

## ***Interactive comment on “Anthropogenic point and non-point nitrogen inputs into Huai River Basin and their impacts on riverine ammonia-nitrogen flux” by W. S. Zhang et al.***

**W. S. Zhang et al.**

wz59@cornell.edu

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We thank the reviewer for assessing our manuscript and providing us with many thoughtful and detailed comments. We have tried to address them in the responses below. The revised MS was attached below.

General Comments and response:

This paper presents an adaptation of the Net Anthropogenic Nitrogen Input (NANI) approach to generate separate values of N inputs by non-point and point source. The authors also use ammonia-N in streamflow to estimate hydrologic N losses and approximate input-output balances. Overall this is an important addition to our understanding

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of N cycling in a watershed that has experienced rapidly increasing N inputs. An important contribution of this paper is the study of N balances in a watershed with very high N inputs - approximately 272 kg/ha/yr for the entire watershed, much derived from fertilizers. It is very surprising and perhaps shocking that of this 272 kgN/ha/yr less than 5% of these extremely high inputs – an estimated 3.8 – 9 kg of TN/ha/yr - were exported from the basin via riverine flows. This combination of high inputs and relatively low exports suggest incredible rates of retention and processing (>250 kgN/ha/yr) within the basin. The authors cite several studies that also found low % nutrient export, which is similar to what they found but for watersheds with much lower inputs, and attribute it as did those authors to retention in dams and water reuse.

(1) In the abstract, the authors state that water consumption, denitrification and dams influenced the export, but this is speculation. There could be other potential explanations including storage in groundwater, high rates of denitrification in hotspots, or some kind of error in accounting.

Authors' response: We agree that other mechanisms (storage in groundwater, high rates of denitrification in hotspots) could also impact riverine exports, but their roles were not addressed in this study. In order to address the reviewer's concern, we have modified the language discussing these and other mechanisms. The parts of the abstract and results have been revised. Please see P1 L27 and P16 L2.

(2) This paper really underplays the implications of this large imbalance. It is hard to imagine how so much nitrogen can be removed by dams, which are a small part of the landscape. If rivers and riparian zones take up 5% of the landscape, then they would have to have a denitrification rate of up to 5000 kg N/ha/yr to remove the N delivered from across the landscape. Are there places that document such high removal rates? Some kind of reality check would be very helpful here, or at least an emphasis on this point. This issue is coming up in many large river balances, and thus more emphasis on this point is warranted.

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Authors' response: We agree with the reviewer's comments and made corresponding revisions in the manuscript. We added one paragraph in section 3.4 to stress the implications of our results (P17 L17). Below are our clarifications: Denitrification in river systems is often considered as an important pathway of N removal from watersheds (Seitzinger, 1990; Seitzinger et al., 2002; Billen et al., 2009) and the construction of dams and impoundments could significantly increase the nitrogen residence time within aquatic ecosystems, and thus increase the proportion of N removal through denitrification losses, assuming that nitrate is sufficiently available. The amount could be significant, given that more than 5,700 impoundments and 5,000 sluices have been constructed in most of the main streams and tributaries of the HRB (Xia et al., 2011). As in other Asian regions (Swaney et al., 2015), irrigation water consumption could be an important factor; the HRB is a very important food-producing region, which has produced nearly one-fourth of the country's marketed grain, cotton, and oilseeds on one-eighth of the nation's farmland (Bai and Shi, 2006). Under such intensive agricultural production, a high amount of riverine N is recycled through irrigation, and is subject to increase in residence times which favor denitrification (Lassaletta et al., 2012). In addition, other factors such as low slope and low runoff in some parts of the watershed (e.g., downstream) also limit NANI exported as riverine N flux (Rock and Mayer, 2006), and storage could be occurring in the soil and groundwater (van Breemen et al., 2002).

Specific comments and response:

(1) The authors have built upon their existing approaches to separate out the fluxes into point and non-point sources. Point sources are calculated from per capita household discharges and industrial N discharges prior to treatment, then applying a flux of waste factor and a treatment N removal factor to allow estimation of the point source inputs to streams. They employ a constant removal factor based on the current technology, a constant concentration in industrial effluent, and constant per capita N excretion rate. The one factor that varies over space is the wastewater volume. This method is quite different from say the most recent SPARROW model runs (JAWRA 2013), which em-

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plugs data on plant-specific discharges AND concentrations, not removal estimates and per capita rates. A statement about the adequacy of this approach as compared to other more spatially explicit approaches is needed in the paper.

Authors' response: Actually, this work is just one part of our series work on N models. This paper focuses on the NANI methodology, but we have another in preparation that discusses the contributions of point and non-point sources to riverine flux, their impacts on water quality, and in particular, the impacts of different methods to N model efficiency and accuracy. Interestingly, we have found that plant-specific methods could be appropriate for developed countries, but not for China. Firstly, there is a considerable gap between high-capacity and low-capacity sewage treatment plants in China. For the high-capacity sewage treatment plants, the data are sufficient, but for low-capacity treatment plants the data are inadequate and extremely difficult to obtain. This means the errors could be very high because of the imbalance of the data; Secondly, almost all of the sewage treatment plants are operated at full capacity, even though large volume of sewage was discharged into rivers directly without any treatment. Thus, it would be more difficult to account these N loads using plant-specific method; Thirdly, it could provide more useful information for decision-making using our method. For example, it allows us to assess the impacts of 'rural-urban' migration on N loads by applying different scenario analyses. However, we think the method comparison should not be isolated alone. It would be more appropriate if we adopt model results or some other quantitative indicators to compare these methods. This work will be shown in our following study on N model.

(2) I am concerned that including the point source inputs via the waste that enters the stream is double counting the N inputs. Doesn't this value represents a fraction of the N in food? Since 100% of food comes back out in the waste according to your paper, this input is double counted. It can't be an input to the watershed as fertilizer then also as an input from waste – those same molecules of N fertilizer were only added once to the basin as fertilizer or imported N. It is a relatively small value, but still appears to be

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double counting.

Authors' response: The point sources would indeed represent double accounting if we did not correct for this. We have already deducted this input from the accounting (please see Eq. (2) and associated text). The point source N inputs were separated from the input of net food and feed import. For a watershed, the amount of net food and feed import could be estimated as (Howarth et al., 1996): Net food & feed imported N = Human N consumption + animal N consumption - Crop N yield - Animal N production. Fertilizer is consumed by crop uptake, producing plant and animal biomass, which is in turn consumed by humans.

Net food and feed import (both in urban and rural regions) is usually based on the assumption that imports and exports are determined by the balance of local production and consumption, and thus defined as total N consumption (by livestock and humans) minus total N production (by crops and livestock). This quantity will be negative (representing an export) when N production exceeds consumption. The crop N yield was initially derived from fertilizer N. Thus, the molecules of N fertilizer were only added once to the basin.

Then, we split the single watershed system as two: rural system (non-point source) and urban system (point source). The equation can be revised as: Net food & feed imported N = Rural residents N consumption + Urban residents N consumption - Crop N yield - Animal N production

Because most of urban residents N consumption comes back as a form of point source, we account this part as point source N inputs (please see Eq. (4)). The remainder (i.e., Eq. (3) in the paper) was accounted as non-point N. Thus, we avoid the double accounting of urban residents' N discharge.

References:

Howarth, R., et al. (1996). "Regional nitrogen budgets and riverine N & P fluxes for the

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drainages to the North Atlantic Ocean: Natural and human influences." *Biogeochemistry* 35(1): 75-139.

(3) P3 L15 – Here it is stated that in heavily polluted rivers more than 70% of the annual N load is ammonia-N, but on page 20 you state that ammonia is “only” 20-50% of total nitrogen export in the Huai Basin. Contradictory. Perhaps an important funding of this paper is that monitoring should include more N forms, particularly in these nutrient polluted waters? I'd be really curious to know what the nitrate concentrations are in a stream with watershed loads of 272 kgN/ha, and how they compare to human health standards in the US and EU. Ammonia can be toxic as well.

Authors' response: We have changed the language slightly to state that heavily polluted rivers exhibit high proportions of ammonia in their N loads. We believe AN can be a major component of the nitrogen dynamics of heavily polluted rivers, but it is critical to measure multiple N species in order to assess their importance to the overall nitrogen load and provide information about the biogeochemical processes controlling the nitrogen dynamics of the river, especially as the overall water quality of a region is changing in response to control measures. This information is critical to the development of appropriate management strategies to improve water quality and safeguard human health. Therefore, we certainly agree that an important conclusion of the paper is that monitoring should include more N species, as we have suggested for other Asian rivers and have added this to the conclusions section (P20 L6).

Because ammonia-nitrogen is a very important assessment indicator for local governments, the priority control of pollutants was usually given to ammonia-nitrogen and organic matter (Xia, et al., 2011). We now address the reason in the paper (P16 L20): “Evidence from the long-term monitoring studies in the mainstream of Huai River revealed that ammonia-nitrogen was the major form of dissolved nitrogen before 2000 (Mao et al., 2003). However, pollution management, especially in treatment of sewage and other sources of organic pollutants, has greatly reduced the possibility of riverine environments being suitable for the persistence of AN (MWR, 2010). In 2008, riverine

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nitrate was measured in a study conducted at several stations in the basin, with concentrations ranging from 0-15.7 mg/L NO<sub>3</sub>-N, with a mean of 2.1 mg/L NO<sub>3</sub>-N (Zhang et al., 2011), suggesting that nitrate is now an important constituent of riverine N flux."

In our study, all of the data were provided by the Huai River Commission. It is a neutral body supported by environmental agencies and local governments to supervise water pollution. Hence, the dataset was usually adopted as the legal basis for assessing pollution accidents. Many scholars believe they are the most accurate data in China (Ongley et al., 2010). However, on the other hand, the list of monitoring indicators was designed according to the Environmental Quality Standards for Surface Water (MEP, 2002). In China, nitrate was not included as a regularly monitored indicator in natural rivers. Although nitrate was recognized as one of the most common pollutants, ammonia-nitrogen is the most common N-related indicator that is monitored in rivers. Total nitrogen is only monitored in some big lakes or reservoirs. Therefore, long-term monitoring of nitrate is not common in China.

However, some research has reported nitrate concentration in the Huai river during a single season (Zhang et al., 2011 (no relation to the lead author of this manuscript)), indicating that nitrate concentration was relatively high when compared with human health standards in the US and EU. The range of nitrate for the entire Huai River Basin was 0 ~ 69.7 mg/L NO<sub>3</sub> ion (0-15.7 mg/L NO<sub>3</sub>-N), with a mean value of 9.5 mg/L NO<sub>3</sub> (2.1 mg/L NO<sub>3</sub>-N), about 20% of the drinking water standard for the US. While high, this value could be an underestimate because the data were collected during the year 2008, the year in which the Beijing Olympic Games were held. (During that time, substantial efforts and resources were invested to alleviate pollution. The trend could be seen in the newly constructed sewage treatment plants. During the years of 2007-2008, more than 120 new plants were constructed in the Huai River Basin, which accounted for 50% of the total numbers of sewage plants, though their capability for reducing N load is unclear). Compare this average value of NO<sub>3</sub>-N with the flow-weighted average concentration of AN (N flux/discharge) across subbasins,

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a value of ~1 mg/L N; range: 0.2-3.3 mg/L N). Note that while there is no drinking water standard for ammonia, the 2013 US EPA chronic ambient water quality criterion for ammonia is 1.9 mg/L TAN (total ammonia nitrogen) at pH 7.0 and temperature 20° C ([http://water.epa.gov/scitech/swguidance/standards/criteria/aqlife/ammonia/upload/AQUATIC\\_LIFE-AMBIENT-WATER-QUALITY-CRITERIA-FOR-AMMONIA-FRESHWATER-2013.pdf](http://water.epa.gov/scitech/swguidance/standards/criteria/aqlife/ammonia/upload/AQUATIC_LIFE-AMBIENT-WATER-QUALITY-CRITERIA-FOR-AMMONIA-FRESHWATER-2013.pdf)).

Given that the limited available evidence suggests a basin-wide average value of riverine NO<sub>3</sub>-N of about twice that of our AN estimates, but that we have no systematic measurements upon which to base solid NO<sub>3</sub> flux estimates, we have added some additional text to indicate the increasing importance of NO<sub>3</sub> (and NO<sub>3</sub> monitoring) in the basin, and suggest that NO<sub>3</sub> is likely a major constituent of current TN flux in the river (P17 L4).

References:

Zhang, L., et al. (2011). "Major element chemistry of the Huai River basin, China." *Applied Geochemistry* 26(3): 293-300.

MEP (Ministry of Environmental Protection of China), M.: *Environmental Quality Standards for Surface Water (GB 3838-2002)*, China Environmental Science Press, Beijing, 1-9 pp., 2002.

Ongley, E. D., et al. (2010). "Current status of agricultural and rural non-point source Pollution assessment in China." *Environ Pollut* 158(5): 1159-1168.

Bai, X. and P. Shi (2006). "Pollution Control: In China's Huai River Basin: What Lessons for Sustainability?" *Environment: Science and Policy for Sustainable Development* 48(7): 22-38.

Xia, J., et al. (2011). "Water Quality Management in China: The Case of the Huai River Basin." *International Journal of Water Resources Development* 27(1): 167-180.

(4) P4, L10. Are effects are being seen in the Huai due to these high N inputs?

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Authors' response: More than 83% of rivers in the Huai River Basin do not meet the national standard (MEP, 2002), giving it the worst water quality in the nation's top seven basins (Xia et al., 2011). Water pollution has further aggravated water shortages and destroyed the river's ecosystem. According to the annual water resource reports (Huai River Commission, 2010), the main pollutants are ammonia-nitrogen, COD and phosphorus. This high N input also has had serious public health consequences. Huangmengying, a village along the Shaying River—the largest tributary of the Huai River—105 out of 204 people who died from 1990 to 2004 died of cancer (The New York Times, 2004). Some public health experts confirmed that with the high level of pollution in the drinking water, it was not surprising to have higher incidences of various cancers (Bai et al., 2006). We have added text to this effect in the introduction (P3 L31).

References:

MEP (Ministry of Environmental Protection of China), M.: Environmental Quality Standards for Surface Water (GB 3838-2002), China Environmental Science Press, Beijing, 1-9 pp., 2002.

Xia, J., et al. (2011). "Water Quality Management in China: The Case of the Huai River Basin." *International Journal of Water Resources Development* 27(1): 167-180.

Huai River Commission: Water Resources Bulletin of Huai River Basin, Bengbu, 1-32, 2010.

Bai, X. and P. Shi (2006). "Pollution Control: In China's Huai River Basin: What Lessons for Sustainability?" *Environment: Science and Policy for Sustainable Development* 48(7): 22-38.

The New York Time, 2004. Web link: <http://www.nytimes.com/2004/09/12/international/asia/1>  
(5) P5, L8. How is this different from other NANI models? What does this add? You never clearly state how this improved the model, it's not just that you label things dif-

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ferently (point source vs. non-point). A statement clearly explaining this to the reader would be very helpful.

Authors' response: We added in P5 L11: "The main differences between Eq. (1) with the old version of NANI methodology are that: 1) human-induced N inputs were recalculated according to their modes of N delivery; 2) some new equations that can represent industrial and urban domestic loads were introduced to estimate the point source N inputs."

(6) P7 L9. Table 1 gives different references for the upland N fixation. This value of 15 kgN/ha seemed high to me, so I looked at the references, and the number of 15 actually comes from "other crops" from Yan et al. 2003, which refers to a string of other papers for this value, so I can't really tell where the 15 kg N/ha originated, except that it is refers to "other non-symbiotic crops" in Yan et al. (2003). So it would be better to clearly state where the value of 15 comes from and what it represents. Yan, W., Zhang, S., Sun, P., & Seitzinger, S. P. (2003). How do nitrogen inputs to the Changjiang basin impact the Changjiang River nitrate: a temporal analysis for 1968– 1997. *Global Biogeochemical Cycles*, 17(4).

Authors' response: Thanks for the correction. In this study, it refers to "other non-symbiotic crops". So we changed the "upland" to "other non-symbiotic crops".

(7) P9 L27. Somehow emission per capita in urban areas is 4.77 kgN/ha/yr but consumption per capita in rural areas is 4.31 kgN/ha/yr. Is this correct? The paper states that people emit 100% of their N, so are rural and urban people eating different diets or ??

Authors' response: Yes, the rural and urban people have different diets. In China, most urban people were wealthier than rural people, which is reflected in their diet. Hence, the N consumption rate in urban regions is also higher than that of rural districts (Wei et al., 2008).

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References:

Wei, J., et al. (2008). "The influence of urbanization on nitrogen flow and recycling utilization in food consumption system of China." *Acta Ecologica Sinica* 28(3): 1016-1025. Abstract link: [http://www.ecologica.cn/stxb/ch/reader/view\\_abstract.aspx?file\\_no=1000-0933200803-1016-10](http://www.ecologica.cn/stxb/ch/reader/view_abstract.aspx?file_no=1000-0933200803-1016-10)

(8) P13 L26. I don't understand why you say the mechanisms for biological N fixation is unclear. The process is well studied. Perhaps you mean that the reason for the positive relationship between N fixation and riverine AN flux is unclear? I expect that the crop N fixers like soybeans are spatially correlated with agricultural areas that receive N fertilizer and thus the relationship is driven as much by a correlation with agricultural areas as something about N fixers. Some N fixers may receive N fertilizers as well.

Authors' response: Thanks for suggesting the clarification. We mean "the reason for the positive relationship between N fixation and riverine AN flux is unclear". We revised this part as: "In contrast, for biological N fixation, it has shown a positive but statistically insignificant relationship ( $P > 0.05$ ) with AN flux (Fig. 4h)."

(9) P15 L23. What's the mechanism for losing N through human consumption, if humans don't retain N?

Authors' response: We mention the drinking water here because the water supply systems usually remove some parts of N load before supplying. This part could be seen as recycled N.

(10) P16 L8-30. This section about %TN export should be renamed to %AN export. The fact that you do not have TN values cannot be understated here. Ammonia nitrogen could be a small component of the flux to 70% of the flux, depending upon the location, etc. I think this is a major limitation of this study for looking at % export. The beginning of this section should acknowledge this limitation and indicate that you are

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going to address in the following paragraphs.

Authors' response: This section has been thoroughly revised, including rearranging its structure. In the beginning of this section, we firstly address the limitation and uncertainties of our analysis according to your suggestion (P16 L11). The implication of this large imbalance (i.e., high inputs but low exports) was also highlighted.

(11) P19 L31. Need to soften these statements as currently they are too speculative and unfounded. These are potential influences, and not components that were evaluated or quantified in any way. Also, I couldn't find where this Tysmans paper specifically mentions the Huai River.

Authors' response: We have adopted more conservative language in response to the reviewer's concern. The corresponding statements had been revised: "The number of dams appears to be related to AN retention in the watershed, while volume of impoundments shows no significant relationship. AN retention could be the result of a combination of factors including biological denitrification and AN sorption onto settling sediment particles (both potentially increased by damming), losses associated with permanent water consumption (including irrigation), and storage in sediments, soils and groundwater. However, it is difficult to provide better assessments because N removal processes are dependent on the form of N. Monitoring of nitrogen in Chinese rivers has been largely focused on AN, neglecting nitrate and other N species. To better understand the processes of N retention, and to better inform N management strategies, we advocate changes in regional water quality monitoring policy to include more measurement of nitrate and total nitrogen in rivers, in addition to AN."

Tysmans et al., (2013) explanations about the reasons for the low export are more general but not specific. In order to address the concern, we now just refer it in a comparison of results (P17 L6).

Technical comments and response:

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(1) P11, L21. Replace “contribute to” to “be attributed to”.

Authors’ response: Revised as recommended.

(2) P12, L3. Here you mention “new N”, why is this distinction important?

Authors’ response: We have deleted “new N”.

(3) P13, L9. Should say “point source N” not “point N”.â€”

Authors’ response: Revised as recommended.

(4) Table 3 should stand alone without having to hunt for abbreviations.

Authors’ response: Revised as recommended.

(5) Figure 2 should label all the fluxes according to their abbreviations in the text. Also, it would really help to indicate what is measured and included in NANI and what is not. The distinction between “direct” and “indirect” is not clear.

Authors’ response: We have made corresponding revisions in manuscript as required. Please see Fig. 2.

Please also note the supplement to this comment:

<http://www.biogeosciences-discuss.net/12/C3367/2015/bgd-12-C3367-2015-supplement.pdf>

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