Point-by-point response to reviewers' comments

W. Zhang

This paper has two merits: The first one is to provide information about one of the highly populated watersheds in the world, with a tremendous level of N contamination. The fact that about 30%-50% of human-induced N would be ended in rivers. That is extremely interesting, given that different findings have been achieved when we compared with similar research in other watersheds. The second one is that the authors can enhance our understanding of factors controlling riverine N exports through the comparison among different watershed groups. Overall, I enjoyed reading this paper and believe that it will make a nice contribution to Biogeosciences.

Reply:

We appreciate that the reviewer recognized the merits of our study. Indeed, it's very surprising that the low-disturbed (semi-pristine) watersheds can retain most of the nitrogen, even when the atmospheric N input reaches as high as 2000 kg-N $km^{-2}yr^{-1}$. For moderately-disturbed (agricultural-dominated) watersheds, the intensive fertilizer application which is common in Southeast Asia is very likely a challenging issue in the near future. The good relationship between agricultural area and DIN export, comparing with the other watersheds in the world, clearly indicates that the non-point source pollution is more severe in this than other regions. The extremely high riverine DIN export and the high NH_4:NO_3 ratio in the highly-disturbed watersheds indicate that the limited wastewater treatment and incomplete sewer drainage system cannot effectively remove DIN from the water and thus pose the potential risk of eutrophication.

However, the methodology used in the study is a little bit different from previous studies, although the discussion is sufficient and the conclusion is noteworthy. In this study, atmospheric N deposition, fertilizer N and human emission was summed as total N input. But this method could be subjected to high error. The commonly used method is NANI methodology, which was proposed by Howarth et al., (1996). NANI has been widely accepted as almost complete inventory for calculating human-induced N. NANI sums N contributions from atmospheric deposition, fertilizer application, agricultural biological fixation, and net import/export of N in food and feed to a watershed. To me, I think your N inventory is incomplete, and hence calculated N input could be underestimated. If N accounting method of this paper is quite different from other studies, how much confidence do we have with the extremely high value of 30%-50%? I would not prefer to argue whether your methodology is suitable or not, but more discusses on the method should be guaranteed. Below, I provide some suggestions for your further consideration:

(1) I cannot quite understand why you exclude N inputs of biological N fixation, food and feed imports and/or livestock excretion (usually, livestock N excretion was incorporated with the estimate of food & feed imports). Can you explain more on this? I can give you more evidence for your further consideration:

(a) As you have mentioned in the paper, many of these watersheds are dominated by forestland and/or cropland. The land cover type is a little bit similar to northeastern U.S.A.. Boyer et al. (2002) had addressed that biological N fixation could be as high as 30% of total N inputs. However, one should be cautious because of the high uncertainties in the estimate of biological N fixation (Sobota et al., 2013). But this really implies that biological N fixation cannot be just omitted.

(b) As a curious idea, I have checked the imported food from other countries in Taiwan. High amount of food (e.g., more that 1 million tons of wheat) was imported annually. In part, this number addresses that N inputs through this source should be significant. You can refer: http://faostat3.fao.org/browse/T/TP/E. More evidence could be seen in other similar watersheds. For example, in Huai River Basin of P.R. China (Zhang et al., 2015), which is also highly populated watershed, about 70% of land cover in this watershed is cropland. Even so, this watershed was still relied on food and feed import. Hence, I believe food and feed imported N may be also significant in Taiwan.

(c) You should mention more on why you exclude feed N (i.e., livestock excretion N). The number is expected to be very small? Can you provide more evidence?

Reply:

We are glad to receive the professional comments raised by the reviewer, which would certainly help us to improve the discussion and strengthen our conclusion. In this review report, the reviewer proposed to use the NANI approach (or model) to complete the N budget, particularly for biological N fixation and net import/export of N in food and feed. First of all, there are many modeling approaches focusing on the N budget at watershed scale, such as NANI, GLOBAL_NEWs, and SPRROW etc. Modeling the N budget is the next step in our study in this subject. However, here we focused on the data compilation and investigation of factors controlling DIN export in the subtropical mountainous region which should be highlighted in global syntheses. For N inputs, it is well recognized that atmospheric N deposition, natural biological N fixation, fertilizer application/agricultural biological fixation, human emission, and livestock excretion are the main N sources. Basically, NANI sums human emission and livestock excretion in the calculation of net import/export of N in food and feed.

Therefore, the reviewer suggested us to elaborate the biological N fixation, net import/export of N in food and feed, respectively. Below, we addressed the 3 points raised by Dr. Zhang.

For biological N fixation (BNF):

We added the following statements to the revised manuscript to clarify our considerations of BNF.

*"For biological nitrogen fixation (BNF), there are two types of BNF, agricultural BNF and natural BNF. Agricultural BNF could be a significant N source. For example, Alfalfa (*Medicago sativa *L.) can fix 21800 kg-N km^{-2} yr^{-1} (McIsaac et al., 2002) which is comparable with that from synthetic fertilizers. A local survey also indicates that the amount of N from green manure crops is close to the amount of synthetic fertilizers commonly applied in the fields and farmers typically do not use synthetic fertilizers following the growth of green manure crops (*http://www.tndais.gov.tw/search_wg.php*). Quality data of agricultural BNF in Taiwan is incomplete and cannot be confidently compiled at an island-wide scale. Therefore, we assume that the agricultural BNF equals the amount of synthetic fertilizers used and it is already included in our calculation of N input from fertilizers. For natural BNF, a global synthesis indicates that natural BNF in forest ecosystems varies from 1600 in temperate region to 2500 kg N km^{-2} yr-1 in tropical region (Cleveland et al., 1999). However, a recent study indicates that BNF in tropical and subtropical regions is not significant and may be overestimated by more than 5 times in previous studies (Sullivan et al., 2014). The study proposes that natural BNF in tropical forests should be less than 600 kg-N km^{-2} yr^{-1}. Using this new estimate, the natural BNF would account for less than 5% of the total N input in our study so that it is not included in our analysis."*

For Net N import/export:

As the reviewer pointed out, food import/export is an important source for calculating N export in NANI approach. Taking net food flow into account is a good way for estimating human emissions in country scale. However, it is very difficult to re-allocate or track the imported foods at to individual watersheds (Swaney et al., 2015). Moreover, food amount is a good surrogate of N export when mainly considering human physiologic responses, but is likely an incomplete estimate for export from human activities (e.g. vehicle combustion and energy consumption). The GDP-based approach proposed by Van Drecht et al. (2009) is also a reasonable alternative surrogate of human activities. We addressed this issue in the section of methodology for clarification.

"N input from human emissions, which are a main source of riverine N, is calculated using a GPD-based estimation proposed by Van Drecht et al. (2009) for per capita N emissions. The average GDP of Taiwan during 2002-2012 is ~30000 US dollars and the per capita human N emissions are ~6.42 kg-N cap^{-1} yr^{-1} following the GDP-based estimation. The population size from county-based censuses is converted to county-based population density and then used to estimate the total human emissions. Similar to the calculation of fertilizers used in each watershed, the watershed polygons are used to calculate human emissions for each watershed."

For Livestock excretion:

We agreed that livestock excretion N is an important source in the temperate region where the cattle and swine are the main sources of protein, because per capita N excretion from livestock excretion is very high, particularly for cattle. We added the following information to the revised manuscript to address this issue.

"Livestock could be an important source of N. The basic information of livestock in Taiwan is listed in supplementary table 1 which also compares the numbers of cattle, cow, and swine in Taiwan, US, and China. From the table, it is clear that the number and density of cattle and cows in Taiwan are much lower than those in the other two countries. Although the density of swine is much higher in Taiwan than in the other two countries, it is important to note that ~ 2/3 of the island is mountainous with very limited number of swine. Most pig farms are located in the west plains and regarded as point sources of pollution so that wastewater treatment is mandatory. Because livestock industry is not a primary source of N in Taiwan and most of the livestock farms are located in the central to southern coastal zones, not in the mountainous region where the studied watersheds are located, livestock execration is not included in our calculation of N inputs."

Table 1 The number and density of cattle, cows, and swine in Taiwan, US, and China (unit: million), from: http://www.indexmundi.com/agriculture

Country (area, 1000 km^2)	cattle	cows	Density (cap km^{-2})	swine	Density (cap km^{-2})
Taiwan (36)	0.03	0.11	3.8	5.5	152.8
US (9388)	89.8	9.2	10.5	118.5	12.6
China (9147)	100.6	16.6	12.8	682.3	74.6

Additional Comment

(2) About the analysis on the impacts of N inputs on DIN, some individual research on nitrate or ammonia could be helpful. I listed some of them for your consideration (please see below).

Reply:
We appreciated the reviewer sharing the papers. We added them in our references and used them in the discussion section to clarify the speciation of the DIN in the three categories.

Referee #1

The study by Huang et al. quantifies DIN fluxes from Taiwanese watersheds across a range of land use, population, and Nitrogen input rates. The results are compared extensively to other world watersheds reported in the literature. The watersheds of Taiwan have greater precipitation and N input rates than is typical in global syntheses, so studying these watersheds is a good rationale for expanding the global response surface for looking at N retention capacity. They find that watershed N retention declines with increasing N loading (or impact), and that much of the decline is due to increasing NH4 exports. The Taiwanese watersheds have a much higher proportion of ammonium export than other world watersheds, especially in the impacted watersheds. Overall this is a good paper, but I am unsure that the export flux estimates are robust. Whereas the ammonium concentrations were estimated monthly, nitrate concentrations were only measured 4x per year. This is very infrequent, and may miss many of the storm events, when concentrations are often quite dynamic compared to base flow. This is particularly true in impacted watersheds (both urban and agricultural). I assume many of the nitrate measurements were collected during relatively lower flows since these are more frequent. If concentrations dilute during storms (as is common for DIN in many agricultural systems), this would be an overestimate of N exports. It will be impossible to address this with the data in hand. However, this must be evaluated (e.g. what is the mean flow during sample periods compared to annual mean flow? What are flow weighted concentrations?), and then discussed for each N form. Perhaps there are some estimates of storm event nutrient samples that can be used to discuss this issue as well. The limited nutrient sampling may also contribute to the patterns in NH4:NO3 in Taiwan compared to other world rivers. Error in this ratio is likely to be greatest in more disturbed watersheds due to dynamic flow and concentration patterns. This also needs some discussion. Further DIN alone does not represent the N export budget. DON and PON are likely also important, the latter particularly in Taiwan with high flows, large storm events, and steep slopes. These are not considered at all. Part of the difference might be due to the relative importance of organic vs. inorganic forms across watersheds. Discussion about how this may influence the results is also needed. The method for estimating fertilizer and human waste loading to each watershed is not described. While N deposition estimates are likely fairly robust, these other loads are not as easy to obtain, and so should be included. It is especially a problem when scaling to watershed boundaries, which likely differ in scale from where the data to estimate loads comes from.

I also think there needs to be more discussion on why export ratio is higher in impacted watersheds. Discussion (e.g. 16412.8-11) doesn't discuss why change in population or land cover result in lower retention rates. Why are these watersheds at more advances stage of N excess. Mechanism of increasing rainfall would also affect low impact watersheds, so this alone not a reason. Is population the best indicator to classify watershed impact? It seems ag land cover would be better, given the sensitivity to this. The writing overall is very understandable, but the text still needs a good edit.

Reply:

We are grateful for the professional comments raised by the reviewer, which made us think more deeply about our study. Through taking the comments into our revision we believe that our revised manuscript is more focused and more readable. In summary, there are 5 concerns in this review report. They are: (1) is sampling frequency sufficient to estimate the 'representative' flux, particularly for nitrate; (2) The role of DON and PN in Taiwanese rivers; (3) Adding clear descriptions of the estimation of fertilizer and human waste loading to each watershed; (4) Explain why the export ratio is higher in impacted watersheds; (5) why population is chosen to classify watersheds. Below is our point-to-point reply.

Comment (1):

Sampling frequency is an important issue for calculating flux, particularly for small mountainous rivers in which the storm discharge variation can surge to 2 or 3 orders of magnitude, compared to the low flows. We appreciated the reviewer's suggestion for comparing mean flow during sample periods with annual mean flow and for the use of the flow weighted concentrations to evaluate the validity of our sampling frequency. In the revised manuscript, we added this in a supplementary table and added the following information to the table.

"*We addressed this issue in our previous studies in several mountainous headwater catchments and a nested watershed in central and northern Taiwan (Huang et al., 2012; Lee et al., 2013; Lee et al., 2014; Lin et al., 2015; Shih et al., revised). In those studies, we also conducted some high-frequency sampling works (every three hours) during typhoons. We found that the relationship between nitrate concentration and streamflow varied from hydrological enhancement to dilution along the urbanization gradient, but most watersheds showed hydrological control over nitrate loading and suggest that that nitrate loading is approximately proportional to streamflow (Lee et al., 2013). For estimation method, we calculated the arithmetic and flow-weighted mean of nitrate to investigate the potential differences resulting from differences in* *methods. In this table, the difference between arithmetic and flow-weighted means of all samples were less than 30 uM, except Site # 1159 which is 37 uM. In terms of yield, the mean difference between arithmetic and flow-weighted means was 271.4 kg-N km-2 yr-1. Most of the differences were less than 1000 kg-N km-2 yr-1, except the Site no. 1159 in which the difference was up to 1339 kg-N km-2 yr-1. For the three categories of watersheds, the mean differences were 169.2, 219.6, and 405.3 kg-N km-2 yr-1, respectively, for the low, moderately, and highly disturbed watersheds. Compared to the N inputs, the differences caused by the estimation methods were ~3% and will not alter the results we presented in this study.*

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 Systems Sciences, 16 (3): 699-714, doi:10.5194/hess-16-699-2012.

Lee, T.Y., Huang, J.C.*, Kao, S.J., Tung, C.P. (2013) Temporal variation of nitrate and phosphate transport in headwater catchments: the hydrological controls and land use alteration, Biogeosciences, 10 (4): 2617-2632, doi: 10.5194/bg-10-2617-2013.

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, doi:10.5194/bg-11-5307-2014.

Lin, T.C., Shaner, P.-J. L., 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, 4493-4504, doi: 10.5194/hess-19-4493-2015.

Comment (2):

The reviewer asked us to describe the role of DON and PN in Taiwanese rivers. First, as our title indicates that this study focused on the riverine DIN export not a comprehensive N budget. We focused on DIN because it is an important indicator of water quality and comprises the majority of total riverine nitrogen in both Taiwan and the world (Galloway et al., 2004; McCrackin et al., 2014). In our previous works and some unpublished data sets, we found that DON accounts for less than 20% of the total dissolved nitrogen in many highly-disturbed watersheds (Lee et al., 2014) and in upstream watersheds, it is less than 5% due to very low DOM in the lotic streams. Because the proportion of DON is not significant for total riverine N, we focused on DIN in this study. For PN, storms transport a large quantity of sediments during high flows in the steep landscape. We agreed that the sediments should contain considerable PN, but the majority of the sediments come from landslides which are not directly caused by human activities (Huang et al., 2012). In fact, we have some observations along a tributary in Danshuei River, which is featured by the urbanization gradient from upstream to downstream. The observations showed that the PN concentration in upstream and downstream are ~4.67 uM and 32.51 uM, respectively which is less than 10% of DIN in normal flow regime. We did a PN sampling during a rainstorm along a river system and found that PN concentration in downstream sites reached ~60.28 uM (Huang unpublished data). However most storms only lasted one to a few days. Thus, our focus on riverine DIN export associated with human activities should not lead to a biased understanding of patterns of overall nitrogen export. Yet, we agreed that the role of DON and PN would be a good next step in our study of N cycling in Taiwan. We included this response with the cited references in the "Discussion" section of our revised manuscript.

Lin, C.H. (2015) Research on biogeochemical condition in Danshuei River midstream and downstream with observation and 1-D advection-diffusion-reaction model simulation (Master dissertation). Graduate Institute of Hydrological and Oceanic Science, National Central University, Zhongli District, Taoyuan, Taiwan.

McCrackin, M.L., Harrison, J.A., Compton, J.E. (2014) Factors influencing export of dissolved inorganic nitrogen by major rivers: A new, seasonal, spatially explicit, global model, Global Biogeochemical Cycles, 28, doi:10.1002/2013GB004723.

Galloway, J.N. et al. (2004) Nitrogen cycles: Past, present, and future. Biogeochemistry, 70(2): 153-226.

Comment (3):

We added the following statements to describe our estimations of N loading from fertilizers and human waste to each watershed in the revision. "*N input from fertilizers is compiled from the crop types and fertilizer applications for each crop type (as partly shown in Table 1). A look-up table for fertilizer applications for each crop type was embedded into the land cover layer (map) so that the crop types could be converted to fertilizer input. Then, we use the individual watershed polygon to clip the land cover layer to estimate fertilizers used in each watershed. N input from human emissions (wastewater), which are a main source of riverine N, is calculated using a GPD-based estimation proposed by Van Drecht et al. (2009) for per capita N emissions. The average GDP of Taiwan during 2002-2012 is ~30000 US dollars and the per capita human N emissions are ~6.42 kg-N* cap^{-1} yr^{-1} *following the GDP-based estimation. The population size from county-based censuses is converted to county-based population density and then used to estimate the total human emissions. Similar* *to the calculation of fertilizers used in each watershed, the watershed polygons are used to calculate human emissions for each watershed.*"

Comment (4):

The high export ratio for the highly disturbed watershed is indeed striking and there are two possible causes. First, most of the high DIN runoff from urban entering streams may be due to the limited wastewater treatment and incomplete sewer drainage system which cannot effectively handle the large quantity of DIN emitted by the large population. For treatment facilities in Taiwan (http://sewagework.cpami.gov.tw/), the average N removal efficiency is ~50% and the installation rate in Taipei and Kaohsiung (the largest two cities in Taiwan) are ~70 and 30% of the household. Extremely high NH_4 concentration, over 300 uM, in the urban drainage systems (Lee et al., 2014) indicating the inadequateness of the water treatment systems. This is likely also the reason for the very high NH_4 concentration in downstream or highly-disturbed watersheds. Second, the farms close to the urban are more heavily fertilized than those in the mountains. For example, most paddy fields are located in the downstream and most of them were very heavily fertilized compared to the farms in the mountainous region. Thus, considering the urban locality, N excess is more likely to occur in the downstream watersheds. The above mentioned information is added to the "Methods" and "Results and Discussion" sections.

Comment (5):

Both population and agriculture land cover are good for classifying the watershed impacts. Agriculture land cover under similar environmental settings and fertilizer practices is a good indicator for non-point pollution as we showed in Figure 4. However, our results (see Fig. 5) clearly show that the changes in riverine DIN export is more closely related to population density than to agriculture land cover at broader scales (as reported in some global syntheses). Thus, we chose to use population for classification watershed impacts.

Referee #2

This paper addresses an important topic of growing concern and interest, the fate of N in watersheds in southeast Asia. The paper is well organized, but needs further editing for English usage. In general the discussion does not provide enough information for the reader (or the authors) to make an informed interpretation of the differences in DIN export among the watershed types. For example, there is no discussion of the sources of wastewater from highly developed lands, are there modern wastewater treatment facilities? Are there areas of septic systems? Are there areas with no treatment of wastewater? What types of wastewater treatment are used and how much do they vary among the watersheds? While I understand the authors are presenting a large scale analysis of N input and export from a number of watersheds across Taiwan, a more thorough investigation of the three broad N sources presented would improve the paper. The different types of agriculture are presented with estimates of N fertilizer use, although it is unclear how those estimates are converted into N input estimates on a watershed scale. A similar investigation of the potential N inputs from the highly populated areas seems appropriate and would improve the discussion. In addition, it would be useful to include a short discussion of the forest history in these watersheds. Are the forests in the moderately and highly disturbed watersheds similar to those in the low disturbed watersheds? If so it would be interesting to note that even with the same retention capacity the moderately and highly disturbed watersheds have completely overwhelmed that capacity. DIN export is estimated based on very few samples which may be one of the reasons the results from this study do not agree with early studies. While the author's explanation of why these results differ may also be true it is very difficult to make the determination based on export calculated with quarterly nitrate samples and monthly ammonium samples. I suspect storm runoff plays an important role in N transport in these watersheds, were any of the samples collected during storms? How well did the sampling strategy capture the range in flow conditions? Furthermore, there is no discussion of organic nitrogen. While the focus of the paper is DIN, I suspect DON is a large contributor to total N export in this region. In general the paper is lacking information for many important components of N inputs and exports and as a result it is difficult to evaluate the accuracy of the conclusions.

Reply:

It's good to receive the constructive comments which certainly help to improve this study and elevate the scientific merit in global syntheses of N export. We summarize the comments into five main points: (1) addressing the sources of the wastewater from the highly impacted watersheds, (2) the estimation of N inputs in relation to agriculture and population, (3) adding a short discussion of the forest history, (4) the effects of sampling frequency and storm event in flux estimation. (5) the proportion of DON in the total riverine N export in the watersheds. Below are our point-by-point reply.

Comment (1):

We added the following information to address the sources of wastewater to the highly disturbed watersheds.

In the Methods:

"*There are a total 49 wastewater treatment centers (most of them located in the cities) with daily capacity of ~2.3 million tons of water in Taiwan (http://sewagework.cpami.gov.tw/). Most of them are equipped with secondary treatments that remove 80% NH_4. Yet, NO_3 removal is not required so that the average N removal efficiency is only ~50%. As of 2003, approximately 70% and 30% of the households in Taipei and Kaohsiung (the largest two cities in Taiwan) had been connected to a sewage system, respectively. The distribution of the water treatment centers and their treatment capacity are given in supplementary Fig. 1*".

In the Results and Discussion

"*The NH_4 concentration (over 300 uM) in the urban drainage systems of Taiwan is very high (Lee et al., 2014) due to the low proportion of households connected to a sewage system. The high human emissions and the short water residence time likely result in the dominance of NH_4 in downstream watersheds unless effective NH_4 removal measures are applied in wastewater treatments*".

Comment (2):

Please see our response to the third comment of Dr. Zhang.

Comment (3):

We added the following land use history when we discuss DIN export of low disturbed watersheds.

"*Prior to 1980s, forests are under extensive exploitation island-wide, only forests in very high elevations with very limited accessibility were not heavily deforested. The large scale deforestation led to serious consequences in soil and water conservation including many catastrophic landslides and debris flows. Then, due to public pressure, deforestation largely stopped in late 1980 and was entirely prohibited since 1991. Many low- to mid-elevation forests are undergoing secondary growth. . It is* *likely that the secondary forests are still capable of taking up large amounts of N leading to the low DIN export ratio and the lack of a close relationship between N input and output.*"….. ""

Comment (4):

Please see our response to the first comment of Reviewer #1.

Comment (5):

Please see our response to the first comment of Reviewer #2.

Dear Dr. Pellerin

My coauthors and I have comprehensively revised the manuscript according to the comments provided by you and the reviewers. We have highlighter major changes in yellow color. We also attached a file with point-by-point responses to each of the three reviewers which is a revised version of the responses that we submitted two weeks ago. We include the responses to general comments only in the point-by-point response file this time. However, we did work carefully on the specific comments and the responses were included in the response files that we submitted on January 18, 2016. Here I would like to highlight some of our major efforts in our revision. First, we considerably extended the "Methods" section to clarify our calculations of nitrogen loading (e.g., biological nitrogen fixation and emissions from livestock in section 2.3) and DIN export (mainly the calculation of river discharge and chemical analysis and our justification for the use of quarterly sampling in section 2.4). Second, we added some supplementary information (F1 figure and two table) to address some of the comments. We believe that although they are important, inserting them to the main text may interrupt the flow of the manuscript so that we included the as supplementary information. For example, the issue of sampling frequency is important in our calculation of DIN export but the somewhat lengthy description (which is necessary to clarify the concerns) may distract the readers. Thus we briefly described it in the main text and give more detail in the supplementary table. Third, we have consulted native speakers in the revision to minimize language problems.

We appreciate the reviewers for their constructive comments which really help to improve the quality of the manuscript. We have tried our best to incorporate them in the revision and believe the manuscript is now much improved from the original version. If you have any question about our revision please contact me via email (tclin@ntnu.edu.tw) or by phone (+886-2-77346241).

Sincerely yours

Chiu

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Effects of different N sources on riverine DIN export and retention in subtropical high-standing island, Taiwan

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Abstract

Increases in nitrogen (N) availability and mobility resulting from anthropogenic activities have substantially altered N cycle both locally and globally. Taiwan characterized by the subtropical montane landscape with abundant rainfall, downwind to the most rapidly industrializing east coast of China can be a demonstration site for extremely high N input and riverine DIN (dissolved inorganic N) export. We used 49 watersheds with similar climatic and landscape settings, but classified into low-, moderate-, and highly-disturbed categories based on population density to illustrate their differences in nitrogen inputs (through atmospheric N deposition, synthetic fertilizers, and human emission) and DIN export ratios. Our results showed that the island-wide average riverine DIN export is ~3800 kg-N/km^2/yr, approximately 18 times of the global average. The average riverine DIN export ratios are 0.30-0.51, which are much higher than the averages of 0.20-0.25 of large rivers around the world indicating excessive N input relative to ecosystem demand or retention capacity. The low-disturbed watersheds have high N retention capacity and DIN export ratios of 0.06~0.18 in spite of the high N input (~4900 kg-N/km^2/yr). The high retention capacity is likely due to effective uptake by secondary forests in the watersheds. The moderately-disturbed watersheds show a linear increase of DIN export with increases in total N inputs and mean DIN export ratios of 0.20 to 0.31. The main difference in land use between low and moderately disturbed watershed is the greater proportion of agricultural land and cover in the moderately-disturbed watersheds. Thus, their greater DIN export could be attributed to N fertilizers used in the agricultural lands. The greater export ratios also imply that agricultural lands have lower proportional N retention capacity and that reforestation could be an effective land management practice to reduce riverine DIN export. The export ratios of the highly-disturbed watersheds are very high, 0.42-0.53, suggesting that much of the N input is transported downstream directly and urges the need of increasing the proportion of households connected to a sewage system and improving the effectiveness of wastewater treatment systems. The increases in riverine DIN export ratio along the gradient of human

disturbance also suggest a gradient in N saturation in subtropical Taiwan. Our results help to improve our understanding of factors controlling riverine DIN export and provide empirical evidence that calls for sound N emission/pollution control measures.

Keywords: dissolved inorganic nitrogen, anthropogenic nitrogen, subtropical mountainous watershed.

1. Introduction

Rapid increases in population and food demand inevitably hasten the emissions of anthropogenic nitrogen (N) via N-rich sewage, fertilizer runoff, and burning of fossil fuels and has led to a 10-fold increase in anthropogenic N emissions since the 1860s (Galloway et al., 2004). The elevated anthropogenic N emissions have increased the availability and mobility of N and as such altered N cycle (Vitousek et al., 1997; Gruber and Galloway, 2008). A substantial proportion of the increased N input is transported to river systems. In riverine systems, N species can be classified into PN (particulate nitrogen), DON (dissolved organic nitrogen), and DIN (dissolved inorganic nitrogen, including NO_2, NO_3, and NH_4), among which DIN is an important indicator of water quality and comprises the majority of total riverine N in most rivers (Galloway et al., 2004; McCrackin et al., 2014). Observed global riverine DIN export varies from 0.60 to 2200 kg-N km^{-2} yr^{-1} (He et al., 2011) while modeled DIN export varies from 0.0004 to 5217 kg-N km^{-2} yr^{-1} (Dumont et al., 2005). The more than 6-order variation reflects large spatial variation and complexity of N input, retention and transport processes (Howarth, 1998; Smith et al, 2005; Seitzinger et al., 2005). The recent high N input may have exceeded the limit of the earth system as a safe operating space for humanity (Rockström et al., 2009). Unfortunately, the increasing trend of N emissions is likely to continue in the near future, especially in Asia (Ohara et al., 2007). High quantity of N fertilizers has been shown to degrade soil fertility, water quality, and creates hypoxic zones in coastal areas (Fitzpatrick et al., 2004; Brown et al., 2009; Tu, 2009; Jiang and Yan, 2010). Because N is a common limiting nutrient element in many ecosystems, availability of N plays a key role in characterizing biodiversity and ecosystem function (Aber 1989, 1998). Anthropogenic N enrichment has been shown to negatively affect ecosystem function and biodiversity at a global scale (Townsend et al., 2009; Hutchison and Henry, 2010).

In freshwater systems, eutrophication is a common consequence of increases in DIN availability, aside from increases in phosphorus levels (Conley et al., 2009). To date, most empirical studies of DIN export were conducted at a geographically limited group of drainage basins in the developed temperate region (Smith et al., 2005; Galloway et al., 2008). In contrast, N deposition and DIN export in subtropical and tropical regions such as East Asia, characterized by high population, intensive agriculture system, and rapid industrialization, is not well documented. Because industrialization in East Asia is among the most rapid in the world, the impact of enhanced anthropogenic N emissions on watershed nutrient cycling is expected to get worse in the near future. Understanding DIN concentration and export in this region is crucial for a thorough understanding of global nutrient cycling in relation to anthropogenic N emissions.

Increases in population, agriculture activities, and atmospheric N deposition are well-recognized sources of elevated riverine DIN export. N retention and transfer processes determine how much of the N entering a watershed will be exported to the river system as DIN. In most riverine systems, DIN export is typically less than the total N input and the riverine DIN export ratio, defined as the DIN export divided by the total input, can be used to evaluate the nutrient-cycling function of a watershed. Quantification of N inputs and outputs of river systems with different levels of human disturbance (e.g., Groffman et al., 2004) provides scientific evidences of how human activities affect N cycling at scales that are relevant to land management. Previous studies indicated that ~20-25% of the N input is transported by river systems and the rest is retained or denitrified in large river basins in North America and Europe (Howarth et al., 2006). Furthermore, it has been proposed that riverine N export from the large rivers will increase 10-27% in the next 3 decades due to the increase of N input, while riverine N export ratio may increase 10-35% due to increases of rainfall which may shorten the water residence time (Howarth et al., 2006). Compared to the temperate region, we have very limited knowledge on riverine N export ratios in relation to human activities in tropical and subtropical regions regardless of their very rapid increases in N emissions.

Taiwan is a 36,000 km^2 subtropical island characterized by rugged topography, high rainfall, high industrialization and a very large population (23 million). Like many countries in East Asia the emissions of N and export of DIN in Taiwan is expected to be very high. In addition, the rich background information on various N inputs, topography and land use intensity make Taiwan an ideal site to assess the relative contributions of major emission sources to total N input and the effects of physical environmental characteristics and human impacts on DIN export. Therefore, this study aims to 1) characterize riverine DIN export in subtropical watersheds in Taiwan and 2) explore the relationship between land use and DIN export in Taiwanese rivers and compare it to riverine systems in other parts of the world.

2. Methods

2.1 Population density and Land use

There are approximately 23 million people living in the 36,000 km^2 Taiwan giving a population density of ~640 cap/km^2 (Fig. 1a). Most people live in the western plains, particularly in cities. For example, approximately 6.7 million people settle in the Taipei metropolitan area and the population density reaches 20,000 cap/km^2. This urges the need of sewage treatment systems for the large quantity of domestic wastewater. There are a total 49 wastewater treatment centers (most of them located in the cities) with daily capacity of ~2.3 million tons of water in Taiwan (http://sewagework.cpami.gov.tw/). Most of them are equipped with secondary treatments that remove 80% NH_4. Yet, NO_3 removal is not required so that the average N removal efficiency is only ~50%. As of 2003, approximately 70% and 30% of the households in Taipei and Kaohsiung (the largest two cities in Taiwan) had been connected to a sewage system, respectively. The distribution of the water treatment centers and their treatment capacity are given in supplementary Fig. 1.

Forests cover approximately 58% of Taiwan (mostly in the mountains) and agricultural lands mainly distributed on the west plains with some scattered on the hillsides. The agriculture in Taiwan is featured by an intensive cropping system with two to five harvests a year (two batches per year for paddy rice) due to intense sunlight, high precipitation and high temperature. The total arable land area is ~8,550 km^2, in which paddy fields account for 4,445 km^2 mostly in the western plain (Fig. 1b). Fodder and sweet maize are planted on the plains from central to southern Taiwan and sugar canes are cultivated in the southern coastal plain (COA, Council of agriculture, executive yuan, Taiwan, http://www.coa.gov.tw). Most of the remaining arable lands (4,100 km^2) spread over the hills, usually along roadsides or streamsides. Still some arable lands distribute in uplands with tea, orchard, vegetable, and bamboo as the main crops. The field area of tea is approximately 190 km^2 and of bamboo is approximately 300 km^2. Agriculture production in Taiwan largely depends on very high applications of synthetic fertilizers and crop protection measures. According to the COA survey, 500 kg-N/ha of N fertilizers are commonly applied for bamboo fields 420 kg-N/ha for tea plantations and 246 kg-N/ha for rice paddy annually (Table 1). For other crops, such as maize, sugar cane, watermelon, banana, and pineapple, more than 100 kg-N/ha of N fertilizers per year are applied (Table 1). The intensive fertilizer applications are not unique to Taiwan as it is also common in other countries of East Asia. For example, synthetic fertilizers applied in Lake Dianchi in China are as high as 150-200 kg-N/ha annually (Gao et al., 2014).

2.2 Basic watershed characteristics

A total of 49 watersheds distributing throughout the island are used for estimating watershed DIN export in this study (Fig. 1c). The watersheds are classified into 3 levels of human disturbance: low disturbed (16 watersheds), moderately disturbed (15 watersheds), and highly disturbed (18 watersheds) based on population density of < 20, 20-200 and >200 cap km^{-2}. The environmental settings of the three categories of watersheds are given in Table 2. Most of the watersheds have drainage areas of less than 1000 km^2. The average slopes and drainage densities of the three categories of watersheds vary from 66 to 29% and 1.4 to 1.6 km^{-1} (Table 2). The mean annual runoff of the 49 watersheds varies from 2200 to 2500 mm and the mean annual precipitation varies from 2000 to 4000 mm.

Forests dominate the landscape of all of the 49 watersheds and the proportion of forest cover decreases from 0.87 for low disturbed watersheds to 0.51 for highly disturbed watersheds (Table 3). Contrarily, the proportion of built-up lands increases from 0.03 for low disturbed watersheds to 0.11 for highly disturbed watershed and the proportion of agricultural lands increases from 0.11 for low disturbed watersheds to 0.38 to 0.38 for highly disturbed watersheds (Table 3). While, non-rice crops and orchards dominate the agricultural lands in all of the three categories of watersheds (> 80%), rice paddy and bamboo are important only in highly disturbed watersheds (Table 3). Unlike many watersheds in Europe and North America where agricultural lands may comprise more than half of the drainage area, agriculture in Taiwan and other mountainous regions is constrained by the rugged topography.

2.3 N loading

Data of atmospheric N deposition, synthetic fertilizer use, and human emissions are collected and compiled for the determination of the N inputs and the computation of riverine N export ratios. Because the emissions from livestock are insignificant, compared to other sources, they are not included in the analysis (see below).

For atmospheric N deposition, two modeling studies estimate a global average of 145 and 283 kg-N km^{-2} yr^{-1} for 1993 and 2050, respectively (Lelieveld and Dentener, 2000; Jeuken et al., 2001). Based on the two studies N deposition in East Asia will surge from ~1600 kg-N km^{-2} yr^{-1} in 1993 to ~3800 kg-N km^{-2} yr^{-1} in 2050 with a cross-year average of 2700 kg-N km^{-2} yr^{-1} (Fig. 2). Our local N deposition is based on a national-wide acid rain monitoring network (11 sites) initiated by Taiwan EPA (Environmental Protection Administration) in 2002. The mean annual wet N deposition, including NO_3 and NH_4, was 1,515 kg-N km^{-2} yr^{-1} between 2007 and 2013 with NH_4-N accounting for 59% of the deposition (http://epr.epa.gov.tw/upload/open/103). A local empirical study indicates that dry deposition of N is approximately 23-50% of wet deposition (Hsu et al., 2013) and thus a factor of 0.4 is used to estimate dry deposition of N from the island-wide wet deposition monitoring network. From the 11 monitoring sites, we interpolate total N deposition (wet + dry) for the island using the inverse distance weighted method with an exponent of 2. From the interpolation we calculate an island-wide mean total N deposition of ~2,121 kg km^{-2} yr^{-1} which is consistent with the N deposition reported by a global modelling (Jeuken et al., 2001) and a local observation (Hsu et al., 2013).

N input from fertilizers is compiled from the crop types and fertilizer applications for each crop type (as partly shown in Table 1). A look-up table for fertilizer applications for each crop type was embedded into the land cover layer (map) so that the crop types could be converted to fertilizer input. Then, we use the individual watershed polygon to clip the land cover layer to estimate fertilizers used in each watershed. N input from human emissions (wastewater), which are a main source of riverine N, is calculated using a GPD-based estimation proposed by Van Drecht et al. (2009) for per capita N emissions. The average GDP of Taiwan during 2002-2012 is ~30000 US dollars and the per capita human N emissions are ~6.42 kg-N cap^{-1} yr^{-1} following the GDP-based estimation. The population size from county-based censuses is converted to county-based population density and then used to estimate the total human emissions. Similar to the calculation of fertilizers used in each watershed, the watershed polygons are used to calculate human emissions for each watershed.

Livestock could be an important source of N. The basic information of livestock in Taiwan is listed in supplementary table 1 which also compares the numbers of cattle, cow, and swine in Taiwan, US, and China. From the table, it is clear that the number and density of cattle and cows in Taiwan are much lower than those in the other two countries. Although the density of swine is much higher in Taiwan than in the other two countries, it is important to note that ~ 2/3 of the island is mountainous with very limited number of swine. Most pig farms are located in the west plains and regarded as point sources of pollution so that wastewater treatment is mandatory. Because livestock industry is not a primary source of N in Taiwan and most of the livestock farms are located in the central to southern coastal zones, not in the mountainous region where the studied watersheds are located, livestock execration is not included in our calculation of N inputs.

For biological nitrogen fixation (BNF), there are two types of BNF, agricultural BNF and natural BNF. Agricultural BNF could be a significant N source. For example, Alfalfa (*Medicago sativa* L.) can fix 21800 kg-N km^2 yr^{-1} (McIsaac et al., 2002) which is comparable with that from synthetic fertilizers. A local survey also indicates that the amount of N from green manure crops is close to the amount of synthetic fertilizers commonly applied in the fields and farmers typically do not use synthetic fertilizers following the growth of green manure crops (http://www.tndais.gov.tw/search_wg.php). Quality data of agricultural BNF in Taiwan is incomplete and cannot be confidently compiled at an island-wide scale. Therefore, we assume that the agricultural BNF equals the amount of synthetic fertilizers used and it is already included in our calculation of N input from fertilizers. For natural BNF, a global synthesis indicates that natural BNF in forest ecosystems varies from 1600 in temperate region to 2500 kg N km^{-2} yr^{-1} in tropical region (Cleveland et al., 1999). However, a recent study indicates that BNF in tropical and subtropical regions is not significant and may be overestimated by more than 5 times in previous studies (Sullivan et al., 2014). The study proposes that natural BNF in tropical forests should be less than 600 kg-N km^2 yr^{-1}. Using this new estimate, the natural BNF would account for less than 5% of the total N input in our study so that it is not included in our analysis.

2.4 Stream water level and DIN monitoring

The Water Resources Agency (WRA, http://www.wra.gov.tw/) and Environmental Protection Administration (http://www.epa.gov.tw) of Taiwan are in charge of monitoring water quantity and quality, respectively. Streamflow and DIN data from 49 water level monitoring stations (Fig. 1c) in which both water level and water quality data are available during 2002-2012 are used in this study. The water level stations are widely deployed in bridge piers and record water levels automatically. The WRA crew measure the stream cross sections two or three times and flow velocity 10 times per year and based on these measurements the discharge at each station is obtained several times per year. From these discharge data and the water levels we develop a rating curve for estimating the discharge from the water levels for each of the 49 stations.

For water quality, the EPA sampling crews take water samples on a monthly basis. Temperature, pH and electrical conductivity (EC) are measured *in-situ* then the samples are transported to laboratories for chemical and biological analysis including dissolved oxygen, cations, anions, *Escherichia coli* (*E. coli*), and selected heavy metals. For DIN species, ammonium is analyzed on a monthly basis using 4500-NH_3 D. Ammonia-selective electrode method (APHA, 2012). Nitrate and nitrite are analyzed every three months using 4500-NO_3 I. (APHA, 2012) or ion exchange chromatography (IC). The mean concentrations of DIN species are multiplied by stream discharge (monthly for NH4 and quarterly for nitrate and nitrite) to obtain the DIN fluxes via global mean approach. The mean DIN concentration, flow-weighted mean concentration, mean discharge during sampling period and mean daily stream discharge are listed in supplementary table 2 for reference. From the data in the table and some of our previous studies we conclude that that although the quarterly sampling of NO_3 and NO_2 is not ideal for representing the variation among seasons and between high and low flow periods, the annual fluxes derived from the 10-year dataset could still fairly represent the differences among watersheds which is the main goal of our analysis. A more comprehensive justification of the use of the quarterly samples is provided in supplementary Table 2.

3 Results and Discussions

3.1 Riverine DIN concentration and flux

The island-wide mean DIN concentration and flux calculated from the 49 watersheds are 148.3 µM and 3,800 kg-N km^{-2} yr^{-1}, respectively. However, they vary considerably among the three categories of watersheds. The mean annual riverine DIN concentrations are 30, 57, 330 µM and the corresponding exports are 909, 1816, and 8020 kg-N km^{-2} yr^{-1} for low-, moderately- and highly-disturbed watersheds, respectively (Fig. 3). For N species, mean NO_3 concentration and export increase from 24 µM and 725 kg-N km^{-2} yr^{-1} for low disturbed watersheds to100 µM and 3243 kg-N km^{-2} yr^{-1} for highly disturbed watersheds (Table 4). Similarly, mean NH_4 concentration and export increase from 5.6 µM and 169 kg-N km^{-2} yr^{-1} for low disturbed watersheds to 214 µM and 4340 kg-N km^{-2} yr^{-1} for highly disturbed watersheds, respectively (Table 4). Nitrite is not shown in the table because it only accounts for a very small proportion (< 0.05) of DIN. The patterns and levels of DIN concentrations and fluxes of the 49 watersheds are consistent with results reported for over 20 sub-catchments within 2 river networks in northern and central Taiwan (Huang et al., 2012; Lee et al., 2014). Note that NO_3 is the dominant species for low and moderately disturbed watersheds, but NH_4 is the dominant species accounting for more than 50% of annual DIN flux for highly disturbed watersheds.

Both NO_3 and NH_4 exports are significantly and positively correlated to population density (r^2 = 0.19 for NO_3 and 0.18 for NH_4, both p values < 0.01) and the proportion of agricultural land cover (r^2 = 0.34 for NO_3 and 0.50 for NH_4, both p values < 0.01) (Fig. 4). The intensive cropping system and dense population likely contribute to the 10-fold greater DIN export at the highly disturbed watersheds relative to the low disturbed watersheds. While the relationship between population density and NO_3 and NH_4 export is very similar, NH_4 increase more dramatically than NO_3 with increases in relative agricultural land cover (Fig. 4). Across the three categories of watersheds, NO_3 export increases gradually with increases in both agricultural land cover and population density. By contrast, NH_4 export does not change much from low to moderately disturbed watersheds (Fig. 4), but increases dramatically with increasing agricultural land cover and population density in highly disturbed watersheds indicating that most of the elevated NH_4 export likely comes from domestic wastewater and agricultural activities.

3.2 Total N input

Mean total annul N input increases from 4893 kg-N km^{-2} yr^{-1} for the low disturbed watersheds, 6578 kg-N km^{-2} yr^{-1} for moderately disturbed watersheds, to 16636 kg-N km^{-2} yr^{-1} for highly disturbed watershed (Table 5). Because atmospheric N deposition is in a small range across the three categories of watersheds (2033-2224 kg-N km^{-2} yr^{-1}), it could not cause the large increases in total N deposition from low to highly disturbed watersheds. Instead the increases are mainly from fertilizer applications and human emissions (Table 5). Assuming synthetic fertilizers are applied only in agriculture lands, the input of N from fertilizers in each percent of agricultural land (a total of 11%, 16% and 38% in low, moderately, and highly disturbed watersheds, respectively) increases only slightly from 236 kg-N km^{-2} yr^{-1} in low disturbed watersheds, 254 kg-N km^{-2} yr^{-1} in moderately disturbed watersheds to 279 kg-N km^{-2} yr^{-1} in highly disturbed watersheds. In contrast, assuming human emissions are entirely from built-up lands the input of N from human emissions of each percent of built-land increases dramatically from 24 kg-N km^{-2} yr^{-1} in low disturbed watersheds, 118 kg-N km^{-2} yr^{-1} in moderately disturbed watersheds to 349 kg-N km^{-2} yr^{-1} in highly disturbed watersheds. The increases in N input from per unit built-up land as its contribution to total watershed area increases possibly reflect disproportional increases in population density as the proportion of build-up land increases which is often associated higher degrees of urbanization. The result suggests that population density control and/or the effectiveness of wastewater treatment could be important control measures of N emissions and the resultant DIN export.

3.3 River DIN exports in Taiwan and the world

Since the 1960s global N flux from land to ocean has elevated by 2-fold (Howarth et al., 2002). Regionally, it has increased by ~4-fold in the Mississippi River basin, 8-fold in northeastern U.S. and more than 10-fold for the rivers draining into the North Sea (Howarth et al., 2002). Dumont et al. (2005) reported that the global DIN export to coastal waters is ~25 Tg N yr^{-1} with more than 60% stemming from anthropogenic sources. Giving the global land of 120 million km^2, the average DIN export per unit land area is 208 kg-N $km^{-2}yr^{-1}$. Comparing to this global picture, the level of riverine DIN export in Taiwan, ~3800 kg-N $km^{-2}yr^{-1}$, is extraordinarily high as it is 18 times of the global average. Generally, the riverine N export is strongly affected by climatic factors and human activities; increasing from temperate to tropical climates and from pristine to disturbed watersheds (Howarth, 1998; Smith et al., 2005; Seitzinger et al., 2005). For example, the riverine N export is 76 kg-N $km^{-2}yr^{-1}$ for the sparsely populated watersheds in northern Canada, but reaches 1450 kg-N $km^{-2}yr^{-1}$ for the developed watersheds of the North Sea (Howarth et al., 1996).

He et al. (2011) reported a positive relationship between DIN export and runoff, population density and proportion of agricultural land cover at the global scale. Adding Taiwan to the global pictures reveals an interesting phenomenon (Fig. 5). Globally the DIN export increases with increases in runoff and Taiwan is clearly on the very high end of both runoff and DIN export. The global pattern exists regardless of the large differences in the efficiency of wastewater treatment among regions and among countries of the same region. Thus, in despite of the large differences in N inputs from wastewater, agriculture and industrial activities, runoff still plays an important role on DIN export.

Interestingly, few sites in the study of global N export by He et al. (2011) have annual runoff greater than 1 m yr^{-1}, while the mean runoff of the 49 watersheds in our study is 2 m yr^{-1}. High runoff is not limited to Taiwan as many tropical and subtropical forested watersheds show a similar pattern. For example, the forested watersheds in north Australia also have high runoff (1.96 m) and high DIN export (2300 kg-N $km^{-2}yr^{-1}$) (Hunter et al., 2008). Compared to the global scale variation of runoff (0.01-1.0 m), the variation within Taiwan is relatively small (1.5-2.5 m), but DIN export of the 49 watersheds varies largely (~900 to ~8000 kg-N $km^{-2}yr^{-1}$) even compared to the global picture (~10-2000 kg-N $km^{-2}yr^{-1}$) (Fig. 5). Yet, even 900 kg-N $km^{-2}yr^{-1}$ is on the high end of the global picture. Thus, adding Taiwan to the figure of global N export fills the gap for regions with both high runoff and high DIN export.

Among the three factors, population density, agriculture activity and runoff, only population density shows a consistent positive relationship with DIN export at both the global scale and our island scale (Fig. 5). Runoff is a good predictor only at the global scale and agriculture is a good predictor only at the island scale (Fig. 5). The lack of predictability of runoff on DIN export in Taiwan might be due to the limited variation in runoff relative to the 10-fold differences in DIN export (Fig. 5). The lack of predictability of agriculture land cover on DIN export at the global scale is not surprising because differences in farming practices (e.g., levels of fertilization and soil disruption) among regions could lead to very different patterns of DIN export even when the proportion of agriculture land cover is similar. In general, fertilizers are applied at much larger quantities in regions with intensive farming systems such as China, Taiwan, and Thailand than in regions with extensive farming systems such as North America, Europe and

Australia. For example, in rice fields N is applied at approximately 418 kg ha^{-1} yr^{-1} in Taiwan (~200 kg ha^{-1} for a harvest; FAO 2002), 194 kg ha^{-1} yr^{-1} in China but only 135 kg ha^{-1} yr^{-1} in California, USA (Yan et al., 2003). As a result of such large differences, DIN export from a watershed with 100% of rice fields in North America may not be different from the export of a watershed with 32% of rice fields in East Asia. Due to the differences in farming systems, the relationship between DIN export and agricultural land cover is likely comparable only between regions with similar management practices (Huang et al., 2012). For global assessments, the amount of N fertilizer application coupling with the proportion of agricultural land cover would be necessary for predicting riverine DIN export from agriculture.

From the global assessment by He et al. (2011), NH_4–N export is 10% to 100% of the total of NO_3- and NO_2-N export in large rivers around the world and this range also applies to the low and moderately disturbed watersheds in Taiwan (Fig. 6). However, while only one of the 49 watersheds has a NH_4 to NO_3+NO_2 ratio less than 0.1, approximately 50% (16/34) of the rivers in He et al. (2011) had a ratio less than 0.1. Moreover, none of the rivers in He et al. (2011) has a ratio greater than 1.0 but 10 of the highly disturbed watersheds in Taiwan have a ratio greater than 1.0 and one of them even reaches 10. Globally NO_3 is the predominant species of DIN export, partly because NO_3 is more stable than NH_4, which is easily oxidized or removed though the treatment processes. In the highly disturbed watersheds, the average DO is ~6.8 mgL^{-1} for watersheds with NH_4 to NO_3+NO_2 ratio greater than 1, and ~8.4 mgL^{-1} for the remaining watersheds suggesting that oxidation potential is important in determining NH_4 relative to NO_3+NO_2 concentration in streamwater. The highly disturbed watersheds are at lower elevations that have higher temperature than low and moderately disturbed watersheds and high temperatures would facilitate the oxidation of NH_4. Thus, the dominance of NH_4 in DIN export for the highly-disturbed watersheds regardless of their greater NH_4 oxidation potential is likely due to high NH_4 input.

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Using ^{15}N isotopic analysis Peng et al. (2012) found very limited NH_4 removal in upstream watersheds of Taiwan and suggested that NH_4 export from these watersheds to streams is very limited.

Water residence time in Taiwan is, in general, very short due to the small drainage area (< 1000 km^2) and steep slopes (>30%) and unfavorable for NH_4 removal (Halbfaβ et al., 2010) because of the limited time available for ammonia oxidization and/or assimilation. Thus, the very low NH_4 content in the low and moderately disturbed watersheds suggests that nitrification and vegetation uptake is substantial compared to mineralization in these watersheds. In contrast, our highly disturbed watersheds have high NH_4 concentrations and fluxes (Fig. 3 and Fig. 4). Although given the high NH_4 concentrations biogeochemical processes such as nitrification may transform a substantial portion of NH_4 (Venohr et al., 2005), it is very likely insufficient for transforming most of the NH_4 in the highly disturbed watersheds. The NH_4 concentration (over 300 uM) in the urban drainage systems of Taiwan is very high (Lee et al., 2014) due to the low proportion of households connected to a sewage system. The high human emissions and the short water residence time likely result in the dominance of NH_4 in downstream watersheds unless effective NH_4 removal measures are applied in wastewater treatments.

3.4 Riverine N export ratio

Although both total N input and output increase from low to highly disturbed watersheds, the increases are greater for output (from 575 to 15689 kg-N $km^{-2}yr^{-1}$) than input (from 3805 to 26668 kg-N $km^{-2}yr^{-1}$) (Table 5). As a result the measured DIN export ratio increases from 0.18 (ranging from 0.05 to 0.20) for the low disturbed watershed, 0.27 (0.11 to 0.38) for the moderately disturbed watersheds, to 0.42 (0.21 to 0.73) for the highly disturbed watersheds, with an average of 0.30 (Table 5). It appears that the highly disturbed watersheds have greater DIN export both in absolute quantity (per unit area) and relative to N input than less disturbed watersheds. Simple linear regression models indicate that the slopes between riverine DIN export and N input for the three categories are 0.06, 0.20, and 0.53 with R^2 of 0.03, 0.62, and 0.51 from low, moderately to highly disturbed watersheds, respectively (Fig. 7c, 7d, and 7e). The regression models support that with per unit increases in N input the rise in DIN export is greater at more disturbed watersheds than less disturbed watersheds. Increases of DIN output in absolute quantity could be at least partially explained by greater N inputs, but other factors must have contributed to the greater DIN export ratios at the more disturbed watersheds.

Although there is an overall increases in DIN export ratio with increases in N input, such a relationship does not exist for the low disturbed watersheds in which DIN export ratio is not significantly related to N input (Fig. 7b). Differences in runoff ratios are often used to explain the differences in export ratios because greater runoff ratios would lead to greater DIN export ratios (Huang et al., 2012; Lin et al., 2015). Watersheds with steeper slopes typically have shorter water residence time and greater runoff ratios than watersheds with less steep slopes. However, regardless of the substantial differences in slope steepness (53-76%) among our low disturbed watersheds, runoff and runoff ratio show very limited differences among the watersheds.

The capacity of plant N uptake and the amount of N that can be hold in the soil (e.g., NH_4 in the inter-layer space of Vermiculite and Montmorillonite and N in soil humus) greatly determine ecosystem N retention capacity. If N input is less than the retention capacity, then DIN export may be irrelevant to N input because most of the additional N input is retained within the watershed until it exceeds the retention capacity. This is probably the case for our low disturbed watersheds in which the riverine DIN export is ~900 kg-N $km^{-2}yr^{-1}$ which is relatively small compared to total input of 2000 to 8000 kg-N $km^{-2}yr^{-1}$.

The high DIN export ratios in alpine watersheds of the Front Range of Colorado with low atmospheric deposition in comparison to other regions where watersheds retain more N regardless of higher N input can be used to illustrate the role of biological uptake (Campbell et al., 2000). The N export ratio in alpine watersheds in Colorado ranges from 0.55 to 0.71 although atmospheric deposition was only 320-550 kg-N $km^{-2}yr^{-1}$ (Campbell et al., 2000) and by contrast the N export ratio for Baltimore LTER sites is less than 0.1 although the input of 1120 kg-N $km^{-2}yr^{-1}$ was much higher (Groffman et al., 2004; Kaushal et al., 2008). It has been suggested that the mature alpine forests in Colorado may have shown symptoms of advanced stages of nitrogen excess so that the forests have very limited capacity to retain N in spite of the low atmospheric N deposition.

Our low disturbed watersheds, which mostly distributed in the mountain ranges are characterized by high atmospheric N input and the mea riverine DIN export ratios (0.18) is slightly less than those of large rivers around the world (0.2-0.25) (Howarth et al., 2006). The low disturbed watersheds are predominately covered by natural forests. Prior to 1980s, forests are under extensive exploitation island-wide, only forests in very high elevations with very limited accessibility were not heavily deforested. The large scale deforestation led to serious consequences in soil and water conservation including many catastrophic landslides and debris flows. Then, due to public pressure, deforestation largely stopped in late 1980 and was entirely prohibited since 1991. Many low- to mid-elevation forests are undergoing secondary growth. It is likely that the secondary forests are still capable of taking up large amounts of N leading to the low DIN export ratio and the lack of a close relationship between N input and output. If forest growth is indeed key to the low DIN export and export ratio, then reforestation could be an effective management practice to reduce DIN export and therefore reduce the risk of downstream eutrophication, especially if the trees are regularly harvested before the forest matures and the ability to take up nutrients declines.

The moderately and highly disturbed watersheds show a linear relationship between DIN export and total N input with a slop of 0.2 for moderately disturbed watersheds and 0.53 for highly disturbed watersheds (Fig. 7d and 7e). The positive linear relationships suggest that the watersheds are unable to retain most of the increased N input and the likeliness of N excess (Liu et al., 2010). The greater export ratios of moderately disturbed watersheds than low disturbed watersheds most likely relate to their greater agricultural land cover (16%) (compared to 11% in low disturbed watersheds) because the proportion of built-up lands is similar between the two categories of watersheds. In addition, compared to the low disturbed watersheds the moderately disturbed watershed have more crops that are heavily fertilized (see section 3-2) and this may also contributed to their greater export ratios. Our results suggest that agricultural lands have lower N retention capacity than forests. Although agricultural lands only cover a small proportion of the watersheds, they have a high impact on riverine DIN export. Thus, concentrating management efforts (e.g. erosion control, precision fertilization) on agricultural lands could have major effects on reducing DIN export. The even greater riverine DIN export ratios of the highly-disturbed watersheds than the moderately disturbed watersheds likely result from their greater population density and greater agriculture intensity.

The considerable variation of export ratio, 0.21-0.73, of the highly disturbed watersheds may result from their differences in wastewater treatment efficiencies and cropping systems. In addition, the very high DIN export ratios in the highly disturbed watersheds suggest that the N input is transported by riverine systems very efficiently and as such the eutrophication threat is high downstream. The high export ratios also suggest that the highly disturbed watersheds are probably at more advanced stages of N excess and that the current removal processes (e.g. denitrification, vegetation uptake) cannot compensate for the increasing N additions (Downing et al., 1999). Additionally, recent studies report increases in rainfall intensity in Taiwan as a result of recent climate change (Huang et al., 2014; Liu et al., 2009). Increases of rainfall intensity would shorten water residence time and therefore further enhance riverine DIN export. Thus, increasing the proportion of households connected to a sewage system and improving the effectiveness of the sewage systems are of particular importance in mitigating riverine N export in Taiwan and other regions with high population densities and intensive cropping systems.

4. Concluding remarks

We characterize riverine DIN export of subtropical watersheds in Taiwan using a total of 49 watersheds classified as low-, moderately-, and highly-disturbed based on population densities (from < 20 to > 200 cap km^{-2}). The average riverine DIN export is ~3800 kg-N $km^{-2}yr^{-1}$, approximately 18 times the global average and is attributable to the high runoff, high atmospheric N deposition, intensive crop systems, and high human emissions. Because the runoff vary only by two fold and atmospheric deposition vary less than 30%, the ~10 times greater DIN export of highly disturbed watersheds (8000 kg-N $km^{-2}yr^{-1}$), compared to low disturbed watersheds (900 kg-N $km^{-2}yr^{-1}$) likely results from their differences in inputs from agricultural lands, human emissions and watershed N retention capacity. Nitrate is the dominant N species for large rivers around the world and our low and moderately disturbed watersheds, whereas NH_4 is the dominant species in the highly-disturbed watersheds possibly due to high human emissions and the short water residence time, which is unfavorable for ammonia removal processes. The high N export to downstream system poses risk of eutrophication.

Our averaged riverine DIN export ratios, 0.30-0.51, are higher than those (0.2-0.25) of many major rivers around the globe. Even the low-disturbed watersheds have very high atmospheric N input (2200 kg-N $km^{-2}yr^{-1}$). However, they only export 6-18% of the N input implying that the watersheds have high N use efficiency and/or retention capacity possibly due to uptake by the still growing secondary forests. The moderately disturbed watersheds export 20-27% of the total N input (3330-15315 kg-N $km^{-2}yr^{-1}$). The positive linear relationship between DIN export and total N input indicates the degradation of nitrogen retention capacity and symptoms of nitrogen excess. The riverine DIN export ratios of the highly-disturbed watersheds are very high (0.42-0.53) and could be attributed to synergistic effects of high population density and agricultural activities. The high N export ratios indicate that the human-associated N inputs are transported to riverine systems very efficiently and that the systems may be in advanced stages of N excess. The result also indicates that current in-stream removal processes (e.g.

denitrification and uptake) cannot effectively reduce riverine N export. Increasing the proportion of households connected to a sewage system and improving the effectiveness of the sewage system are important measures for reducing N export.

Acknowledgements

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Table 1.Crop area and yield and estimated quantities of fertilizers used in Taiwan (from FAO, 2002)*

Crop	Harvested area (ha)	Average yield (kg/ha)	Est. quantities of fertilizers used** (ton)		
			N	P_2O_5	K_2O
Paddy and rice	353065	10646	41793	15314	16462
Maize (fodder & sweet)	34854	11970	3485	2440	1742
Groundnut	26495	2535	539	1192	1060
Sugar cane	30657	81337	6438	1073	2146
Tea	19142	1103	8040	2680	2680
Bamboo shoot	29819	12030	14910	3727	5069
Watermelon	19720	19685	3550	2366	3944
Banana	8961	23718	2216	1090	4433
Pineapple	7340	47474	2422	440	1321
Mango	18700	11065	449	299	673
Litchi	10530	9385	316	211	284

*Only the primary crops are listed

** The fertilizer amount are suggested by COA (Council of Agriculture, Taiwan) which surveys the crop plantation and declares the suggested values for farmers

Table 2. Watershed environmental settings of the three categories of watersheds

category	number	N deposition ($kg\text{-}N/km^2$)	Area (km^2)	Runoff (mm)	Avg. slope (%)	DD* (km^{-1})	Pop. Den. (cap/km^2)
Low disturbed	16	2224 (369)	592 (486)	2250 (554)	66.3 (5.6)	1.35 (0.05)	11.4 (4.2)
Moderately disturbed	15	2030 (458)	1030 (913)	2420 (638)	55.3 (7.6)	1.40 (0.10)	55.2 (22.2)
Highly disturbed	18	2200 (352)	379 (462)	2270 (542)	29.1 (14.0)	1.63 (0.18)	598 (586)

*DD: Drainage density defined as the total stream length over drainage area, the unit is (km^{-1})

The values and the parentheses indicate the means and the standard deviations of the individual category

Table 3. Relative land cover composition of the three categories of watersheds

category	Forest	Built-up	Agriculture				
			total	paddy	crops	orchard	bamboo
Low	0.87	0.03	0.11	0.0	0.05	0.05	0.01
disturbed	(0.06)	(0.01)	(0.08)	N/A	(0.06)	(0.03)	(0.01)
Moderately	0.81	0.03	0.16	0.02	0.05	0.08	0.02
disturbed	(0.11)	(0.01)	(0.10)	(0.03)	(0.06)	(0.08)	(0.04)
Highly	0.51	0.11	0.38	0.06	0.09	0.23	0.08
disturbed	(0.22)	(0.05)	(0.19)	(0.08)	(0.06)	(0.13)	(0.11)

Parentheses indicate the standard deviation of the individual category

N/A: No paddy in the low-disturbed watersheds

Note that the national land use classification put bamboo field as part of the forest cover but farmers use fertilizers for their bamboo fields so that they also appear in the Agriculture part in the table.

Table 4. Mean annual NO_3, NH_4 and DIN concentrations and riverine fluxes of the three categories of watersheds between 2002 and 2012.

category	NO_3		NH_4		DIN	
	conc.	flux	conc.	flux	conc.	flux
Low disturbed	23.8 (9.9)	725 (243)	5.60 (3.20)	169 (86.8)	29.9 (11.0)	909 (285)
Moderately disturbed	50.2 (31.1)	1600 (854)	5.70 (2.80)	182 (87.9)	56.9 (31.5)	1820 (854)
Highly disturbed	99.6 (42.9)	3240 (1580)	214 (205)	4340 (3700)	329 (216)	8020 (4200)

Parentheses indicate the standard deviation of the individual category

Unit for concentration and flux are μM and kg-N/km^2, respectively

Table 5. Nitrogen inputs, riverine output and riverine export ratios of the three categories of watersheds.

	Low-disturbed	Moderate-disturbed	Highly-disturbed	All watersheds
Atmospheric deposition	2220	2030	2200	2160
Synthetic fertilizer	2600	4190	10600	6020
[1]Human emission	73.4	354	3840	1540
Total input	4900	6580	16600	9720
Riverine DIN output	909	1820	8020	3800
[2]Averaged export ratio	0.18	0.27	0.42	0.30
[3]Regressive export ratio	0.06	0.20	0.53	0.51

Unit for inputs and output is kg-N $km^{-2}yr^{-1}$

1. Human emissions are calculated from per capita emissions using GDP-based estimation proposed by Van Drecht et al. (2009).
2. Averaged export ratio is the arithmetical mean of the export ratios in the category.
3. Regressive export ratio indicates the regressive slope of DIN output with DIN input in the category.

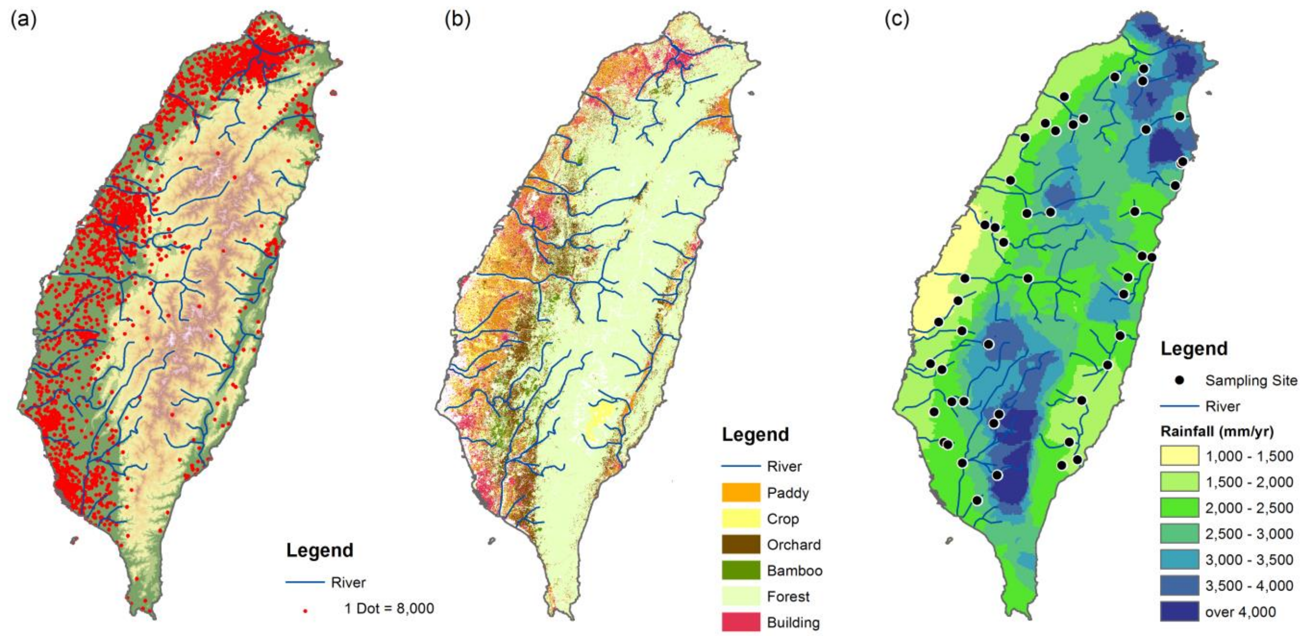

Figure 1. Three maps of Taiwan to show the population density (a), land cover (b), and mean annual rainfall (c). The annual rainfall dataset is provided from water resources agency during 2002-2012. Population dataset is derived from county census from Ministry of Interior. Land cover dataset is distributed by Ministry of Interior in 2006.

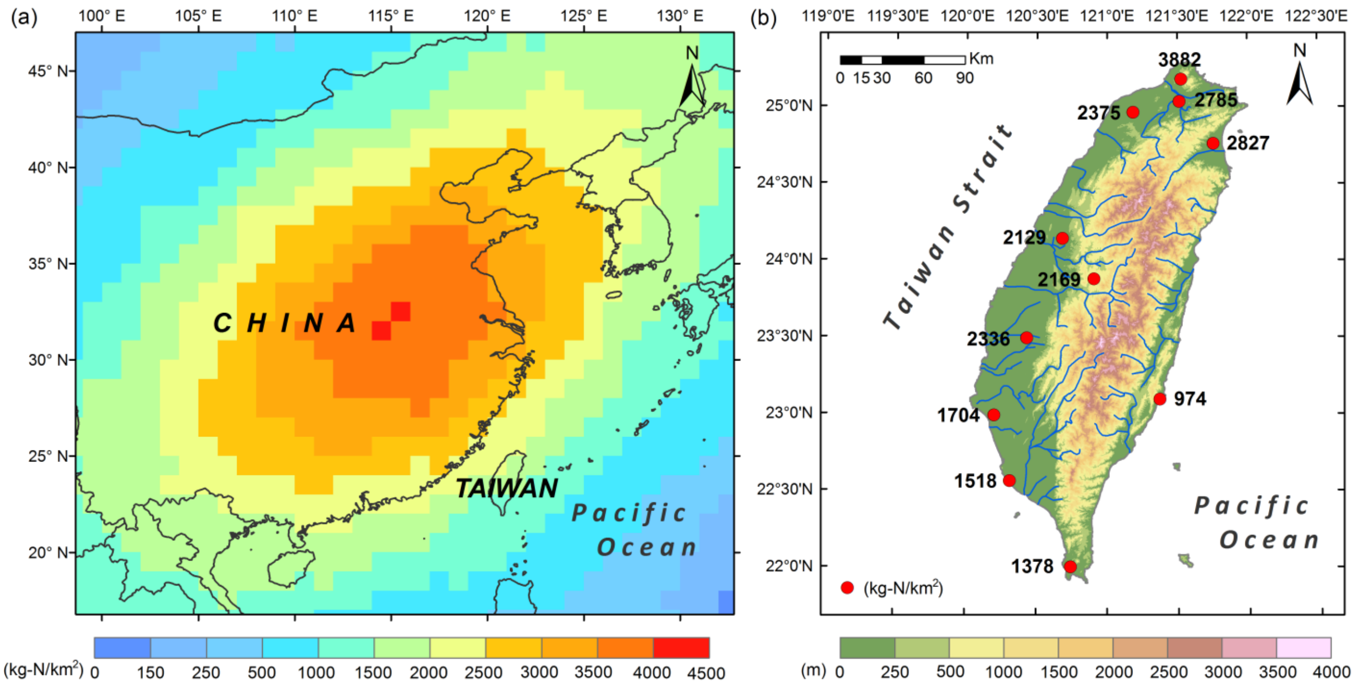

Figure 2. Atmospheric N deposition in eastern Asia (dataset: from ORNL DAAC, NASA, http://daac.ornl.gov) (a). This dataset was generated using a global three-dimensional chemistry-transport model (Lelieveld and Dentener, 2000; Jeuken et al., 2001 re-sampled to 1degree × 1 degree). The observational long-term N deposition (including NO_3 and NH_4) in Taiwan (Lin NH, unpublished data) (b). The observed wet deposition is used to estimate the dry deposition by an empirical factor of 0.4 based on (Lin NH, unpublished data).

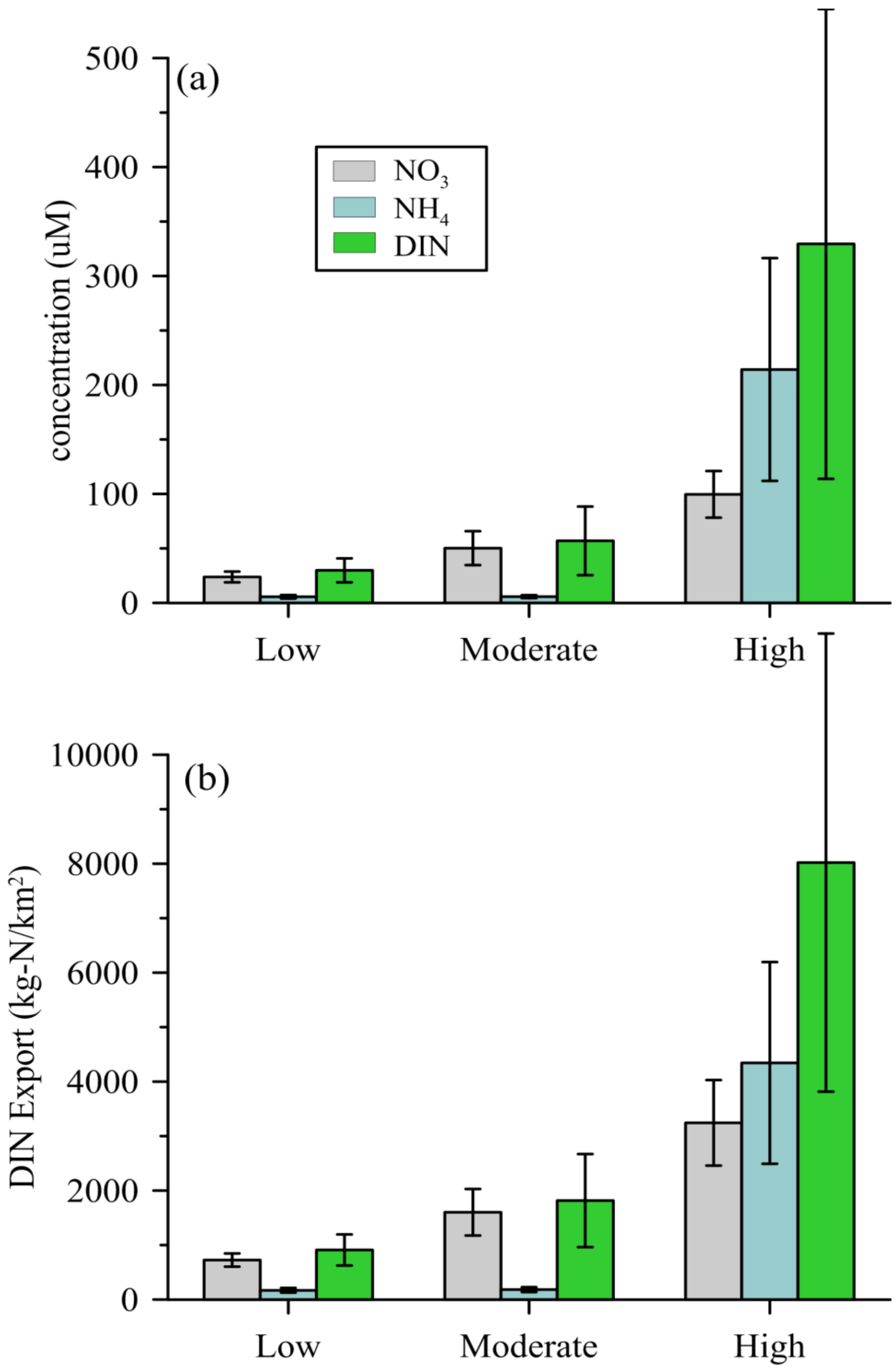

Figure 3. Mean riverine DIN concentration (a) and annual export (b) of the low, moderately and highly disturbed watersheds during 2002-2012. The gray, sky blue, and green bars represent the NO_3, NH_4, and DIN of the three classes. Standard deviation for each bar is given as well.

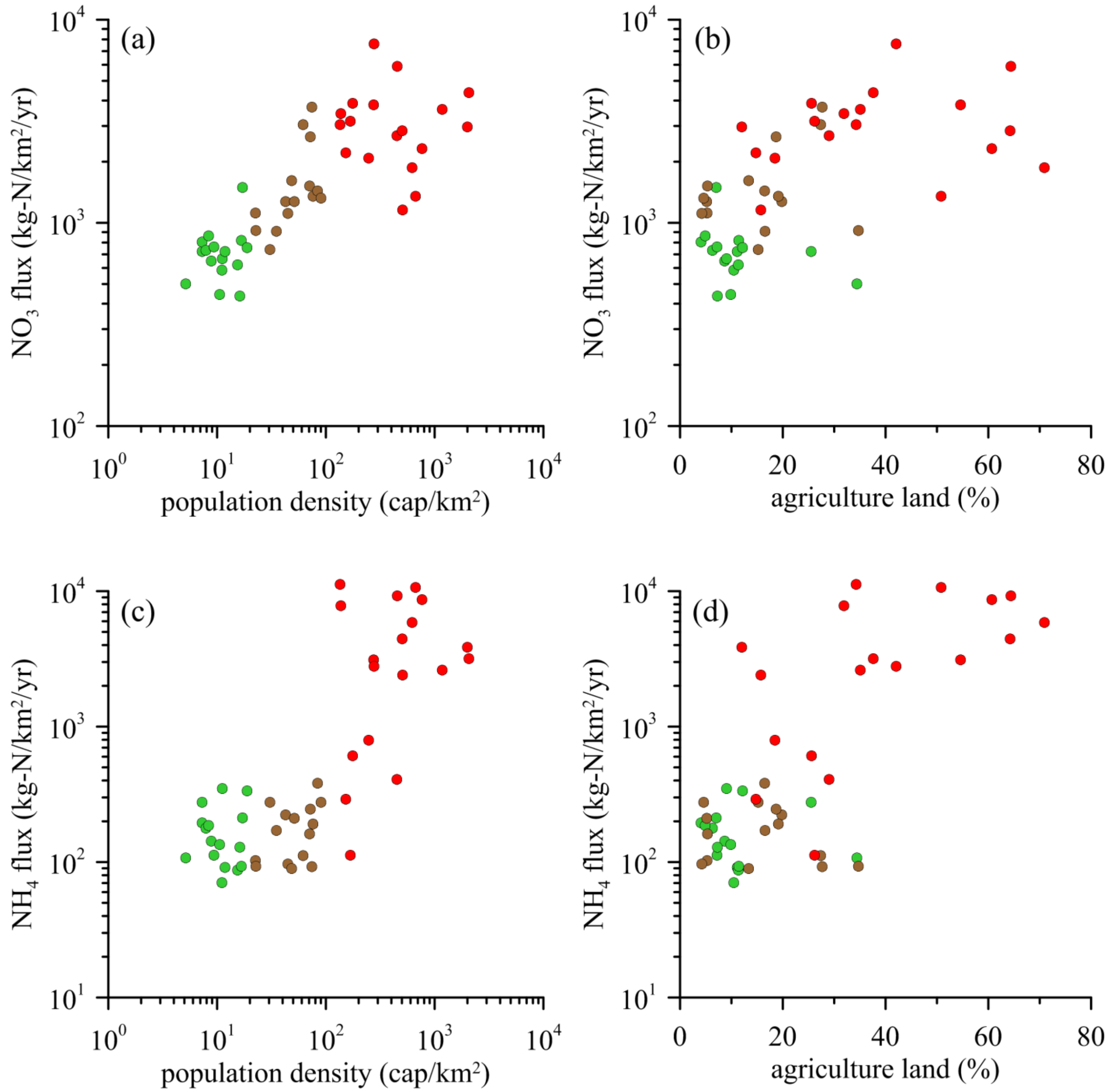

Figure 4. Scatter plot of NO_3 and NH_4 export associated with population density (a) and (b), and relative agricultural land cover (c) and (d). The green, brown, and red dots show the low, moderately, and highly disturbed watersheds, respectively. The *r*-squared values for (a), (b), (c) and (d) are 0.19, 0.34, 0.18, and 0.50 with *p* values < 0.01, respectively.

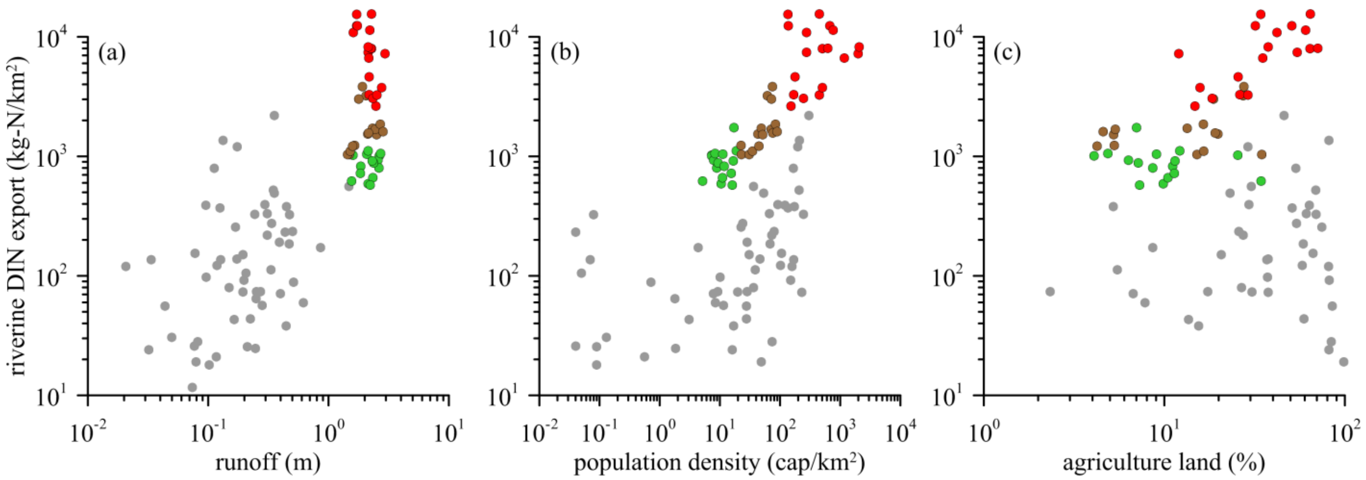

Figure 5. Scatter plot of riverine DIN export associated with runoff (a), population density (b), and relative agricultural land cover (c). The gray dots represent the global river data retrieved from He et al. (2011). The green, brown, and red dots show the low, moderately, and highly disturbed watersheds, respectively.

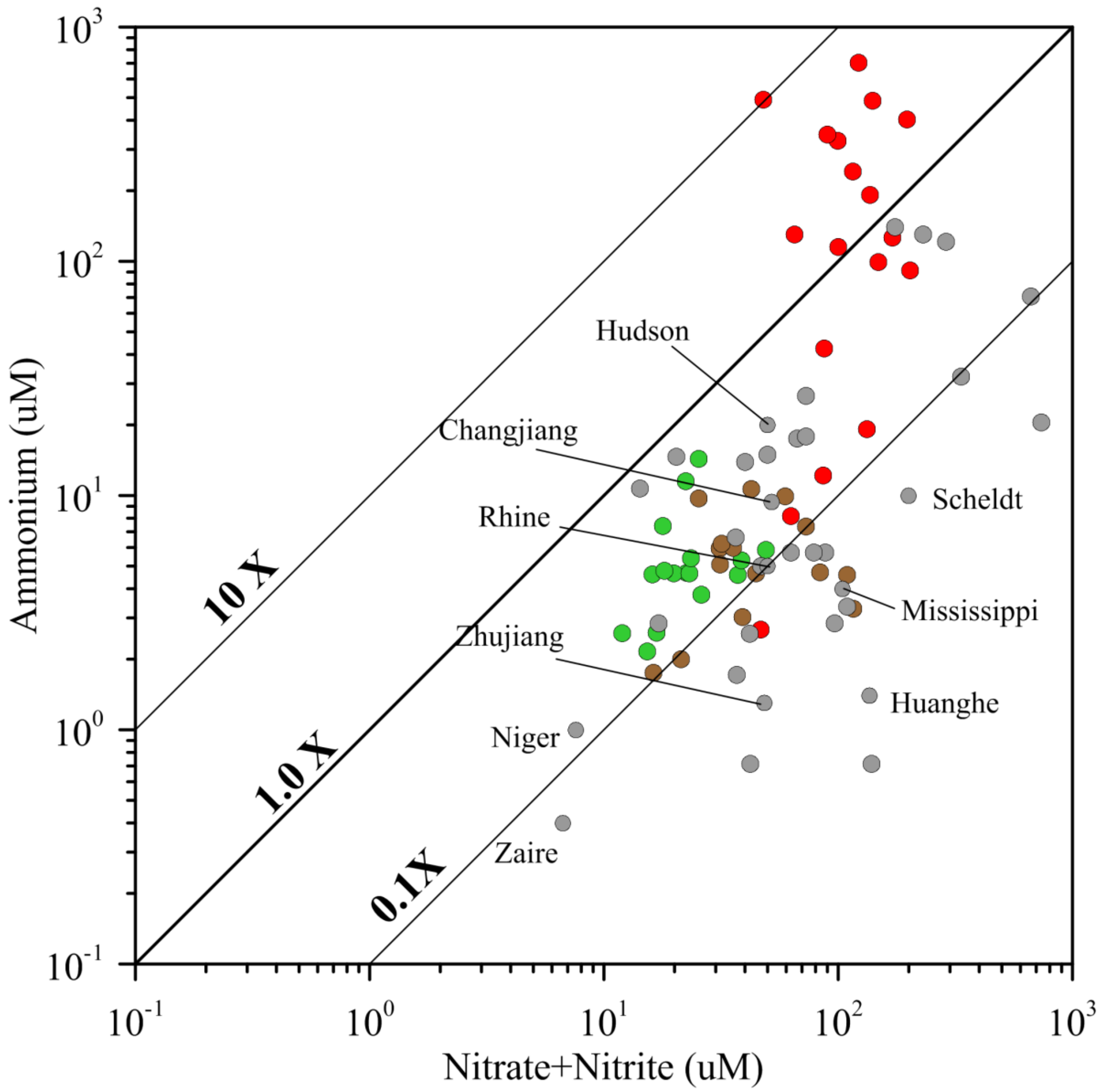

Figure 6. The DIN composition of large rivers around the world (He et al., 2011) and the 49 rivers in Taiwan. The green, brown, and red dots represent the rivers of the low, moderately and highly disturbed watersheds

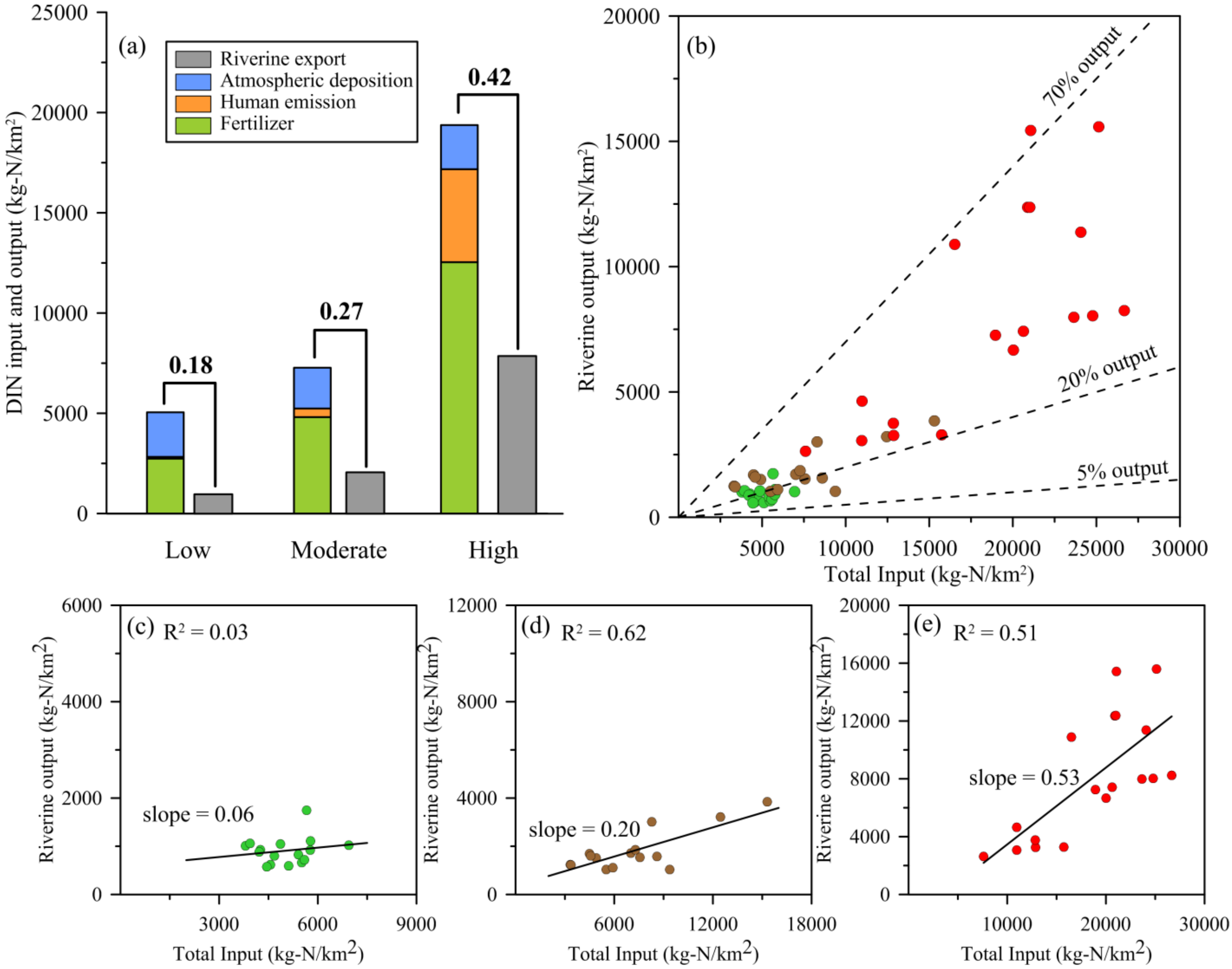

Figure 7. Nitrogen input and riverine output in the low, moderately and highly disturbed watersheds (a). Riverine DIN export against the total nitrogen input (b). The regressive slope of riverine output for the low disturbed (green dots)(c), moderately (brown dots)(d), and highly disturbed (red dots)(e) watersheds.

Supplementary

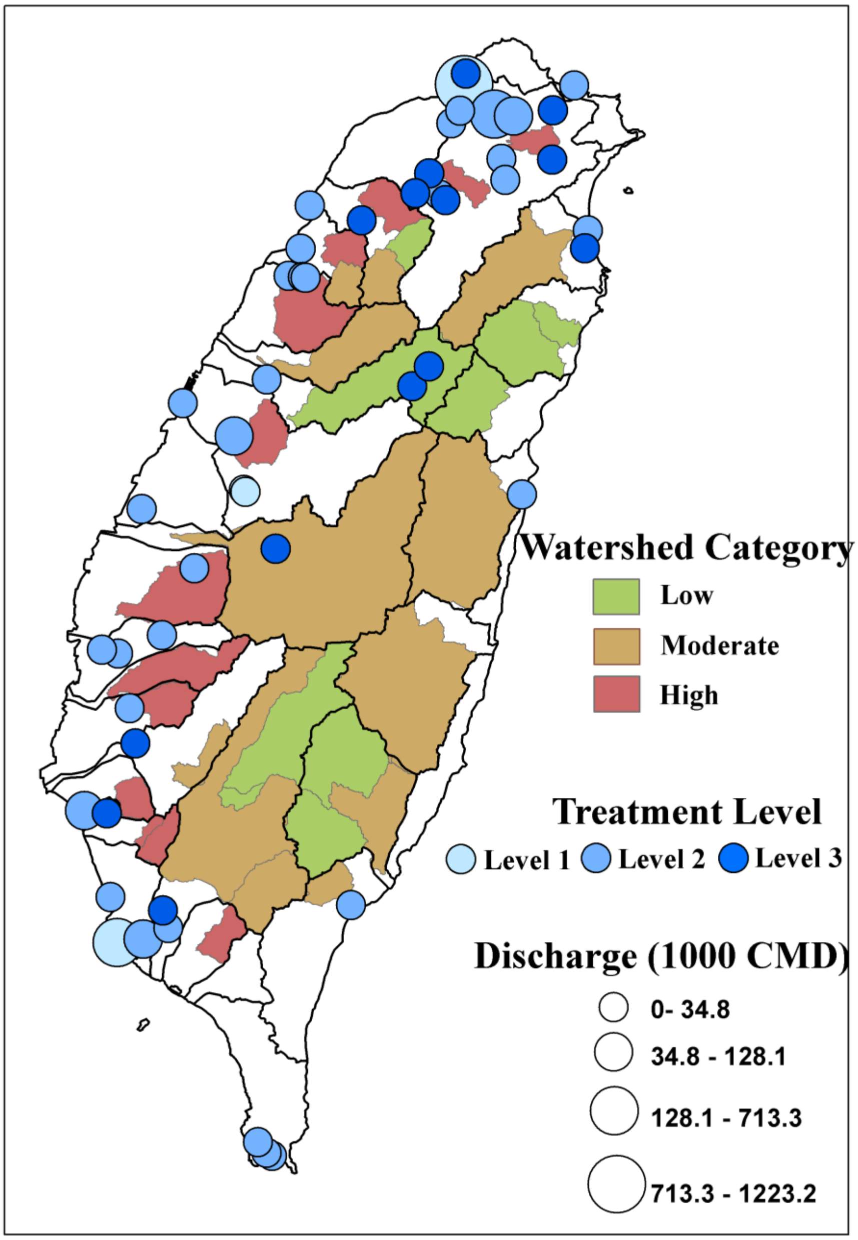

Figure 1. The distribution of wastewater treatments. The size color of circles indicate the treatment capacity and treatment levels

Table 1. The numbers and densities of cattle, cows, and swine in Taiwan, US, and China (unit: million)

Country (area, 1000 km^2)	cattle	cows	Density (cap km^{-2})	swine	Density (cap km^{-2})
Taiwan (36)	0.03	0.11	3.8	5.5	152.8
US (9388)	89.8	9.2	10.5	118.5	12.6
China (9147)	100.6	16.6	12.8	682.3	74.6

Data from: http://www.indexmundi.com/agriculture

Table 2. The arithmetic and flow-weighted means of NO_3 concentration and the mean stream discharge of 49 monitoring stations during sampling period and 2002-2012

Station	category	NO_3 conc. (uM)		runoff	Flux estimation (kg-N km^{-2} yr^{-1}) by		Relative Diff.
		Arithmetic Mean	Flow-Weighted Mean	(mm day^{-1})	AM	FWM	|AM-FWM|
1084	1	38.2	40.4	7.1	1385.9	1465.8	79.8
1109	1	36.0	29.2	3.2	1306.1	1059.4	246.7
1110	1	48.2	32.7	3.2	1748.7	1186.4	562.4
1136	1	24.8	30.8	5.0	899.8	1117.5	217.7
1238	1	22.8	24.5	6.8	827.2	888.9	61.7
1239	1	19.6	18.5	7.4	711.1	671.2	39.9
1240	1	25.2	24.8	6.5	914.3	899.8	14.5
1249	1	21.5	18.9	6.1	780.0	685.7	94.3
1250	1	15.8	15.9	8.9	573.2	576.9	3.6
1252	1	17.9	16.7	5.2	649.4	605.9	43.5
1256	1	13.0	18.2	10.8	471.7	660.3	188.7
1257	1	18.1	17.9	8.4	656.7	649.4	7.3
1327	1	23.1	18.6	6.8	838.1	674.8	163.3
1337	1	20.8	31.2	5.9	754.6	1132.0	377.3
1346	1	22.9	30.0	4.6	830.8	1088.4	257.6
1509	1	15.4	25.0	7.8	558.7	907.0	348.3
1085	2	30.6	35.8	7.7	1110.2	1298.9	188.7
1091	2	44.9	48.1	6.3	1629.0	1745.1	116.1
1106	2	84.2	92.9	3.7	3054.9	3370.5	315.6
1139	2	57.4	65.4	4.2	2082.5	2372.8	290.2
1176	2	116.2	131.8	5.6	4215.9	4781.8	566.0
1177	2	108.2	85.8	4.6	3925.6	3112.9	812.7
1201	2	70.7	79.6	7.4	2565.1	2888.0	322.9
1225	2	41.9	42.2	6.6	1520.2	1531.1	10.9
1251	2	34.9	33.4	7.3	1266.2	1211.8	54.4
1253	2	25.3	27.5	5.7	917.9	997.7	79.8
1255	2	30.4	31.5	5.8	1102.9	1142.9	39.9
1258	2	38.4	35.6	5.8	1393.2	1291.6	101.6
1262	2	21.6	26.4	9.0	783.7	957.8	174.1
1271	2	31.8	33.0	8.7	1153.7	1197.3	43.5
1654	2	17.0	21.9	10.0	616.8	794.6	177.8
1024	3	93.2	92.9	7.2	3381.4	3370.5	10.9
1042	3	58.5	78.2	5.2	2122.4	2837.2	714.7
1071	3	125.8	122.1	4.3	4564.1	4429.9	134.2
1093	3	61.6	63.2	7.1	2234.9	2293.0	58.0
1099	3	80.9	82.5	5.4	2935.1	2993.2	58.0
1118	3	81.4	73.0	7.7	2953.3	2648.5	304.8
1119	3	134.8	139.6	5.7	4890.7	5064.8	174.1

1126	3	147.3	152.5	6.0	5344.2	5532.9	188.7
1149	3	76.6	89.8	5.5	2779.1	3258.0	478.9
1150	3	87.5	94.6	4.2	3174.6	3432.2	257.6
1154	3	181.9	203.2	6.5	6599.5	7372.3	772.8
1159	3	47.9	84.8	9.1	1737.9	3076.6	1338.8
1163	3	90.3	96.9	6.5	3276.2	3515.6	239.5
1167	3	118.9	129.3	5.1	4313.8	4691.1	377.3
1186	3	41.8	65.7	5.4	1516.5	2383.7	867.1
1191	3	86.2	81.4	6.4	3127.4	2953.3	174.1
1207	3	190.9	217.1	7.8	6926.0	7876.6	950.6
1305	3	103.1	97.7	6.4	3740.6	3544.7	195.9

Riverine substance load or yield (per area load), defined as the product of concentration and stream discharge is a function of flow regimes, watershed characteristics, substance characteristics, sampling frequency, and estimation method (Ferguson, 1987; Preston et al., 1989; Lee et al., 2009). Therefore, sampling frequency and estimation methods play an important role in calculating flux, particularly for small mountainous river basins in which the storm discharge variation can surge to 2 or 3 orders of magnitude, compared to the base low. We addressed the issue of sampling frequency and estimation method in our previous studies in several mountainous headwater catchments and a nested watershed in central and northern Taiwan (Huang et al., 2012; Lee et al., 2013; Lee et al., 2014; Lin et al., 2015; Shih et al., revised). In those studies, we also conducted some high-frequency sampling works (every three hours) during typhoons. We found that the relationship between nitrate concentration and streamflow varied from hydrological enhancement to dilution along the urbanization gradient, but most watersheds showed hydrological control over nitrate loading and suggest that that nitrate loading is approximately proportional to streamflow (Lee et al., 2013). For estimation method, we calculated the arithmetic and flow-weighted mean of nitrate to investigate the potential differences resulting from differences in methods. In this table, the difference between arithmetic and flow-weighted means of all samples were less than 30 uM, except Site # 1159 which is 37 uM. In terms of yield, the mean difference between arithmetic and flow-weighted means was 271.4 kg-N km^{-2} yr^{-1}. Most of the differences were less than 1000 kg-N km^{-2} yr^{-1}, except the Site no. 1159 in which the difference was up to 1339 kg-N km^{-2} yr^{-1}. For the three categories of watersheds, the mean differences were 169.2, 219.6, and 405.3 kg-N km^{-2} yr^{-1}, respectively, for the low, moderately, and highly disturbed watersheds. Compared to the large N inputs, the differences caused by the estimation methods were ~3% and will not alter the results we presented in this study.