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Speciation and dynamics of dissolved inorganic nitrogen export in the Danshui River, Taiwan

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Abstract

Dissolved inorganic nitrogen (DIN, including ammonium, nitrite and nitrate) export from land to ocean is becoming dominated by anthropogenic activities and severely altering the aquatic ecosystem. However, rare observational analyses have been conducted in the Oceania, the hotspot of global DIN export. In this study a whole watershed monitoring network (20 stations) was conducted in 2003 to investigate the controlling factors of DIN export in the Danshui River of Taiwan. The results showed that DIN concentration ranged from ~ 16 µM in the headwater and up to ~ 430 µM in the estuary. However, the dominating DIN species transformed gradually from NO_3^- in the headwater (~ 97 %) to NH_4^+ in the estuary (~ 70 %), which well followed the descending dissolved oxygen (DO) distribution (from ~ 8 mg L^{-1} to ~ 1 mg L^{-1}). NO_2^- was observed in the transition zone from high to low DO. DIN yield was increasing downstream, ranging from ~ 160 to ~ 6000 kg N km^{-2} yr^{-1} as population density increases toward the estuary, from ~ 15 pop km^{-2} to ~ 2600 pop km^{-2}. Although the individual DIN export, ~ 2.40 kg N $person^{-1}$ yr^{-1}, was comparable to the global average, the close-to-top DIN yield was observed owing to abundant rainfall, dense population, and the sensitive response to population increase. The Danshui River occupies 1.8×10^{-3} % of the land surface area of the Earth but discharges disproportionately high percentage, ~ 60×10^{-3} % (~ 14 000 t N yr^{-1}) of the annual global DIN export to the ocean. Through this study, regulating factors and the significance of human population on DIN export were identified, and the regional databases were supplemented to promote the completeness of global models.

1 Introduction

Stemming from population increase, the huge demand of food and energy consumption for supporting human activities have been increasing significantly (Galloway and Cowling, 2002; Seitzinger et al., 2010). Human disturbances, such as cultivation, fertilizer, livestock industry, and fossil fuel combustion, have emitted doubled biologically available nitrogen to the biosphere in the past five decades (Galloway et al., 2004). Massive discharges of dissolved inorganic nitrogen (DIN) transporting to rivers have caused dramatic changes of nutrient status in freshwater, adjacent estuarine and coastal ecosystems (Jickells, 1998; Turner et al., 2003; Galloway et al., 2004; Duan et al., 2007; Conley et al., 2009), resulting in seasonal hypoxia, harmful algal blooms, and losses in fishery production in aquatic ecosystems (Lu et al., 2011; Diaz and Rosenberg, 2008; Wen et al., 2008; Billen and Garnier, 2007; Howarth et al., 1996; Rabalais, 1996). The anthropogenic DIN has hence significantly altered the original global nitrogen cycles and the relevant biogeochemical processes.

Oceania, a region centered on the islands of the tropical Pacific Ocean, is surrounded by stratified oligotrophic water with limited bio-available nutrients, particularly nitrogenous nutrients (Jiao et al., 2007; Martha and Kristen, 2012). Annually, ~ 27 tropical cyclones (typhoon) pass through this region bringing torrential rainfall and often subsequent floods that flush and erode the mountainous watersheds (Webster et al., 2005; Tu and Chou, 2013). Most typhoon events last only for a few days yet carry remarkable amount of particulate and dissolved material including dissolved inorganic nitrogen from land to fuel the primary production in the surrounding seas (Kao and Liu, 2000; Kao et al., 2004). However, the speciation and dynamics of DIN in Oceania islands remains unclear.

Model studies have demonstrated that Oceania rivers are significant sources of global DIN export (Seitzinger et al., 2005, 2010). However, relatively limited data were actually collected from Oceania rivers (Meybeck, 1982; Caraco and Cole, 1999; Smith et al., 2003). Taiwan has geographic and climatic features similar to Oceania islands, i.e., high precipitation, steep slopes, small basin areas, and frequent flood events, and has relatively well resources for river studies (Lee et al., 2013; Kao et al., 2005; Kao and Liu, 2000). With 23 million people living on a surface area of ~ 36 000 km^2, the population of the urban areas are highly concentrated. For example, the capital city, Taipei, has 2.6 million people living on an area of 271 km^2, which is equivalent to a population

density of 9869 people km^{-2}, in contrast to less than 20 people km^{-2} in the suburbs. Changing land use and wastewater disposal have resulted in major changes in the receiving water bodies (Wen et al., 2008). From the headwater to the estuary, the Danshui River draining through Taipei city records the impacts of human activities within the watershed. The findings in Taiwan rivers could be analogous to typical Oceania rivers (Lee et al., 2013; Kao and Milliman, 2008).

In this paper, we investigated the DIN fluxes from the headwater to the estuary along the Danshui river in 2003. The nitrate, nitrite and ammonium concentrations were measured at 20 sites representing urbanization gradient. The study highlights (1) the extremely high DIN export in the Danshui River indicating most of the global models may have very likely underestimated DIN export in the Oceania; (2) the change of controlling factors to DIN export from the headwater to the estuary, revealing the different sources of DIN along the urbanization gradient.

2 Materials and methods

2.1 Danshui watershed

The Danshui River located in northern Taiwan is the third largest river in Taiwan (Fig. 1). The drainage area is 2726 km^2 including Taipei City in the downstream. The annual precipitation is around 2500–4000 $\mathrm{mm\,yr}^{-1}$; average temperature is about 22 °C. Three major tributaries, i.e. Dahan, Sindian and Keelung River, merge in Taipei City (Huang et al., 2012). Among the three major tributaries, Dahan River draining from south to north is the longest one with the stream length of 135 km. The Shihmen reservoir in the middle of Dahan River is one of the most important hydrologic constructions for irrigation, hydroelectric power, water supply, and flood prevention in Taiwan. It serves 365 km^2 irrigation area and 1.8 million people. Another reservoir, Feitsui, located in the branch of Sindian River was designed for the domestic water supply to Taipei city. Human activities are restrained in the upstream of the reservoir. Community development along Keelung River began from the late 19th century because of coal mining. With the development of railway and road system, communities spread along the valley and the industrial zones occupied the downstream area in the middle 20th century. For the entire Danshui watershed, forest is the dominant landuse type but its proportion gradually decreases from upstream toward downstream due to the expansion of human-associated landuses. Consequently, population increases from the headwater to the downstream and reaches the maximum in the district of Taipei City.

2.2 Water sampling and chemistry

In this study, the stream water samples were collected at 20 sites in 2003. There were 5, 8, and 7 sites along Dahan River (D), Keelung River (K) and Sindian River (S), respectively (Fig. 1). Table 1 shows the fundamental watershed characteristics and landuse compositions for each sampling site. The sites in Table 1 were arranged in accordance with their distances to the estuary. These 20 sampling sites covered wide human-altered levels, providing the opportunity to distinguish the urbanization impacts on water quality through inter-comparisons among sites. Site ids with the prefix of EPA indicate that the water chemistry data at those sites were actually collected by Environment Protection Administration, EPA (www.epa.gov.tw). EPA regularly implements the monthly stream water sampling for most downstream reaches in Taiwan.

Different sampling schemes were applied to cover the entire watershed. Two samples per week were taken at D13, K05, K06, S05, and S07 resulting in ~ 100 samples at each station in a year. Monthly sampling frequency, the same as the EPA, was applied onto the other sites. The water samples taken from the river were immediately filtered through GF/F filters (0.7 µm). The filtrates were quick-frozen in liquid nitrogen for water chemistry analyses. Nitrate, nitrite and ammonium content were determined by ion chromatography (IC) using a Dionex ICS-1500 instrument with a detection limit of 0.2, 0.2, and 0.4 µM, respectively. The dissolved oxygen (DO) was measured in situ using the HI9828 probe produced by HINNA with the accuracy of 0.1 $\mathrm{mg\,L^{-1}}$.

2.3 Rainfall and discharge data

There are over 80 rain gauges maintained by Central Weather Bureau (CWB) in the Danshui watershed (Fig. 1). The precipitation distribution of rainfall was interpolated by the built-in Kriging module in ArcGIS and then retrieved the annual precipitation for individual watershed by overlaying the watershed polygons. As for discharge, the Taiwan Water Resource Agency (WRA) is responsible for monitoring of river discharge of Taiwan Rivers. The river discharge was estimated by substituting the consecutive water levels to the individual rating curve which is calibrated by field measurements every year. Among the 20 sampling sites, 8 of them have discharge gauges. For the other sampling sites, the daily discharges could be derived from an area proportion of the adjacent gauges (Kao et al., 2004; Lee et al., 2013). The annual rainfall and discharge data at each sampling in 2003 are shown in Table 1.

2.4 Flux calculation

The flux is defined as the total amount of exported elements from a watershed within a given period. The measured concentrations multiplying the corresponding discharge are the main concept to obtain the elemental mass load. However, compared to the consecutive discharge, the measured concentration is discrete, which implies the requirement of flux estimator to complement the unsampled days. Therefore, the uncertainties, due to sampling frequency, hydrological behaviors, and hydrologic response, in estimations are unavoidable (Lee et al., 2009). In this study, four commonly used methods (i.e., linear interpolation (LI), global mean (GM), flow weighted (FW), and the rating curve (RC) method) were applied to estimate the individual DIN flux of the 20 sites. The four method-derived fluxes at each site were then averaged and normalized by drainage area to represent flux and yield, respectively.

The linear interpolation (LI) method interpolates the unsampled daily DIN concentrations by two adjacent measured nitrate concentrations, as shown in Eq. (1). The main merit of this method is to supplement the discrete DIN concentration to pair with the consecutive discharge records (Moatar and Meybeck, 2005).

$$\text{FLUX} = m\sum_{j=1}^{T} C_j^{\text{int}} \times Q_j \tag{1}$$

Where FLUX is annual DIN load ($\text{kg}\,\text{yr}^{-1}$); C_j^{int} is the DIN concentration on jth day linearly interpolated between two measured samples ($\text{mg}\,\text{L}^{-1}$); Q_j is the monitored daily discharge ($\text{m}^3\,\text{s}^{-1}$); m is the conversion factor to convert the calculated values into a specific unit ($\text{kg}\,\text{yr}^{-1}$). T stands for the number of days of the studied period, which is a year for this study.

Another method, global mean (GM) method, is to multiply the average concentration of all samples by the total discharge within the study period as shown in Eq. (2) (Birgand et al., 2010).

$$\text{FLUX} = m\frac{\sum_{i=1}^{n} C_i}{n} \times Q_t \tag{2}$$

Where C_i is the DIN concentration of the water sample ($\text{mg}\,\text{L}^{-1}$); Q_t is the annual total discharge ($\text{m}^3\,\text{yr}^{-1}$); and n is the number of water samples in a year. This method does not yet take the hydrological responses into account.

The flow weighted (FW) method which weighs the sampled concentration by discharge for considering the hydrological responses is also widely used as shown in Eq. (3). Annual DIN flux equals the annual discharge volume multiplied by the flow-weighted DIN concentration.

$$\text{FLUX} = m\frac{\sum_{i=1}^{n} C_i Q_i}{\sum_{i=1}^{n} Q_i} \times Q_t \tag{3}$$

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Where Q_i ($\text{m}^3\,\text{s}^{-1}$) is the corresponding discharge on the discrete sampling day. The rating curve (RC) method has been widely used in small mountainous rivers with highly fluctuating hydrodynamic range (Kao and Liu, 2000; Kao et al., 2004; Kao and Milliman, 2008). The method aims to construct a regression equation between discrete observations and corresponding discharges with a power function, $C = aQ^b$, which represents the hydrological influence on transport. The parameter b denotes the hydrological influence. A larger b value (> 0) indicates concentration is enhanced with the increase of discharge. By contrast, a smaller b value reflects the dilution effect because the concentration decreases with the increase of Q. Similar to LI, the RC method can estimate the DIN concentration on the unsampled days. However, the RC method-estimated DIN concentrations are dependent on the corresponding discharge

$$\text{FLUX} = m\sum_{j=1}^{T} Q_j C_j = m\sum_{j=1}^{T} aQ_i^{b+1} \tag{4}$$

Where Q_j ($\text{m}^3\,\text{s}^{-1}$) is the daily water discharge; C_j ($\text{mg}\,\text{L}^{-1}$) is an estimated DIN concentration on the jth day Yield denotes the flux divided by the watershed area.

3 Results

3.1 Rainfall and discharge distribution

The main characteristics of spatial rainfall distribution in the Danshui watershed is that the rainfall was highest in the north-eastern part and gradually decreasing toward west and south (Fig. 1). This rainfall distribution is attributed to the north-eastern monsoon and the orographic enhancement in winter (November to January), given that the rainfall amount in wet season (May to October) was relatively evenly-distributed spatially. The annual rainfall amount ranged from 1593 mm to 2569 mm among our study watersheds (Table 1). The rainfall amount in Keelung River was the largest among the three

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rivers, followed by Sindian and Dahan River. The rainfall seasonality was less evident in Keelung River, also because of the north-eastern monsoon bringing abundant rainfall in dry season.

The discharge (in terms of runoff depth) at the sampling sites ranged from 595 mm to 4259 mm per year. The annual discharge for each watershed generally followed the rainfall ($\rho = 0.89$) after removing data at S05, S07 and S12 where the annual discharges were higher than the rainfall amount. The correlation coefficients between annual discharge and rainfall were 0.97 and 0.82 for the upstream and downstream watersheds, respectively. Generally, the runoff depths in the downstream sites were lower compared to the upstream ones. Note that there are two reservoirs located in between D13-D01 and S05-EPA1910. We will discuss this later in the Discussion section.

3.2 DIN concentrations and species changes

DIN concentrations and species compositions at the 20 sampling sites are shown in Table 2. In Dahan River, the annual mean concentration changed from 18 µM at D13 (in the upstream) to 385 µM at EPA1907 (downstream). The increase of mean concentration corresponded to the increase of population density, from 16 pl km^{-2} (people km^{-2}) to 1492 pl km^{-2}, revealing the impacts of urbanization along the main channel. In terms of seasonal pattern, mean DIN concentration in wet season was lower than in dry season except at D03. DO concentration held relatively steady until EPA1907 where it dropped to 1.09 mg L^{-1}. With regard to species composition, nitrate is the dominant species in the upstream (high DO) and ammonium gradually dominated the DIN composition in the downstream (low DO), corresponding to DO concentration. Besides, nitrite plays a secondary role in DIN composition which only accounted for < 7 % of DIN.

In Keelung River, annual mean DIN concentration was ~ 24 µM at the upstream sites and elevated to above 103 µM from K02 toward the downstream (Table 2). DIN concentration reached the maximum of 355 µM in EPA1905 and was slightly moderated

to 305 µM at EPA1906. In the upstream reach where population density was less than 157 pl km^{-2}, the DIN concentrations in wet season were higher compared to those in the dry season (except at K05), which were contrary to the cases in the downstream. Population density rose to 475 pl km^{-2} at K02 and then abruptly elevated to 2617 pl km^{-2} at EPA1906 that is only 46 km downstream of K02. DO concentration began to decrease when river flowed by K03 where DIN concentration and population density were rising. DO concentrations were ~ 8 mg L^{-1} in the upstream and were decreasing at a rate of ~ 0.11 mg L^{-1} km^{-1} to 0.98 mg L^{-1} at EPA1906. DIN compositions also corresponded well to the DO concentration. Nitrate could contribute ~ 94 % of DIN where DO concentrations were higher than 7.8 mg L^{-1} (upstream reach). When river flowed by the middle reach of Keelung River (K02 and K01), both nitrate and ammonium were similarly occupied ~ 47 % of DIN and nitrite contributed the remaining 7 %. While in the lower reach where DO concentrations were < 2 mg L^{-1} (EPA1905 and EPA1906), ammonium dominantly accounted for ~ 85 % of DIN concentration. Nitrate only contributed ~ 14 % of DIN. Nitrite, as an intermediate product of nitrification or denitrification process, was merely ~ 2 % of the DIN.

In Sindian River, water sampling sites were actually distributed in three main branches of Sindian River. At S12 where population density was 15 pl km^{-2}, annual mean DIN concentration was 19 µM comparable to the background sites in Danhan and Keelung River. At S07 and S05 that were located in another branch, the population densities were higher at 57 pl km^{-2} and 35 pl km^{-2}, respectively. S05 was at a small tributary entering the main branch downstream of S07. Less population density and smaller proportion of agricultural/building landuse at S05 (35 µM) resulted in lower DIN concentration than that at S07 (57 µM). EPA1910, EPA1908, S03, and EPA1909 in the main stream were located in the urban district. Population density hence rose to 644 pl km^{-2} at EPA1908 and abruptly increased to 2060 pl km^{-2} at EPA1909. In the downstream reach (between EPA1910-EPA1909), the annual mean DIN concentration ranged between 161 µM to 431 µM. Following the general DIN pattern, the DIN concentration increased downstream-ward but dropped at S03 right after the afflux of a small tributary (not shown). The observations revealed that the most downstream sites of the three tributaries have the highest DIN concentration of each tributary. Like in Dahan and Keelung River, DIN concentrations in the upstream sites were enhanced in wet season but were diluted in the downstream. Besides, the differences between wet and dry season in DIN concentration seemed increasing toward the downstream. DO concentrations decreased toward the downstream except at S05 (a tributary) and S03 (after the afflux of a small tributary). The DIN compositions were evidently changed with DO concentrations, like all the above-mentioned cases.

For the entire Danshui watershed, the overall pattern of DIN concentrations and population densities toward the estuary is shown in Fig. 2a and b, respectively. It is apparent that the annual DIN concentrations well followed the population density ($\rho = 0.89$). The DIN species changed as well toward the estuary as Fig. 3 shows. Ammonium gradually replaced nitrate as the dominant species toward the estuary. Nitrite proportion reached its maximum in the middle reach where DO concentration remained in a medium level. Nitrite seemed to appear in the most upstream site where DO concentration tended to decrease. Figure 4 shows the mean DIN concentrations in wet season against those in dry season. For the upstream sites, the DIN concentrations were prone to be higher in wet season than in dry season (except K05). On the contrary, the downstream sites had opposite tendency (except D03).

3.3 DIN yields in the Danshui watershed

Four method-derived DIN yields for each sampling site are shown in Table 3. The mean value of the four method-derived DIN yields were used to represent the actual yield to smooth the method-associated uncertainty. In general, the differences among four method-derived DIN yields were relatively small; most of the coefficients of variation (CV) were less than 30 %, except K04 and EPA1907. Therefore, the mean values can be regarded as a good estimator to present and compare the DIN yields among all sites. In Dahan River, DIN yields ranged from 175 at D13 to 2244 $\mathrm{kg\,N\,km^{-2}\,yr^{-1}}$ at EPA1907, which followed the trend of increasing DIN concentration and population

density toward the estuary. In Keelung River, DIN yield was ~ 605 $\mathrm{kg\,N\,km^{-2}\,yr^{-1}}$ for the upstream sites and abruptly elevated to larger than 1989 $\mathrm{kg\,N\,km^{-2}\,yr^{-1}}$ from K02 toward the downstream. Although the CV of the calculated yields at K04 was 66 %, it did not influence the overall trend of increasing DIN toward the estuary. DIN yield at EPA1906 was ~ 6000 $\mathrm{kg\,N\,km^{-2}\,yr^{-1}}$ representing the highest DIN yield among all the study watersheds. In Sindian River, S12 represented a background DIN yield at 532 $\mathrm{kg\,N\,km^{-2}\,yr^{-1}}$. At S07, although it was located in the upstream reach, it represented a high DIN yield at 3400 $\mathrm{kg\,N\,km^{-2}\,yr^{-1}}$. We speculate it was owing to the higher proportion of agricultural landuse (tea farm). With the decrease of agricultural landsue proportion, the DIN yield may decrease as at S05 (~ 1500 $\mathrm{kg\,N\,km^{-2}\,yr^{-1}}$). For the downstream sites, the DIN yields were more than 2500 $\mathrm{kg\,N\,km^{-2}\,yr^{-1}}$ according to the relatively consistent estimations among four methods. At EPA1909, DIN yield reached 5295 $\mathrm{kg\,N\,km^{-2}\,yr^{-1}}$. For the entire Danshui watershed, DIN yields also showed an evident increasing trend toward the estuary (Fig. 5a), which was similar to the patterns of DIN concentration and population density.

4 Discussion

4.1 Changes of controlling factors for DIN concentration

We demonstrate the correlation coefficients between the observed mean DIN concentrations and the potential controlling factors, including population density, discharge, and landuse compositions in Table 4. For the all dataset, the DIN concentrations are highly and positively correlated to population density ($\rho = 0.89$) and building proportion ($\rho = 0.85$) but negatively correlated to natural forest proportion ($\rho = -0.75$) (owing to the competitive relation among natural and building landuse, $\rho = -0.80$). The results imply that the increasing population density-associated inputs (e.g. domestic and industrial sewage) very likely control the spatial distribution of DIN (Fig. 2). Population density is one of the well-known factors regulating DIN export both on global and regional scale (Smith et al., 2005; Boyer et al., 2006). As a result of urbanization, particularly in the developing countries, nitrogen input to the surface water is increasing (Bouwman et al., 2005). On the catchment scale, given the similar climate among the sub-basins as in this study, it might be clearer to specify the contribution of urbanization to DIN export.

If we take a closer examination into the upstream and downstream dataset, their controlling factors are different. For the subset of the upstream data, the DIN concentrations (dominated by nitrate) are significantly and positively correlated to discharge (ρ = 0.86) and agricultural landuse proportion (ρ = 0.87). Basically, nitrate concentrations increase with the increase of discharge which illustrates a typical diffuse source where nitrate is carried along the flow pathways (Salmon et al., 2001; Kao et al., 2004). Agricultural landuse along with fertilization superimposes the background nitrate which represents the leaching status of the forest (Lee et al., 2013). In the upstream, higher DIN concentration in wet season, compared to that in dry season, again indicates that higher discharge can result in more DIN export to the stream (Fig. 4). However, K05 shows a contrary case owing to higher building landuse proportion (4.6 %, Table 1) than the agricultural one (2.3 %). Therefore, population-associate inputs dominate river DIN at K05. Domestic and industrial sewages are usually characterized as point sources owing to the built-in sewer system. Given that DIN concentration is constant from a point source, more water discharge dilutes the riverine DIN concentration. On the contrary, agriculture-associated inputs, e.g. fertilizer, are non-point sources which are diffused by various flow pathways (e.g. surface, subsurface, and groundwater). More water discharge can purge out more non-point source from the soil (Lee et al., 2013). It could hence be concluded that higher DIN concentration in wet season indicates the dominance of diffuse sources to riverine DIN. On the other hand, point source dominates while DIN concentration in dry season is higher (Fig. 4).

For the downstream dataset, as expected, DIN concentrations are significantly and positively correlated to two population-associated factors, i.e. population density (ρ = 0.78, Table 4) and building landuse proportion (ρ = 0.71). Seasonal DIN concentration pattern in the downstream is opposite to that in the upstream. All the downstream sites show higher DIN concentrations in dry season except D03 where agricultural landuse (13.1 %, Table 1) is higher than building one (4.0 %). Diffuse sources overwhelm point sources at D03. The contrary cases at D03 and K05 reveal DIN concentrations are very sensitive to human disturbances, even when the anthropogenic proportion is quite low. Huang et al. (2012) reviewed the relation between agricultural landuse proportion and nitrate concentration (flux as well) and concluded that even small piece of agriculture would result in considerable nitrate export due to over-fertilization and abundant rainfall in Taiwan.

4.2 Transformation among DIN species

Dissolved oxygen of the stream water plays a superior role on influencing the compositions of DIN species due to nitrification and denitrification processes. The correlation coefficients between DO and nitrate/ammonium proportion are 0.87 and −0.87, respectively (not shown). DIN appears in the form of nitrate at higher dissolved oxygen. On the contrary, ammonium appears at lower dissolved oxygen. Nitrite shows little correlation with dissolved oxygen (ρ = −0.28) and is hardly detected due to its low stability in the water.

In the upstream, the riverine nitrate is mainly influenced by leaching from the soil. Warmer temperature in Taiwan may enhance the rates of decomposition of organic matter and nitrification within a watershed. In Taiwan, excess rainfall forces farmers to apply much more ammonium sulfate and urea in hope to help crop growth. Ammonium in the leachate is quickly oxidized to nitrite (which being quickly oxidized as well) and then to nitrate in the upstream reaches. Fertilization raises the background nitrate concentration in the leachate (Lee et al., 2013). In addition, rapid infiltration diminishes denitrification potentials in the upstream mountainous watersheds. The denitrification signals cannot be detected in stream water even in the cultivated watersheds (Peng et al., 2012). Previous study also shows that ammonium and nitrite concentrations in the headwater catchments of Taiwan are not detectable (Wen et al., 2008; Lee et al., 2013).

In the downstream, concentrated population and sewage system facilitate the input of pollutant into the river. While the samples were taken in 2003 there was only one waste water treatment plant conducting primary treatment for waste water along the Danshui River (Fig. 1). The dissolved inorganic nitrogen of the effluents from the waste water treatment plant was measured in a previous study in 2001. It was found that nitrite and nitrate concentration were both below 0.2 µM while ammonium was ~ 1718 µM (Wen et al., 2008), supporting ammonium being the dominant DIN species in the downstream. Current research found that particulate organic matter in the estuary mainly consists of phytoplankton feeding ammonium as the major nutrient source (Cheng, 2010). Eutrophication has resulted in hypoxia, the depletion of oxygen in the estuarine water column. A modeling work also suggests that the Danshui estuary is a heterotrophic ecosystem. More organic matter is consumed than produced in the estuary (Lin et al., 2007), leading to the depletion of dissolved oxygen and the release of ammonium (from decomposition of organic matter) in the water. Low dissolved oxygen further impedes the oxidation of ammonium, resulting in the dominance of ammonium in DIN species (Fig. 3).

4.3 DIN yield estimation equations

The controlling factors regulating spatial DIN yield changes were also examined. The correlation between the calculated DIN yields and watershed characteristics are shown in Table 5. The DIN yield data were also grouped into two subsets. As for the all data set, DIN yields are positively correlated to population-associated factors, i.e. population density ($\rho = 0.85$) and building proportion ($\rho = 0.88$) as the DIN concentration tendency indicates (Table 4). The correlations are more robust while only looking into the downstream subsets. However, the controlling factors for DIN yields actually change from upstream do downstream. In the upstream where diffuse source pollution prevails, discharge ($\rho = 0.89$) and agricultural proportion ($\rho = 0.86$) dominates the DIN export.

Downstream dataset mask the upstream DIN behaviors while pooling all the dataset as a whole. DIN yields are well correlated to annual DIN concentrations regardless of which subsets.

Previous studies have investigated less populated large river basins, e.g. Mediterranean and Black Sea river basins where pollution densities are less than 200 pl km^{-2} with basin areas ranging 68–5526 × 10^{3} km^{2}. They found that DIN yields are generally best correlated with N fertilizer usage and runoff ratio as a quantitative measure of water production in the river basins (Ludwig et al., 2010). However, in the global spectrum, population density and discharge are the two main controlling factors while addressing the nutrient export from land to ocean (Smith et al., 2003). With the comprehensive investigation from the headwater to the estuary as we did in this study, it is critical to discover the changes of controlling factors from upstream to downstream and to understand how the controlling factors influence DIN export from forest and from the city. It is found that the influence of diffuse source pollution is masked by the point source pollution toward the estuary. Further investigations, e.g. the measurement of nitrogen isotope (δ^{15}N), are essential to identify the sources of DIN through more direct evidence (Ohte et al., 2010).

Following previous studies (Smith et al., 2003, 2005), we used logarithmic linear regression model to estimate DIN export (Table 6). Inclusion of annual runoff depth and population density in the logarithmic linear regression model, as in the global model, produces the best estimation. Both the coefficients of population and runoff depth are statistically significant, i.e. p value $\ll 0.01$. Population density directly reflects human-associated waste effluent, and runoff depth is a carrier of nutrient (Caraco and Cole, 1999). In this study, there is a reservoir in the mid reach of Sindian and Dahan River resulting in runoff depths much higher in the upstream than downstream (Fig. 5b), a poor correlation coefficient of annual runoff depth and DIN yield for all sites is found (0.04, Table 5); nevertheless, runoff depth actually correlates closely with DIN yield in the upstream or downstream, respectively ($\rho = 0.89$ for upstream and $\rho = 0.67$ for downstream). The significance of runoff depth on DIN yield can be also revealed from the DIN yield in the global spectrum (Fig. 6b).

Figure 6 clearly shows that the runoff (Fig. 6a) and population density (Fig. 6b) are positively correlated to DIN export in the global spectrum, while DIN export decreases when the agricultural proportion is over 10 %. The dominance of agriculture may be diminished as the population increases. Our results also support this argument (in Sect. 4.1). Danshui River has a special position having high runoff depth and dense population density. Table 6 shows the equations derived from this study and those from the references. The intercepts and coefficients of the equation shown in Table 6 are all statistically significant. For our all data set, the runoff depth coefficient, 0.77 ± 0.41, is comparable to those of global rivers. However, the population density coefficient, 0.53 ± 0.13, presents a ~ 50 % larger value than those derived from rivers worldwide. The Danshui River exports ~ 2×10^5 mol $\mathrm{km^{-2}\,yr^{-1}}$ of DIN, which is closed to the world's highest DIN yield revealing the specific characteristics of this region. In terms of DIN flux, the Danshui River could export ~ 14 000 t N $\mathrm{yr^{-1}}$, that is ~ 20× higher than the estimation by the equation of Smith et al. (2003). To consider the regional differences and watershed scale, Smith et al. (2005) updated their database and constructed watershed area-dependent equations to re-calculate global DIN export. However, the updated equation still underestimates ~ 40 % of the DIN yield compared to our observations. These diverse estimations imply the uncertainty in the estimated DIN export from the Oceania rivers.

The equation for the downstream dataset is similar to the one for all dataset but with lower runoff depth coefficient and larger population density coefficient (Table 6), emphasizing again the significance of population-associated impacts on DIN exports. For the upstream dataset, the population density factor is removed from the equation due to its statistical insignificance. Agricultural landuse proportion is not included in the equation for the same reason, although agricultural proportion is highly correlated to DIN yield in the upstream (Table 5). It turns out that only runoff depth explains the DIN yield changes, leading to ~ 1.42 in runoff depth coefficient. Our analyses indicate

that different DIN export behaviors should be considered while constructing equations. Overall, the DIN yield equations derived from this study that indicate the efficiency of the Oceania rivers in transporting DIN according to the features of high DIN yield rate per increment of runoff depth and population density.

4.4 The nitrogen budget in sub-basins

In terms of nitrogen budget, Howarth (1998) built an empirical model relating net anthropogenic N inputs (y_1) per landscape area to the total N export (x) for 10 temperate regions surrounding the North Atlantic Ocean. The results revealed a strong positive linear relationship between the two ($y_1 = 102.5 + 0.2x$, $R^2 = 0.73$, $p = 0.002$) (Fig. 7). Boyer et al. (2006), in addition to the anthropogenic N inputs (y_2), have modified the approach to include new inputs of N from natural biological N fixation to a region, and extended the modified model of Howarth to other regions of the world including a total of 39 watersheds ($y_2 = 90.3 + 0.2x$, $R^2 = 0.61$, $p < 0.001$). Although the inputs of the two models are different, they consistently indicate that ~ 72–85 % (95 % confidence interval) of the input nitrogen is retained in the basins. It may imply that most of the biological N fixation is stored within the watershed, i.e. soil and vegetation. For the upstream sites in this study, K03–K06, and S12, have medium DIN yield ranging 531–643 kg N $\mathrm{km^{-2}\,yr^{-1}}$. These basins show a comparable retention capability (79–81 %) in the given condition of ~ 2100 to ~ 3400 kg N $\mathrm{km^{-2}\,yr^{-1}}$ atmospheric N deposition which comes mainly from China via long-range transport (King et al., 1994; Chen et al., 1998; Lin et al., 2000; Fang et al., 2008). However, if the N input from fertilization is counted, the retention percentage would increase. D13 exports 175 kg N $\mathrm{km^{-2}\,yr^{-1}}$, indicating the retention of ~ 94 % of the atmospheric N deposition in the basin. It has been clear from many studies that the greater the N loadings are to a region, the greater the potential for riverine N losses (Howarth et al., 1996; Seitzinger et al., 2002; Van Drecht et al., 2003; Galloway et al., 2004; Green et al., 2004; Dumont et al., 2005). However, the heterogeneity of the landscape, reflecting many complex factors, can result in variable retention of N inputs (Boyer et al., 2006). Howarth et al. (2006) suggested that the unexplained (residual) variance in the relationship between N inputs and N export can be explained by climatic factors (precipitation and discharge). For example, the relatively lower discharge at D13 might explain such a large retention because DIN export will follow the flow pathways (Lee et al., 2013). For S05 and S07, higher discharge and relatively more agricultural activities (compared to building proportion) result in N yield comparable to the atmospheric deposition, noted that the considerable fertilization is not yet taken into account. If the global retention rate of 80 % are applied to our cases, the estimated N input would be ~ 7800 and ~ 17 000 kg N $\text{km}^{-2}\,\text{yr}^{-1}$ for S05 and S07, respectively. In other words, the additional N input of ~ 5400 and ~ 14 300 kg N $\text{km}^{-2}\,\text{yr}^{-1}$ should be mainly from fertilization. Over-fertilization is a common way among local farmers to complement the substantial fertilizer loss due to abundant rainfall (Huang et al., 2012). More investigation relevant to nitrogen budget should be conducted further at S05 and S07 where tea is the major crop.

For the downstream sites in this study, the riverine DIN export at most of the sites are so large that additional N input must be superimposed on the atmospheric deposition and fertilization. Urbanization has been made possible by increasing longdistance import of agricultural goods from rural regions. Human population actually consumes agricultural products from other areas, e.g., headwater catchments. The wastes produced by human that are far from the site of crop production can no longer be easily recycled in the agricultural sector (Howarth et al., 2002; Galloway et al., 2007; Smaling et al., 2008). Nevertheless, urbanization transfers the crop fixed nitrogen in the rural areas to the waste in the sewage system of cities and renders an unprecedented opening of the nitrogen cycle on regional and global scales (Billen et al., 2010). To quantify the impacts of population on DIN export, the equation describing DIN export in the upstream was applied at the downstream sites to remove the impacts from diffuse sources. The contribution of population and diffuse source to the downstream DIN export is significant and shown in Fig. 7b. It reveals that more than 80 % DIN export in the downstream could be attributed to the population. We further estimated the population-induced DIN export after excluding the contribution of diffuse source. The average individual DIN export

is ~ 2.2 kg N $\text{person}^{-1}\,\text{yr}^{-1}$, though the individual DIN export varies among sub-basins (1.0–3.4 kg N $\text{person}^{-1}\,\text{yr}^{-1}$). The determination of variability among sub-basins would be helpful for local environmental management. For the entire Danshui watershed, the annual total DIN export divided by the total population derives ~ 2.4 kg N $\text{person}^{-1}\,\text{yr}^{-1}$ which is comparable to the global mean value of 2.99 kg N $\text{person}^{-1}\,\text{yr}^{-1}$ (compiled 79 of 88 rivers around world, mainly from dataset used in Liu et al., 2010 and He et al., 2011; 9 outliers were excluded). The extremely concentrated population of Taipei City results in the high DIN yield in Danshuei River.

4.5 Implication for global DIN estimation

From the point of view of global DIN export, the export from Oceania rivers is a significant source (Seitzinger et al., 2005, 2010). Our study reveals that the Danshui River occupies 1.8×10^{-3} % of the land surface area of the Earth but discharges ~ 60×10^{-3} % (~ 14 000 t N yr^{-1}) of the annual global DIN export to the ocean (24.8 Tg N, Seitzinger et al., 2005), implying a disproportionate DIN production from small mountainous rivers and emphasizing their importance on global biogeochemistry cycles. Smith et al. (2005) compiled 496 rivers with different drainage areas around the world and suggested that runoff coefficient and population density are dominant factors for DIN export estimation; nonetheless, this model underestimated the DIN export in the Danshui River considerably (Table 6). Although agricultural landuse does not have a primary effect on DIN yield in the global spectrum (Fig. 6c), it has been found that more DIN can be flushed out with increasing extent of agricultural activities in a watershed (Huang et al., 2012; Lee et al., 2013). Hence, more investigations on areas where diffuse source dominates with low population density are suggested. This might be important in the global DIN export estimations for regions having such condition, e.g. Australia, South Africa and South America where fertilization is considered the most significant source of DIN export to the ocean (Dumont et al., 2005; Seitzinger et al., 2005).

Besides statistical models, Seitzinger et al. (2005) developed a conceptual model, NEWS (Nutrient Export from Watersheds), to estimate nutrient export from 5761 watersheds. Their DIN yield estimation for the Oceania, as a function of land use, nutrient inputs, hydrology, and other factors, is ~ 720 $\mathrm{kg\,N\,km^{-2}\,yr^{-1}}$. However, their estimation is far lower than our yield of ~ 5200 $\mathrm{kg\,N\,km^{-2}\,yr^{-1}}$ from the Danshui River, Although the global DIN load to the ocean can probably be adequately estimated from large systems, our observational estimation in Danshui River can facilitate the dataset in Oceania rivers. Moreover, an accurate estimation of riverine DIN export may be a key for understanding the primary production surrounding the Oceania where the ocean is oligotrophic and limited by bio-available nutrients, particularly nitrogenous nutrients. This challenging issue is getting important because the scenario analysis shows that the riverine N flux in the Oceania will increase to over 10 % by 2030 as the consequence of urbanization, sanitation, development of sewerage systems, and lagging wastewater treatment (Bouwman et al., 2005). It may imply that the DIN export from the Oceania in the near future may be more than the current estimation. This study supplemented the global databases and will benefit the completeness of global models, considering the fact that the results and inferences of the previous studies are mainly extrapolation from large rivers with limited data from the Oceania rivers (Meybeck, 1982; Caraco and Cole, 1999; Smith et al., 2003). The significant hydrologic and demographic heterogeneity of the small basins can result in varied geographic distribution of nutrient loading (Smith et al., 2005). High-resolution regional and local analysis is necessary for environmental assessment and management. We hence highlight the importance of DIN export survey for the Oceania rivers here in this study.

5 Conclusion

Global nitrogen cycle is a hot issue due to its significance in biogeochemical cycles. DIN, occupying more than one-third of nitrogen export from land to ocean, deserves more detailed investigations. Previous studies mainly focused on large river systems

for the fact that data from Oceania rivers are not easily accessible, even though the Oceania has been identified as a hotspot of global DIN export. The Danshui River exports close-to-top DIN yields among the world rivers at given the abundant rainfall, dense population, and the sensitive responses of DIN yields to the increase of runoff depth and population density. The Danshui River demonstrates the feature of small mountainous rivers in terms of the high efficiency in DIN transport. Given the unit runoff depth and population density, Danshui River can discharge, respectively, ~ $1.2x$ and ~ $1.4x$ DIN yield estimated by the global model (Smith et al., 2005). The complement of regional data will make the global estimations more robust. Moreover, it is found that different DIN transport mechanisms from watersheds would alter the regression model, and an accurate DIN export estimation should include more than one model which is adjusted in accordance with suitability to different conditions.

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References

Billen, G. and Garnier, J.: River basin nutrient delivery to the coastal sea: assessing its potential to sustain new production of nonsiliceous algae, Mar. Chem., 106, 148–160, doi:110.1016.j.marchem.2006.1012.1017, 2007.

Billen, G., Beusen, A., Bouwman, L., and Garnier, J.: Anthropogenic nitrogen autotrophy and heterotrophy of the world's watersheds: past, present, and future trends, Global Biogeochem. Cy., 24, GB0A11, doi:10.1029/2009GB003702, 2010.

Birgand, F., Faucheux, C., Gruau, G., Augeard, B., Moatar, F., and Bordenave, P.: Uncertainties in assessing annual nitrate load and concentration indicators, 1. Impact of sampling frequency and load estimation algorithms, Trans. ASABE, 53, 1–10, 2010.

Bouwman, A. F., Van Drecht, G., Knoop, J. M., Beusen, A. H. W., and Meinardi, C. R.: Exploring changes in river nitrogen export to the world's oceans, Global Biogeochem. Cy., 19, GB1002, doi:10.1029/2004GB002314, 2005.

Boyer, E. W., Howarth, R. W., Galloway, J. N., Dentener, F. J., Green, P. A., and Vorosmarty, C. J.: Riverine nitrogen export from the continents to the coasts, Global Biogeochem. Cy., 20, GB1S91, doi:10.1029/2005GB002537, 2006.

Caraco, N. F. and Cole, J. J.: Human impact on nitrate export: an analysis using major world rivers, Ambio, 28, 167–170, 1999.

Chen, Z. S., Liu, J. C., and Cheng, C. Y.: Acid deposition effects on the dynamic of heavy metals in soils and their biological accumulation in the crops and vegetables in Taiwan, in: Acid Deposition and Ecosystem Sensitivity in East Asia, edited by: Bashkin, V. and Park, S. U., Nova Science Publishers, Hauppauge, NY, 188–225, 1998.

Cheng, C. S.: A Study of Particulate Organic Carbon and Nitrogen and Dissolved Inorganic Nitrogen and Their Isotopic compositions in the Danshuei Estuary, Institute of Hydrological & Oceanic Sciences, National Central University, 2010.

Conley, D. J., Paer, H. W., Howarth, R. W., Boesch, D. F., Seitzinger, S. P., Havens, K. E., Lancelot, C., and Likens, G. E.: Controlling eutrophication: nitrogen and phosphorus, Science, 323, 1014–1015, 2009.

Diaz, R. J. and Rosenberg, R.: Spreading dead zones and consequences for marine ecosystems, Science, 321, 926–929, doi:10.1126/science.1156401, 2008.

Duan, S. W., Xu, F., and Wang, L. J.: Long-term changes in nutrient concentrations of the Changjiang River and principal tributaries, Biogeochemistry, 85, 215–234, 2007.

Dumont, E., Harrison, J. A., Kroeze, C., Bakker, E. J., and Seitzinger, S. P.: Global distribution and sources of DIN export to the coastal zone: results from a spatially explicit, global model, Global Biogeochem. Cy., 19, GB4S02, doi:10.1029/2005GB002488, 2005.

Fang, Y. T., Gundersen, P., Mo, J. M., and Zhu, W. X.: Input and output of dissolved organic and inorganic nitrogen in subtropical forests of South China under high air pollution, Biogeosciences, 5, 339–352, doi:10.5194/bg-5-339-2008, 2008.

Galloway, J. N. and Cowling, E. B.: Reactive nitrogen and the world: 200 years of change, Ambio, 31, 64–71, 2002.

Galloway, J. N., Dentener, F. J., Capone, D. G., Boyer, E. W., Howarth, R. W., Seitzinger, S. P., Asner, G. P., Cleveland, C. C., Green, P. A., Holland, E. A., Karl, D. M., Michaels, A. F., Porter, J. H., Townsend, A. R., and Vorosmarty, C. J.: Nitrogen cycles: past, present, and future, Biogeochemistry, 70, 153–226, 2004.

Galloway, J. N., Burke, M., Bradford, G. E., Naylor, R., Falcon, W., Chapagain, A. K., Gaskell, J. C., McCullough, E., Mooney, H. A., Oleson, K. L. L., Steinfeld, H., Wassenaar, T., Smil, V.: International trade in meat: the tip of the pork chop, Ambio, 36, 622–629, doi:10.1579/0044-7447(2007)36[622:ITIMTT]2.0.CO;2, 2007.

Green, P. A., Vorosmarty, C. J., Meybeck, M., Galloway, J. N., Peterson, B. J., and Boyer, E. W.: Pre-industrial and contemporary fluxes of nitrogen through rivers: a global assessment based on typology, Biogeochemistry, 68, 71–105, 2004.

Howarth, R. W.: An assessment of human influences on fluxes of nitrogen from the terrestrial landscape to the estuaries and continental shelves of the North Atlantic Ocean, Nutr. Cycl. Agroecosys., 52, 213–223, 1998.

Howarth, R. W., Billen, G., Swaney, D., Townsend, A., Jaworski, N., Lajtha, K., Downing, J. A., Elmgren, R., Caraco, N., Jordan, T., Berendse, F., Freney, J., Kudeyarov, V., Murdoch, P., and Liang, Z. Z.: Regional nitrogen budgets and riverine N and P fluxes for the drainages to the North Atlantic Ocean: natural and human influences, Biogeochemistry, 35, 75–139, 1996.

Howarth, R. W., Sharpley, A., and Walker, D.: Sources of nutrient pollution to coastal waters in the United States: implications for achieving coastal water quality goals, Estuaries, 25, 656–676, 2002.

Howarth, R. W., Swaney, D. P., Boyer, E. W., Marino, R., Jaworski, N., and Goodale, C.: The influence of climate on average nitrogen export from large watersheds in the northeastern United States, Biogeochemistry, 79, 163–186, doi:10.1007/s10533-006-9010-1, 2006.

Huang, J.-C., Lee, T.-Y., Kao, S.-J., Hsu, S.-C., Lin, H.-J., and Peng, T.-R.: Land use effect and hydrological control on nitrate yield in subtropical mountainous watersheds, Hydrol. Earth Syst. Sci., 16, 699–714, doi:10.5194/hess-16-699-2012, 2012.

Jiao, N. Z., Zhang, Y., Zeng, Y. H., Hong, N., Chen, F., Liu, R. L., and Wang, P. X.: Distinct distribution pattern of abundance and diversity of aerobic anoxygenic phototrophic bacteria in the global ocean, Environ. Microbiol., 9, 3091–3099, 2007.

Jickells, T. D.: Nutrient biogeochemistry of the coastal zone, Science, 281, 217–222, 1998.

Kao, S. J. and Liu, K. K.: Stable carbon and nitrogen isotope systematics in a human-disturbed watershed (Lanyang-Hsi) in Taiwan and the export of biogenic particulate matter, Global Biogeochem. Cy., 14, 189–198, 2000.

Kao, S. J. and Milliman, J. D.: Water and sediment discharge from small mountainous rivers, Taiwan: the roles of lithology, episodic events, and human activities, J. Geol., 116, 431–448, 2008.

Kao, S. J., Shiah, F. K., and Owen, J. S.: Export of dissolved inorganic nitrogen in a partially cultivated subtropical mountainous watershed in Taiwan, Water Air Soil Poll., 156, 211–228, 2004.

Kao, S. J., Lee, T. Y., and Milliman, J. D.: Calculating highly fluctuated suspended sediment fluxes from mountainous rivers in Taiwan, Terr. Atmos. Ocean Sci., 16, 653–675, 2005, http://www.ocean-sci.net/16/653/2005/.

King, H. B., Hsia, Y. J., Liou, C. B., Lin, T. C., Wang, L. J., and Hwong, J. L.: Chemistry of precipitation, throughfall, stem flow and streamwater of six forest sites in Taiwan, in: Biodiversity and Terrestrial Ecosystem, edited by: Peng, C. I. and Chou, C. H., Institute of Botany, Academia Sinica, Taiwan, 355–362, 1994.

Lee, T. Y., Huang, J. C., Carey, A. E., Hsu, S. C., Selvaraj, K., and Kao, S. J.: Uncertainty in acquiring elemental fluxes from subtropical mountainous rivers, Hydrol. Earth Syst. Sci. Discuss., 6, 7349–7383, doi:10.5194/hessd-6-7349-2009, 2009.

Lee, T.-Y., Huang, J.-C., Kao, S.-J., and Tung, C.-P.: Temporal variation of nitrate and phosphate transport in headwater catchments: the hydrological controls and land use alteration, Biogeosciences, 10, 2617–2632, doi:10.5194/bg-10-2617-2013, 2013.

Lin, H. J., Shao, K. T., Jan, R. Q., Hsieh, H. L., Chen, C. P., Hsieh, L. Y., Hsiao, Y. T.: A trophic model for the Danshuei River Estuary, a hypoxic estuary in northern Taiwan, Mar. Pollut. Bull., 54, 1789–1800, doi:10.1016/j.marpolbul.2007.07.008, 2007.

Lin, T. C., Hamburg, S. P., King, H. B., and Hsia, Y. J.: Throughfall patterns in a subtropical rain forest of northeastern Taiwan, J. Environ. Qual., 29, 1186–1193, 2000.

Lu, X. X., Li, S., He, M., Zhou, Y., Bei, R., Li, L., and Ziegler, A. D.: Seasonal changes of nutrient fluxes in the upper Changjiang basin: an example of the Longchuangjiang River, China, J. Hydrol., 405, 344–351, 2011.

Ludwig, W., Bouwman, A. F., Dumont, E., and Lespinas, F.: Water and nutrient fluxes from major Mediterranean and Black Sea rivers: past and future trends and their implications for the basinscale budgets, Global Biogeochem. Cy., 24, GB0A13, doi:10.1029/2009GB003594, 2010.

Martha, G. and Kristen, N. B.: The organic complexation of iron in the marine environment: a review, Front. Microbiol., 3, 69, doi:10.3389/fmicb.2012.00069, 2012.

Meybeck, M.: Carbon, nitrogen, and phosphorus transport by world rivers, Am. J. Sci., 282, 401–450, 1982.

Milliman, J. D., Farnsworth, K. L., and Albertin, C. S.: Flux and fate of fluvial sediments leaving large islands in the East Indies, J. Sea. Res., 41, 97–107, 1999.

Moatar, F. and Meybeck, M.: Compared performances of different algorithms for estimating annual nutrient loads discharged by the eutrophic river Loire, Hydrol. Process., 19, 429–444, 2005.

Ohte, N., Tayasu, I., Kohzu, A., Yoshimizu, C., Osaka, K., Makabe, A., Koba, K., Yoshida, N., and Nagata, T.: Spatial distribution of nitrate sources of rivers in the Lake Biwa watershed, Japan: controlling factors revealed by nitrogen and oxygen isotope values, Water Resour. Res., 46, W07505, doi:10.1029/2009WR007871, 2010.

Peng, T. R., Lin, H. J., Wang, C. H., Liu, T. S., and Kao, S. J.: Pollution and variation of stream nitrate in a protected high-mountain watershed of Central Taiwan: evidence from nitrate concentration and nitrogen and oxygen isotope compositions, Environ. Monit. Assess., 184, 4985–4998, doi:10.1007/s10661-011-2314-1, 2012.

Rabalais, N. N., Wiseman, W. J., Turner, R. E., SenGupta, B. K., and Dortch, Q.: Nutrient changes in the Mississippi River and system responses on the adjacent continental shelf, Estuaries, 19, 386–407, 1996.

Salmon, C. D., Walter, M. T., Hedin, L. O., and Brown, M. G.: Hydrolgoical controls on chemical export from an undisturbed old-growth Chilean forest, J. Hydrol., 253, 69–80, 2001.

Seitzinger, S. P., Kroeze, C., Bouwman, A. F., Caraco, N., Dentener, F., and Styles, R. V.: Global patterns of dissolved inorganic and particulate nitrogen inputs to coastal systems: recent conditions and future projections, Estuaries, 25, 640–655, 2002.

Seitzinger, S. P., Harrison, J. A., Dumont, E., Beusen, A. H. W., and Bouwman, A. F.: 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 Biogeochem. Cy., 19, GB4S01, doi:10.1029/2005GB002606, 2005.

Seitzinger, S. P., Mayorga, E., Bouwman, A. F., Kroeze, C., Beusen, A. H. W., Billen, G., Van Drecht, G., Dumont, E., Fekete, B. M., Garnier, J., and Harrison, J. A.: Global river nutrient export: a scenario analysis of past and future trends, Global Biogeochem. Cy., 24, GB0A08, doi:10.1029/2009GB003587, 2010.

Smaling, E. M. A., Roscoe, R., Lesschen, J. P., Bouwman, A. F., and Comunello, E.: From forest to waste: assessment of the Brazilian soybean chain, using nitrogen as a marker, Agric. Ecosyst. Environ., 128, 185–197, doi:10.1016/j.agee.2008.06.005, 2008.

Smith, S. V., Swaney, D. P., Talaue-McManus, L., Bartley, J. D., Sandhei, P. T., McLaughlin, C. J., Dupra, V. C., Crossland, C. J., Buddemeier, R. W., Maxwell, B. A., and Wulff, F.: Humans, hydrology, and the distribution of inorganic nutrient loading to the ocean, Bioscience, 53, 235–245, 2003.

Smith, S. V., Swaney, D. P., Buddemeier, R. W., Scarsbrook, M. R., Weatherhead, M. A., Humborg, C., Eriksson, H., and Hannerz, F.: River nutrient loads and catchment sizes, Biogeochemistry, 75, 83–107, 2005.

Tu, J. Y. and Chou, C.: Changes in precipitation frequency and intensity in the vicinity of Taiwan: typhoon vs. non-typhoon events, Environ. Res. Lett., 8, 014023, doi:10.1088/1748-9326/8/1/014023, 2013.

Turner, R. E., Rabalais, N. N., Justic, D., and Dortch, Q.: Global patterns of dissolved N, P and Si in large rivers, Biogeochemistry, 64, 297–317, 2003.

Van Drecht, G., Bouwman, A. F., Knoop, J. M., Beusen, A. H. W., and Meinardi, C. R.: Global modeling of the fate of nitrogen from point and nonpoint sources in soils, groundwater and surface water, Global Biogeochem. Cy., 17, 1115, doi:10.1029/2003GB002060, 2003.

Webster, P. J., Holland, G. J., Curry, J. A., and Chang, H.-R.: Changes in tropical cyclone number, duration and intensity in a warm environment, Science, 309, 1844–1846, 2005.

Wen, L. S., Jiann, K. T., and Liu, K. K.: Seasonal variation and flux of dissolved nutrients in the Danshuei Estuary, Taiwan: a hypoxic subtropical mountain river, Estuar. Coast. Shelf S., 78, 694–704, 2008.

Table 1. Watershed characteristics, landuse compositions, discharge and rainfall for each sampling site and represented watersheds. Upstream sites are bold.

Site ID	Tributary	Watershed characteristics			Landuse Composition						Discharge			Rainfall		
		Distance	Area	Population	Building	Agricultural	Natural	Water	Bare	Gauge	Annual	Dry	Wet	Annual	Dry	Wet
		(km)	(km^2)	($pl\,km^{-2}$)	(%)	(%)	(%)	(%)	(%)		(mm)	(mm)	(mm)	(mm)	(mm)	(mm)
D13	**D**	**125**	**119**	**16**	**0.2**	**1.4**	**96.7**	**0.7**	**1.0**	**SL**	**632**	**223**	**407**	**1593**	**374**	**1219**
D01	D	40	857	158	3.6	4.8	87.7	2.9	1.0	XY	740	264	474	1798	440	1358
D03	D	39	126	489	4.0	13.1	81.9	0.9	0.1	HS	606	285	321	1830	576	1254
D02	D	37	54	488	5.0	23.1	70.8	0.7	0.5	HS	1003	574	431	1661	641	1019
EPA1907	D	16	2101	1492	8.9	5.6	82.3	2.7	0.5	XY, SGS	595	197	397	1894	607	1287
K06	**K**	**93**	**7**	**81**	**1.5**	**1.3**	**96.4**	**0.6**	**0.2**	**GSC**	**2243**	**1088**	**1155**	**2524**	**1077**	**1447**
K05	**K**	**90**	**9**	**81**	**4.6**	**2.3**	**91.9**	**1.0**	**0.2**	**GSC**	**2170**	**1052**	**1117**	**2311**	**1035**	**1277**
K04	**K**	**87**	**37**	**81**	**3.1**	**2.2**	**93.4**	**1.1**	**0.2**	**GSC**	**2305**	**1118**	**1187**	**2375**	**1038**	**1337**
K03	**K**	**74**	**85**	**157**	**3.2**	**1.7**	**93.6**	**1.4**	**0.1**	**GSC**	**2279**	**1105**	**1173**	**2569**	**1281**	**1288**
K02	K	62	124	476	6.9	1.9	89.5	1.7	0.1	GSC	1741	844	897	2510	1317	1193
K01	K	47	203	1054	11.4	2.6	84.0	1.9	0.0	WD	1757	959	799	2508	1373	1135
EPA1905	K	32	328	1930	15.4	3.5	79.2	1.9	0.0	WD	1757	959	799	2269	1175	1094
EPA1906	K	16	361	2618	19.9	3.2	74.6	2.1	0.0	WD	1757	959	799	2178	1107	1071
S12	**S**	**72**	**163**	**15**	**0.3**	**0.1**	**98.4**	**0.5**	**0.6**	**FS**	**2401**	**1109**	**1290**	**2271**	**664**	**1607**
S07	**S**	**72**	**111**	**54**	**2.0**	**4.8**	**91.8**	**1.3**	**0.1**	**PL**	**4259**	**1718**	**2534**	**2419**	**1042**	**1377**
S05	**S**	**71**	**79**	**38**	**0.8**	**2.1**	**96.0**	**0.9**	**0.1**	**DYJ**	**3158**	**1295**	**1858**	**2094**	**776**	**1318**
EPA1910	S	40	91	645	8.6	7.5	82.8	1.1	0.0	BC	1378	635	741	2066	811	1255
EPA1908	S	36	106	1737	13.0	7.7	78.1	1.1	0.0	BC	1375	634	740	2001	774	1227
S03	S	34	111	1969	13.9	8.5	76.5	1.2	0.0	BC	1311	605	706	1991	769	1222
EPA1909	S	31	115	2061	16.0	8.2	74.5	1.2	0.0	BC	1273	587	685	1976	760	1216
Danshui River			2697	2187	14.1	5.4	77.2	2.8	0.4		1938	971	968	1870	661	1209

Table 2. Observed dissolved oxygen (DO), DIN concentrations and compositions of DIN species. Upstream sites are bold.

Site ID	Sample number	DIN concentration (μM)						DIN species (%)			DO(mg L^{-1})
		Annual		Dry season		Wet season		NO_3^-	NO_2^-	NH_4^+	
		mean	std	mean	std	mean	std				
D13	**98**	**17.9**	**8.3**	**13.8**	**2.7**	**21.8**	**8.7**	**93**	**1**	**6**	**5.14**
D01	8	77.6	54.6	94.4	87.0	67.6	33.0	55	4	41	4.90
D03	8	118.9	67.0	90.9	35.0	135.7	73.0	47	7	46	4.49
D02	8	103.2	20.3	104.6	16.3	102.3	24.2	83	3	14	5.69
EPA1907	9	385.2	325.5	570.0	340.7	237.3	251.8	30	1	70	1.09
K06	**99**	**22.2**	**6.6**	**20.7**	**4.7**	**23.7**	**7.8**	**97**	**0**	**3**	**8.55**
K05	**99**	**23.3**	**10.3**	**27.9**	**7.9**	**18.7**	**10.5**	**93**	**1**	**6**	**8.55**
K04	**3**	**20.9**	**20.0**	**10.3**	**NA**	**26.2**	**25.1**	**94**	**1**	**5**	**7.90**
K03	**3**	**30.1**	**16.3**	**27.1**	**NA**	**31.5**	**22.8**	**94**	**1**	**5**	**7.77**
K02	3	103.4	31.5	NA	NA	103.4	31.5	49	7	44	6.57
K01	8	165.4	90.2	171.4	147.4	161.9	57.7	44	7	49	5.08
EPA1905	9	355.5	242.1	431.6	237.1	294.6	254.2	9	3	88	2.08
EPA1906	9	305.7	210.2	361.0	201.0	261.5	229.2	18	1	81	0.98
S12	**3**	**18.9**	**8.1**	**10.2**	**NA**	**23.3**	**4.2**	**79**	**1**	**21**	**8.07**
S07	**105**	**57.3**	**15.9**	**49.2**	**NA**	**64.7**	**17.3**	**87**	**1**	**12**	**5.50**
S05	105	35.4	12.3	32.9	8.0	37.7	14.9	98	0	2	7.75
EPA1910	9	163.7	69.0	209.6	42.3	127.0	66.3	43	5	51	3.41
EPA1908	9	247.9	130.7	291.1	82.1	213.3	160.4	30	5	65	3.67
S03	8	161.4	109.9	205.5	168.7	128.4	NA	54	6	35	3.48
EPA1909	9	431.5	233.6	520.6	238.8	360.2	228.1	26	5	69	2.86

Table 3. The calculated DIN yields at each sampling sites. Four calculation methods are applied in this study. Upstream sites are bold.

	DIN yield (kg N km^{-2} yr^{-1})						
Site ID	LI	GM	FW	RC	Mean	Std	CV(%)*
D13	**183**	**160**	**179**	**178**	**175**	**10**	**5.8**
D01	789	831	738	684	760	64	8.4
D03	936	1055	1183	1048	1056	101	9.6
D02	1354	1294	1236	1210	1274	64	5.1
EPA1907	2684	2931	2167	1193	2244	770	34.3
K06	**586**	**528**	**632**	**576**	**581**	**43**	**7.3**
K05	**619**	**543**	**666**	**746**	**643**	**85**	**13.2**
K04	**222**	**394**	**618**	**1105**	**585**	**383**	**65.5**
K03	**389**	**560**	**720**	**781**	**613**	**176**	**28.7**
K02	2465	2146	1913	1431	1989	435	21.9
K01	3886	3698	3708	3066	3590	360	10.0
EPA1905	6180	6525	5136	3799	5410	1226	22.7
EPA1906	6455	5611	5672	6257	5999	421	7.0
S12	**495**	**485**	**565**	**581**	**532**	**48**	**9.1**
S07	**3444**	**3424**	**3465**	**3265**	**3400**	**91**	**2.7**
S05	**1554**	**1569**	**1598**	**1518**	**1560**	**33**	**2.1**
EPA1910	2652	2787	2296	2358	2523	235	9.3
EPA1908	3473	4211	2799	2905	3347	648	19.3
S03	2929	2614	2446	2206	2549	304	11.9
EPA1909	5649	6790	4242	4501	5295	1169	22.1

* CV denotes coefficient of variation.

Table 4. The correlation matrix among population density, discharge and landuse composition. The correlation coefficients are shown. The observed DIN concentrations are grouped into two subsets, i.e. upstream and downstream data.

	Pop (pl km^{-2})	Q (mm)	Building (%)	Agri. (%)	Natural (%)	Water (%)	Bare (%)
Pop (pl km^{-2})	1	−0.30	0.97*	−0.11	−0.70*	0.19	−0.38
Q (mm)		1	−0.29	−0.41	0.49	−0.26	−0.35
Building (%)			1	0.16	−0.80*	0.42	−0.51
Agricultural (%)				1	−0.71*	−0.16	−0.03
Natural (%)					1	−0.28	0.33
Bare Land (%)						1	1
All data	0.89*	−0.38	0.85*	0.22	−0.75*	0.49	−0.33
Upstream	0.08	0.86*	0.06	0.87*	−0.53	0.87	−0.56
Downstream	0.78*	0.14	0.71*	−0.28	−0.38	0.53	−0.29

* denotes the significant correlation

Table 5. The correlation coefficients correlating the calculated DIN yields to annual mean DIN concentration, runoff depth, population density, and landuse composition. The DIN yields are grouped into two subsets, i.e. upstream and downstream data.

	DIN (µM)	Pop (pl km^{-2})	Q(mm)	Building (%)	Agri. (%)	Natural (%)	Water (%)	Bare (%)
All data	0.82*	0.85*	0.04	0.88*	0.07	−0.66	0.38	−0.55
Upstream	0.97*	−0.10	0.89*	−0.01	0.86*	−0.46	0.42	−0.49
Downstream	0.76*	0.86*	0.67	0.94*	−0.43	−0.42	0.08	−0.57

* denotes the significant correlation

Table 6. Yield equations as a function of annual runoff and population density. Smith et al. (2005) generated different yield equations for different basin size groups.

Data source	Basin size (km^2)	Intercept*	Runoff coeff.	Population coeff.	No. data	R^2	Est. Danshui DIN export ($t\,N\,yr^{-1}$)/yield ($kg\,N\,km^{-2}\,yr^{-1}$)
This study (Upstream)	6–162	4.22 ± 0.27	1.42 ± 0.66	–	8	0.82	NA
This study (Downstream)	53–2101	3.55 ± 0.56	0.64 ± 0.39	0.55 ± 0.19	12	0.92	NA
This study (All data)	6–2101	3.58 ± 0.37	0.77 ± 0.41	0.53 ± 0.13	20	0.81	14 073/5218
Smith et al. (2003)	10^1–10^7	3.99	0.75	0.35	165	0.59	659/244
Smith et al. (2005)	$< 10^2$	4.32 ± 0.14	0.82 ± 0.23	0.20 ± 0.07	62	0.19	NA
	10^2–10^3	4.09 ± 0.09	0.61 ± 0.10	0.38 ± 0.06	157	0.33	NA
	10^3–10^4	3.97 ± 0.06	0.64 ± 0.08	0.38 ± 0.05	155	0.39	10 001/3708

* Yield equation: $\log(DIN_y) = \text{Intercept} + \text{Runoff coefficient} \times \log(Q/1000) + \text{Population coefficient} \times \log(\text{Pop})$, DIN_y is DIN yield in ($mol\,km^{-2}\,yr^{-1}$), Q is annual runoff depth in (mm), Pop is population density in ($people\,km^{-2}$), all the coefficients in the table are statistically significant, i.e. p value < 0.01; – denotes the parameter is not used in the equation.

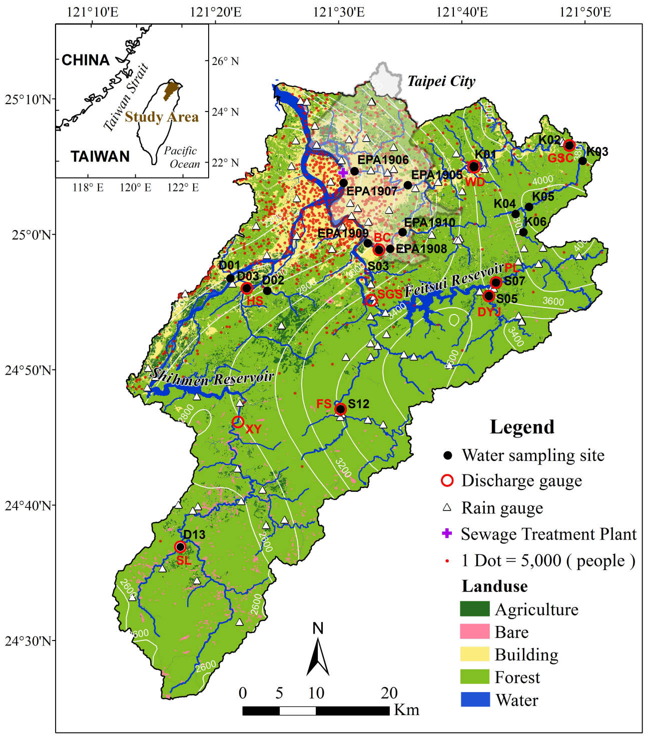

Fig. 1. The landuse and poupulation density in Danshui River. The landuse and population data is derived from the Minstry of Interior. Water sampling sites (black dots), discharge gauges (red circle), rain gauges (triangles), and sweage treatment plant (cross symbol) are shown as well. The contour shows the annual rainfall distribution and the shaded area is the district of Taipei City.

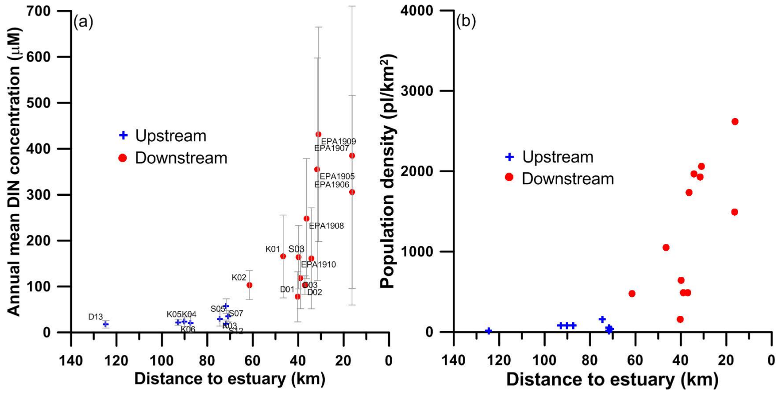

Fig. 2. **(a)** Annual mean DIN concentration and **(b)** population density along Danshui River. Error bars in **(a)** represent standard deviation among samples. The blue cross and red circle indicate the upstream and downstream sites, respectively.

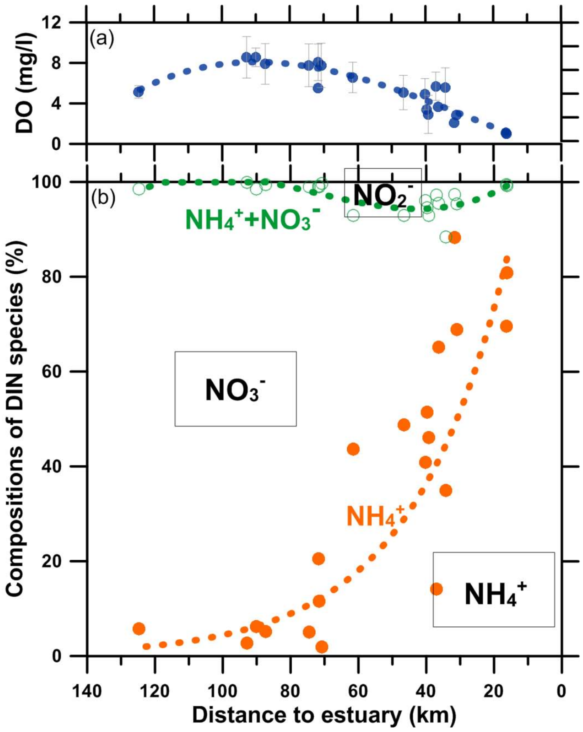

Fig. 3. **(a)** Annual mean dissolved oxygen and **(b)** relative proportions of three DIN species along Danshui River. Orange curve stands for NH_4^+ proportion in total DIN. Green curve stands for the summed proportion of NH_4^+ and NO_3^-. Hence, the range in between green curve and orange curve represents the NO_3^- proportion. Similarly, the area above the green curve is the NO_2^- proportion in total DIN along Danshui River.

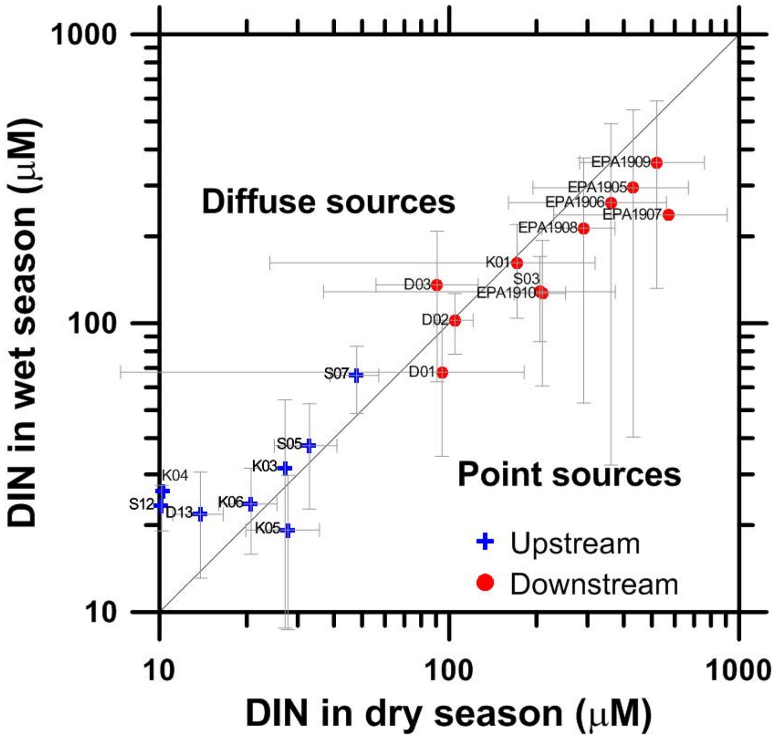

Fig. 4. The mean DIN concentration in wet season (May–October in 2003) against mean DIN concentration in dry season (other months in 2003). Horizontal and vertical error bars represent standard deviations among samples taken in dry season and wet season, respectively. Please read the text for the determination of DIN sources, i.e. diffuse and point source.

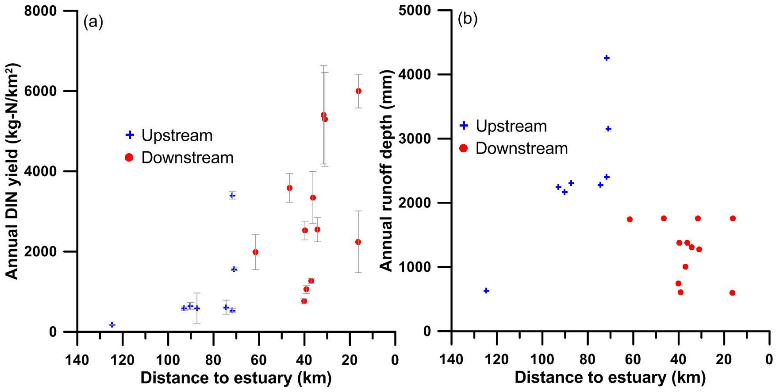

Fig. 5. (a) Calculated annual DIN yield and **(b)** annual runoff depth along Danshui River. Error bars in **(a)** are the standard deviations among four flux calculation methods.

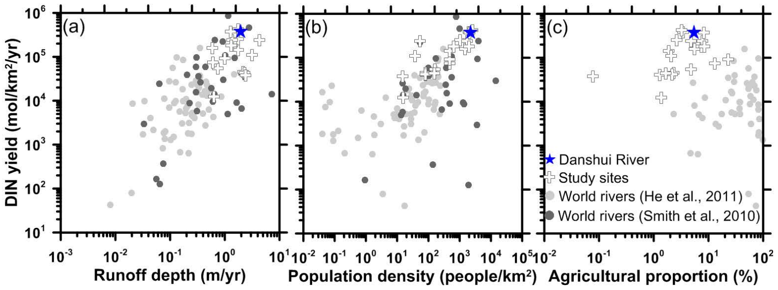

Fig. 6. Scatter plots of DIN yields against **(a)** runoff depth, **(b)** population density, and **(c)** agricultural proportion. Not only Danshui River data but also some world river data are shown for comparison. Blue star represents the DIN yield for Danshui River based on the equation established in this study. Please see more detail in the text.

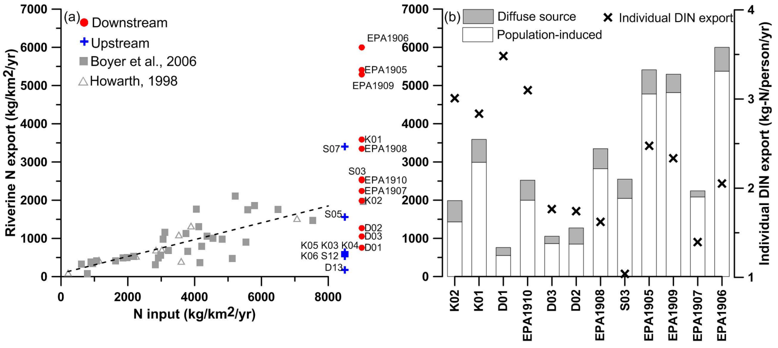

Fig. 7. (a) Scatter plot of riverine N export against N input published in Boyer et al. (2006) and Howarth (1998), the riverine DIN exports in this study were plotted aside for comparison; **(b)** the percentage of diffuse source and population-induced N in the riverine export and the individual DIN export for only the downstream sites. The cross symbols in **(b)** stands for the estimated individual DIN export.