity. Results from this study confirm predictions that climate change will drive changes in C, N, and P stoichiometry and have far-reaching effects on aquatic ecosystems.

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