Point-to-point Reply and Rebuttal to Anonymous Referee #1

Anonymous Referee #1

General Comments:

This paper describes fluxes of dissolved inorganic nitrogen (DIN) from the Dashui River in Taiwan. The novelty of data describing DIN fluxes in a river draining to Oceania makes this analysis potentially interesting. However, the paper as written contains a number of significant flaws in its presentation, analysis, and discussion of results. Perhaps the most significant flaw is the lack of a coherent message that advances our understanding of how DIN moves and is transformed throughout the catchment. At the forefront, there are no objectives or testable hypotheses stated in the introduction. As far as the results go, the shifts in nitrate, nitrite, and ammonium seen here have been seen in other river systems, and in of themselves are not groundbreaking.

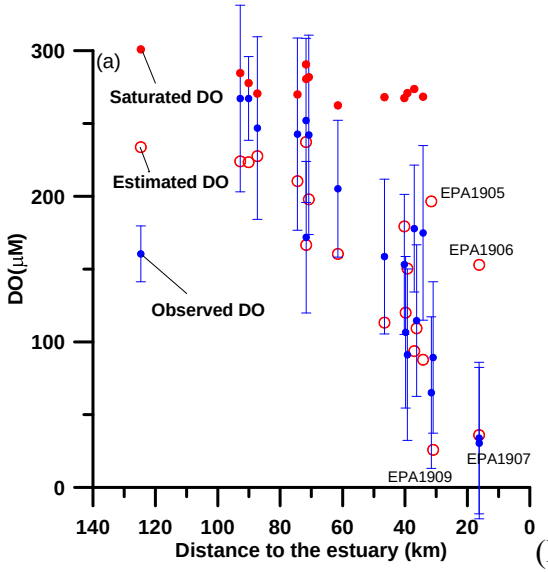
According to this comment and below, we extended our data from a single year to four years, rewrote our Abstract, Introduction, added new plots of C-Q relation into Results, gave examples of how Q controls the cumulative DIN export, and elaborated the stoichiometric relation between DO and DIN in Discussions. We appreciated reviewer's comments indeed since the scientific level of this version is now significantly improved. Though not groundbreaking, this is the first paper investigating DIN speciation and distribution in basin scale networks in Oceania region under wide range of human alteration. Results may serve as a scientific background for stream restoration and nutrient mitigation in Oceania rivers. The objectives of this study are (1) to explore the effective factors governing the DIN export and speciation; (2) to construct a more practical equation of DIN discharge for mountainous watershed. These points have been highlighted in the revised manuscript.

Neither is the change in instantaneous DO concentrations, which may not be the appropriate way to represent DO here (no diel DO curves were sampled, which would have been more interesting and informative).

We agree with reviewer when this question is for a large watershed. The mountainous small rivers in Taiwan or Oceania are characterized by shallow depth, short length and high speed flow. In Taiwan, the flow rate of water parcel ranges from 1 to 5 m/sec. Thus, the water parcel only takes 5 hours in high flow condition and ~24 hours in low flow traveling from upstream at 2000 m elevation to downstream outlet. Apparently, the short residence time, intensive physical process coupled with inputs from variable water sources make the on-site nutrient uptake and/or diel variation of DO difficult to be detected by concentration changes. However, the biological effect accumulates longitudinally downstream.

The spatial correlation patterns among DO, NH_4^+, NO_2^- and NO_3^-, in fact, were derived from integrated measures over different seasons and various stations in monitoring network. Such spatial pattern is supportive of our illustration above. Nevertheless, in Figure 3a we extended the data to 4 years and additionally included the standard deviations of measured DO to partly present the DO variability at each site. Besides, the unit of DO has been changed to μM for further stoichiometric

calculations to reproduce the spatial pattern of DO along Danshui River. For nitrification process, the productions of 1 mole NO_2^- and NO_3^- from NH_4^+ require 1.5 and 2 moles DO, respectively. In the calculation, we assumed the DO consumption merely resulted from the nitrification and DO began to decrease at 267 μM, the highest mean DO among the sites. The figure below (Figure 7a in the revised version) shows the estimated DO (black dots) could follow the spatial pattern of measured DO (blue dots) and fall within the measured variability of DO, although the DO consumption due to organic decomposition and aeration in the air-water interface were not considered in our calculations. Nitrification alone could explain the DO along the river, implying the organic decomposition is insignificant or the DO consumption due to organic decomposition and the aeration cancel each other out which need more investigations. The DO pattern makes sense and explainable, and hence we argue that the DO represented here is not inappropriate.



(Figure 7a)

Attempting to relate DIN fluxes observed here more broadly to the Oceania region is of greater interest to biogeochemists, but is not done effectively here and requires more thought. In reality the discussion focuses mainly on nuances of how DIN speciation changes along the Danshui River. Also, the discussion section contains material that mostly should be placed in the results section.

We've reorganized this article and made every paragraph in the appropriate section. We also extended our discussion focusing on three aspects, including 4.1 Changes of controlling factors on DIN export, 4.2 Implications of DIN yields in Danshui River, and 4.3 Transformation among DIN species, to satisfy readers with boarder interest.

Specific Comments: I also see two significant flaws in the analysis. The first concerns the calculation of DIN fluxes. Using four separate methods to calculate DIN fluxes seems like overkill, and taking the average of the four methods to estimate flux is not valid statistically. This is because each estimate relies on the same two parameters, concentration and discharge, violating the assumption of independence.

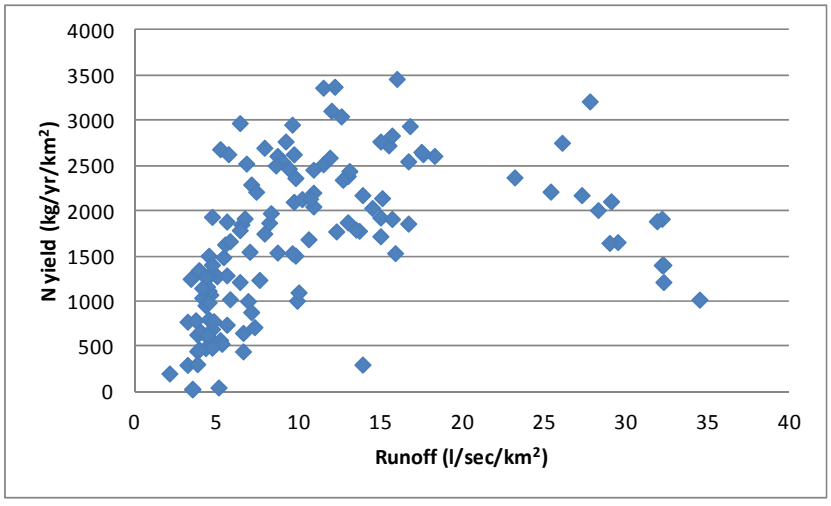
Moreover, the second flux estimate (equation 2) is thoroughly dismissed in the literature. I would suggest only using the calculation from equation 4 for the flux estimate.

To derive an accuracy material flux from discrete samples is view-dependent. For example, Reviewer#1 suggested to keep the RC method (equation 4) alone but Reviewer#2 suggested us to remove the RC method. The second reviewer, in fact, suggested us to elaborate more about comparison of all methods to prevent subjective or arbitrary choice. Accordingly, we added more illustrations for the second estimate but still kept four estimates. Worthwhile to note that our inference remained unchanged since similar fluxes came up no matter what estimate is applied.

The second flaw pertains to the investigation of factors controlling DIN yield from the Dashui River watershed. Although examining the role of runoff in DIN export seems attractive (as in Figure 6a), this analysis is inherently flawed because runoff is used to calculate DIN yield (meaning the axes are autocorrelated). More importantly, attempting to relate DIN fluxes in Danshui to NANI model estimates (as in Figure 7a) is an apples to oranges comparison because NANI (or NTNI) uses TN flux as a base comparison. I do not see any information on DON or particulate N presented here.

We've removed NANI-relevant paragraphs in the revised version.

As for the autocorrelation, the rating curve method, in fact, inherently admits the "autocorrelation" between flux/yield and runoff in order to achieve flux estimation more effectively. The purpose of our application is to examine the runoff control on DIN "yield or export" rather than concentration, the behavior. Nevertheless, we add one more example, of which limited N supply during high flow leads to decreasing N yield (Wit, 2000, see figure below), to illustrate the importance of supply. Moreover, the hydrological control on nutrient export is a common feature for Taiwan rivers (Lee et al., 2013) since DIN fluxes or yields are always positively correlated to runoff owing to abundant nitrogen supply from the watershed (please also see Figure 4 in the revised version).



<Reference>

Wit, M. 2000. Modelling nutrient fluxes from source to river load: a macroscopic analysis applied to the Rhine and Elbe basins. Hydrobiologia 410: 123–130.

Technical Comments:

The authors should consult with a native English speaker. Overall, this paper was extremely difficult to read because there were numerous grammatical errors, awkward phrases, and misspelled words. There also are several items that are incorrectly described in the text (highlighted below).

Thanks for the comments and the corrections. In this revised manuscript, we've asked a professional editor to check the English of this article thoroughly and carefully.

line 15, p2498: "close-to-top"?

We rewrote the abstract and therefore removed the sentence.

lines 19-23, p2498: Not a real strong or informative statement to conclude the abstract

We rewrote the abstract. In the end of the abstract, we highlight the very high DIN yield and the dominance of ammonium in the DIN export which are both special features compared to large rivers. We also highlight our networking monitoring, given the analogous ranges of watershed characteristics of Oceania rivers, could provide a good example to infer the DIN export from the Oceania rivers.

line 24, p2498: "huge" is not a scientific term

We rewrote the Introduction and therefore removed the sentence.

line 24, p2498 - line 10, p2499: This a general review that can be found in many other places; need to get to relevance of your study quickly.

Thanks for the valuable suggestion. We rewrote the Introduction and highlighted the significance of our study. It now reads "However, most of current knowledge about dissolved inorganic nitrogen (DIN) export was obtained mainly from larger river systems and developed countries in Europe and North America with much less efforts paid for developing countries in Oceania in tropical western Pacific Ocean, where is occupied by stratified oligotrophic water with limited bio-available nutrients, particularly nitrogenous nutrients (Jiao et al., 2007; Martha and Kristen, 2012)" in the end of the first paragraph of the Introduction.

line 1, p2499: "doubled biologically available nitrogen"?

Removed owing to we rewrote the introduction.

line 13, p2499: "nitrogenous nutrients"? Nitrogen is a nutrient.

We keep the term "nitrogenous nutrients" which being used a lot in journal articles. It indicates nitrogen-associated nutrients, i.e. ammonium, nitrate, and nitrite.

lines 11-20, p2499: This paragraph needs a better transition into it. It does not fit well with the previous paragraph.

The introduction has been rewritten to make it smoothly linked with the previous paragraph.

lines 7 - 14, p2500: Need objective and hypotheses here.

It now reads “The objectives of this study are (1) to explore the effective factors governing the DIN export and speciation; (2) to construct a more practical equation of DIN discharge for mountainous watershed”.

lines 14-15, p2502: flux is defined as the movement of mass over time through a defined cross-sectional area.

Corrected as suggested and moved the description of the methods to the Supplementary Information as suggested by Reviewer#2.

lines 16 - 18, p2502: This sentence is really awkwardly worded.

We’ve modified the first few sentences and moved to the Supplementary Information. Now it reads “Flux is defined as the movement of mass over time through a defined cross-sectional area, and can be derived by the product of measured concentrations and discharge. It will not be a problem if continuous measured concentration and discharge is available. However, the measured concentration is often discrete. Therefore, flux estimators are often used to overcome the situation, and will derive the unavoidable uncertainties due to sampling frequency, hydrological behaviors, and hydrologic response (Lee et al., 2009)”.

line 21, p2503: Don’t the Qi’s in the numerator and denominator cancel out?

We’ve modified the equation by adding brackets in the numerator. It now reads

$$FLUX = m\frac{\sum_{i=1}^{n}(C_i Q_i)}{\sum_{i=1}^{n} Q_i} \times Q_t .$$

lines 11-12, p2505: Delete the last sentence of the paragraph.

Deleted.

line 12, p2506: delete “were”

Deleted.

lines 22-25, p2507: Not appropriate to calculate means and st deviations because the flux estimates are not independent of one another.

Right, it is not statistically meaningful to calculate means and standard deviation of the four flux estimates. However, the relatively small standard deviation indicates that using any one of the four flux estimates in this study will not much influence the inferences. We kept all four estimators to prevent subjective or arbitrary choice of flux estimate. See reply above also.

lines 18-20, p2508: This is a weak start to the discussion section. This sentence really belongs in the results.

Moved to the Results.

lines 23-25, p2508: This is not surprising. Overall, the start to the discussion section should really describe how the study results are novel and contribute to global understanding of N cycling.

We reorganized the section of Discussion starting with the controlling factors of DIN export and its relevance to the global models.

lines 3-5, p2509: Not really sure what this means.

Sorry for the confusion. We've modified the sentence and moved the section of 4.2. It now reads "Along the Danshui River, given the wide ranges of watershed characteristics, it might be clearer to specify the changes of DIN export"

line 17, p2509: "population-associate"?

It should be more specific here. We've changed it to "domestic and industrial sewage".

lines 11-17, p2510: This belongs in the results section.

Moved to the section of 3.3.

lines 25-26, p2510: "denitrification signals"?

It should be more specific. It now reads "In addition, basing on the isotopic compositions of δ15N and δ18O in nitrate denitrification process was inhibited in the upstream mountainous watersheds even in the cultivated watersheds due to rapid infiltration (Peng et al., 2012)"

lines 20 - 29, p2511: More results.

Moved to the section of 3.6.

line 13 page 2513: "closed"?

Changed to "almost". It now reads "In the global spectrum, the Danshui River exports ~$2x10^5$

mol/km^2/yr of DIN, which is almost the world's highest DIN yield in the condition of high runoff and dense population density which are specific characteristics of this region."

line 16 p2515 "longdistance"?

Removed owing to the reorganization of the article.

lines 11-12, p2516: Assume that you mean the watershed area here, although this is not stated.

Thanks for your kindly reminding. We've added the watershed area into the sentence, and now it reads "Our study reveals that the watershed area of Danshui River occupies $1.8x10^{-3}$% of the land surface area……".

line 1, p2517: NEWS is a hybrid statistical-process based model, not a conceptual model.

Thanks for the correction. We've modified the description.

Tables and Figures: Captions need to be written so that they can stand alone independent of the paper. Referring the reader to the text for details is not appropriate.

Making tables and figures being able to stand alone is also one of our principles in writing captions. We may have obscured the captions in the previous manuscript. Hence, we've checked them carefully and modified them in this revised version.

Table 4: Missing a row for Water (%)

Thanks for your careful reviewing. We've added a row for Water into the new Table 3.

Figure 1: Difficult to pick out details on map.

We've redrawn the Figure 1 by eliminating rainfall relevant legends, including rain gauges and rainfall contour. We also removed the rainfall relevant paragraph in the revised manuscript because it is relatively irrelevant to this study.

Figure 3: Difficult to see NO2; suggest moving NO2 to bottom.

We've modified the entire old Figure 3 to make it clearer.

Figue 6: More detail is needed in caption on data sources.

More detail about the data sources is added in the caption. The old Figure 6 now is Figure 5.

Figure 6a: autocorrelation between axes.

It's common method to present and estimate flux. Please also see the reply above.

Figure 7a: Can’t compare this because NANI data are total N fluxes.

Removed the old Figure 7 and no more discussion about NANI in the revised manuscript.