



Temporal variation of stable isotopic values for dissolved nitrogen compounds in paddy water environment

Makoto Saiki¹, Thu Nga Do², Thi Thuy Hai Cao¹, Takashi Nakamura¹,
Thi Thao Ta³ and Kei Nishida¹

¹University of Yamanashi, 4-4-37 Takeda, Kofu, Yamanashi 400-0016, Japan,

²Electric Power University, 235 Hoang Quoc Viet, Hanoi, Vietnam

³Vietnam National University, University of Science, 19 Le Thanh Tong, Hanoi, Vietnam

Email: g18dtk02@yamanashi.ac.jp, dothu_nga2005@yahoo.com, g18dtkal@yamanashi.ac.jp,
tnakamura@yamanashi.ac.jp, tathithao@hus.edu.vn, nishida@yamanashi.ac.jp

Abstract: Vietnam is the second-largest rice exporter worldwide and the amount of applied fertilizer is increasing rapidly in recent years. Overuse of chemical fertilizers in the paddy fields strongly contributes to the pollution of water bodies. This study aimed to understand the temporal variation of nitrogen concentrations and stable isotope values as environmental tracers based on the observed data in a selected paddy field in Vietnam, which provides basic and useful clues for tracing sources and identifying processes of nitrogen. The results from the field survey showed that, in accordance with the changes in concentrations, $\delta^{15}\text{N}$ values of ammonium and nitrate in ponded water drastically varied from -3.6‰ to 17.2‰ and from -18.2‰ to 8.5‰, respectively. The present study implied that not only chemical fertilizers but also irrigation water was the major source of nitrogen into the paddy. In addition, microbiological nitrification and denitrification were presumed based on the temporal isotopic variations.

Keywords: Nitrogen source, Nitrogen processes, Environmental tracer

I. INTRODUCTION

Vietnam is the world second-largest (after Thailand) exporter and the seventh-largest consumer of rice. Forty percent of the agricultural land in Vietnam is paddy field. Recently, in Vietnam, the amount of applied fertilizer is increasing rapidly, which resulted in the increase of rice yield [2]. Overused amount of chemical fertilizers in the paddy fields strongly contributes to the pollution of water bodies [11]. For example, the loss of total nitrogen from paddy field due to runoff accounts for approximately 66% of the total applied chemical fertilizer [3], and the nitrogen loss is closely related to nitrogen application

rates [10]. In Vietnam, nitrogen runoff from paddy fields is also an alarming pollution source [4,13]. Identification of nitrogen sources and flows is needed for controlling the pollutions from paddy fields. However, nitrogen cycle in the paddy is very complex because multiple sources and biochemical processes are involved.

Nitrogen isotope analysis is a well-known tool for tracing the sources and identifying physicochemical and biological reactions [14]. Dissolved nitrogen is the main form of nitrogen (50 to 80% of total nitrogen) in ponded water [8] and, among the dissolved nitrogen compounds, nitrate accounts for 48–92% of total nitrogen losses in runoff water

[12]. Previous studies reported the observed isotope value of nitrate in drainage and percolation water at the outlet of paddy fields [9], in which the irrigation water was supposed to be one of the nitrogen sources in drainage water and nitrate in percolation water was microbiologically affected. Nitrogen isotope value possibly changes during a cropping season because of the transportation and/or transformation processes and differs based on regional characteristics such as hydro-meteorological conditions and agricultural practices [7].

This study aimed to understand the temporal variation of nitrogen stable isotope values of ponded water based on the

observed data in a selected paddy field in Hai Duong province, Vietnam. The results are expected to provide basic and useful clues for tracing sources and identifying processes of nitrogen.

II. CONTENT

A. Subjects and methods

The study area locates at 20.8°N and 106.8°E in Hai Duong Province, Vietnam that includes the targeted paddy field (2.2ha) managed by four practical farmers as Fig. 1.

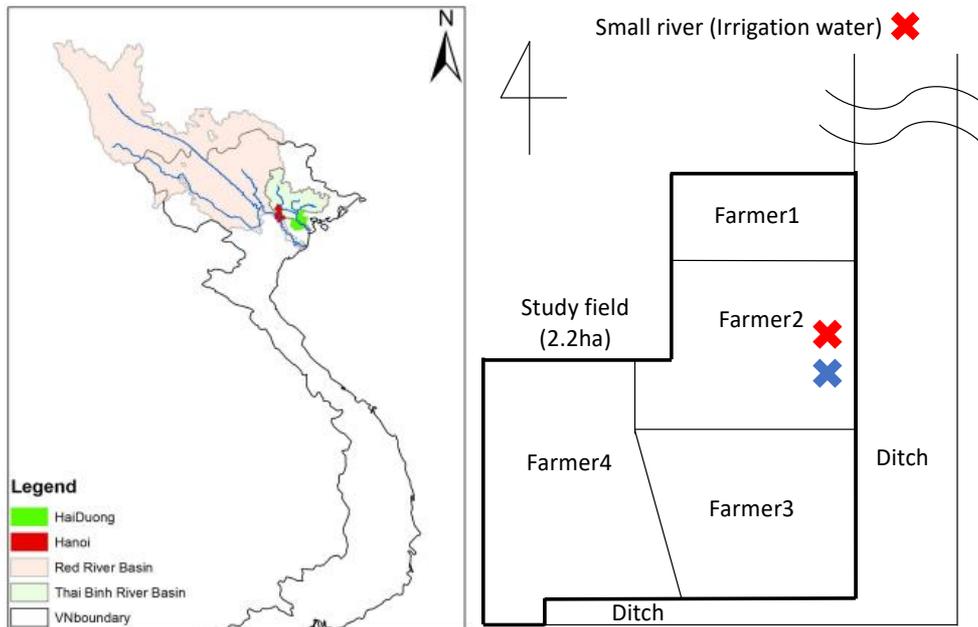


Fig. 1. Study site location and sketch map of the four paddy fields. Red cross marks are sampling points for irrigation water and ponded water, and blue one is place of an installed water level sensor.

An adjacent small river provided the irrigation water to this paddy field and received the drainage water from this field. The irrigation and drainage waters flew through the same ditch. Agricultural practices and types and amounts of fertilizers among the four farmers were occasionally different.

Information of agricultural practice of Farmer 2 was collected by interviewing the farmer in the field survey.

Monthly water samples were collected during January to June 2016. Especially, daily sampling were conducted after 1st irrigation and fertilization at spring season. In this study,

nitrogen concentrations and stable isotope values in irrigation and pond water samples were measured. The values of drainage water were assumed as similar to those in pond water. Electric conductivity, pH and water level of ponded water were measured at water sampling. Also fertilizer samples were collected in the field survey. Concentrations of ammonium nitrogen ($\text{NH}_4\text{-N}$) and nitrate nitrogen ($\text{NO}_3\text{-N}$) in water samples were measured using an ion chromatography in the environmental laboratory at University of Yamanashi, Japan. The nitrogen stable isotope values of $\text{NH}_4\text{-N}$ ($\delta^{15}\text{N-NH}_4$) and

$\text{NO}_3\text{-N}$ ($\delta^{15}\text{N-NO}_3$) in the water samples were measured by diffusion method [1] and microbial denitrified method [9], respectively, when the samples contained over 1.0mg/L of $\text{NH}_4\text{-N}$ and 0.05mg/L $\text{NO}_3\text{-N}$. The $\delta^{15}\text{N}$ in fertilizer samples was also measured by using elemental analyzer mass spectrometer [9].

B. Results

The agricultural practice, including schedule of water irrigation, water drainage, paddling and fertilization of Farmer 2's paddy field, was shown in Table I.

Table I. Agricultural practices of the experimental field (by Farmer 2)

Month	Date	Practices	Fertilizer type, amount of nitrogen
Jan.	20	Irrigation	
	28	Paddling	
Feb.	7	Paddling	
	10	Drainage	
	11	Fertilization and transplanting	NPK chemical fertilizer, 18.8kgN/ha
Mar.	1	Irrigation	
	2	Drainage	
	27	Irrigation	
	29	Fertilization	Urea, 65kgN/ha
May	3	Fertilization	Urea, 32.2kgN/ha
	5	Fertilization and irrigation	Urea, 32.2kgN/ha
Jun.	10	Harvesting	

Nitrogen concentrations in irrigation and ponded water were shown in Fig. 2. The concentrations of $\text{NO}_3\text{-N}$ in irrigation water (river water) and ponded water in the paddy field were similar, and ranging from 0.02 to 0.95

mg/L. The $\text{NH}_4\text{-N}$ concentration in ponded water had highest value at the fertilization period (approximately 10–50 mg/L), but the one in irrigation water was significantly smaller, from 1.0 mg/L to 6.0 mg/L.

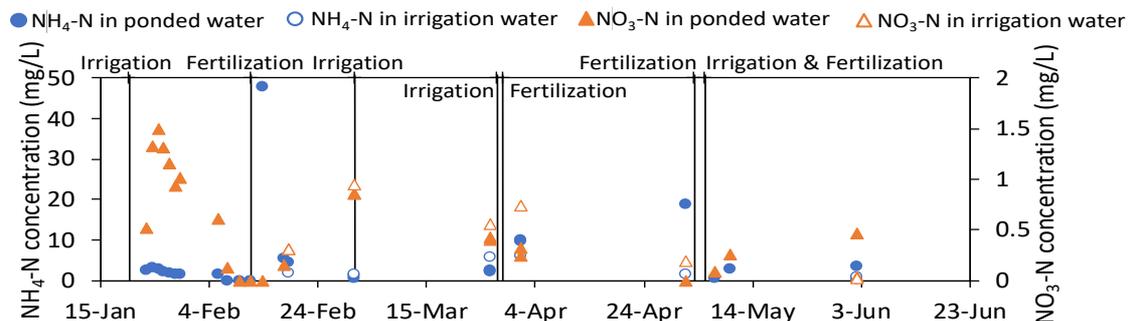


Fig. 2. Temporal changes of concentrations of ammonium and nitrate-nitrogen in ponded and irrigation water during spring season (January to June 2016)

Nitrate-isotope values of chemical fertilizer, irrigation and ponded water were shown in Figure 3. The $\delta^{15}\text{N}$ values of the two type fertilizers were -4.4‰ and -3.8‰ as NPK and Urea, respectively. The $\delta^{15}\text{N}$ values for ammonium and nitrate in

ponded water ranged from -3.6‰ to 17.2‰ and from -18.2‰ to 8.5‰, respectively. The values in irrigation water samples ranged from 7.2‰ to 13.1‰ for ammonium and from -5.8‰ to 7.5‰ for nitrate, respectively.

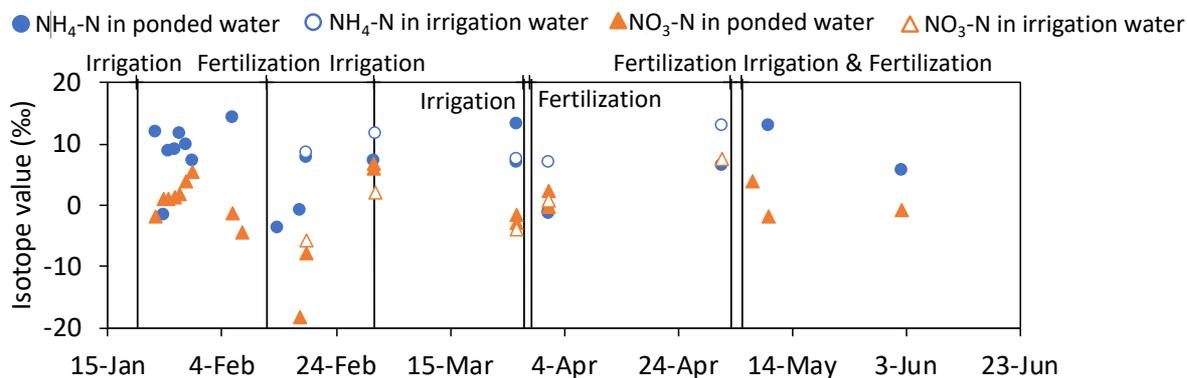


Fig. 3. Temporal changes of isotope values of ammonium and nitrate-nitrogen in ponded and irrigation water during spring season (January to June 2016)

C. Discussion

Fig. 2 and Fig. 3 presents the value of $\delta^{15}\text{N}-\text{NO}_3$ in ponded water monotonically increased with decreasing concentration of NO_3-N in ponded water before the first fertilization. This could be explained by the possible denitrification because no additive nitrogen was observed during this period.

After fertilization, ammonium-nitrogen isotope values in ponded water closed to that of fertilizer. In the 2nd day after 1st

fertilization, no nitrate but only ammonium was detected in the ponded water sample with -3.62‰ of $\delta^{15}\text{N}-\text{NH}_4$.

When a large amount of ammonium is applied in the paddy, microbial nitrification is stimulated and a large fractionation of $\delta^{15}\text{N}-\text{NH}_4$ would likely be observed [6]. Feigin [5] indicated that $\delta^{15}\text{N}-\text{NO}_3$ in the agricultural soil decreased to below -10‰ after application of anhydrous ammonia as a fertilizer. Hence, when $\delta^{15}\text{N}-\text{NO}_3$ value was the lowest (-18.2‰), NH_4-N of fertilizer contained plenty

amount of light nitrogen and was oxidized to $\text{NO}_3\text{-N}$ with the lighter $\delta^{15}\text{N}$ value compared to that of $\text{NH}_4\text{-N}$. On the other hand, an input of nitrogen contained in irrigation water was detected because the $\delta^{15}\text{N}$ values in ponded water were similar to those in irrigation water when irrigation water came to the studied field.

III. CONCLUSIONS

By applying isotope technique as an environmental tracing analysis, this study presented the temporal variation of $\delta^{15}\text{N}$ values of ammonium and nitrate in ponded water and irrigation water in a paddy in Vietnam. The results showed that $\delta^{15}\text{N}$ values of ammonium and nitrate in ponded water drastically varied from -3.6‰ to 17.2‰ and from -18.2‰ to 8.5‰, respectively. Fertilizer and irrigation water were identified as the major sources for nitrogen flow in the paddy field. Nitrification and denitrification process in the paddy were presumably observed.

ACKNOWLEDGEMENTS

We are grateful to Prof. Hiroshi Ishidaira, Dr. Junko Shindo and Dr. Tadashi Toyama for assessing the research methodology. We would like to thank Mr. Cao Van Nam and his family for kindly providing access to his paddy field. This study was financially supported by Grant-in-Aid for Scientific Research (No. 15K06270) from Japan Society for the Promotion of Science (JSPS), a research grant from The Yanmar Environmental Sustainability Support Association (YESSA), Akiyama Scholarship for Global Young Researchers and Fund of Special Graduate Program on River Basin Environmental Science from University of

Yamanashi.

REFERENCE

- [1]. Cao TTH, Nakamura T, Saiki M, Ta TT, Toyama T, Nishida K. "Effect of dissolved organic nitrogen concentration on $\delta^{15}\text{N}$ - NH_4 determination in water samples by modification of the diffusion method with gas – phase trapping", *Rapid Communications in Mass Spectrometry*, 32, 635-638, 2018.
- [2]. CGIAR. "Fourth Edition Rice Almanac", *CGIAR*, 137-140, 2013.
- [3]. Cho JY, Han KW. "Nutrient losses from a paddy field plot in central Korea" *Water, Air, and Soil Pollution*, 134, 215-228, 2002.
- [4]. Do TN, Nishida K. "A nitrogen cycle model in paddy fields to improve material flow analysis: the Day-Nhue River Basin case study", *Nutrient Cycling on Agroecosystems*, 100 (2), 215–226, 2014.
- [5]. Feigin A, Shearer G, Kohl DH, Commoner B. "The amount and nitrogen-15 content of nitrate in soil profiles from two Central Illinois fields in corn-soybean rotation", *Soil Science Society of America, Proceedings*. 38, 465-471, 1974.
- [6]. Kendall C, McDonnell JJ. "Isotope tracers in catchment hydrology", *Elsevier*, 528-529, 1998.
- [7]. Lee KS, Lee DS, Lim SS, Kawak JH, Jeon BJ, Lee SI, Lee SM, Choi WJ, "Nitrogen isotope ratios of dissolved organic nitrogen in wet precipitation in a metropolis surrounded by agricultural areas in southern Korea", *Agriculture, Ecosystems and Environment*, 159, 161-169, 2012.
- [8]. Liang XQ, Chen YX, Li H, Tian GM, Ni WZ, He MM. Zhang ZJ, "Modeling transport and fate of nitrogen from urea applied to a near-

- trench paddy field”, *Environment Pollution*, 150 (3), 313-320, 2007.
- [9]. Nguyen TPM, Nakamura T, Shindo J, Nishida K, “Application of Stable Isotopes to Identify Nitrogen Sources in the Outflow Waters from Paddy”, *Journal of Water Environment Technology*, 13(5) 371–381, 2015.
- [10]. Qiao J, Yang L, Yan T, Xue F, Zhao D, “Nitrogen fertilizer reduction in rice production for two consecutive years in the Taihu Lake area”, *Agriculture, Ecosystems and Environment*, 146, 103-112, 2012.
- [11]. Shindo J, Okamoto K, Kawashima H, “Prediction of the environmental effects of excess nitrogen caused by increasing food demand with rapid economic growth in eastern Asian countries, 1961–2020”, *Ecological Modelling*, 193, 703-720, 2006.
- [12]. Tian YH, Yin B, Yang LZ, Yin SX, Zhu ZL, “Nitrogen runoff and leaching losses during rice-wheat rotations in Taihu Lake region, China”, *Pedosphere*, 17 (4), 445-456, 2007.
- [13]. Tran VB, Ishidaira H, Nakamura T, Do TN, Nishida K, “Estimation of nitrogen load with multi-pollution sources using the SWAT model: a case study in the Cau river basin in northern Vietnam”, *Journal of Water and Environment Technology*, 15 (3), 106-119, 2017.
- [14]. Umezawa Y, Hosono T, Onodera S, Siringan F, Buapeng S, Delinom R, Yoshimizu C, Tayasu I, Nagata T, Taniguchi M, “Erratum to “Sources of nitrate and ammonium contamination in groundwater under developing Asian megacities””, *Science of The Total Environment*, 407 (9), 3219-3231, 2009.