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Master Thesis

流況轉移對溶解性有機氮輸出之碳氮耦合關係的影響：以福山試驗集水區為例

Influence of flow regime shift on the carbon-nitrogen coupling relationship of dissolved organic nitrogen export: a case study of the Fushan Experimental Forest catchment

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國立臺灣大學碩士學位論文
口試委員會審定書

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本論文係游昱霖君（R09228011）在國立臺灣大學地理環境資源學系、所完成之碩（博）士學位論文，於民國 111 年 6 月 28 日承下列考試委員審查通過及口試及格，特此證明。

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摘 要

溶解性有機氮(DON)作為一種在氮循環中生物可利用的活性氮，由於其量測上的困難度，導致在過往的研究中常被忽略，可能對氮營養狀態飽和的評估有所低估，因此了解溶解性有機氮的輸出量以及輸出行為有其必要。本研究在福山試驗林集水區，藉由及每週以及颱風事件時採集的雨水、河水、地下水、土壤水資料，透過平日與颱風事件中的營養鹽輸出狀況的比較，進一步討論當中的溶解性有機氮輸出的模式以及碳氮耦合關係的改變。研究結果顯示在福山試驗林集水區中，溶解性有機氮(DON)的平均濃度為~0.31 mg-N L^{-1}，年輸出產量為~18.96 kg ha^{-1} yr^{-1}，暴雨約佔了全年 20%的溶解性有機氮輸出佔比;溶解性無機氮(DIN)的平均濃度為~0.53 mg-N L^{-1}，年輸出產量為~24.04 kg ha^{-1} yr^{-1}，暴雨約佔了全年 17%的溶解性無機氮輸出佔比;溶解性有機碳(DOC)的平均濃度為~0.32 mg-N L^{-1}，年輸出產量為~23.97 kg ha^{-1} yr^{-1}，颱風約佔了全年 38%的溶解性有機碳輸出佔比。福山試驗林集水區的氮輸出在溶解性有機氮和無機氮上呈現負相關，另外溶解性有機碳和溶解性有機氮卻呈現解耦的狀態，並顯示出遠低於世界平均的河川碳氮比(約為 0.88)。本研究認為流況的轉移特別是颱風，可能在福山試驗林的碳氮耦合模式貢獻上扮演一個重要的媒介，在不同流況上會改變平常福山試驗林的碳氮耦合，導致集水區呈現出極低的碳氮比，讓我們對於溶解性有機氮的輸出假設以及看法提供了更近一步的了解。

關鍵詞： 溶解性有機氮、颱風、流況、碳氮耦合、碳氮比、福山試驗林

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Abstract

Dissolved organic nitrogen (DON) is a kind of reactive nitrogen in the nitrogen cycling processes, which has been neglected for decades because of the difficulty in measurement, leading to underestimating the nitrogen saturation in the ecosystem. This study compares the pattern of DON losses to previous studies, focusing on the carbon-nitrogen coupling between weekly normal flow and rainstorm event data. We analyze the stream water, groundwater, rainfall, and soil water collected at the Fushan Experimental Forest (FEF) in northeastern Taiwan. Results show that the mean DON concentration of ~0.31 mg-N L^{-1}, the mean DON yield of~18.96 kg ha^{-1} yr^{-1}, and the rainstorms accounted for 20% of the annual DON yield; the mean DIN concentration of ~0.53 mg-N L^{-1}, the mean DIN yield of~24.04 kg ha^{-1} yr^{-1}, and the rainstorms accounted for 17% of the annual DIN yield; the mean DOC concentration of ~0.32 mg-N L^{-1}, the mean DOC yield of~23.97 kg ha^{-1} yr^{-1}, and the rainstorms accounted for 38% of the annual DOC yield. Furthermore, the pattern of DON losses shows the negative correlation between DIN and DON concentration, the relationship between carbon and nitrogen shows decoupling, and the riverine CN ratio of~0.88 is lower than the global average. Our study considers that the shift of flow regimes, especially typhoons/rainstorms, may play an essential role in the change of pattern of the DON losses, which causes the meager CN ratio and provides valuable insights for improving our understanding of carbon-nitrogen coupling in the Fushan Experimental Forest (FEF).

Keywords: dissolved organic nitrogen (DON), typhoon, flow regimes, carbon-nitrogen coupling, CN ratio, Fushan Experimental Forest (FEF).

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CONTESTS

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1 Introduction

1.1 Motivation

Reactive nitrogen, including inorganic nitrogen (e.g., ammonium [NH_4^+], nitrate [NO_3^-]) and organic nitrogen (e.g., urea and amino acids) available to support the growth of plants and microbes (Dittman et al., 2007), has doubled the amount supplied to the biosphere via the emergence of the Haber-Bosch process in the early 19 century (Galloway et al., 2008). The increasing accumulation of anthropogenic N might exceed biological demand. The plenty of excess N likely exports to downstream aquatic ecosystems and causes severe eutrophication and dead zones in the environment (Conley et al., 2009). In the past concept, the conceptual model of nitrogen cycling assumed that nitrate is the export form predominantly because nitrate is thought to be particularly mobile (Aber et al., 1998). However, many catchments in South America showed that dissolved organic nitrogen (DON) not merely be a significant part of nitrogen losses but indicates the gaps of understanding about nitrogen export in nitrogen cycling (Perakis & Hedin, 2002).

The DON pool is frequently treated like a heterogeneous mixture of compounds, a subset of the dissolved organic carbon (DOC) pool containing N (Sipler et al., 2015). Various molecules, ranging from low to high molecular weight, constitute this organic nitrogen, differing in chemical bonds, element ratios, and condensation states (e.g., monomers or polymers) (Bronk et al., 2002). Different chemical bonds and condensation states resulted in parts of the DON pool on the surface waters being in the form of labile form–assimilated to the DON by phytoplankton or mineralized to dissolved inorganic nitrogen (DIN) by bacteria within days. In contrast, parts of the DON pool are characterized by slower turnover–ranging from weeks or months to decades–often denoted as refractory DON (Bronk et al., 2007). In addition, different element ratios, especially in carbon and nitrogen of DON, resulted in DON uptake sometimes from carbon or nitrogen source, even both by bacteria (Andersson et al., 2006).

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In order to discuss the pattern of dissolved organic nitrogen (DON) losses, three hypotheses have been developed based on the relationship between DON, DIN, and DOC in streams. The first hypothesis is the Passive Carbon Vehicle Hypothesis, which shows no relationship between DON and DIN concentration and a positive relationship between DON and DOC concentration. Therefore, it is assumed that DON and DOC are passively transported from soil to stream together (Hedin et al., 1995; Rastetter et al., 2005; Brookshire et al., 2007). The second hypothesis Stoichiometric enrichment hypothesis, which shows the positive relationship between DON and DIN concentration, and no relationship between DON and DOC concentration, is assumed that the biological demands of DON, like the DIN (Brookshire et al., 2007). The third hypothesis is the Carbon Indirect Control Hypothesis, which shows the negative relationship between DON and DIN concentration. Therefore, it is assumed that DON is consumed because of the biological demand for carbon sources, not the nitrogen source of DON (Lutz et al., 2011). The current studies propose some hypotheses according to the several carbon-nitrogen relationships in their survey, which mean to discuss the combination of allochthonous (i.e., land-derived) and autochthonous (i.e., intra-stream-generated) DON, DOC, and DIN (Brookshire et al., 2007; Lutz et al., 2011). However, our understanding of the contribution of allochthonous versus autochthonous sources to the total flow of DON, DOC, and DIN and its variability over time and space, especially in rainstorm events, is far from complete (Wymore et al., 2015). To research how the sources of dissolved organic nitrogen (DON) concentrations in these streams vary seasonally, sources, or in response to rainstorm events, we plan to do relative sampling and experiments in the Fushan Experimental Forest (FEF) in northeastern Taiwan.

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1.2 Objectives

In this study, we compared the DON export behaviors to previous studies (Brookshire et al., 2007; Lutz et al., 2011; Wymore et al., 2015), discussing the relationship between DON, dissolved inorganic nitrogen (DIN), dissolved organic carbon (DOC), and carbon-nitrogen coupling by using weekly and typhoon events rainwater, stream water, groundwater, and soil water collected at the Fushan Experimental Forest (FEF) in northeastern Taiwan. This study has two specific objectives. The first is to discuss the relationship between DON losses and CN coupling, especially between each pool. The second is to sketch how the different flow regimes affect nutrient transport in subtropical mountain watersheds. In addition, the sketch of various nutrient interactions in subtropical forest ecosystems with periodic tropical cyclone disturbance can provide insights into the patterns.

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2 Literature review

2.1 Nitrogen cycling

Nitrogen (N) is essential for life, but organisms cannot directly use most nitrogen, such as N_2. The only minor nitrogen-associated species of living organisms can use "reactive nitrogen." *Reactive nitrogen* is defined as various fixed nitrogen compounds that directly or indirectly support growth (Galloway et al., 2003). To utilize N_2, biological nitrogen fixation (Figure 1.; Zhang et al., 2020) refers to the process by which specialized groups of prokaryotic organisms known as "diazotrophs" or "N_2-fixers" reduce nitrogen gas (N_2) to ammonia (NH_3) to meet their anabolic needs and is the only way to generate reactive nitrogen in natural processes.

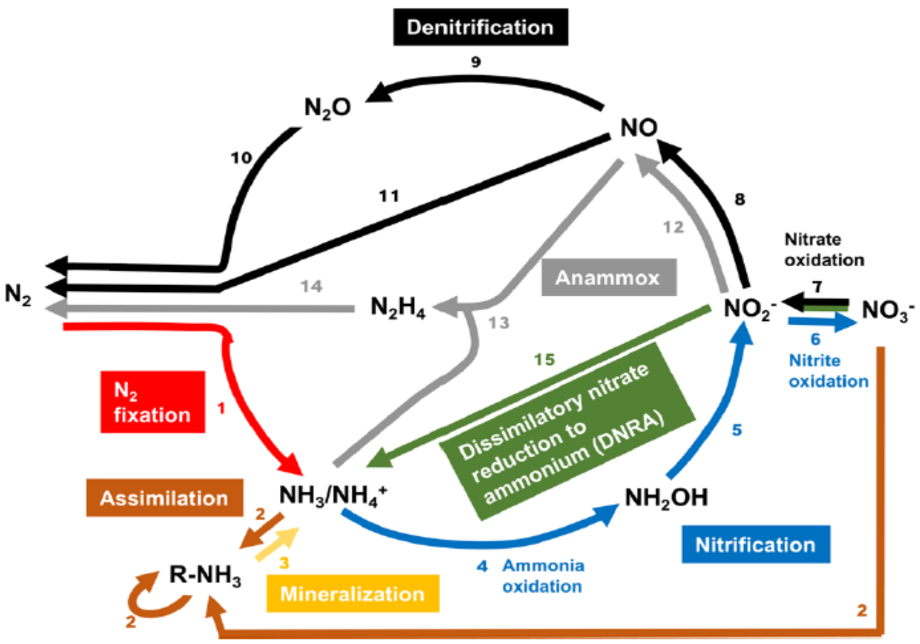

Figure 1. Nitrogen cycling (Zhang et al., 2020). N2 is fixed to ammonium and ammonia by Nitrogen (N_2) fixation (step1, red arrow). Dissolved inorganic nitrogen (DIN) such as ammonium, ammonia, and nitrate transfer to dissolved organic nitrogen (DON), which molecular formula showed $R\text{-}NH_3$ by assimilation processes (step2, brown arrow) and redox by mineralization (step 3, yellow arrow). Ammonium and ammonia transfer to a more stable status like nitrate and nitrite by nitrification (steps 4-6, blue arrow). Nitrate and nitrite will transfer to the ammonium and ammonia

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by DNRA process (step 5, green arrow) at the hypoxia condition. Denitrification and Anammox convert reactive nitrogen back into N_2 (steps 7-14, black and gray arrows).

In the following discussion, nitrification, assimilation, and mineralization are our focus processes. These processes will directly affect the generation of DIN and DON, the two primary nutrients discussed in this study. The DNRA process has also been associated with DIN production. However, it is generally much less critical for DIN production than other processes (Kuypers et al.,2018) and is not discussed further.

The nitrification process (steps 4-6, Figure 1.), in which ammonia is oxidized to nitrate by O_2, is usually carried out by specialized chemoautotrophic nitrifying microorganisms that use ammonia or nitrite as a source of energy and biomass N. Ammonia oxidation Bacteria (e.g., proteobacterium Nitrosomonas) and archaea (e.g., thaumarchaeon Nitrosopumilus) oxidize ammonia to nitrite with O_2 (steps 4 and 5, Figure 1.). Nitrite-oxidizing bacteria (e.g., Proteobacteria Nitrobacter, Nitrospina) use O_2 to oxidize nitrite to nitrate (step 6, Figure 1.). In addition, various fungi and heterotrophic bacteria oxidize reduced organic forms of N to nitrite and nitrate, a process known as heterotrophic nitrification (Hillel et al., 2005). Heterotrophic nitrification is generally less well understood than autotrophic nitrification and may be an essential nitrification process in soils (Daims et al., 2015).

Nitrogen assimilation refers to producing organic nitrogen by cells from allochthonous inorganic and organic nitrogen species (step 2, Figure 1.). Assimilation of dissolved inorganic nitrogen in the form of ammonium or nitrate is joint in plants, phytoplankton, fungi, and microorganisms (Glibert et al., 2016). Ammonia assimilation into biomass typically involves diffusion or transport of ammonia into cells, where it is then converted to amino acids by glutamine synthase and glutamate synthase (Leigh et al., 2007). The metabolic cost of nitrate assimilation is

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high because nitrate must first be reduced to ammonia by nitrate and nitrite reductases before nitrogen can be assimilated into biomolecules. At lower concentrations, phytoplankton prefers ammonium as an inorganic fixed nitrogen source compared to nitrate because their nitrogen is already in the redox state of nitrogen in amino acids (Glibert et al., 2016). Plants prefer ammonium or nitrate, depending on the type of plant function and environmental conditions (e.g., the external ratio of ammonium/nitrate) (Xu et al., 2019). Due to its ease of assimilation into biomass, ammonium accumulation is rarely observed in the environment except under dark, anoxic conditions, when no autotrophic growth or chemical oxidants limit its removal. Organic nitrogen assimilation traditionally associated with animals has also been observed in plants, fungi, and microorganisms (Näsholm et al., 2009).

The return of biomass-derived organic nitrogen to the inorganic form of ammonium is called mineralization (step 3, Figure 1.). This process is related to the excretion of organisms and the microbial degradation of organic matter during the cycle of macromolecules. During mineralization, biomass PON may first break down into the DON form (e.g., by physical breakdown, dissolution, at C-C bonds), followed by deamination of protein and nucleotide macromolecules, ultimately resulting in the release of ammonium to the environment middle (Zhang et al., 2020).

In this section, compared with the traditional concept, Recently studies found that heterotrophic microbes can also uptake the inorganic nitrogen, and autotrophs or plants can also uptake the organic nitrogen. However, we lack direct evidence that organic nitrogen contributes substantial amounts of nitrogen to plant nutrition in any ecosystem. Although a single experiment has shown unequivocally that plant N can be explained mainly by organic N uptake (Näsholm et al., 2009), this is a severe disadvantage. Of course, this is also the most critical challenge for future research. Nevertheless, we can also conclude that several lines of evidence indicate that plants inhabiting particular ecosystems may largely depend on organic nitrogen forms (Kielland, 1994;

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Lipson et al., 2001). These disruptions to the traditional concept of inorganic and organic nitrogen also affect our biogeochemical thought about nutrient export in the environment.

2.2 Global N budget

The global N budget in the form of reactive nitrogen is understood as the terrestrial and oceanic budget that fixes N through atmospheric and riverine transfers. Numerous studies have estimated the nitrogen reservoirs and natural and anthropogenic fluxes over the past few decades. The largest N reservoir is N_2 in the atmosphere (~4x109 Tg N, Figure 2.), which transfers to fixed N into the land reservoir (~1x105 Tg N) and ocean reservoir (~6.5X105 Tg N) (Johnson & Goldblatt, 2015). Among these N reservoirs, the fluxes of N into and out of the reservoirs can be viewed as the much smaller pools of chemically diverse, biologically available, “fixed” N forms present in the biosphere, oceans, freshwaters, soils, and shallow sediments. In particular, the amount of anthropogenic nitrogen such as agricultural N2 fixation (~60 Tg N yr^{-1}), Haber-Bosch N2 fixation (~136 Tg N yr^{-1}), and fossil fuel combustion (~40 Tg N yr^{-1}) is increasing, and comparable to the quantity generated by earth systems (numbered arrows, Figure 2.) (Fowler et al., 2015; Zhang et al., 2020). This excess reactive nitrogen causes serious hazards, such as eutrophication and the dead zone in the environment (Conley et al., 2009).

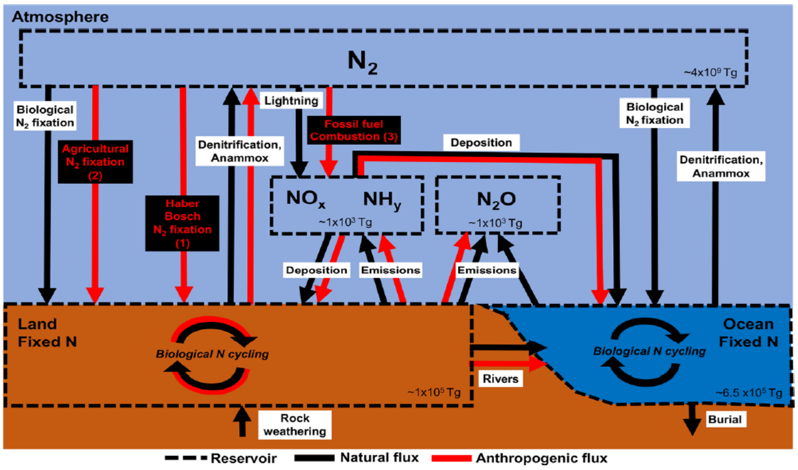

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Figure 2. Global N cycling between the atmosphere, terrestrial, and marine (Zhang et al., 2020). Black arrows indicate the N fluxes by natural processes; red arrows show the fluxes influenced by anthropogenic processes; numbered arrows mean the direct anthropogenic new N inputs.

In the DIN, A considerable amount of N was exported to the oceans through rivers, which greatly affected nutrient balance in coastal ecosystems. An estimation derived from Global Nutrient Export from Watersheds models (global NEWS) in 5,761 watersheds around the globe was 66 Tg-N yr^{-1}, including 25 Tg-N yr^{-1} of DIN (**Figure 3.**) (Seitzinger et al., 2005). The mentioned studies also show that river N exports differ in each region. Generally, Eastern Asia, Eastern America, and Europe contributed more DIN (Boyer et al., 2006).

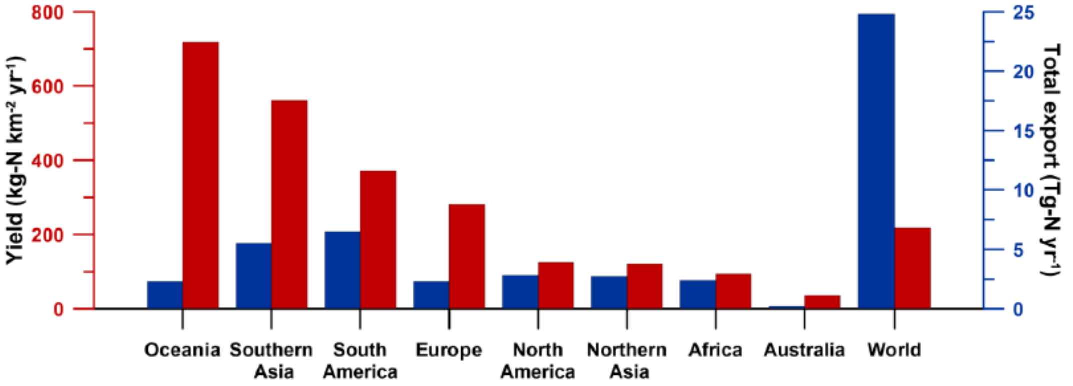

Figure 3. NEWS-Model-Estimate river DIN yield (kg-N km^2 yr^{-1}) and total export (Tg-N yr^{-1}) (Seitzinger et al., 2005).

Taiwan is located in East Asia, which has been rapidly developed recently. The atmospheric deposition also increased with increased local human activities and long-range transport from China (Figure 4.). When atmospheric deposition is more significant than 1,000 kg-N km^{-2} yr^{-1}, N leaching would gradually increase: when it grows to 2,500 kg-N km^{-2} yr^{-1}, N leaching would rapidly increase (Dentener et al., 2006). In Taiwan, during the 2007 - 2013 period, the nitrate and ammonium

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deposition was 2,100 kg-N km^{-2} yr^{-1} (Huang et al., 2016), which is much higher than the global mean and potentially results in N saturation.

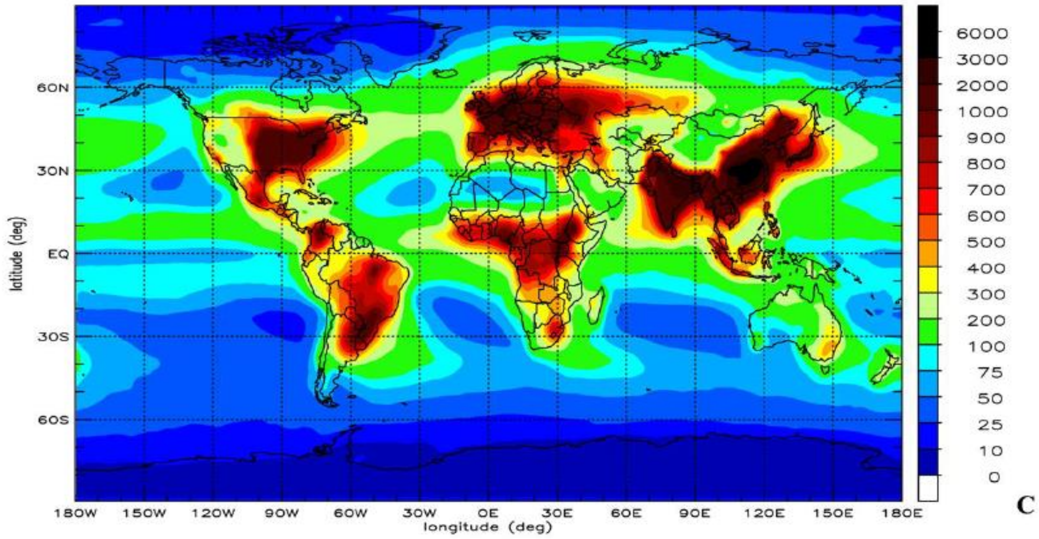

Figure 4. Modeled total deposition (kg-N km^{-2} yr^{-1}) of Nr for year 2000 (Dentener et al., 2006).

In Taiwan, the river DIN export in Guandaushi experimental forest, central Taiwan, was 623 kg-N km^{-2} yr^{-1} (Liu & Sheu, 2003). Regarding the Danshui river, northern Taiwan, the DIN export of relative natural catchments in the upper stream was 720 kg-N km^{-2} yr^{-1} (Lee et al., 2014). Still, the DIN export downstream is much higher (8,689 kg-N km^{-2} yr^{-1}) and coincidental with human activities. In the relatively natural catchment in Pinyin, upstream of Danshui River, the DIN export was 560 kg-N km^{-2} yr^{-1}, while it could reach 10,570 kg-N km^{-2} yr^{-1} in the nearby catchment because of tea plantation (Lin et al., 2015). In Chichiawan catchment, central Taiwan, the nitrate yield was 351± 62 kg-N km^{-2} yr^{-1}, while it could reach 308,170 kg-N km^{-2} yr^{-1} in intensively farming sub-catchment (Huang et al., 2012). River DIN export is 3,800 kg-N km^{-2} yr^{-1} in Taiwan, about 18-folds higher than the world average. The average DIN export ratio (output/input) was 0.30 - 0.51, higher than 0.20-0.25 in larger eutrophic rivers (Huang et al., 2016). However, these catchments more or less contained human activities such as agricultural land and urban. In other

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words, the natural N export ratio should be less if the human impacts were removed. Compared to the highest-estimated global NEWS, unit area DIN export in Taiwan was still much higher than in other regions. Taiwan is a subtropical island with high deposition, high temperature and precipitation, and thus high river DIN export. Therefore, Taiwan could be an appropriate site to study how global change could affect the N cycle.

Because DIN is highly mobile in most soils (Vitousek, 1982), increased DIN export is the primary symptom of ecosystem N saturation (Stoddard, 1994). Some studies have hypothesized that DIN availability exerts a more substantial biological control than DON (Hedin et al., 1995). All published studies to date point in this direction. In many cases, low nitrate concentrations during the growing season have been attributed to higher biological demands. However, one study showed that nitrate was consistently only a tiny fraction (average 5%, range 0.1~18%) in North and South America (Perakis & Hedin, 2002). Nitrate concentrations were uniformly low in the 13 different sample areas of the study, ranging from 0.02 to 7.7 mg-N l^{-1} (average 1.9 mg-N l^{-1}). Dissolved organic nitrogen (DON) concentrations were high, accounting for 61~97% of total N (average 80%). The range in DON concentrations among the sample areas (8~135 mg-N l^{-1}) was much more significant than that of dissolved inorganic nitrogen (DIN; range 0.5~18 mg-N l^{-1}) (Figure 5.) (Perakis & Hedin, 2002). Thus, dissolved organic nitrogen is responsible for the majority of nitrogen losses from these forests (Perakis & Hedin 2002). Therefore, we suggest that future studies consider organic nitrogen losses in models of forest nutrient cycling, which could help explain observations of nutrient limitation in forest ecosystems.

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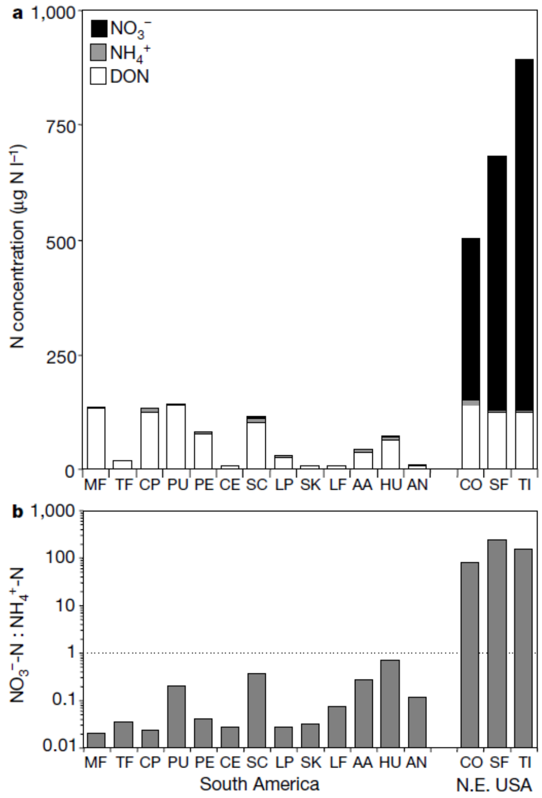

Figure 5. Hydrologic nitrogen losses from temperate forest watersheds in 13 areas of South America and three areas of eastern North America (Perakis & Hedin, 2002). (A) Average concentrations of NH_4^+, NO_3^- and DON; (B) Ratios of NO_3-N: NH_4-N. Sites arranged from left to right in order of increasing contribution of NO3-N to total dissolved nitrogen. The dashed line in b indicates equal NO_3-N and NH_4-N.

Compared to the DIN budget, our understanding of DON is low. In addition to the previous studies focusing on DIN more than DON, another reason is that the measurement of DON concentration is problematic. There are several methods for analyzing DON, such as persulfate oxidation (Menzel and Vaccaro, 1964), ultraviolet oxidation (Armstrong et al., 1968), and high-temperature oxidation (Sharp et al., 2004; Walsh, 1989), but none exist A single accepted method. The concentration of DON is determined as the difference between the concentrations of total

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dissolved nitrogen (TDN), the sum of dissolved inorganic nitrogen (DIN) to form ammonium (NH4+), nitrate (NO_3-) and nitrite (NO_2-). Therefore, there is three uncertainty in separate analyses: TDN, NH_4^+, NO_3^-, and $N0_2^-$. This uncertainty results in problems for samples with proportionally high DIN concentrations.

Some studies indicated that global Riverine DON concentrations average 0.33 ± 0.25 mg N L^{-1} and comprise 57.7 ± 23.7% of the TDN pool, with a C: N ratio of 32.5 ± 16.3 (Bronk, 2002; Wiegner et al., 2006; Cooper et al., 2008; Letscher et al., 2013). Seitzinger and Harrison (2008) estimated that 23.8 Tg N $year^{-1}$ is delivered to the marine by the largest 25 rivers of the world, and 5.02 Tg N $year^{-1}$ of which is DON. Goolsby et al. (2001) found that 24% of the annual total N flux was DON. These studies demonstrate that DON constitutes a significant portion of the total nitrogen content in rivers and should be included in the nitrogen load budget for coastal waters.

2.3 Carbon-nitrogen coupling

Carbon and Nitrogen cycling in the ecosystems are coupled to elemental stoichiometry in both plant autotrophy and soil microbial heterotrophy (Soussana et al., 2014). Terrestrial ecosystem carbon (C) storage is determined by net primary productivity (NPP) and mean residence time (MRT), both of which are strongly influenced by terrestrial nitrogen (N) availability (Vitousek et al., 1991; Hungate et al., 2003; Luo et al., 2004). Since nitrogen limitation is prevalent in terrestrial ecosystems (LeBauer and Treseder, 2008; Xia and Wan, 2008), nitrogen availability is often highly correlated with critical ecological processes, such as C assimilation (Du et al., 2017), allocation (Kuzyakov and Xu, 2013), plant respiration (Sprugel et al., 1995), and litter and soil organic matter (SOM) decomposition (Terrer et al., 2016). Therefore, nitrogen dynamics play an essential role in controlling C storage in terrestrial ecosystems (García-Palacios et al., 2013; Shi et al., 2015).

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Terrestrial nitrogen storage is mainly affected by nitrification, assimilation, and mineralization. Taylor (2010) found that when DOC: NO_3^- ratio is under the minimal threshold ratio of around 4, carbon limitation may allow NO_3^- to accumulate (Figure 6. (a)). The concept (Figure 6. (b)) indicates that a trio of microbial-driven nitrogen transformations governs inverse DOC：NO_3^- relationships by responding to discrete changes in resource stoichiometry (Taylor et al., 2010).

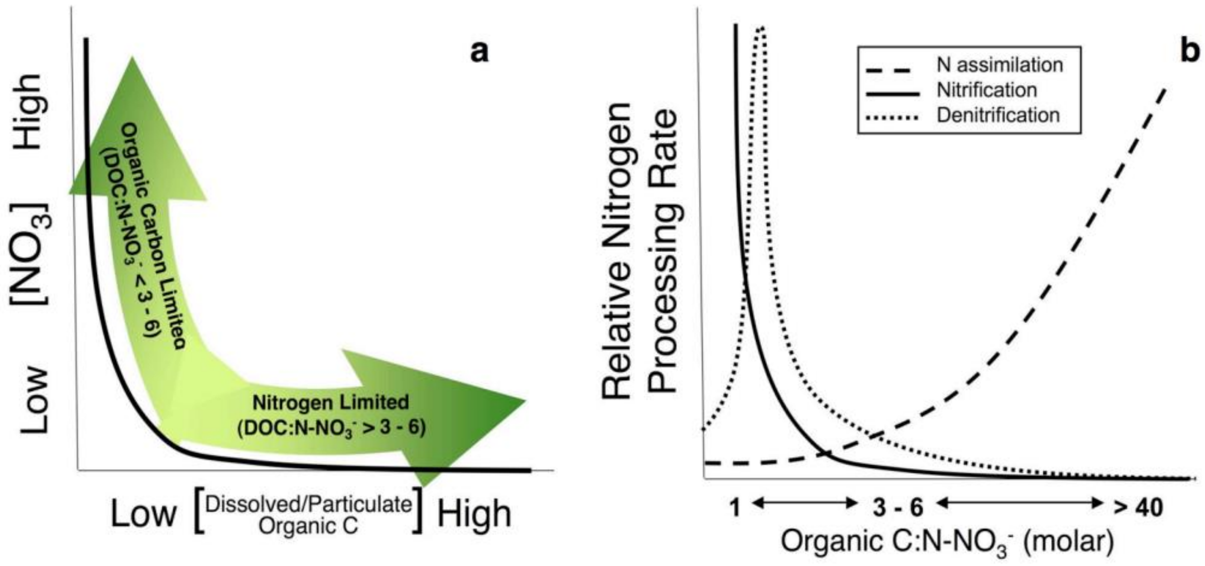

Figure 6. Conceptual schematic illustrating how changes in resource stoichiometry along inverse DOC- NO_3^- patterns alter microbial processes that couple the C and N cycles (Taylor et al., 2010).

In addition to the DOC: NO_3^- ratios that affect nitrogen transformation, there will also be a strong coupling between DON and DOC because both DOC and DON are organic compounds. The simplest definition of an organic compound contains a C, C-H, or C-C bond, which means that dissolved organic nitrogen (DON) is a subset of the N-containing dissolved organic carbon (DOC) pool. To discuss the coupling of DOC and DON, we must consider the lability of DON, meaning the uptake ability by the organism in the ecosystem. In this sense, the first fraction within the DON

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box likely includes the refractory components that persist in the environment for months to hundreds of years (Bronk, 2002). A second fraction of the pool can be described as semi-labile (Carlson and Ducklow, 1995). This fraction likely includes compounds such as proteins, dissolved combined amino acids (DCAA), and amino polysaccharides, which turnover on annual time scales. The third fraction is highly labile moieties, including urea, dissolved free amino acids (DFAA), and nucleic acids (Bronk, 2002). These labile forms uptake on timescales of minutes to days (Bronk et al., 1998).

Previous studies have shown that DON is a vital nitrogen source for phytoplankton (Fan & Glibert, 2005) and heterotrophic bacteria (Rosenstock & Simon 2001). However, it is unclear whether nitrogen-containing dissolved organic compounds are used for Nitrogen(N), carbon (C), or both. Peterson et al. (2004) showed that heterotrophic and nitrifying bacteria could absorb carbon from urea. For phytoplankton, results have been variable and sometimes conflicting, e.g., Fan & Glibert (2005) found urea to be a carbon source during dinoflagellate flowering, and Mulholland et al. (2004) concluded that urea is used for nitrogen during phytoplankton blooms. Mulholland et al. (2003) reported nitrogen was uptake preferentially over carbon in the DON along the estuarine gradient. To sum up, more observations are needed to determine natural communities' differential uptake of carbon and nitrogen in the DON.

Because dissolved organic matter (DOM) contains carbon and nitrogen, the mechanisms influencing their metabolism might be expected to be coupled. Strong correlations between dissolved organic carbon (DOC) and nitrogen (DON) in temperate and boreal streams have suggested that soil organic pools are an essential factor in controlling the fate and form of riverine DOM (Brookshire et al., 2007; Hedin et al., 1995; Perakis and Hedin, 2002). A growing number of studies report differences in DOC:DON ratios between allochthonous sources and stream water. For instance, Some studies showed that DOC: DON ratios in stream water were around 26, except

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during the months following drought when DOC: DON ratios ranged between 42 and 20 during baseflow and stormflow conditions, respectively (Bernal et al., 2005). The DOC:DON ratio decreased during the storm, indicating that the water flow path passed through organic-rich compartments that contained high-N-content organic matter, such as straight-through waterfalls or shallow subsurface riparian soils. However, humic organic matter is mainly composed of recalcitrant N with low C/N (below 10), which has been described in deep soils (depth of 50 cm or less) (Avila et al., 1995). Therefore, another plausible explanation for the low DOC:DON ratio might be the movement of soluble compounds from deep soils in riparian areas due to rising water tables (Bernal et al., 2018). In addition, stream biota can exhibit robust DOM processing (Bernhardt and McDowell, 2008), with whole-reach DOM uptake even higher than essential nutrients such as nitrate (Brookshire et al., 2005). Treatment of DOM in streams may lead to a decoupling between stream DOC and DON concentrations, as stream DOC is used as a carbon source for consumption, but when DIN and DOC are sufficient, DON can also be used as a nitrogen source for production (Figure 7.) (Kaushal & Lewis, 2005; Lutz et al., 2011; Wymore et al., 2015).

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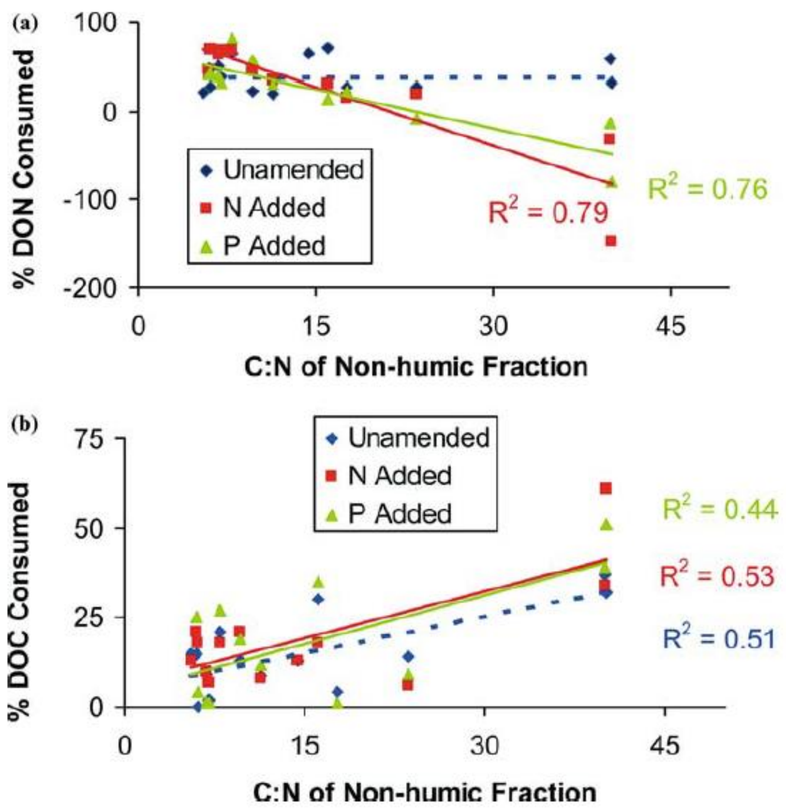

Figure 7. Relationship of the C:N ratio of non-humic fractions with % DOC (a) and % DON (b) consumed in incubations (Kaushal & Lewis, 2005). The percentage of DON consumed showed no significant relationship to the C:N ratio of the non-humic fraction in unamended incubations; it remained relatively high (ca. 50%) regardless of substrate quality. The percentage of DON consumed showed a negative relationship to the C:N ratio of the non-humic fraction, however, when inorganic N or P was added (**Figure 7.**a). In contrast, the percentage of DOC consumed showed a significant positive relationship to C:N ratio of the non-humic fraction and was unaffected by the addition of inorganic nutrients (**Figure 7.**b).

In this section, we could find that DON uptake or losses were affected by the coupling with DOC. However, the knowledge of the contribution of allochthonous vs. autochthonous sources to total stream DOC, DON, and its variability over time and space is far from complete. The work is

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needed for disentangling the different mechanisms underlying DOC and DON processing within the streams and understanding how environmental factors such as nutrient availability and water residence time drive in-stream DOM processing and changes in DOM quality during different hydrological conditions.

2.4 Hypotheses of riverine dissolved organic nitrogen losses

According to the previous chapters, we can find that the loss of DON is affected by the interaction between DIN and DOC, so it must be further clarified through the coupling of the three nutrients. In the past few decades, three hypotheses have been proposed to explain the loss of DON through the relationship between DON, DIN, and DOC. They are the Passive Carbon Vehicle Hypothesis, the Stoichiometric Enrichment Hypothesis, and the Carbon Indirect Control Hypothesis. We will discuss these hypotheses in this chapter.

In the past few thousand years, nitrogen limitation in most forests has been maintained due to low atmospheric nitrogen deposition (<4 kg ha^{-1} y^{-1}), resulting in an insufficient supply of biological nitrogen fixation (Holland et al., 1999). Under this condition, DON is the primary source of nitrogen nutrient loss in the ecosystem (Sollins and McCorision, 1981; Perakis and Hedin, 2002) and is produced by soil organic matter (SOM) like humus in the soil, making it essentially impossible for organisms and plants to use directly. These observations lead to the first hypothesis to explain DON losses from temperate forests, the Passive Carbon Vehicle Hypothesis. The hypothesis argues that the export of DON is largely biounavailable compounds leaching from slowly converted SOM by the strict stoichiometry with dissolved organic carbon (Hedin et al., 1995; Rastetter et al., 2005). Therefore, DON losses remain stable simply because dissolved organic matter (DOM) export is dominated by refractory compounds whose production is not directly tied

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to nitrogen cycling. The observed correlation between DOC and DON fluxes in soil and stream waters (Perakis and Hedin 2002) supports this hypothesis.

However, more and more watersheds have observed different DON losses from the carbon passive vehicle hypothesis. For example, some studies have shown an increase in the organic nitrogen in the soil solution (Aber et al., 1989; Gundersen et al., 1998; McDowell et al., 2004; Pregitzer et al., 2004). In addition, some studies have observed a decrease in DOC : DON in river water, indicating that the DOM leached from the soil may not be as stoichiometrically fixed as predicted by the Passive Carbon Vehicle Hypothesis (Figure 8.) (Brookshire et al., 2007). Therefore, the second DON losses hypothesis was proposed, called the Nitrogen Stoichiometric Enrichment Hypothesis or the DON release hypothesis (Brookshire et al., 2007; Lutz et al., 2011). DON is currently considered the stoichiometric enrichment of DOM in this hypothesis. It can happen in two main ways. The first is affected by stoichiometric changes in the exogenous SOM (observed under nitrogen deposition) (Aber et al., 1989; Gundersen et al., 1998; McDowell et al., 2004; Pregitzer et al., 2004), which means that the DOM leached from the soil pond is directly transported to the river. The second is the direct enrichment of N by the DOM in the river. In the case of the second hypothesis, the C:N of the river DOM ratio will be lower than SOM, and the output of DON is mainly positively correlated with DIN but has nothing to do with DOC (Brookshire et al., 2007; Lutz et al., 2011).

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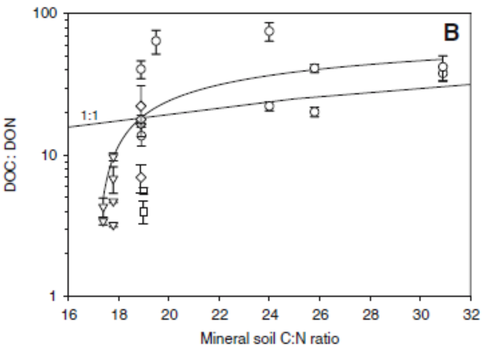

Figure 8. The relationship between soil and river water CN ratio (Brookshire et al., 2007). The Y-axis is the river water DOC:DON ratio, and the X-axis is the soil C:N ratio. The 1:1 straight line refers to the value when the soil CN ratio is the same as the river water CN ratio. The equation for the relationship between soil and river water CN ratio is y = 11.06 + 13.54 x ln (x – 16.93); r^2 = 0.52, P = 0.0184.

Compared with the Passive Carbon Vehicle Hypothesis and Nitrogen Stoichiometric Enrichment Hypothesis, there is currently a third hypothesis of DON output behavior proposed, the Carbon Indirect Control Hypothesis (Figure 9.). Lutz et al. (2011) observed that the relationship between DON and DIN concentrate showed a negative linear relationship in the stream, which differed from the previous two hypotheses. Therefore, they did an incubation experiment, and founding DON will show a significant consumption trend when there is carbon limitation (Lutz et al., 2011). According to the foundation, Lutz proposes the Carbon Indirect Control Hypothesis, which considers that under limited carbon, organisms and plants will tend to use DON instead of DOC as a carbon source for the consumption of organic matter.

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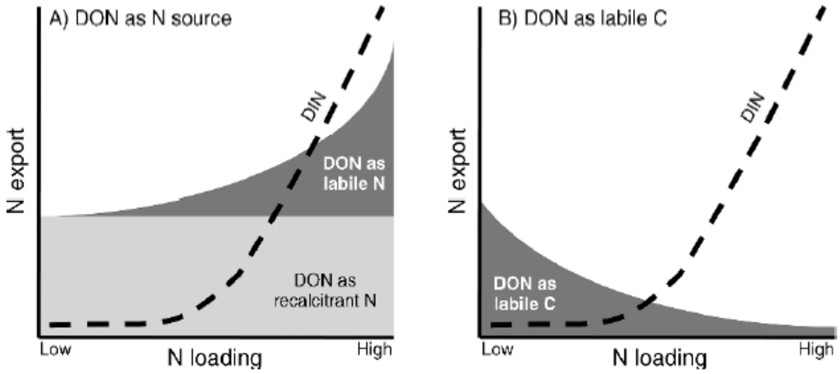

Figure 9. DON release hypothesis and carbon indirect control hypothesis (Lutz et al., 2011). (A) DON release hypothesis. This hypothesis believes that DON is composed of humus (unavailable to organisms) and bioavailable parts. When nitrogen deposition decreases, the basin tends to use DON as the main source of output. When nitrogen deposition is high, When both the DIN input and the DON input exceed the biological requirements, both DON and DN will be enriched in a large amount at this time. (B) The hypothesis of indirect carbon control. When the watershed presents carbon limitation, DON is used as a source of biologically-replaced organic matter, showing a coupling relationship with DOC.

In summary, the three hypotheses discuss the DON export with the relationship between DON, DOC, and DIN in rivers (Figure 10.; Hedin et al., 1995; Rastetter et al., 2005; Brookshire et al., 2007; Lutz et al., 2011). The pattern in which DON and DIN have no relationship is called the Passive Carbon Vehicle Hypothesis. The positively correlated pattern is called the Stoichiometric Enrichment Hypothesis. The negative correlation is called the Carbon Indirect Control Hypothesis. However, different studies found these patterns in several couplings with carbon. In the pattern investigation of the Passive Carbon Vehicle Hypothesis, previous studies mentioned that DOC and DON are positively correlated (Hedin et al., 1995; Rastetter et al., 2005; Brookshire et al., 2007).

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However, from the nutrient addition experiment in southeastern New Hampshire, different patterns were seen in the relationship between DOC and DON or CN and DIN (Wymore et al., 2015).

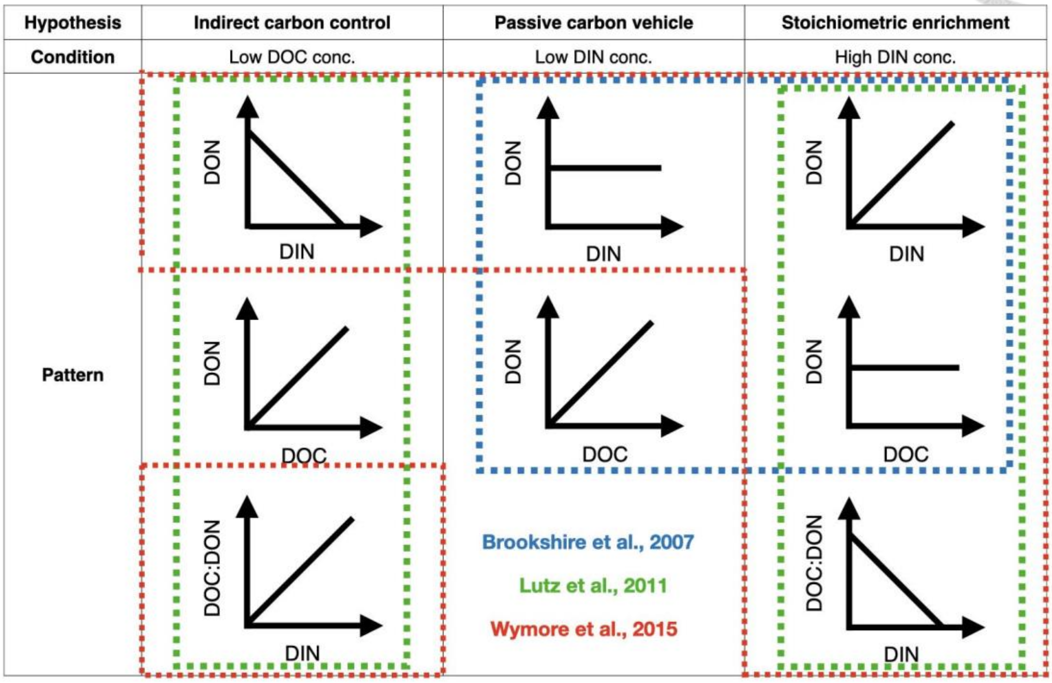

Figure 10. The pattern of DON losses. Each color frame presented the three studies. The blue frame investigated the relationship between DON and DIN and the relationship between DON and DOC in the river, respectively (Brookshire et al., 2007). The other two studies investigated the relationship between DON and DIN, DON and DOC, and the relationship between Carbon-nitrogen and DIN in the river (Lutz et al., 2011; Wymore et al., 2015).

The DON in stream water is a mixture of inputs of terrestrial surface DOM, the leaching of DON from the subsurface, and the production of DON by stream biota. How these sources of DON in stream water change seasonally or respond to storm events is mainly unknown (Lutz et al., 2011). Much of our current knowledge about watershed DON export is derived from single synoptic surveys, with very few long-term research sites monitoring DON regularly or under high N-loading

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conditions (Pellerin et al., 2006). Previous studies demonstrate that patterns of DON export across landscapes may change significantly over seasons and storm hydrographs (Lutz et al., 2011; Wymore et al., 2015). Therefore, this study conducted different seasonal periodic and extreme event-intensive nutrient observations supportive with other reservoirs (stream water, rainwater, falling water, soil water, groundwater) in the Fushan watershed to discuss the export and interaction of the nutrient coupling.

2.5 Fushan Experimental Forest (FEF)

Fushan Experimental Forest (FEF) is Taiwan's first long-term ecological research site, established in 1992. This site has accumulated many studies associated with forest structure and dynamics, water chemistry, sediment transport, and erosion, as well as a biogeochemical cycle (precipitation, throughfall, soil water, and streamwater) over the past few decades (e.g., Lin, 1994; Owen et al., 2010; Lu et al., 2017; Chi et al., 2015; Lin, 1994; West et al., 2011; Lin et al., 2003). Therefore, we consider FEF is a suitable area for experimenting further to understand the hypotheses of DON losses in our study. In this section, we will review the previous studies, especially about the nitrogen, carbon-nitrogen coupling, or typhoon disturbance in the Fushan Experimental Forest (FEF).

The estimated pool size of the total soil nitrogen in FEF was 6909 ± 81 kg-N ha^{-1} (Owen et al., 2010). For inorganic nitrogen, the pool size is much smaller: about 1 ± 3 kg-N ha^{-1} for NO_3-N in the organic layer (2-0 cm) and 0.6 ± 2 kg-N ha^{-1} for NH_4-N. In mineral soils (0-30 cm depth), the NO_3-N pool was calculated to be 1.7 ± 4.1 kg-N ha^{-1} and NH_4-N to be 2.8 ± 9.3 kg-N ha^{-1}. For organic nitrogen, it is estimated that approximately 682 ± 74 kg-N ha-1 in the organic layer and 6227 ± 311 kg-N ha^{-1} are stored in the mineral layer. The carbon-nitrogen ratio decreases from the organic layer at around 12.9 to the mineral soil at around 10.7(Owen et al., 2010).

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In the terrestrial N cycling processes (Figure 11.), the N fixation rate was low at FEF, which estimated a 247 ±18 kg-N ha^{-2} yr^{-1} (Lu et al., 2017). On the other hand, the annual nitrification rate echoed mineralization, ~1748 kg-N ha^{-2} yr^{-1} at FEF, implying high microbial activities. The nitrification and mineralization processes are controlled mainly by temperature and soil water content, are most active in topsoils, and decrease with soil depth. In order of descending importance, plant uptake, riverine N transport, and denitrification were the three main processes responsible for N removal at FEF. In the study, Lu (2017) suggested that FEF may be in advanced stages of N excess because of the high riverine DIN flux to atmospheric N deposition ratio, 0.45, implying a high N deposition environment.

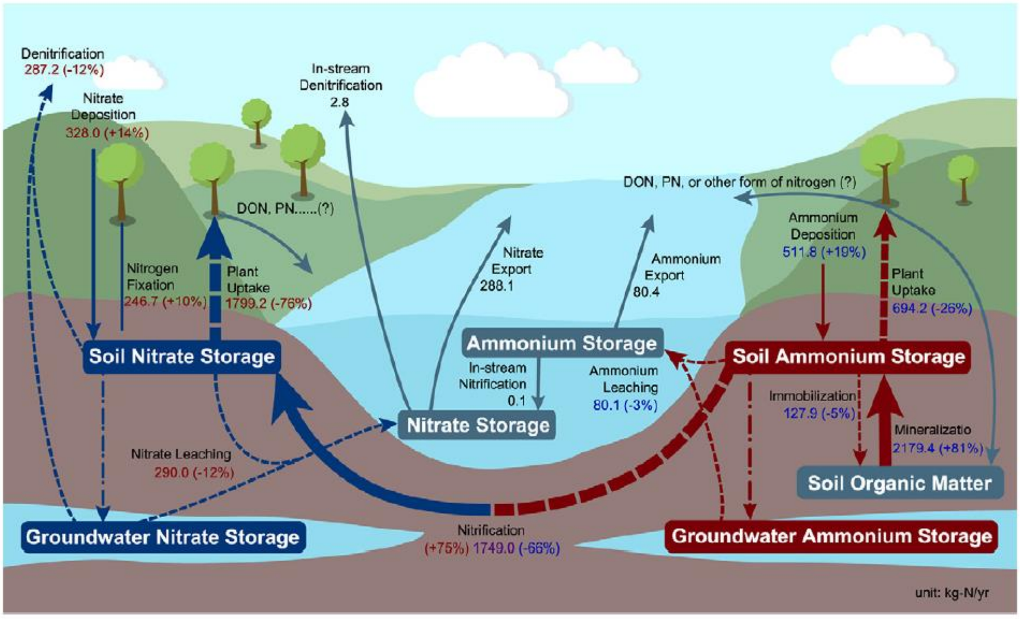

Figure 11. The N cycling at FEF (Lu et al., 2017). The unit is kg-N yr^{-1} at this 38-ha site.

FEFs have low biomass (200-290 ton ha-1) compared to many tropical humid forests, which typically have a biomass of 400 ton ha^{-1} (Lin, 1994), and the biomass showed a CN ratio of around 25 (Jian et al., 2013). The low biomass is attributed to frequent typhoon disturbances, which

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transfer large amounts of biomass (such as litter and wood debris) to downstream systems (Chi et al., 2015; Lin, 1994; West et al., 2011). Annual litter in FEFs varied from 3.0 to 11.0 Mg ha^{-1} yr^{-1}; in years with multiple typhoons, typhoon-ravaged litter may account for N50% of total annual litter production (Lin et al., 2003). Typhoon-induced litter contributes to soil DON and increases N output through streams. However, so far, particulate nitrogen (PN) and dissolved organic nitrogen (DON) carried away by typhoon storms have not been included in the study. Therefore, incorporating the transport of DON into the discussion can improve our understanding of the N cycle in regions where tropical cyclones frequently disturb regions.

In conclusion, combining the above advantages of testing hypotheses at FEF, we will collect weekly and typhoon events samples, such as rainwater, stream water, groundwater, and soil water. The results will discuss the relationship between DON losses and CN coupling and how the different flow regimes affect nutrient transport in subtropical mountain watersheds.

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3 Material and methods

3.1 Study site

The experimental watershed 1 (WS1; 38 hectares) of the Fushan Experimental Forest (FEF) is the upstream catchment of Harpen Creek (Figure 12.). The elevation of WS1 varied from 660 to 1027 m, and the slope varied from 40% to 90% (Chang et al., 2002). From 1993 to 2013, the annual average temperature was 18.2℃ (11.7℃ in January and 24.1℃ in July), and the average annual precipitation was 4240 mm, two-thirds of which were mainly affected by the typhoon in the summer (June to November) (Lin et al. People, 2011). There is no observable dry season due to frequent rainfall (>220 days per year) and high humidity (95%) (Lin et al., 2011). Common tree species for FEF include *Machilus thunbergii*, *Engelhardtia roxburghiana*, *Castanopsis carlesii var. sessilis*, *Ma-chilus zuihoensis*, and *Litsea acuminate*; common shrub species are *Cyathea podophylla*, and *Blast cochinchinensis* and the ground vegetation is dominated by *Diplazium dilatatum* (Lin, 1996). The biomass of FEF is between 200 and 290 Mg ha-1, of which 75 - 94% was contributed by trees (Lin, 1994). The forest's soil (Typic Dystrochrepts) is thin and rough in texture, with few plant roots found at depths above 60 cm (Liu et al., 2008). Soils are very acidic (pH 3.8 - 5.0) with low bulk density (0.5 - 0.8 Mg m^{-3}) and very low base saturation (2 - 5 %) (Horng, 1996).

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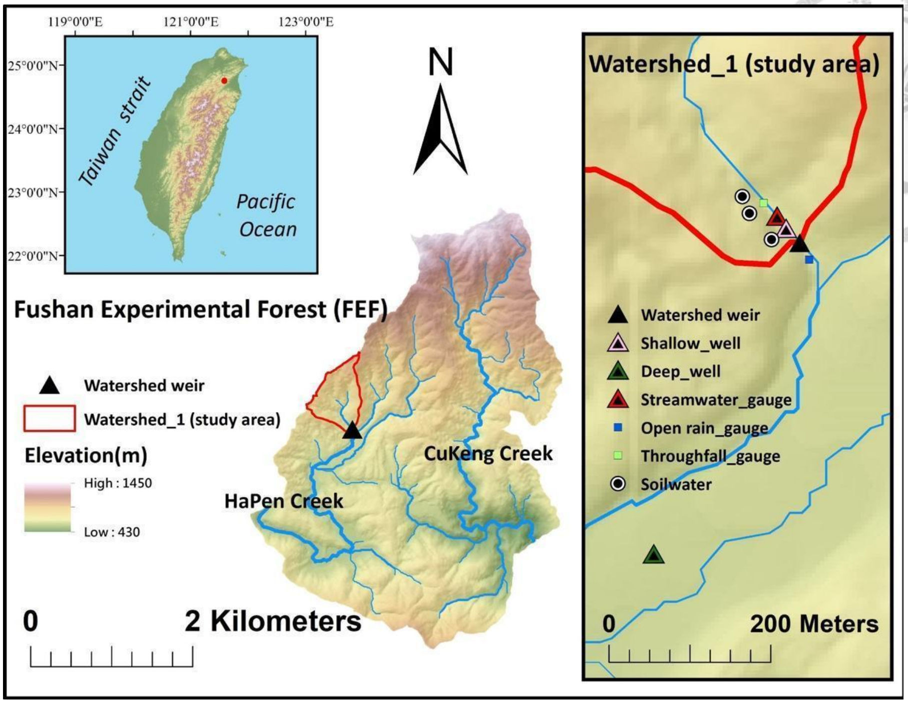

Figure 12. Location of Fushan experimental forest (FEF), Taiwan. The stream network and boundary of FEF, left panel, and the experimental watershed (WS1), right panel. The black circles are the location of the soil water samplers. The pink and green triangles represent the groundwater. The black triangle is the location of the streamflow station.

3.2 Field sampling methods

3.2.1 Regular sampling

We sampled the stream water, soil water, groundwater, and rainwater weekly during the sampling campaign from 2016 to 2022. We collected the stream water sample directly in 1-L low-density polyethylene (LDPE) bottles. The sample was divided into two sub-samples. The first one was used to measure temperature, conductivity, and pH value by PC 450 Waterproof Portable Meter *in situ*. A 0.45 uM filter filtered the other sample, and the filtrate was preserved in an icebox for transportation and further lab analysis. Three soil water sampling sites with depths of 10 cm, 30 cm,

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and 50 cm were installed by tensiometers for collecting soil water for soil water samples. The capacity of each water pipe is a total of 120 ml. We sampled the water and then pumped it with negative pressure (60 hPa) in the pipe to let it collect the soil water during the next week's sampling period. For the groundwater, there are two wells with depths of 7-meter (deep well) and 3-meter-deep wells (shallow well) at 300 meters and 30 meters from the water weir, respectively. We washed the well 30 times with Baylor tubes and then collected a water sample of 500ml and filtered it using the same procedure mentioned above. The groundwater's water temperature and depth will be recorded in the log and manually taken to the computer every month. An automatic rainwater sampler is set 10 meters next to the water weir for collecting rainwater samples. Twenty-four 60ml glass bottles were mounted on a turntable which would rotate to the next bottle incrementally every 12 hours. We mixed every two samples into one day's samples in each survey. After collecting the samples, we sent samples to the laboratory by a three-hour drive. After samples were filtered through GF/F filters (0.45 um), 35 ml of the samples were transferred into 40 ml glass bottles for the DOC (dissolved organic carbon) measurement. It is important to note that the glass bottles were baked at 450 degrees for three hours before removing the carbon in all glass bottles. Moreover, 12 ml of the samples were transferred into two 15 ml polypropylene centrifuge tubes for TDN (total dissolved nitrogen) and DIN (dissolved inorganic nitrogen) samples. 2ml of 85% phosphoric acid was injected into the DOC (dissolved organic carbon) samples and TDN (total dissolved nitrogen) samples for storage. All the filtrates distributed to each glass bottle or centrifuge tube were preserved for water chemistry analyses in a refrigerator.

3.2.2 Event sampling

We collected the sample at three typhoon events in September 2016 and one typhoon event in July 2021. In September 2016, three typhoons disturbed Taiwan. A high-frequency (2-3 hours)

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scheme was applied during this period for collecting the stream water for three typhoons, Meranti, Malakas, and Megi, by automatic stream water sampler. All water samples were collected by 1-L low-density polyethylene (LDPE) bottles. The bottle was used to measure the water temperature, pH, electronic conductivity (EC) by PC-450 in situ and filtered through GF/F filters (0.45 um). The filtrates were preserved in a refrigerator for water chemistry analyses. In July 2021, we collected the stream, soil, groundwater, and rainwater during the typhoon In-fa disturbed Taiwan. We collected the sample for a high frequency (2-3 hours) by the automatic stream water sampler for stream water. For the soil water, we collected the samples every six hours. We pumped the negative pressure (60 hPa) to the soil water pipe for collecting soil water. We washed the well 30 times with Baylor tubes and collected 500ml of water every six hours for the groundwater. We collected the samples every half an hour for the rainwater by the automatic rainwater sampler. All samples would be filtered and aliquoted into 40 ml glass bottles for the DOC (dissolved organic carbon) and two 15 ml polypropylene centrifuge tubes for TDN (total dissolved nitrogen) and DIN (dissolved inorganic nitrogen) samples. After we injected the acid into the DOC and TDN samples, the samples were stored in the refrigerator. After the typhoon event, we were sent the samples back to the laboratory refrigerator for storage.

3.3 Chemical analyses

3.3.1 Anions analysis - Ion chromatography (IC)

For all water samples prepared for DIN analysis, we filtered them with Whatman glass fiber filters GF/F (0.7um) in situ. Then, we transferred them into the 15 ml polypropylene centrifuge tubes stored in the ice refrigerator at -7℃. In the DIN are the anions such as the NO_2^-, NO_3^-, and the cations such as NH4+, respectively. Ion chromatograph Metrohm(R) Basic-883 plus a Metrohm A5 column with a detection limit of 0.01 mg-N L^{-1} is used to analyze the concentration of anions, and

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Ion chromatograph ICS-1100 with a detection limit of 0.01 mg-N L^{-1} is used to analyze the concentration of cations. These two instruments integrated an ion chromatography system containing a pump, injection valve, and conductivity detector. Other system components, including a guard column, separator column, and suppressor, vary depending on the analyses performed. In the detection, IC (ion chromatography) consists of stationary and mobile phases; in the stationary phase, the substance stays fixed inside the column. In the mobile phase, the solvent moves through the column. Different components of the anion samples exhibit varying degrees of adhesion to the anions; thus, the travel time is additional. When the members adhere firmly, they spend more time in the stationary phase and vice versa. Hence, the conductivity fluctuates to the diverse arrival time. By comparing the difference in the arrival time, the conductivity detector estimates the concentration of each anion and cation.

3.3.2 TDN analysis

We collected the sample and filtered them in situ with Whatman glass fiber filters GF/F (0.7um). Then, we injected the 12ml sample and the 2 ml 85% phosphoric acid into the 15 ml polypropylene centrifuge tubes stored in the ice refrigerator at -7℃. The Formacs ^***HT*** TN Analyzer & ND25 Nitrogen Detector with a detection limit of 0.01 mg-N L^{-1} was used to determine the total dissolved N (TDN) by high-temperature potassium persulfate oxidation. The sample is injected into the high-temperature furnace in the instrument, where it is catalytically combusted at 850℃. Oxidative pyrolysis causes the chemically bound nitrogen to be converted to nitric oxide (NO). NO is reacted with ozone (O_3) to form metastable nitrogen dioxide (NO_2). The photons emitted from the rapid decay of the NO_2, in the 590-2900 nanometer range, are detected by a photomultiplier tube. The DON value is determined in two steps, i.e., the analysis of TDN, which the ND25 Nitrogen Detector determines, and the analysis of NO_3-N and NH_4-N via an Ion chromatography instrument. The DON value is obtained by subtraction: DON = TDN – (NO_3-N + NH_4-N).

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3.3.3 DOC analysis

Before analyzing, We collected the samples in amber glass vials with Teflon-lined caps. First, the glass bottle must be soaked in acid and repeatedly washed with reagent water. After being wrapped with aluminum foil, we placed the glass in a 450℃ oven for heating for at least 3 hours. Next, the Teflon lining is washed with detergent and then repeatedly washed with reagent water, wrapped with aluminum foil, and heated in an oven at 45℃ for 3 hours. Suppose the collected sample cannot be analyzed immediately. In that case, phosphoric acid should be added to the sample to make the pH value less than or equal to 2, and it can be stored at 4±2℃ for 14 days. Because the water sample contains large particles or insoluble substances, we need to filter the water sample with a 0.45 μM pore size filter.

The Model 1030W/1088 Total Carbon Analyzer has been used to analyze DOC with a detection limit range from 10 ppb to 30,000 ppm. After the treated water sample is introduced into the reaction chamber to react with concentrated phosphoric acid, the inorganic carbon in the sample is converted into carbon dioxide. After blowing air to discharge it, sodium persulfate solution is added to the residual water sample to oxidize the organic carbon into carbon dioxide. Then the carrier gas is introduced into the non-dispersive infrared analyzer to detect the water—the total organic carbon concentration in the sample. In the standard line, We prepare at least five concentrations (excluding blanks) of organic carbon standard line depending on the concentration range of the water sample. Use the signal obtained from the reaction between the calibration line standard solution and the instrument. Then plot the standard product's organic carbon content (mg C/L) to draw the calibration line. The calibration line should be re-created before each sample analysis. Its linear correlation coefficient Should be greater than or equal to 0.995. The relative error value of calibration line confirmation should be within ± 15%. A calibration line check is performed at the end of every ten samples or each analysis batch.

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3.4 Discharge data collection and analysis

3.4.1 Observational data collection and processing

We measure the discharge with the weir in the Fushan experimental watershed (WS1). First, the discharge is converted from the water level (Eq.1 & Eq. 2), which the sensor records under the mouth in the weir. The weir in Fushan is constructed in a compound weir considering the significant difference between high and low discharge. Therefore, a more petite triangular mouth is opened at the bottom weir, and an enormous rectangular mouth is opened at the top. When the water level does not exceed 0.6 meters, the flow rate is based on the record of the triangular weir; if the water level exceeds 0.6 meters, the water level record of the rectangular weir is used as the basis for flow conversion.

$$Q = 1.3794\, h^{2.5}, (Eq. 1)$$

$$Q = 1.837\, (bc - 0.2h)\, h^{1.5}, (Eq. 2)$$

Equation 1 is the discharge conversion formula of the triangular weir, and Equation 2 is the rectangular weir. Q is the discharge in which the unit is cms. H is the height of the water level in meters. Bc is the depth of the rectangular weir, which is 4.996 meters. Sometimes in rectangular or triangular weirs, the water level data may not be received, or there will be some errors because of the moves due to external force interference. Therefore, we filled in the missing water level data according to the relationship between the two water level data from rectangular and triangular weirs (Figure 13.).

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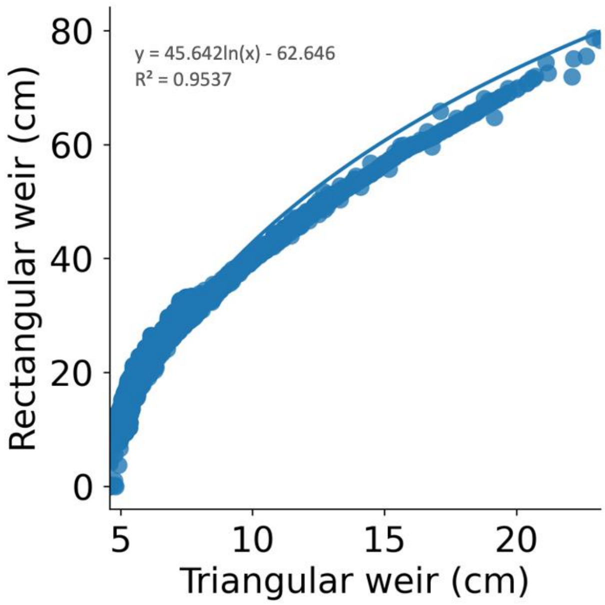

Figure 13. The relationship between the two water level data from rectangular and triangular weirs.

3.4.2 HBV simulation

The sensors in rectangular weirs and triangular weirs collected water level data every ten minutes, but in 2016 the silting in the weirs was so severe that the data could not be used until the silt was cleared. Therefore, we simulated the discharge in the stream by the HBV model of that year. We use the TUW model, which version is 1.1-1(Parajka et al., 2007), a lumped conceptual rainfall-runoff model, following the structure of the HBV model in the R package. The model treats the catchment as two reservoirs (S1 and S2) connected by a percolation flow. Inflow to the first reservoir is calculated as surface runoff, which is left over from initial precipitation after calculating infiltration and evapotranspiration. The outflow from the first reservoir is split into two separate flows (Q1 and Q2), where Q1 represents the fast flow triggered after some user-defined threshold L, and Q2 is the intermediate flow. The constant K1 is used to find the outflow as a stored function in S1. The constant Kd accounts for permeability as long as the storage is S1. The outflow from the

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second reservoir is considered a function of groundwater flow (Q3) with constant K2 and storage in S2. The total flow from a rainfall event is the sum of the three flows. The results of the model are compared with the actual measured flow values.

For good model calibration, we use the Monte-Carlo simulation to properly define the parameters and the uncertainty, showing the model's max nash value (Figure 14.). The NSE coefficients range from -∞ to 1, where 1 indicates a perfect simulation, i.e., absolute equality between the observed and simulated flows.

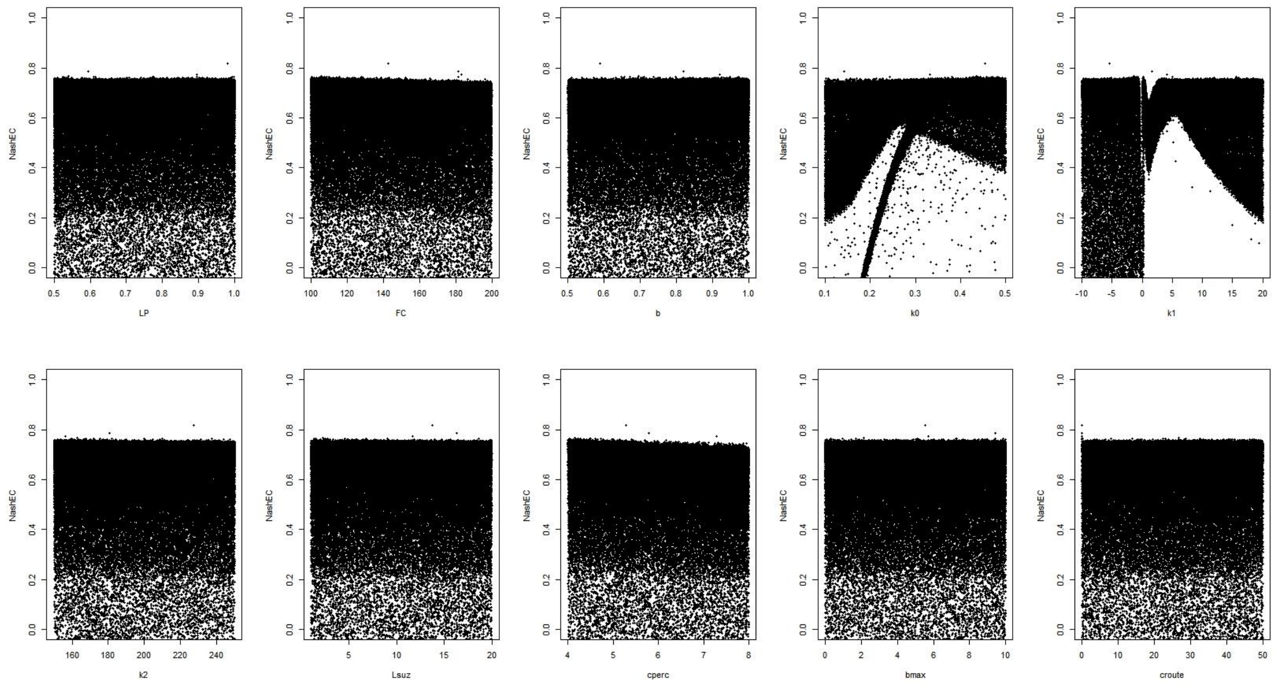

Figure 14. NSE formulas in parameters. We used the ten parameters to simulate the runoff, such as the LPrat parameter related to the limit for potential evaporation, FC field capacity (max soil moisture storage), BETA, the non-linear parameter for runoff production, k0 storage coefficient for very fast response, k1 storage coefficient for fast response, k2 storage coefficient for the slow response, lsuz threshold storage state (the very fast response start if exceeded), cperc constant percolation rate, bmax maximum base at low flows, and croute free scaling parameter.

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3.4.3 Probability of exceedance

To discuss the relationship between flow regimes and the patterns of nutrient export, we use the concept of probability of exceedance. The probability of exceedance is a statistical metric describing the probability that a particular value will be met or exceeded (Eq.3). We use the hourly-scale runoff for calculation and sort the hourly-scale runoff data from 2016 to 2021 according to size. In this equation, (P) represents the percent (%) probability that a given flow will be equaled or exceeded; (m) represents the rank of the inflow value, with 1 being the largest value. Finally, the (N) represents the record's total number of events or data points.

$$Pexd = \frac{m}{N+1}, (Eq. 3)$$

To make the rainfall and runoff comparable, we changed the runoff unit to mm per hour, as shown in Figure 15. In addition, to further discuss the influence of flow conditions on nutrient export, we divided runoff into three sections. According to the definition of the Central Weather Bureau, we divided runoff less than 20mm/hr as low flow conditions (blue line), and which probability of exceeding is between 99% and 13%. The runoff between 20mm/hr and 40mm/hr is defined as high flow conditions (black line), with a probability of exceeding 13%~3%. Finally, the runoff larger than 40mm/hr is defined as rainstorm events (orange line), with less than a 3% probability of exceeding.

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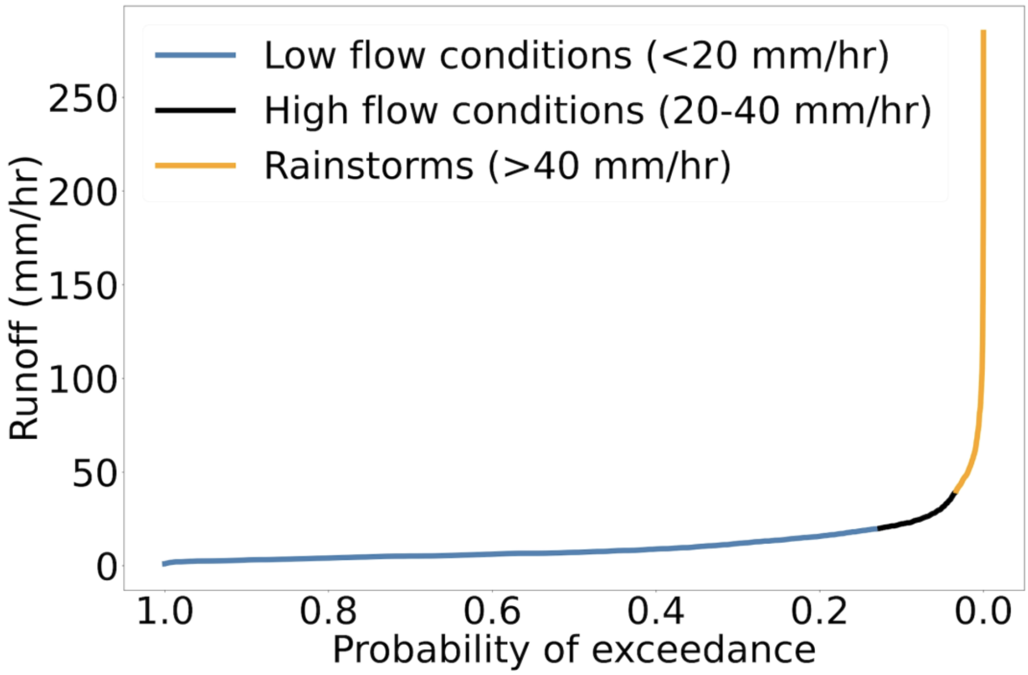

Figure 15. Probability of exceedance. The blue line represents low flow conditions which mean runoff less than 20 mm/hr, the black line represents high flow conditions which mean runoff between 20 mm/hr and 40 mm/hr, and the yellow line represents rainstorms which mean runoff larger than 40 mm/hr.

3.4.4 Flux and yield calculation

The flux can be obtained by multiplying the collected concentration and runoff and dividing it with the catchment area to get the yield. However, nutrient flux estimates have much uncertainty. First, runoff is often derived from stage measurements and rating curves developed for individual sites (ISO 1100-2, 2010). However, this approach relies on the existence of a temporally stable relationship between stage and runoff. Many studies discussed the uncertainty of rating curves and attempted to quantify the impact on estimated runoff (Di Baldassarre and Montanari, 2009; McMillan et al., 2010; Jalbert et al., 2011; Westerberg et al. et al., 2011; Birgand et al., 2013; Juston et al., 2014). Second, the most significant source of uncertainty is the extrapolation of rating curves beyond the lowest or highest stage runoff measurements (Montanari, 2009). Suppose the period of

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hydrological interest is an extremely low or high flow, especially for the latter when the flow becomes offshore. These periods are significant for nutrient-related water quality studies because sediment-related nutrients are transported into and within streams during peak flow events.

In order to solve the above two uncertainty, we will divide the flux algorithm into two types: rainstorms and normal flow regimes. We definite the runoff larger than 40mm/hr is rainstorms, and lower than 40mm/hr is normal flow regimes. Then, we multiply the known concentration by the runoff of the hourly scale to get the flux. The linear relationship of flux (Figure 16. (A)-(C)) is the relationship between flow and flux during the typhoon and non-typhoon periods. Then we used this linear formula to obtain other hourly runoff without sample concentration data to obtain hourly-scale flux. Finally, we added them together to get the annual-scale flux and yield. During the 2016-2021 typhoon period, we mainly defined which flow periods were the flow during a typhoon by comparing the typhoon warning issued by the Central Meteorological Administration and the peak flow data.

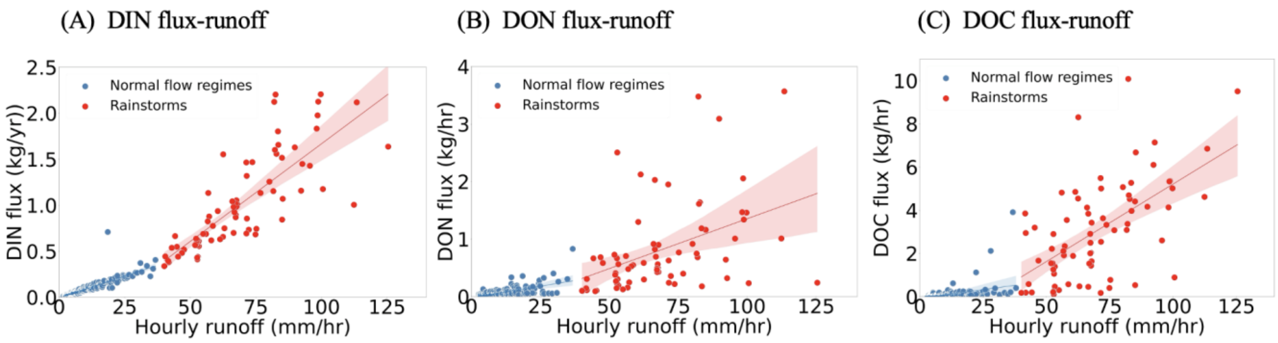

Figure 16. The flux-Q relationship between the normal flow regime and rainstorms in the WS1 (watershed 1) of the Fushan Experimental Forest (FEF) catchment. (A) Relationship between dissolved inorganic nitrogen (DIN) flux (kg-N hr^{-1}) and hourly runoff (mm hr^{-1}). (B) Relationship between dissolved organic nitrogen (DON) flux (kg-N hr^{-1}) and hourly runoff (mm hr^{-1}). (C) Relationship between dissolved organic carbon (DOC) flux (kg-C hr^{-1}) and hourly runoff (mm hr^{-1}).

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4 Results

4.1 Nutrient concentrations and yields

To investigate DON export derived from long-term surveys, we collected the samples from Sept. 2016 to Dec. 2021. The chronosequence of rainfall, air temperature, runoff, and nutrient concentrations at the Fushan Experimental Forest (FEF) is shown in Figure 17. The annual rainfall in the catchment is 3745 ± 22 mm, and the runoff is 3099 ±11mm (Table 1.). Overall, the FEF is humid, and the relative humidity is always higher than 90%. The frequent rainfall quickly responds to the runoff. The mean annual temperature is stable at around 18.33 ℃, and the apparent daily and seasonal temperature variations can be found. The annual carbon-nitrogen ratio has a low CN ratio of about 0.88 at FEF.

Table 1. Mean annual riverine nutrient concentrations and the environmental metrics of each year in the WS1 (watershed 1) of the Fushan Experimental Forest (FEF) catchment. *Mean value ± one standard deviation.

year	Rainfall (mm)	Annual runoff (mm)	Mean annual Temp. (°C)	NO_3-N conc. (mg-N L^{-1})	DON conc. (mg-N L^{-1})	DOC conc. (mg-C L^{-1})	DOC:DON (molar ratio)
2017	4296 ± 27	3724 ± 17	18.14 ± 5.31	0.63 ± 0.11	0.21 ± 0.11	0.27 ± 0.16	1.1
2018	3614 ± 18	3149 ± 7	18.15 ± 4.98	0.47 ± 0.07	0.58 ± 0.16	0.21 ± 0.14	0.31
2019	3769 ± 22	3299 ± 10	18.37 ± 4.48	0.56 ± 0.27	0.29 ± 0.42	0.37 ± 0.4	1.09
2020	3888 ± 22	2869 ± 11	18.44 ± 4.85	0.54 ± 0.08	0.19 ± 0.13	0.39 ± 0.58	1.76
2021	3158 ± 20	2452 ± 8	18.54 ± 5.05	0.47 ± 0.07	0.15 ± 0.08	0.36 ± 0.29	2.05
Average	3745 ± 22	3099 ± 11	18.33 ± 4.93	0.54 ± 0.15	0.31 ± 0.29	0.32 ± 0.36	0.88

In the DIN concentration, except for the mean riverine nitrogen concentrations of nitrate (NO_3-N), which was 0.54 ± 0.15 mg-N L^{-1}, the other anions (NO_2-N) or cations (NH_4-N) were lower than those detected by the detection limit. In the DON concentration, the mean concentration

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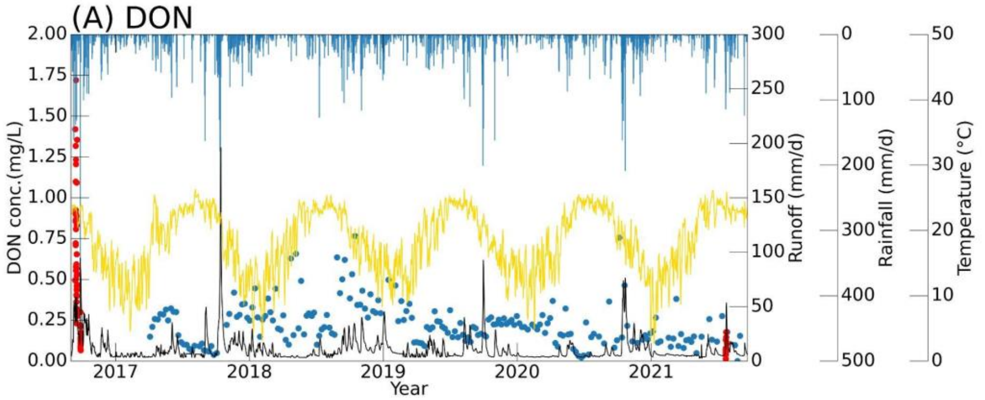
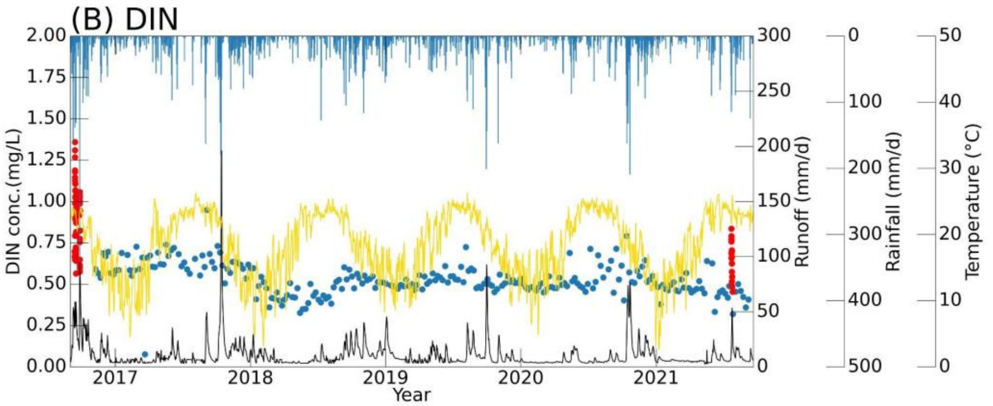
of dissolved organic nitrogen (DON) was 0.31 ± 0.29 mg-N L^{-1}, and the concentration of DON accounted for 57% of the total nitrogen. There were no apparent regular variations in the chronosequence of DON concentration. In contrast, DIN concentration showed apparent regular variations in the chronosequence.





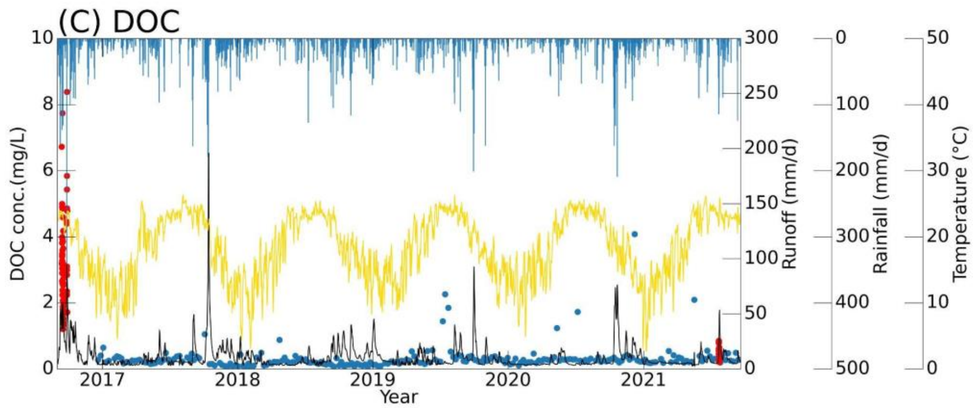


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Figure 17. The runoff, air temperature, and riverine nutrient concentrations in the WS1 (watershed 1) of Fushan Experimental Forest (FEF) catchment during Sept. 2016-Dec. 2021. (A) Dissolved organic nitrogen (DON) concentration during Sept. 2016-Dec. 2021, (B) dissolved inorganic nitrogen (DIN) concentration during Sept. 2016-Dec. 2021, and (C) dissolved organic carbon (DOC) concentration during Sept. 2016-Dec. 2021. The red and blue dots represent the observed riverine nutrient concentrations during typhoon and non-typhoon periods (corresponding to the left y-axis). The blue, black, and yellow lines indicate the rainfall, runoff, and temperature (corresponding to right y-axes).

The dissolved organic carbon (DOC) concentration was 0.32 ± 0.31 mg-C L^{-1}. It is particularly noteworthy that the standard deviation of the mean DOC concentration was substantial, and the DOC concentrations were deficient (<1.0 mg L^{-1}) under a normal flow regime (Table 1.). The red dots represent the nutrient concentration obtained through our intensive sampling during the typhoon. It can be seen that when the rainfall and runoff are large enough, whether it is dissolved organic nitrogen (DON), dissolved inorganic nitrogen (DIN), or DOC, the concentrations will increase significantly during the typhoon.

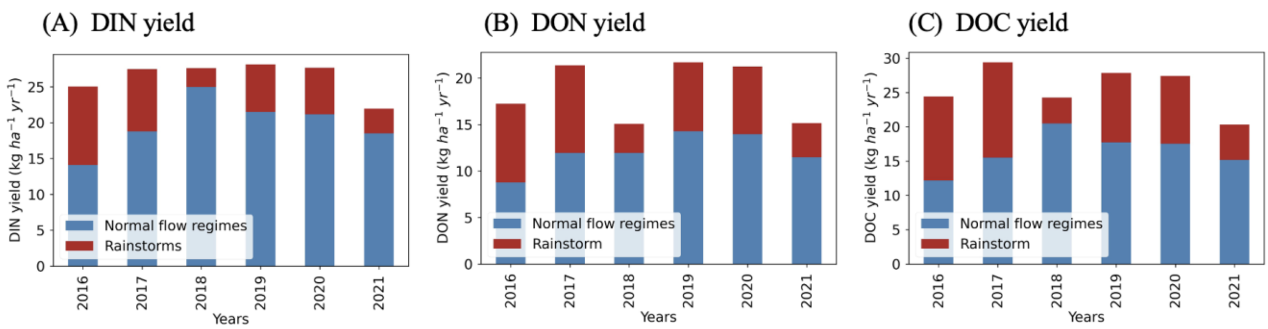

Figure 18. Nutrient yields between the normal flow regime and rainstorms in the WS1 (watershed 1) of the Fushan Experimental Forest (FEF) catchment. (A) Riverine DIN annual yield (kg-N ha^{-1}

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year^{-1}). (B) Riverine DON annual yield (kg-N ha^{-1} year^{-1}). (C) Riverine DOC annual yield (kg-C ha^{-1} year^{-1}).

In the Fushan Experimental Forest (FEF), the runoff from rainstorm events accounts for about 17% of the total runoff. The mean annual dissolved organic nitrogen (DON) yield was 18.96±1.63 kg-N ha^{-1} yr^{-1}, the mean annual yield during normal flow regimes was 15.28±3.13 kg-N ha^{-1} yr^{-1}, and the mean annual yield during rainstorms was 3.68±1.97 kg-N ha^{-1} yr^{-1}. The rainstorms accounted for 20% of the DON yield (Figure 18. (A)). The mean annual dissolved inorganic nitrogen (DIN) yield was 24.04±2.48 kg-N ha^{-1} yr^{-1}, the mean annual yield of normal flow was 20.01±4.18 kg-N ha^{-1} yr^{-1}, and the mean annual yield during rainstorms was 4.03±2.77 kg-N ha^{-1} yr^{-1}, and the rainstorms were about accounted for 17% of the DIN yield (Figure 18. (B)). The mean annual dissolved organic carbon (DOC) yield was 23.97±3.67 kg-C ha^{-1} yr^{-1}, the mean annual yield of normal flow regimes was 14.21±2.76 kg-C ha^{-1} yr^{-1}, and the mean annual yield during rainstorms was 9.77±6.09 kg-C ha^{-1} yr^{-1}. The rainstorms accounted for 38% of the DOC yield (Figure 18. (C)).

4.2 The pattern of DON losses at the FEF catchment

In the Fushan Experimental Forest (FEF), we showed the pattern of dissolved organic nitrogen (DON) losses and carbon-nitrogen coupling during non-typhoon and typhoon events (Figure 19.). The pattern of DON losses showed the carbon indirect control hypothesis in the normal flow regimes, with a negative correlation between DIN and DON concentration, no correlation between DOC and DON concentration, and CN ratio and DIN concentration showing a positive correlation.

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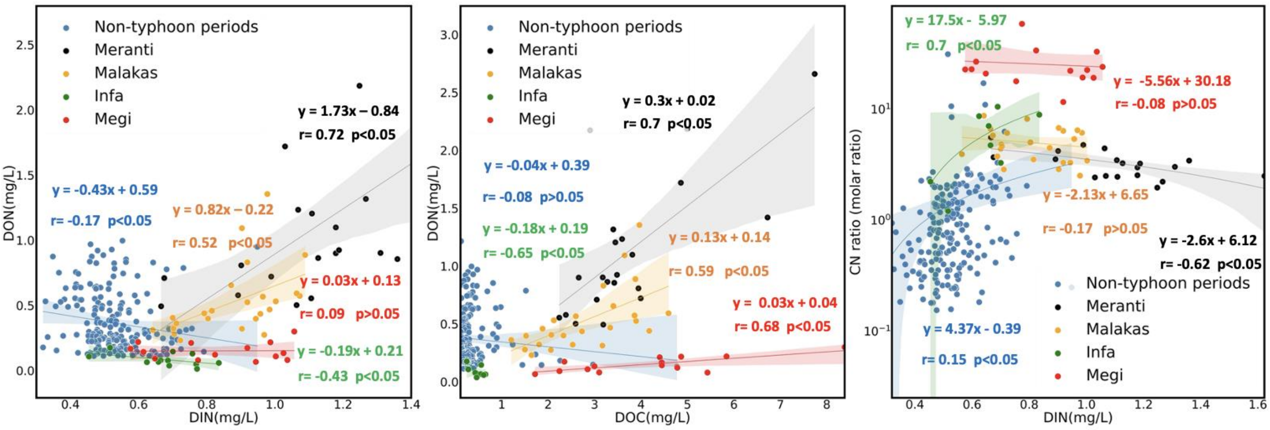

Figure 19. Relationships between streamwater dissolved organic nitrogen (DON) concentration and the molar C:N ratio of dissolved organic matter (DOM) against variation in streamwater dissolved inorganic nitrogen (DIN) concentrations for non-typhoon periods and typhoon events at the Fushan Experimental Forest (FEF). Blue dots represent nutrient concentrations during non-typhoon periods, and other colors represent nutrient concentrations in different typhoon events. r and P values are based on Pearson's correlation.

We collected the nutrient data from four typhoon events. Typhoon Meranti (Figure 19, black dots), Typhoon Malakas (Figure 19, yellow dots), and Typhoon Megi (Figure 19, red dots) were three consecutive typhoon events that disturbed the Fushan Experimental Forest (FEF) directly in September 2016. On the other hand, Typhoon Infa (green dot) was a rainstorm between a tropical depression and a typhoon. It did not make landfall at Fushan Experimental Forest (FEF), which was only the outer weather system of the typhoon that impacted FEF in July 2021. From the non-typhoon periods, Typhoon Infa, to the other three typhoon events, the relationship between DON and DIN showed a shift from the pattern that fits the Carbon Indirect Control Hypothesis to the pattern that fits the Nitrogen Stoichiometric Enrichment Hypothesis. In addition, different typhoon events also caused different patterns of DON losses and carbon-nitrogen coupling.

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The pattern of DON losses in the Typhoon Infa (Figure 19, green dots) was the same as the non-typhoon periods (Figure 19, blue dots), showing the negative correlation between DIN and DON concentration which fits the Carbon Indirect Control Hypothesis. However, it can be found that the concentration range, especially in DON concentration displayed by Typhoon Infa was very different from the non-typhoon periods. The concentration of DON was significantly lower than that in the non-typhoon periods. In addition, compared with non-typhoon periods, the relationship showed a negative correlation between DOC and DON; dissolved organic carbon (DOC) and CN ratio concentration increased significantly in Typhoon Infa.

In the other three typhoons, the DON losses and carbon-nitrogen coupling patterns differ from the non-typhoon periods. Typhoon Meranti, a severe typhoon, disturbed the Fushan Experimental Forest (FEF) in September 2016 from 9/13 to 9/14. Typhoon Meranti showed a positive correlation between dissolved organic nitrogen (DON) and dissolved inorganic nitrogen (DIN) and also a positive correlation between dissolved organic carbon (DOC) and DON. However, in the relationship between DIN and CN ratio, it can be seen that there was a negative correlation. Typhoon Malakas disturbed the FEF in September 2016 from 9/17 to 9/18. The relationship between dissolved organic nitrogen (DON) and dissolved inorganic nitrogen (DIN) and the relationship between dissolved organic carbon (DOC) and DON still showed a positive correlation. However, it can be found that DIN, DON, and DOC concentrations all showed a downward trend. There was no relationship between DIN and CN ratio, and the CN ratio was higher than in typhoon Meranti. The Typhoon Megi, a super typhoon, disturbed FEF in September 2016 from 9/27 to 9/28. The relationship between DON and dissolved inorganic nitrogen (DIN) did not show a relationship even though Typhoon Megi was the largest typhoon of than other three typhoons. On the other hand, the dissolved organic carbon (DOC) and DON relationship showed a positive correlation. The

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pattern showed no relationship between DIN and CN ratio, but the CN ratio was larger than the other three typhoon events.

4.3 Riverine nutrient endmember in each pool

To understand how the different sources of nutrients are transported to the stream, we collected samples from each pool, such as rainfall, soil water, and groundwater. In addition, the pattern of DON losses and CN coupling of streamwater during Typhoon Meranti, Typhoon Malakas, and Typhoon Megi brought about we are full of curiosity about how the different sources of nutrients respond to storm events. Therefore, we further surveyed the nutrient of each pool during Typhoon Infa. However, Typhoon Infa did not make landfall at Fushan Experimental Forest (FEF), which means the data shown in Figure 20. and Table 2. only represent a typhoon's outer weather system, not a typhoon event.

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Table 2. Nutrient concentrations of stream and each end-members between normal flow regimes and Typhoon Infa in the WS1 (watershed 1) of Fushan Experimental Forest catchment. *Mean value ± one standard deviation；*N.D., not detected；*N.A., not available.

Normal flow regimes						
	Rainfall	Stream	Ground water (shallow)	Ground water (deep)	Soil water (30cm_depth)	Soil water (50cm_depth)
DIN conc. (mg-N L-1)	0.91 ± 0.91	0.54 ± 0.15	0.57 ± 0.1	0.45 ± 0.06	1.21 ± 1.92	1.89 ± 3.03
DON conc. (mg-N L^{-1})	0.5 ± 0.8	0.31 ± 0.29	0.17 ± 0.17	0.12 ± 0.12	0.91 ± 0.97	1.18 ± 1.56
DOC conc. (mg-C L^{-1})	N.A.	0.32 ± 0.36	0.31 ± 0.21	0.23 ± 0.16	17.54 ± 18.75	18.74 ± 19.19
DOC:DON (molar ratio)	N.A.	1.69 ± 2.47	3.93 ± 6.37	4.86 ± 7.48	29.7 ± 30.56	56.64 ± 52.6
Typhoon Infa						
	Rainfall	Stream	Ground water (shallow)	Ground water (deep)	Soil water (30cm_depth)	Soil water (50cm_depth)
DIN conc. (mg-N L^{-1})	0.01 ± 0.01	0.65 ± 0.11	0.99 ± 0.13	0.57 ± 0.04	1.5 ± 1.62	1.17 ± 1.47
DON conc. (mg-N L^{-1})	0.16 ± 0.07	0.08 ± 0.05	0.27 ± 0.13	0.69 ± 0.33	0.7 ± 0.1	0.67 ± 0.19
DOC conc. (mg-C L^{-1})	0.43 ± 0.28	0.45 ± 0.17	0.3 ± 0.09	0.3 ± 0.09	7.12 ± 2.98	7.83 ± 3.89
DOC:DON (molar ratio)	0.92 ± 0.6	5.8 ± 3.43	1.25 ± 0.71	0.46 ± 0.3	12.1 ± 1.2	13.02 ± 11.02

The nutrient concentration of each pool during normal flow regimes and Typhoon Infa was shown in Table 2, and the nutrient endmembers of the pattern of DON losses and CN coupling were shown in Figure 20. In the normal flow regime (Figure 20. (A)-(C); Table 2.), It can be found that all of the nutrient concentrations of soil water are high but not homogeneous. In addition, the nutrient concentration of the soil water was higher than that of stream water and groundwater, which means that the nutrient concentration of the soil water does not transport to the groundwater and stream water. Focusing on the riverine nutrient concentration of each three patterns during the normal flow regime (Figure 20 (A)-(C)), they are close to the nutrient concentration of groundwater than the nutrient concentration of soil water, especially in the section of DIN and DOC

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concentration. In each range of nutrient concentration during the normal flow regime, the standard deviation of the DIN concentration of each pool is minimal, and the standard deviation of the DOC concentration of each pool is significant. It is worth noting that the riverine DON concentration was higher than the DON concentration of groundwater, which also caused the CN ratio of the stream water to be significantly lower than that of the groundwater.

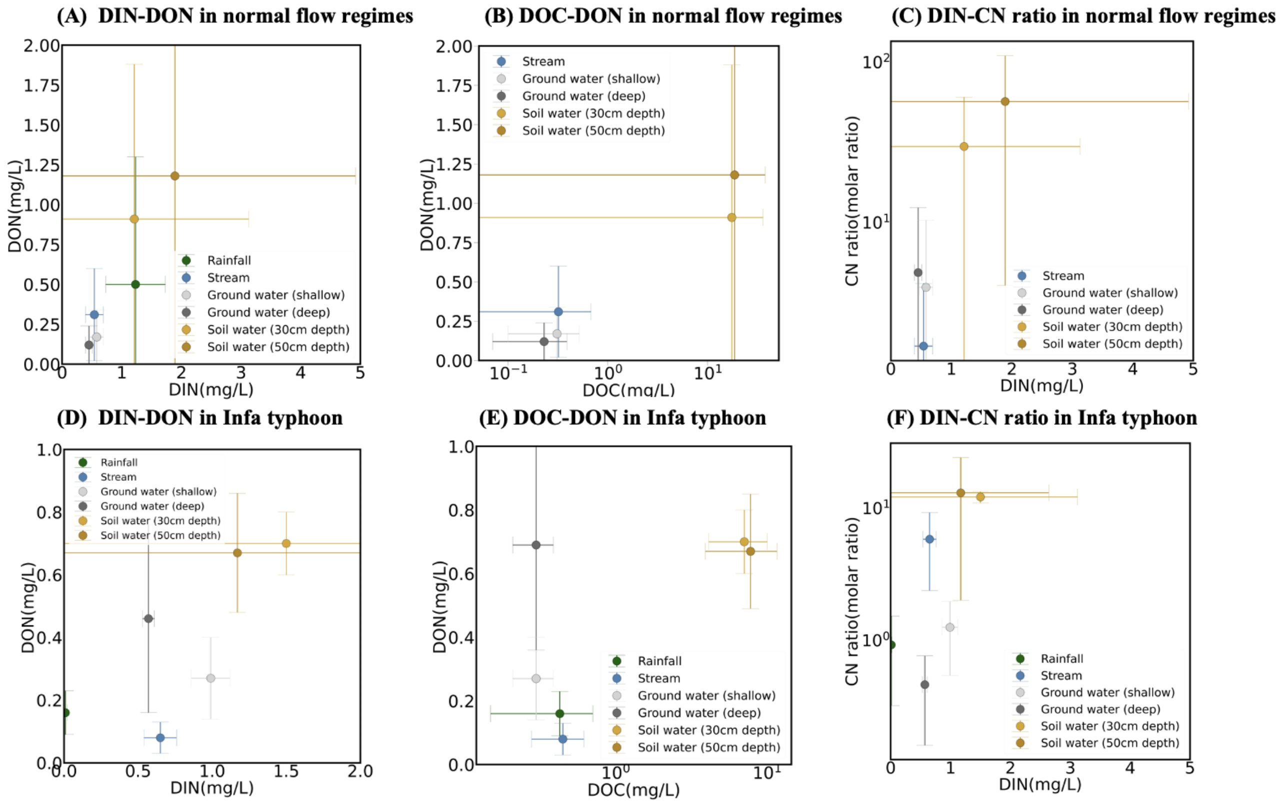

Figure 20. The pattern of dissolved organic nitrogen (DON) losses and the nutrient between each pool between normal flow regimes and Typhoon Infa. The green dot and green error bar mean the rainfall. The blue dot and blue error bar mean the stream water. The shallow and dark grey dots and error bars mean the shallow groundwater with depths of 3-meter and deep groundwater with depths of 7-meter. The shallow and dark brown dots and error bars mean the shallow soil water with depths of 30-centimeter and deep soil water with depths of 50-centimeter. The error bar means the standard deviation.

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In Typhoon Infa, although it did not make land at the FEF, the data (Figure 20. (D)-(F); Table 2.) can still represent the nutrient concentration of each pool under the rainfall of the outer weather system of the typhoon. Overall, the nutrient concentration of the soil water decreased significantly compared with the normal flow regimes. In contrast, the DON concentration of the groundwater during Typhoon Infa increased more than the DON concentration during normal flow regimes. In the part of stream water, the DON concentration decreased significantly to that of normal flow regimes, and the DOC concentration increased significantly, resulting in the CN ratio of stream water being higher than that of groundwater.

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5 Discussion

Our research aimed to examine the carbon and nitrogen coupling and decoupling at the Fushan Experimental Forest (FEF) to understand the pattern of DON losses. To accomplish our objective, we investigated the nutrient of each pool during long-term periods and rainstorm events, which avoids the problem of data derived from single synoptic surveys and allows us to analyze the sources of DON in stream water response to storm events.

5.1 The DON sources at Fushan Experimental Forest (FEF)

Our results of long-term surveys support the negative correlation between DON and DIN concentrations in the Fushan Experimental Forest (FEF) (blue dots in Figure 19.), as the Indirect Carbon Control Hypothesis predicted. Lutz (2011) considered DON a labile carbon source in this hypothesis according to the incubation experiment from two synoptic surveys. However, our results show little support for coupling DOC and DON concentrations, and dissolved organic matter (DOM) C: N ratios changed systematically with increasing DIN concentrations, which was different from the survey of Lutz (2011).

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Table 3. **Total dissolved nitrogen (TDN) and dissolved organic nitrogen (DON) concentrations in the literature.**

Rivers	DON Concentration (mg -N L−1)	DON:TDN %	C:N DOM ratio	References
Ob Rive	0.26 ± 0.01	59.2	39.8	Letscher et al. (2013); Cooper et al. (2008)
Yenisey River	0.18 ± 0.01	68.3	36.3	
Lena River	0.23 ± 0.01	82.6	45.9	
Kolyma River	0.15 ± 0.01	67.7	41.1	
Mackenzie River	0.1 ± 0.01	51.4	49.2	
Yukon River	0.23 ± 0.01	70	24.1	
Bass River	0.05 ± 0.01	58 ± 1	87 ± 5	Wiegner et al. (2006)
Delaware River	0.11 ± 0.01	12 ± 1	26 ± 1	
Hudson River	0.17 ± 0.03	28 ± 4	28 ± 5	
Altamaha River	0.18 ± 0.03	35	32 ± 4	
Savannah River	0.12 ± 0.03	20 ± 4	31 ± 7	
Pocomoke River	0.49 ± 0.01	94	22 ± 1	
Choptank River	0.37 ± 0.04	83 ± 2	15 ± 2	
Peconic River	0.22 ± 0.01	59 ± 1	32 ± 2	
Bronk (2002) mean (n = 13, representing River)	0.49 ± 0.29	60.1 ± 23.5	25.7 ± 12.5	Bronk (2002)
Average	0.33 ± 0.25	57.7 ± 23.7	32.5 ± 16.3	

Compared to the riverine DOC and DON concentrations at the FEF in the world, the average riverine concentration of DOC in FEF is 0.32±0.36 mg/L, which is significantly lower than the world average of 5.6 mg/L (Lee et al., 2019). Furthermore, it is extraordinary that the riverine DON concentration and DON: TDN ratio at the FEF catchment (Table 2.; Table 3.) are similar to the world average (Bronk, 2002; Wiegner et al., 2006; Cooper et al., 2008; Letscher et al., 2013). In general, DOC and DON have strongly stoichiometric (Bernal et al., 2005; Bernal et al., 2018) because the dissolved organic nitrogen (DON) is that subset of the dissolved organic carbon (DOC) pool containing N (Bronk et al., 2015). However, our results show the extreme low DOC concentration and high DON concentration in the stream, which may imply some interaction

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between the allochthonous and autochthonous sources between DOC and DON, causing the decoupling in the FEF (Kaushal & Lewis, 2005; Bernal et al., 2018).

To explain the pattern of non-coupling DOC and DON concentrations in stream water, we further focus on the DON losses and CN coupling between each pool. Firstly, we need to discuss the DON and DOC sources from allochthonous or autochthonous sources. In the carbon-nitrogen relationship of groundwater, it does not support coupling in the normal flow regimes (Figure 21.), which may imply that DON is not passively transported together with DOC from allochthonous sources to stream water at the FEF catchment (Brookshire et al., 2007). Because the nutrient in the groundwater comes from allochthonous sources mainly, we consider that DON and DOC show the different lability of DOM at FEF (Bronk et al., 2007； Bronk, 2002； Carlson and Ducklow, 1995； Bronk et al., 1998).

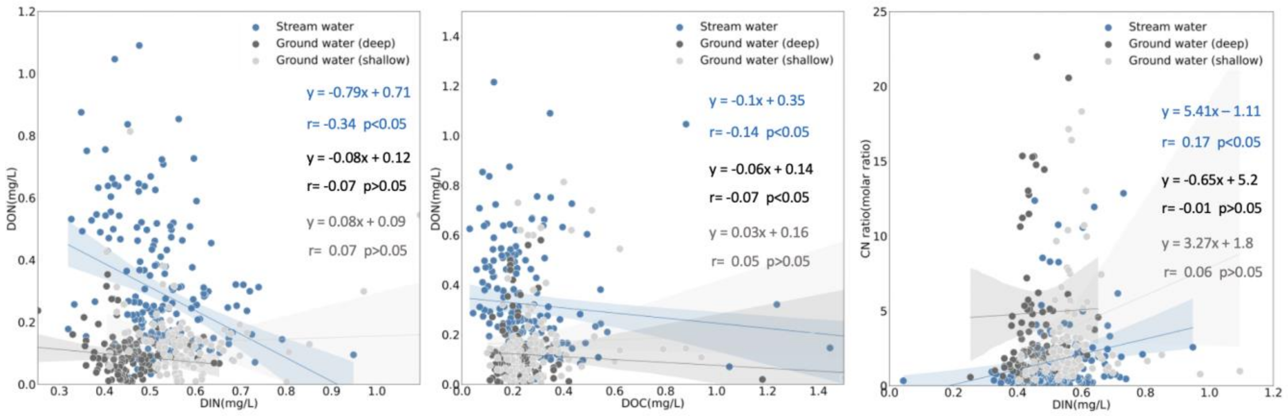

Figure 21. The pattern of DON losses and the carbon-nitrogen relationship between stream water and groundwater in the normal flow regimes. The blue dot means the stream water. The shallow and dark grey dots mean shallow groundwater with depths of 3-meter and deep groundwater with depths of 7-meter. P values and r are based on Pearson’s correlation.

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In the relationship between stream water and groundwater, the concentration of riverine DON is higher than the DON concentration of groundwater (Figure 21.). We consider that riverine DON is likely to come from autochthonous sources at the FEF because nitrogen assimilation is more likely to produce organic nitrogen by autotrophic microbes in stream water than groundwater without the sun (Näsholm et al., 2009). From the relationship between CN and DIN, it can also be seen that only stream water has a correlation, which may imply that the conversion between DIN and DON in stream water affects the change in CN ratio.

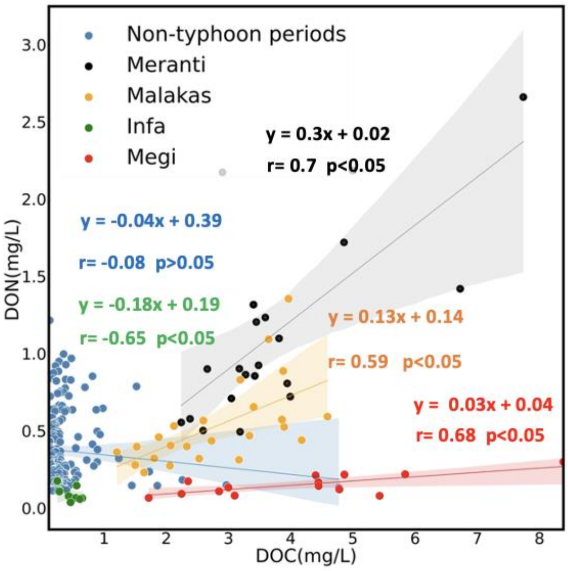

Figure 22. Relationships between streamwater dissolved organic nitrogen (DON) concentration and streamwater dissolved organic carbon (DOC) concentration for non-typhoon periods and typhoon events at the Fushan Experimental Forest (FEF). Blue dots represent nutrient concentrations during non-typhoon periods, and other colors represent nutrient concentrations in different typhoon events. r and P values are based on Pearson's correlation.

From the relationship between stream DOC and DON concentrations under the typhoon (Figure 22.), it can be found that under the continuous disturbance of three typhoons in September

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2016, DOC could be continuously transported to the stream water when the typhoon disturbs the FEF. DON was exhausted during Typhoon Malakas and Typhoon Megi. However, the DON storage capacity in FEF was estimated at 682 ± 74 kg-N ha^{-1} in the organic layer and 6227 ± 311 kg-N ha^{-1} in the mineral layer (Owen et al., 2010). This estimated DON storage capacity was even higher than the annual yield we estimate (Figure 18.), indicating that it is unlikely that the nitrogen reservoirs in the hillslope are exhausted. We consider that the refractoriness of DON in soil may be much higher than that of DOC (Bronk et al., 2002), resulting in the continuous reduction of DON concentration in stream water despite the continuous generation of subsurface flow under event. (Figure 22.). Previous studies considered that the short-term change in the nutrient export path flow during the event would not affect the riverine carbon and nitrogen coupling (Lutz et al.,2011; Wymore et al., 2015; Bernel et al., 2018). However, in the case of FEF, we consider that changing the refractory content of allochthonous and autochthonous DON under rainstorm events is a factor that should be considered. However, it should be noted that both DON and DOC are just large substances. Therefore, in addition to being divided into refractory, semi-labile, and labile fractions, they can be further subdivided into various substances (Bronk et al., 2002), requiring further identification investigations and related experiments.

5.2 Flow regime shifts the carbon-nitrogen coupling of DON losses

The discussion in 5.1 shows that the DOC and DON are decoupled, and DON may come from autochthonous sources in normal flow regimes at FEF. According to the riverine nutrient data of three typhoon events in 2016, we further collected the nutrient data of each pool during Typhoon Infa. However, Typhoon Infa did not make landfall at FEF, which was only the outer weather system of the typhoon that impacted FEF. Therefore, we found that the DON losses and CN

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coupling at Typhoon Infa are very different from the other three typhoons, implying that the pattern of the DON losses and the CN coupling is affected by the flow regime of different intensities.

In order to further discuss how different flow regimes affect the pattern of DON losses and the CN coupling, we use the concept of probability of exceedance to classify the riverine data collected on weekdays and events to different flow regimes. The runoff less than 20mm/hr is defined as low flow conditions, which represent flow regimes between 99% and 13% of the probability of exceedance; the runoff between 20mm/hr and 40mm/hr is defined as high flow conditions, which represent flow regimes between 13% and 3% of the probability of exceedance; the runoff higher than 40mm/hr are defined as typhoon/rainstorms, representing the flow conditions with the probability of exceedance lower than 3%. Our classification method divides all nutrient data into three flow conditions rather than a chronosequence of events, which may mislead the analysis of the DON losses and CN coupling pattern. However, compared with the more predictable peaks and sampling arrangements for typhoon events, it is challenging to perform relevant sampling based on practical considerations regarding the unpredictability of rainfall, which is a limitation of our research.

In the past, it was believed that different watershed environments would show different patterns of DON losses and CN coupling (Brookshire et al., 2007; Lutz et al., 2011). However, the other study proposed that even the same catchment will show different patterns under different seasons (Wymore et al., 2015). In the FEF catchment, we can find that different flow conditions present different patterns of DON losses and CN coupling, and the patterns proposed by three past hypotheses are presented (Figure 23.). The FEF catchment presents a pattern similar to the Carbon Indirect Control Hypothesis under low flow conditions, the Passive Carbon Vehicle Hypothesis under high flow conditions, and the Nitrogen Stoichiometric Enrichment Hypothesis under typhoons/rainstorms.

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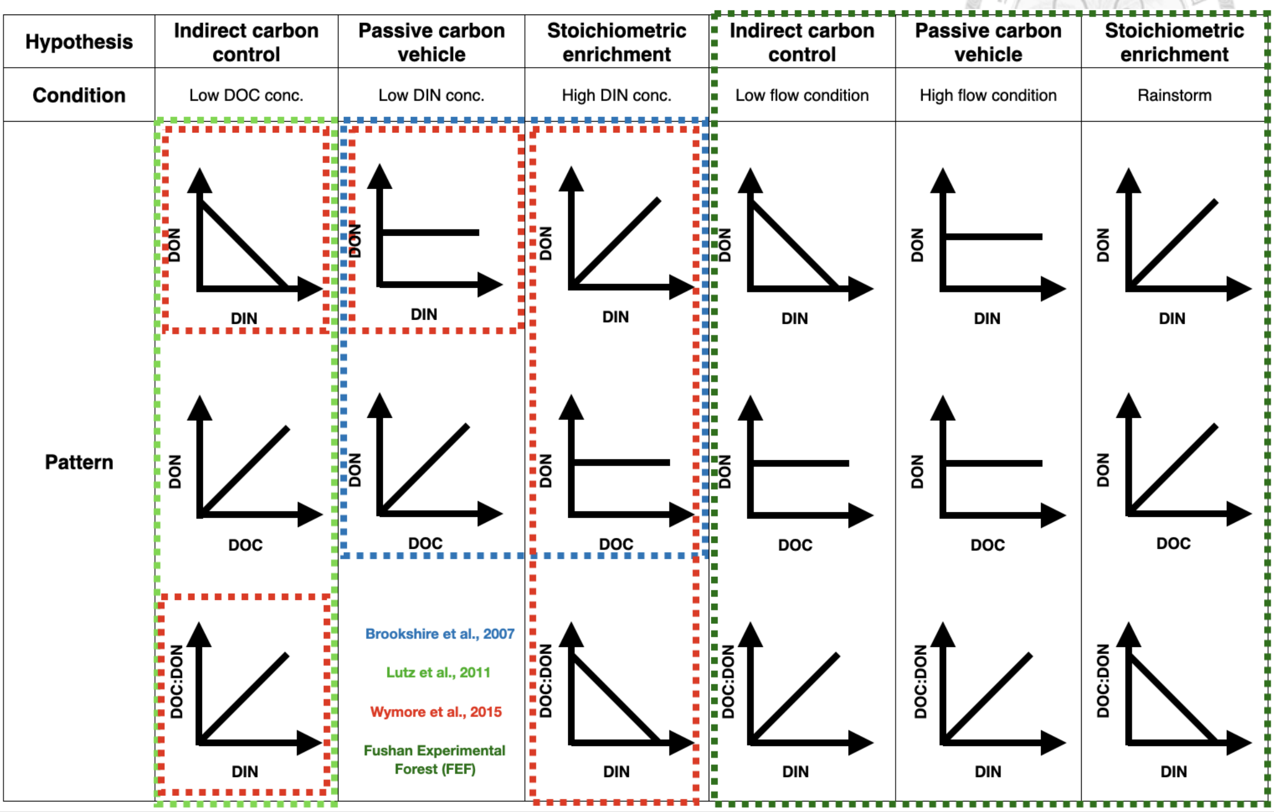

Figure 23. Hypothesized relationships between dissolved inorganic nitrogen (DIN) and dissolved organic nitrogen (DON), dissolved organic carbon (DOC) and DON, and dissolved inorganic nitrogen (DIN) and DOC:DON ratio. Each color frame means the pattern that the hypothesis assumed or the results they investigated or found in the experiment (Brookshire et al., 2007; Lutz et al., 2011; Wymore et al., 2015).

In conclusion, the pattern of DON losses and carbon-nitrogen coupling in FEF does not change with the seasons. However, there are three patterns shown during different flow regimes in FEF. The results imply that the pattern of DON losses and carbon-nitrogen coupling may not be judged solely by a single background environmental parameter but to further discuss how allochthonous and autochthonous nutrient sources change the pattern in stream water under different flow regimes (Lutz et al., 2011; Bernel et al., 2018).

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Turning now to the DOC and DON relationship on different flow conditions (Figure 24.), it can be found that DIN is a very labile substance compared to other dissolved organics and will increase significantly with the change in flow conditions (Vitousek, 1982). In low flow conditions, DON and DOC are decoupled. From the discussion in 5.1, we know that DON here is likely to come from autochthonous nitrogen assimilation. We can see the allochthonous DOC and DON in the environment are rare, resulting in the carbon-containing part of autochthonous DON being preferentially used (Kaushal & Lewis, 2005; Bernal et al., 2015), as the concept proposed by the Carbon Indirect Control Hypothesis (Lutz et al., 2011).

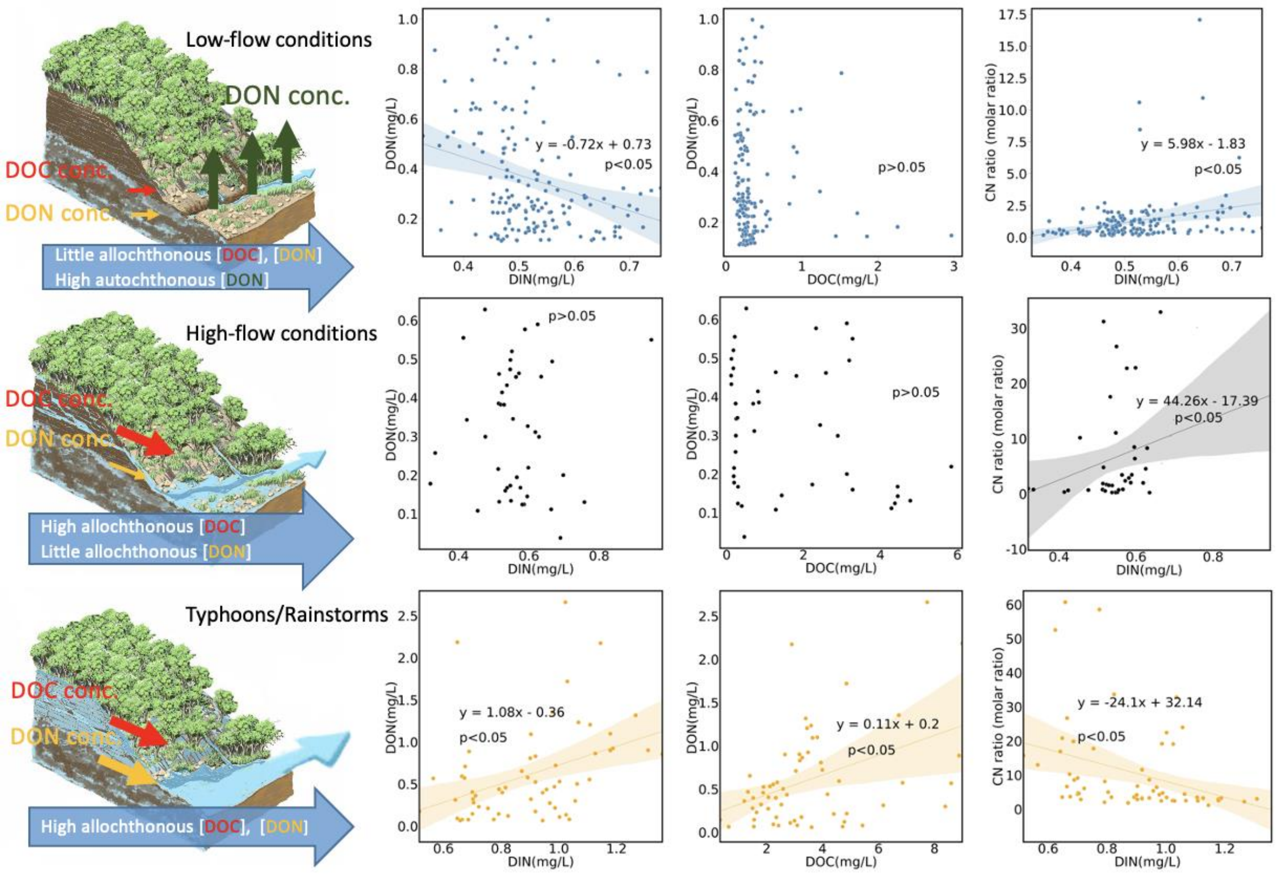

Figure 24. The schematic diagram of the conceptual model illustrates nutrient export in low-flow conditions, high-flow condition, and typhoons/rainstorms at the Fushan Experimental Forest (FEF).

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The arrow represents the nutrient concentration. The Dissolved organic nitrogen (DON) (yellow arrow, green arrow) and dissolved organic carbon (DOC) (red arrow) concentrations are shown.

In the high flow conditions, the relationship of DON and DIN or DOC and DON are all decoupling (Figure 24.). Further observation can see that the DON concentration of high flow conditions is significantly lower than that of low flow conditions, which may imply that In the state of high flow conditions, there is no source of DON in the autochthonous source of the stream water. On the other hand, the increasing DOC concentration is significantly higher than that of DON, which means that the availability of DOC is likely to be higher than that of DON in FEF (Bronk et al., 2015). Therefore, our results may imply that the transport of DON and DOC in the FEF differs from the Passive Carbon Vehicle Hypothesis concept that DON is transported together with DOC (Hedin et al., 1995; Brookshire et al., 2007). Moreover, From the CN relationship, the CN ratio is mainly controlled by the DOC input from the allochthonous source. Therefore, the CN ratio is significantly improved rather than the low flow condition. In typhoons/rainstorms, the allochthonous nutrients in the hillslope are transported to the stream in large quantities, showing a positive correlation between DIN and DON or DOC and DON (Figure 23.). The negative correlation between the CN ratio and DIN is worth paying particular attention. We consider that when the rainfall intensity increases enough, the refractory allochthonous DON begins to transport to the stream, causing the pattern of CN ratio to descend with DIN increasing.

In conclusion, our results show that FEF presents a meager CN ratio compared to the other literature (Bronk, 2002; Wiegner et al., 2006; Cooper et al., 2008; Letscher et al., 2013). A closer look at this CN ratio shows that the low DOC concentration with the DON concentration is close to the average of other rivers worldwide. We judged that typhoons/ rainstorms might play an essential

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role in the FEF to cause this special CN ratio. We assume that typhoons/ rainstorms washed clean and brought the decomposed part of refractory DON into stream water (Bronk et al., 2015). After the event, because there was no allochthonous available DON in the river, DON was produced by autochthonous nitrogen assimilation in the stream water. However, in these DON compounds, the carbon-containing part is preferentially used by organisms in the form of labile carbon so that we cannot detect the signal of DOC concentration in the river, thus showing the pattern of the Indirect Carbon Control Hypothesis in the FEF (Kaushal & Lewis, 2005; Lutz et al., 2011; Bernal et al., 2018). In order to further verify whether the rainstorm affects the pattern of DON losses and CN coupling, we suggest that future research can analyze the nutrient monitoring after the rainstorm peak until the normal flow condition is fully restored.

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6 Conclusions

Global studies highlight that riverine DON is the essential source of nutrients and energy sources for the ecosystem (Perakis & Hedin, 2002; Kaushal & Lewis, 2005; Lutz et al., 2007; Wymore et al., 2015; Berbal et al., 2018). In order to discuss the pattern of dissolved organic nitrogen (DON) losses and the carbon-nitrogen coupling, three hypotheses have been developed based on the relationship between DON and dissolved inorganic nitrogen (DIN) in rivers. The first hypothesis is the Passive Carbon Vehicle Hypothesis that DON and DIN have no relationship, which assumes that DON and dissolved organic carbon (DOC) are passively transported from soil to rivers together (Hedin et al. al., 1995; Rastetter et al., 2005; Brookshire et al., 2007). The second hypothesis is that DON and DIN are positively correlated, the Nitrogen Stoichiometric Enrichment Hypothesis. The hypothesis is that the biological demands of DON, like the DIN (Brookshire et al., 2007). The third hypothesis is the Carbon Indirect Control Hypothesis that DON and DIN are negatively correlated. The hypothesis assumes that DON is consumed instead of the biological demand for DOC, and the patterns of DON export reflect complex changes in the coupling and decoupling of carbon and nitrogen (Bronk et al., 2002; Lutz et al., 2011). However, the potential role of streams in mineralizing allochthonous DON and DOC and its consequences at the catchment scale is still largely unknown (Wymore et al.,2015; Bernal et al., 2018).

In the Fushan Experimental Forest (FEF), There is an extreme low CN ratio than in the other stream of the world (Bronk, 2002; Wiegner et al., 2006; Cooper et al., 2008; Letscher et al., 2013). Our study sheds new light on this issue by showing that typhoons/rainstorms may play an important role, causing the stream water in the FEF to have a strong capacity to produce, transform, and consume DOM internally. The results of flow regimes revealed that after the decomposed part of refractory allochthonous nitrogen experiences the nutrient transport of rainstorm events. As a result, the autochthonous biological action converts the riverine DIN to DON, increasing the riverine

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DON's concentration and decreasing DIN. Moreover, we found that this converted DON only detects the DON concentration, not the DOC concentration, which provides evidence that this stream autochthonous DOM as labile carbon sources preferentially used.

To sum up, our findings suggest that the changes in flow conditions shift the carbon and nitrogen transport mainly by autochthonous sources or allochthonous groundwater, subsurface flow, and overland flow to the stream. Further work is needed to disentangle the different mechanisms of DOC and DON processing in streams and to understand how environmental factors such as nutrient availability and water retention time drive DOM processing in streams and changes in DOM quality under different hydrological conditions.

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7 References

Aber, J., McDowell, W., Nadelhoffer, K., Magill, A., Berntson, G., Kamakea, M., ... & Fernandez, I. (1998). Nitrogen saturation in temperate forest ecosystems: hypotheses revisited. *BioScience*, *48*(11), 921-934.

Andersson, M. G., van Rijswijk, P., & Middelburg, J. J. (2006). Uptake of dissolved inorganic nitrogen, urea and amino acids in the Scheldt estuary: comparison of organic carbon and nitrogen uptake. *Aquatic Microbial Ecology*, *44*(3), 303-315.

Avila, A., Bonilla, D., Rodà, F., Piñol, J., & Neal, C. (1995). Soilwater chemistry in a holm oak (Quercus ilex) forest: inferences on biogeochemical processes for a montane-Mediterranean area. *Journal of Hydrology*, *166*(1-2), 15-35.

Armstrong, F. A. J., & Tibbitts, S. (1968). Photochemical combustion of organic matter in sea water, for nitrogen, phosphorus and carbon determination. *Journal of the Marine Biological Association of the United Kingdom*, *48*(1), 143-152.

Battin, T. J., Kaplan, L. A., Findlay, S., Hopkinson, C. S., Marti, E., Packman, A. I., Newbold, J. D., & Sabater, F. (2008). Biophysical controls on organic carbon fluxes in fluvial networks. *Nature geoscience*, *1*(2), 95-100.

Bernal, S., Butturini, A., & Sabater, F. (2005). Seasonal variations of dissolved nitrogen and DOC: DON ratios in an intermittent Mediterranean stream. *Biogeochemistry*, *75*(2), 351-372.

Bernal, S., Lupon, A., Catalán, N., Castelar, S., & Martí, E. (2018). Decoupling of dissolved organic matter patterns between stream and riparian groundwater in a headwater forested catchment. *Hydrology and Earth System Sciences*, *22*(3), 1897-1910.

Bernhardt, E., & McDowell, W. (2008). Twenty years apart: Comparisons of DOM uptake during leaf leachate releases to Hubbard Brook Valley streams in 1979 versus 2000. *Journal of Geophysical Research: Biogeosciences*, *113*(G3).

doi:10.6342/NTU202203583

Birgand, G., Armand-Lefevre, L., Lolom, I., Ruppe, E., Andremont, A., & Lucet, J. C. (2013). Duration of colonization by extended-spectrum β-lactamase-producing Enterobacteriaceae after hospital discharge. *American journal of infection control*, *41*(5), 443-447.

Boyer, J. N., Dailey, S. K., Gibson, P. J., Rogers, M. T., & Mir-Gonzalez, D. (2006). The role of dissolved organic matter bioavailability in promoting phytoplankton blooms in Florida Bay. *Hydrobiologia*, *569*(1), 71-85.

Bronk, D. A., Glibert, P. M., Malone, T. C., Banahan, S., & Sahlsten, E. (1998). Inorganic and organic nitrogen cycling in Chesapeake Bay: autotrophic versus heterotrophic processes and relationships to carbon flux. *Aquatic microbial ecology*, *15*(2), 177-189.

Bronk, D. A. (2002). Dynamics of DON. *Biogeochemistry of marine dissolved organic matter*, 153-247.

Bronk, D. A., See, J. H., Bradley, P., & Killberg, L. (2007). DON as a source of bioavailable nitrogen for phytoplankton. *Biogeosciences*, *4*(3), 283-296.

Brookshire, E., Valett, H., Thomas, S., & Webster, J. (2007). Atmospheric N deposition increases organic N loss from temperate forests. *Ecosystems*, *10*(2), 252-262.

Brookshire, E. N. J., Valett, H. M., Thomas, S. A., & Webster, J. R. (2005). Coupled cycling of dissolved organic nitrogen and carbon in a forest stream. *Ecology*, *86*(9), 2487-2496.

Capone, D. G., Bronk, D. A., Mulholland, M. R., & Carpenter, E. J. (Eds.). (2008). *Nitrogen in the marine environment*. Elsevier.

Carlson, C. A., & Ducklow, H. W. (1995). Dissolved organic carbon in the upper ocean of the central equatorial Pacific Ocean, 1992: Daily and finescale vertical variations. *Deep Sea Research Part II: Topical Studies in Oceanography*, *42*(2-3), 639-656.

Chi, C.-H., McEwan, R. W., Chang, C.-T., Zheng, C., Yang, Z., Chiang, J.-M., & Lin, T.-C. (2015). Typhoon disturbance mediates elevational patterns of forest structure, but not species

doi:10.6342/NTU202203583

diversity, in humid monsoon Asia. *Ecosystems*, *18*(8), 1410-1423.

Cole, J. J., Prairie, Y. T., Caraco, N. F., McDowell, W. H., Tranvik, L. J., Striegl, R. G., Duarte, C. M., Kortelainen, P., Downing, J. A., & Middelburg, J. J. (2007). Plumbing the global carbon cycle: integrating inland waters into the terrestrial carbon budget. *Ecosystems*, *10*(1), 172-185.

Conley, D. J., Paerl, H. W., Howarth, R. W., Boesch, D. F., Seitzinger, S. P., Havens, K. E., ... & Likens, G. E. (2009). Controlling eutrophication: nitrogen and phosphorus. Science, 323(5917), 1014-1015.

Cooper, C. E., & Brown, G. C. (2008). The inhibition of mitochondrial cytochrome oxidase by the gases carbon monoxide, nitric oxide, hydrogen cyanide and hydrogen sulfide: chemical mechanism and physiological significance. *Journal of bioenergetics and biomembranes*, *40*(5), 533-539.

Daims, H., Lebedeva, E. V., Pjevac, P., Han, P., Herbold, C., Albertsen, M., ... & Wagner, M. (2015). Complete nitrification by Nitrospira bacteria. *Nature*, *528*(7583), 504-509.

Dentener, F., Drevet, J., Lamarque, J.-F., Bey, I., Eickhout, B., Fiore, A. M., Hauglustaine, D., Horowitz, L. W., Krol, M., & Kulshrestha, U. (2006). Nitrogen and sulfur deposition on regional and global scales: A multimodel evaluation. *Global Biogeochemical Cycles*, *20*(4).

Di Baldassarre, G., & Montanari, A. (2009). Uncertainty in river discharge observations: a quantitative analysis. *Hydrology and Earth System Sciences*, *13*(6), 913-921.

Dittman, J. A., Driscoll, C. T., Groffman, P. M., & Fahey, T. J. (2007). Dynamics of nitrogen and dissolved organic carbon at the Hubbard Brook Experimental Forest. *Ecology*, *88*(5), 1153-1166.

DU, Y. D., CAO, H. X., LIU, S. Q., GU, X. B., & CAO, Y. X. (2017). Response of yield, quality, water and nitrogen use efficiency of tomato to different levels of water and nitrogen under

doi:10.6342/NTU202203583

drip irrigation in Northwestern China. *Journal of integrative agriculture*, *16*(5), 1153-1161.

Fan, C., & Glibert, P. M. (2005). Effects of light on nitrogen and carbon uptake during a Prorocentrum minimum bloom. *Harmful Algae*, *4*(3), 629-641.

Fowler, D., Steadman, C. E., Stevenson, D., Coyle, M., Rees, R. M., Skiba, U. M., ... & Galloway, J. N. (2015). Effects of global change during the 21st century on the nitrogen cycle. *Atmospheric Chemistry and Physics*, *15*(24), 13849-13893.

Galloway, J. N., Aber, J. D., Erisman, J. W., Seitzinger, S. P., Howarth, R. W., Cowling, E. B., & Cosby, B. J. (2003). The nitrogen cascade. *Bioscience*, *53*(4), 341-356.

Galloway, J. N., Townsend, A. R., Erisman, J. W., Bekunda, M., Cai, Z., Freney, J. R., ... & Sutton, M. A. (2008). Transformation of the nitrogen cycle: recent trends, questions, and potential solutions. Science, 320(5878), 889-892.

García- Palacios, P., Maestre, F. T., Kattge, J., & Wall, D. H. (2013). Climate and litter quality differently modulate the effects of soil fauna on litter decomposition across biomes. *Ecology letters*, *16*(8), 1045-

1053.

Glibert, P. M., Wilkerson, F. P., Dugdale, R. C., Raven, J. A., Dupont, C. L., Leavitt, P. R., ... & Kana, T. M. (2016). Pluses and minuses of ammonium and nitrate uptake and assimilation by phytoplankton and implications for productivity and community composition, with emphasis on nitrogen- enriched conditions. *Limnology and Oceanography*, *61*(1), 165-197.

Goolsby, D. A., Battaglin, W. A., Aulenbach, B. T., & Hooper, R. P. (2001). Nitrogen input to the Gulf of Mexico. *Journal of Environmental Quality*, *30*(2), 329-336.

Hedin, L. O., Armesto, J. J., & Johnson, A. H. (1995). Patterns of nutrient loss from unpolluted, old- growth temperate forests: Evaluation of biogeochemical theory. *Ecology*, *76*(2), 493-509.

Hillel, D., & Hatfield, J. L. (Eds.). (2005). *Encyclopedia of Soils in the Environment* (Vol. 3).

doi:10.6342/NTU202203583

Amsterdam: Elsevier.

Horng, F. (1996). Soil nutrient pool and available nutrient dynamics in the Fushan mixed hardwood forest ecosystem. *Taiwan J. For. Sci., 11*, 465-473.

Huang, J.-C., Lee, T.-Y., Kao, S.-J., Hsu, S.-C., Lin, H.-J., & Peng, T.-R. (2012). Land use effect and hydrological control on nitrate yield in subtropical mountainous watersheds. *Hydrology and Earth System Sciences*, *16*(3), 699-714.

Huang, J.-C., Lee, T.-Y., Lin, T.-C., Hein, T., Lee, L.-C., Shih, Y.-T., Kao, S.-J., Shiah, F.-K., & Lin, N.-H. (2016). Effects of different N sources on riverine DIN export and retention in a subtropical high-standing island, Taiwan. *Biogeosciences*, *13*(6), 1787-1800.

Hungate, B. A., Dukes, J. S., Shaw, M. R., Luo, Y., & Field, C. B. (2003). Nitrogen and climate change. *Science*, *302*(5650), 1512-1513.

Jalbert, J., Mathevet, T., & Favre, A. C. (2011). Temporal uncertainty estimation of discharges from rating curves using a variographic analysis. *Journal of Hydrology*, *397*(1-2), 83-92.

Johnson, B., & Goldblatt, C. (2015). The nitrogen budget of Earth. *Earth-Science Reviews*, *148*, 150-173.

Juston, J., Jansson, P. E., & Gustafsson, D. (2014). Rating curve uncertainty and change detection in discharge time series: case study with 44- year historic data from the Nyangores River, Kenya. *Hydrological Processes*, *28*(4), 2509-2523.

Kaushal, S. S., & Lewis, W. M. (2005). Fate and transport of organic nitrogen in minimally disturbed montane streams of Colorado, USA. *Biogeochemistry*, *74*(3), 303-321.

Kielland, K. (1994). Amino acid absorption by arctic plants: implications for plant nutrition and nitrogen cycling. *Ecology*, *75*(8), 2373-2383.

Kuypers, M. M., Marchant, H. K., & Kartal, B. (2018). The microbial nitrogen-cycling network. *Nature Reviews Microbiology*, *16*(5), 263-276.

doi:10.6342/NTU202203583

Kuzyakov, Y., & Xu, X. (2013). Competition between roots and microorganisms for nitrogen: mechanisms and ecological relevance. *New Phytologist*, *198*(3), 656-669.

LeBauer, D. S., & Treseder, K. K. (2008). Nitrogen limitation of net primary productivity in terrestrial ecosystems is globally distributed. *Ecology*, *89*(2), 371-379.

Lee, L.-C., Hsu, T.-C., Lee, T.-Y., Shih, Y.-T., Lin, C.-Y., Jien, S.-H., Hein, T., Zehetner, F., Shiah, F.-K., & Huang, J.-C. (2019). Unusual roles of discharge, slope and SOC in DOC transport in small mountainous rivers, Taiwan. *Scientific reports*, *9*(1), 1-9.

Lee, T.-Y., Shih, Y.-T., Huang, J.-C., Kao, S.-J., Shiah, F.-K., & Liu, K.-K. (2014). Speciation and dynamics of dissolved inorganic nitrogen export in the Danshui River, Taiwan. *Biogeosciences*, *11*(19), 5307-5321.

Leigh, J. A., & Dodsworth, J. A. (2007). Nitrogen regulation in bacteria and archaea. *Annu. Rev. Microbiol.*, *61*, 349-377.

Letscher, R. T., Hansell, D. A., Carlson, C. A., Lumpkin, R., & Knapp, A. N. (2013). Dissolved organic nitrogen in the global surface ocean: Distribution and fate. *Global Biogeochemical Cycles*, *27*(1), 141-153.

Lin, K. (1994). Biomass and leaf area index estimates of broadleaf forest in Fu-shan forest. *Bull Taiwan For Res Inst New Ser*, *9*, 299-315.

Lin, K. (1996). Soil survey and classification of the Fushan Experimental Forest. *Taiwan J For Sci*, *11*, 159-174.

Lin, K.-C., Hamburg, S. P., Tang, S.-l., Hsia, Y.-J., & Lin, T.-C. (2003). Typhoon effects on litterfall in a subtropical forest. *Canadian Journal of Forest Research*, *33*(11), 2184-2192.

Lin, T.-C., Hamburg, S. P., Lin, K.-C., Wang, L.-J., Chang, C.-T., Hsia, Y.-J., Vadeboncoeur, M. A., McMullen, C. M. M., & Liu, C.-P. (2011). Typhoon disturbance and forest dynamics: lessons from a northwest Pacific subtropical forest. *Ecosystems*, *14*(1), 127-143.

doi:10.6342/NTU202203583

Lin, T.-C., Shaner, P.-J., Wang, L.-J., Shih, Y.-T., Wang, C.-P., Huang, G.-H., & Huang, J.-C. (2015). Effects of mountain tea plantations on nutrient cycling at upstream watersheds. *Hydrology and Earth System Sciences*, *19*(11), 4493-4504.

Lipson, D., & Näsholm, T. (2001). The unexpected versatility of plants: organic nitrogen use and availability in terrestrial ecosystems. *Oecologia*, *128*(3), 305-316.

Liu, C.-P., Lu, S.-Y., Wang, C.-H., & Hwang, L.-S. (2008). Soil solution chemistry on the three slopes of a natural hardwood stand in the subtropics of the Fushan Forest. *Soil science*, *173*(12), 845-856.

Liu, C. P., & Sheu, B. H. (2003). Dissolved organic carbon in precipitation, throughfall, stemflow, soil solution, and stream water at the Guandaushi subtropical forest in Taiwan. *Forest Ecology and Management*, *172*(2-3), 315-325.

Lu, M.-C., Chang, C.-T., Lin, T.-C., Wang, L.-J., Wang, C.-P., Hsu, T.-C., & Huang, J.-C. (2017). Modeling the terrestrial N processes in a small mountain catchment through INCA-N: A case study in Taiwan. *Science of The Total Environment*, *593*, 319-329.

Luo, Y., Su, B. O., Currie, W. S., Dukes, J. S., Finzi, A., Hartwig, U., ... & Field, C. B. (2004). Progressive nitrogen limitation of ecosystem responses to rising atmospheric carbon dioxide. *Bioscience*, *54*(8), 731-739.

Lutz, B. D., Bernhardt, E. S., Roberts, B. J., & Mulholland, P. J. (2011). Examining the coupling of carbon and nitrogen cycles in Appalachian streams: the role of dissolved organic nitrogen. *Ecology*, *92*(3), 720-732.

McDowell, W. H., Magill, A. H., Aitkenhead-Peterson, J. A., Aber, J. D., Merriam, J. L., & Kaushal, S. S. (2004). Effects of chronic nitrogen amendment on dissolved organic matter and inorganic nitrogen in soil solution. *Forest Ecology and Management*, *196*(1), 29-41.

McMillan, H., Freer, J., Pappenberger, F., Krueger, T., & Clark, M. (2010). Impacts of uncertain

doi:10.6342/NTU202203583

river flow data on rainfall- runoff model calibration and discharge predictions. *Hydrological Processes: An International Journal*, *24*(10), 1270-1284.

Menzel, D. W., & Vaccaro, R. F. (1964). THE MEASUREMENT OF DISSOLVED ORGANIC AND PARTICULATE CARBON IN SEAWATER 1. *Limnology and Oceanography*, *9*(1), 138-142.

Montanari, M., Hostache, R., Matgen, P., Schumann, G., Pfister, L., & Hoffmann, L. (2009). Calibration and sequential updating of a coupled hydrologic-hydraulic model using remote sensing-derived water stages. *Hydrology and Earth System Sciences*, *13*(3), 367-380.

Mulholland, P. J. (2003). Large-scale patterns in dissolved organic carbon concentration, flux, and sources. In *Aquatic ecosystems* (pp. 139-159). Academic Press.

Mulholland, P. J., Valett, H. M., Webster, J. R., Thomas, S. A., Cooper, L. W., Hamilton, S. K., & Peterson, B. J. (2004). Stream denitrification and total nitrate uptake rates measured using a field 15N tracer addition approach. *Limnology and Oceanography*, *49*(3), 809-820.

Näsholm, T., Kielland, K., & Ganeteg, U. (2009). Uptake of organic nitrogen by plants. *New phytologist*, *182*(1), 31-48.

Owen, J. S., King, H. B., Wang, M. K., & Sun, H. L. (2010). Net nitrogen mineralization and nitrification rates in forest soil in northeastern Taiwan. *Soil Science & Plant Nutrition*, *56*(1), 177-185.

Parajka, J., Merz, R., & Blöschl, G. (2007). Uncertainty and multiple objective calibration in regional water balance modelling: case study in 320 Austrian catchments. *Hydrological Processes: An International Journal*, *21*(4), 435-446.

Pellerin, B. A., Kaushal, S. S., & McDowell, W. H. (2006). Does anthropogenic nitrogen enrichment increase organic nitrogen concentrations in runoff from forested and human-dominated watersheds? *Ecosystems*, *9*(5), 852-864.

doi:10.6342/NTU202203583

Perakis, S. S., & Hedin, L. O. (2002). Nitrogen loss from unpolluted South American forests mainly via dissolved organic compounds. *Nature, 415*(6870), 416-419.

Parajka, J., Merz, R., & Blöschl, G. (2007). Uncertainty and multiple objective calibration in regional water balance modelling: case study in 320 Austrian catchments. *Hydrological Processes: An International Journal*, *21*(4), 435-446.

Qualls, R. G., & Haines, B. L. (1992). Biodegradability of dissolved organic matter in forest throughfall, soil solution, and stream water. *Soil Science Society of America Journal*, *56*(2), 578-586.

Rastetter, E. B., Perakis, S. S., Shaver, G. R., & Ågren, G. I. (2005). Terrestrial C sequestration at elevated CO_2 and temperature: the role of dissolved organic N loss. *Ecological Applications*, *15*(1), 71-86.

Rodríguez-Cardona, B., Wymore, A. S., & McDowell, W. H. (2016). DOC: NO_3^- ratios and NO_3^- uptake in forested headwater streams. *Journal of Geophysical Research: Biogeosciences*, *121*(1), 205-217.

Sarmiento, J. L., & Gruber, N. (2006). Air-Sea Interface. *Ocean Biogeochemical Dynamics. Princeton University Press, Princeton, New Jersey*, 503.

Schulten, H. R., & Schnitzer, M. (1997). The chemistry of soil organic nitrogen: a review. *Biology and Fertility of Soils*, *26*(1), 1-15.

Seitzinger, S. P., Harrison, J. A., Dumont, E., Beusen, A. H., & Bouwman, A. (2005). Sources and delivery of carbon, nitrogen, and phosphorus to the coastal zone: An overview of Global Nutrient Export from Watersheds (NEWS) models and their application. *Global Biogeochemical Cycles*, *19*(4).

Seitzinger, S. P., & Harrison, J. A. (2008). Land-based nitrogen sources and their delivery to coastal systems. In *Nitrogen in the marine environment*. Academic Press, New York.

doi:10.6342/NTU202203583

Sharp, J. H., Beauregard, A. Y., Burdige, D., Cauwet, G., Curless, S. E., Lauck, R., ... & Styles, R. (2004). A direct instrument comparison for measurement of total dissolved nitrogen in seawater. *Marine Chemistry*, *84*(3-4), 181-193.

Shi, Q., Zhang, R., Lv, Y., Deng, Y., Elzatahrya, A. A., & Zhao, D. (2015). Nitrogen-doped ordered mesoporous carbons based on cyanamide as the dopant for supercapacitor. *Carbon*, *84*, 335-346.

Shih, Y. T., Chen, P. H., Lee, L. C., Liao, C. S., Jien, S. H., Shiah, F. K., ... & Huang, J. C. (2018). Dynamic responses of DOC and DIC transport to different flow regimes in a subtropical small mountainous river. *Hydrology and earth system sciences*, *22*(12), 6579-6590.

Soussana, J. F., & Lemaire, G. (2014). Coupling carbon and nitrogen cycles for environmentally sustainable intensification of grasslands and crop-livestock systems. *Agriculture, Ecosystems & Environment*, *190*, 9-17.

Sipler, R. E., & Bronk, D. A. (2015). Dynamics of dissolved organic nitrogen. *Biogeochemistry of marine dissolved organic matter*, 127-232.

Sprugel, D. G., Ryan, M. G., Brooks, J. R., Vogt, K. A., & Martin, T. A. (1995). Respiration from the organ level to the stand. In *Resource physiology of conifers* (pp. 255-299). Academic Press.

Stoddard, J. L. (1994). Long-term changes in watershed retention of nitrogen: its causes and aquatic consequences.

Taylor, P. G., & Townsend, A. R. (2010). Stoichiometric control of organic carbon–nitrate relationships from soils to the sea. *Nature*, *464*(7292), 1178-1181.

Terrer, C., Vicca, S., Hungate, B. A., Phillips, R. P., & Prentice, I. C. (2016). Mycorrhizal association as a primary control of the CO2 fertilization effect. *Science*, *353*(6294), 72-74.

Tranvik, L. J., Downing, J. A., Cotner, J. B., Loiselle, S. A., Striegl, R. G., Ballatore, T. J., Dillon,

doi:10.6342/NTU202203583

P., Finlay, K., Fortino, K., & Knoll, L. B. (2009). Lakes and reservoirs as regulators of carbon cycling and climate. *Limnology and oceanography*, *54*(6part2), 2298-2314.

Vitousek, P. (1982). Nutrient cycling and nutrient use efficiency. *The American Naturalist*, *119*(4), 553-572.

Walsh, J. J., McRoy, C. P., Coachman, L. K., Goering, J. J., Nihoul, J. J., Whitledge, T. E., ... & Dean, K. (1989). Carbon and nitrogen cycling within the Bering/Chukchi Seas: Source regions for organic matter effecting AOU demands of the Arctic Ocean. *Progress in Oceanography*, *22*(4), 277-359.

West, A., Lin, C.-W., Lin, T.-C., Hilton, R., Liu, S.-H., Chang, C.-T., Lin, K.-C., Galy, A., Sparkes, R., & Hovius, N. (2011). Mobilization and transport of coarse woody debris to the oceans triggered by an extreme tropical storm. *Limnology and oceanography, 56*(1), 77-85.

Westerberg, I. K., Guerrero, J. L., Younger, P. M., Beven, K. J., Seibert, J., Halldin, S., ... & Xu, C. Y. (2011). Calibration of hydrological models using flow-duration curves. *Hydrology and Earth System Sciences*, *15*(7), 2205-2227.

Wiegner, T. N., Seitzinger, S. P., Glibert, P. M., & Bronk, D. A. (2006). Bioavailability of dissolved organic nitrogen and carbon from nine rivers in the eastern United States. *Aquatic Microbial Ecology*, *43*(3), 277-287.

Wymore, A. S., Rodríguez-Cardona, B., & McDowell, W. H. (2015). Direct response of dissolved organic nitrogen to nitrate availability in headwater streams. *Biogeochemistry*, *126*(1), 1-10.

Xia, J., & Wan, S. (2008). Global response patterns of terrestrial plant species to nitrogen addition. *New Phytologist*, *179*(2), 428-439.

Xu, L., Cheng, S., Fang, H., Xin, X., Xu, X., & Tang, H. (2019). Soil inorganic nitrogen composition and plant functional type determine forage crops nitrogen uptake preference in the temperate cultivated grassland, Inner Mongolia. *Soil Science and Plant Nutrition*, *65*(5),

doi:10.6342/NTU202203583

501-510.

Vitousek, P. M., & Howarth, R. W. (1991). Nitrogen limitation on land and in the sea: how can it occur?. *Biogeochemistry*, *13*(2), 87-115.

Zhang, X., Ward, B. B., & Sigman, D. M. (2020). Global nitrogen cycle: critical enzymes, organisms, and processes for nitrogen budgets and dynamics. *Chemical Reviews*, *120*(12), 5308-5351.

doi:10.6342/NTU202203583