

# QUANTITATIVE ANALYSIS OF NITROGEN COMPOUNDS IN PADDY FIELDS AMMENDED WITH UREA FERTILIZER

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## Abstract

A field experiment was conducted to quantitatively analyze nitrogen (N) compounds as both inorganic and organic N (measured as total Kjeldahl N (TKN),  $\text{NH}_4^+\text{-N}$ ,  $\text{NO}_2\text{-N}$ ,  $\text{NO}_3\text{-N}$ , organic N and total N) and N pollution loading (measured as total N load) in paddy fields after the application of various dosages of urea [ $\text{CO}(\text{NH}_2)_2$ ] fertilizer. Three urea levels (0, 200, and 300 kg urea/ha) and IR64 rice were used in a factorial designed experiments. The irrigation water in both outlet and inlet water flow was sampled after urea surface application at 0, 15 and 35 days after planting (DAP) and those of N concentrations were determined. In general, the urea fertilizer application of three N levels showed significantly increased inorganic and organic N concentrations in outlet irrigation water ( $P < 0,05$ ) but did not increase total N load ( $P > 0,05$ ) compared to inlet irrigation water. When no urea fertilizer was applied (0 kg urea/ha), high N concentration was measured in irrigation water, indicating that irrigated water system had carried N compounds other than urea fertilizer applied. All the N compounds increased significantly except for  $\text{NO}_2\text{-N}$  and total N at 0 kg urea/ha,  $\text{NO}_2\text{-N}$  and organic N at 200 kg urea/ha, and TKN at 300 kg urea/ha, which were not significantly different between outlet and inlet irrigation water ( $P > 0,05$ ). These results revealed that although the three urea fertilizer application levels did not increase N loading, they have a significant effect on both inorganic and organic N concentrations in surface water runoff, thus eventually entering and polluting the water receiving bodies with the subsequent increase of eutrophication.

Key words: eutrophication, nitrogen compound, paddy field, urea fertilizer

## 1. INTRODUCTION

Nitrogen (N) for agriculture includes fertilizer, biologically fixed, manure, recycled crop residue, and soil-mineralized N (Follett and Hatfield, 2001). For N fertilizers, they are often employed in agricultural areas to gain high rate of crop yield and improve its quality. The effective use of N fertilizers to achieve maximum yield is a very important determinant of crop yield in both developed and developing countries. One of the N fertilizers is urea that is gaining more importance among N fertilizers because of its low cost per unit of nitrogen. When placed in soil, urea is hydrolyzed to ammonium through the action of the extracellular enzyme urease (Kumar and Wagenet, 1984).

Application of N as urea is recommended for rice. It is also one of the most expensive inputs in crop production. Nonetheless, urea is presently a major source of N and its potential environmental impacts are increasing rapidly with increasing world populations due to its inefficient use; N can be transported immense

distances and transformed into soluble and/or gaseous forms that pollute water resources with the subsequent increase of eutrophication (Bellos et al., 2003) and cause greenhouse effects. Thus, the efficient management of N by farmers with limited resource is a very important part of successful soil and crop management systems (Le Gouis et al., 1999; Ankumah et al., 2003). In general, N losses are caused by leaching, erosion, volatilization, denitrification and fixation in soil organic matter. Low N recovery by crops increases N losses from the rice fields, causing a negative impact on the environment (Fernandez-Escobar et al., 2004).

Correspondingly, waters that contain mostly organic and ammonia nitrogen are considered to have been recently polluted and therefore of great potential danger, while the drinking waters with high nitrate content often cause methemoglobinemia in infants (also called "blue baby"). The methemoglobinemia results from the oxidation of the ferrous iron in hemoglobin to the ferric iron state (Gold and Bithoney, 2003) and may result from congenital deficiencies of enzymes that normally convert methemoglobin to hemoglobine, alterations in the hemoglobin molecule itself or, most commonly, from

the ingestion of medications or toxin that oxidize the ferrous iron of hemoglobin (Groeper et al. 2003).

The objective of this study is to quantitatively analyze N compounds as both inorganic and organic N (measured as total Kjeldahl N (TKN),  $\text{NH}_4^+$ -N,  $\text{NO}_2^-$ -N,  $\text{NO}_3^-$ -N, organic N and total N) and N loading (measured as total N load) in paddy fields after the application of various dosages of urea [ $\text{CO}(\text{NH}_2)_2$ ] fertilizer.

## 2. MATERIALS AND METHODS

### *Study sites and experimental design*

The experimental study area was located in Pameungpeuk, Wanasari Village, Wanayasa Subdistrict, Purwakarta Regency, West Java, Indonesia. The experiment was conducted in paddy field which consisted of nine plots. Each plot size was 2 m  $\times$  2 m (Fig. 1). Nitrogen fertilizer as urea [ $\text{CO}(\text{NH}_2)_2$ ] at three N levels (0, 200, and 300 kg urea/ha) and IR64 rice were used in a factorial designed experiments. The IR64 rice was planted in 20-cm rows. The urea was supplied three times at 0, 15 and 35 days after planting (DAP). The irrigation water runoff in both outlet and inlet water flow was sampled after urea surface application at 0, 15 and 35 DAP and those of N concentrations were determined. The irrigation water runoff samples were immediately returned to the laboratory for analysis. Dissolved oxygen (DO), temperature (T) and pH of irrigation water were also measured in the field.

### *Analytical procedures and statistical analysis*

The water flow rate (Q) was measured by a V-notch. Since Q was relatively small, the measurement was performed with the following formula:  $Q = 2,5 (\tan \theta/2) H^{5/2}$ ; where Q = flow rate (cfs), H = head over angle of V-notch (ft), and  $\theta$  = angle of the notch ( $\theta = 60^\circ$ ).

Measurements of N compounds were performed with the Nesslerization method for  $\text{NH}_4^+$ -N, the spectrophotometric method (Diazotization method) for  $\text{NO}_2^-$ -N, the spectrophotometric method (Brucine method) for  $\text{NO}_3^-$ -N, and Kjeldahl method for total N (APHA, 1998). Total Kjeldahl N (TKN) was determined by digestion using the reagents of sulfuric acid ( $\text{H}_2\text{SO}_4$ ), potassium sulfate ( $\text{K}_2\text{SO}_4$ ) and cupric

sulfate ( $\text{CuSO}_4$ ) catalyst, followed by steam distillation.

TKN is the sum of organic N and ammonia nitrogen. Organic N was obtained by difference between total N and inorganic N (the sum of  $\text{NH}_4^+$ -N,  $\text{NO}_2^-$ -N, and  $\text{NO}_3^-$ -N). Total N load (expressed as mg N/day) was calculated as the product of N concentration and the volume of flow, which was measured at the sampling time of 15 days (for 0 and 35 DAP) and 20 days (for 15 DAP).

Statistical analysis was performed to determine the significance of differences between N runoff concentrations in outlet and inlet irrigation water for three urea application levels. This analysis was conducted by the one-way ANOVA at significance levels of  $P < 0,05$ , using the software SigmaStat version 2.03 (SPSS Inc., Chicago, Illinois).

## 3. RESULTS AND DISCUSSION

### *Physico-chemical characteristics of irrigation water*

Physico-chemical analysis of irrigation water was performed to provide a detail description of the irrigation water used on the study site. The physico-chemical characteristics of irrigation water showed that irrigation water temperatures ranged from  $26,5 \pm 2,1$  to  $28,4 \pm 1,1^\circ\text{C}$ ; dissolved oxygen from  $5,4 \pm 0,7$  to  $6,2 \pm 0,4$  mg/L, indicating aerobic condition during the day time; and the water flow ranged from  $0,007 \pm 0,004$  to  $0,015 \pm 0,005$  L/s. Throughout the study period; the pH of the irrigation water remained constant, maintaining the initial pH of 7.

### *N compounds as urea fertilizer associated with N pollution in aquatic environment*

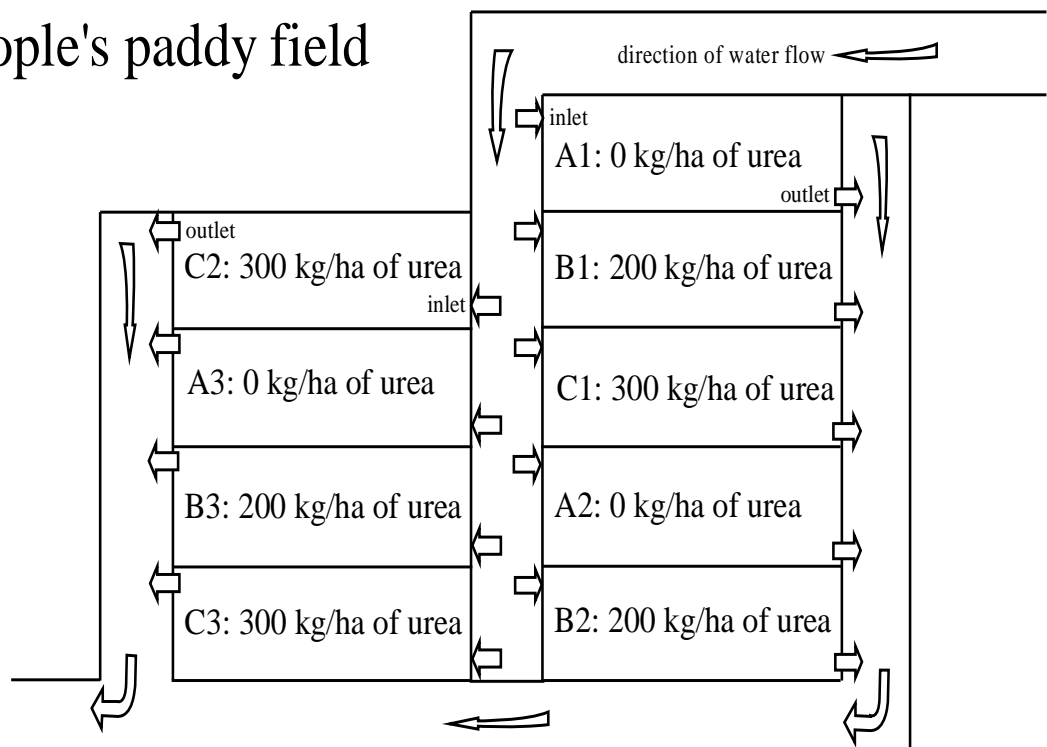
N compound concentrations are reported in Table 1. Nitrogenous compounds included total Kjeldahl N (TKN),  $\text{NH}_4^+$ -N,  $\text{NO}_2^-$ -N,  $\text{NO}_3^-$ -N, organic N, total N, and total N load. The application of urea fertilizers at three N levels, particularly at high N application (300 kg urea/ha) led to a marked increase in N runoff concentrations as total N. The irrigation water runoffs for all N levels (0, 200, and 300 kg urea/ha) were characterized by low  $\text{NO}_2^-$ -N and  $\text{NO}_3^-$ -N contents, moderate  $\text{NH}_4^+$ -N contents as well as high organic N, TKN and total N contents (Tables 1).

Generally, all the urea applications caused an increase in N runoff concentrations and their increases were statistically significant, as determined by the one-way ANOVA analyses of the data ( $P <$

0,05) obtained by difference between outlet and inlet N runoff concentrations. However, there were no consistent statistically significant differences among all N application levels for total N loading during the experiment ( $P > 0,05$ ); the average total N load for all N levels ranged from 14469,94 to 23037,02 mg/day (Tables 1). The average N concentrations for TKN, organic N and total N were extremely high compared with those for inorganic N ( $\text{NO}_2^-$ -N,  $\text{NO}_3^-$ -N and  $\text{NH}_4^+$ -N): TKN, organic N, and total N concentrations ranged from  $3,08 \pm 0,43$  to  $6,01 \pm 1,74$  mg/L,  $1,79 \pm 0,43$  to  $5,20 \pm 1,67$  mg/L, and  $3,29 \pm 0,43$  to  $6,74 \pm 1,46$  mg/L, respectively.

When no urea fertilizer was applied (0 kg urea/ha), high N concentration was measured in irrigation water, indicating that irrigated water system had carried N compounds other than urea fertilizer applied. Thus, nitrogenous compounds increased significantly except for  $\text{NO}_2^-$ -N and total N at 0 kg urea/ha,  $\text{NO}_2^-$ -N and organic N at 200 kg urea/ha, and TKN at 300 kg urea/ha, which were not significantly different between outlet and inlet irrigation water ( $P > 0,05$ ). However, although the three urea fertilizer application levels did not increase N loading, they have a significant effect on both inorganic and organic N concentrations in surface water runoff.

### Local people's paddy field



Note:

Each plot size was 2 m × 2 m. Nitrogen fertilizer as urea [ $\text{CO}(\text{NH}_2)_2$ ] was supplied three times at 0, 15 and 35 days after planting (DAP) at three N levels: (A) 0 kg urea/ha, (B) 200 kg urea/ha, and (C) 300 kg urea/ha. The irrigation water samples were collected at both inlet and outlet water flow from each plot, and the N runoff concentrations were measured.

**Figure 1.** Schematic diagram of the experimental study area that was the paddy field consisting of nine plots.

**Table 1.** N Compound Concentration and Total N Load of Irrigation Water for Inlet and Outlet Volumetric Flow Rate (Q inlet and outlet) at Urea Level of 0, 200 and 300 kg/ha

Urea level		TKN (mg/l)	NH <sub>4</sub> <sup>+</sup> -N (mg/l)	NO <sub>2</sub> <sup>-</sup> -N (mg/l)	NO <sub>3</sub> <sup>-</sup> -N (mg/l)	Organic N (mg/l)	Total N (mg/l)	Total N Load (mg/day)
0 kg/ha	Inlet	3,41 (0,95)	1,21 (0,24)	0,001 (0,000)	0,27 (0,22)	2,18 (1,12)	3,65 (1,08)	16224,36
	Outlet	3,08 (0,43)	1,36 (0,44)	0,002 (0,000)	0,21 (0,06)	1,79 (0,43)	3,29 (0,43)	15445,94
200 kg/ha	Inlet	3,63 (0,79)	1,17 (0,15)	0,002 (0,000)	0,21 (0,12)	2,61 (0,84)	3,86 (0,90)	14469,94
	Outlet	5,02 (1,13)	1,46 (0,44)	0,003 (0,000)	0,25 (0,18)	3,55 (1,30)	5,27 (1,14)	23037,02
300 kg/ha	Inlet	3,73 (0,86)	1,21 (0,28)	0,002 (0,000)	0,21 (0,14)	2,59 (1,08)	3,94 (0,99)	15920,51
	Outlet	6,01 (1,74)	1,50 (0,50)	0,002 (0,000)	0,17 (0,07)	5,20 (1,67)	6,74 (1,46)	16613,84

**Note:**

The values are means with standard deviation in parentheses based on three times of urea fertilizer application [at 0, 15 and 35 days after planting (DAP)] of three field replicates (n=5 for 0 and 15 DAP and n=4 for 35 DAP). Unit of total N load is mg/15 day for 0 and 35 DAP and mg/20 day for 15 DAP. Measurement of N compounds was performed three times (at 0, 15, and 35 DAP). TKN is the total Kjeldahl N that is the sum of organic N and ammonia nitrogen.

The NO<sub>2</sub><sup>-</sup>-N contents of irrigation water runoffs were extremely low, ranging from 0,001 mg/L to 0,003 mg/L, while the NO<sub>3</sub><sup>-</sup>-N contents were slightly higher than NO<sub>2</sub><sup>-</sup>-N contents, ranging from 0,17 ± 0,07 to 0,26 ± 0,18 mg/L. A low nitrite content was probably due to the high bacterial activity of the genus *Nitrobacter* to oxidize nitrite to nitrate under aerobic condition (Gaudy and Gaudy, 1980) as evidenced by DO content of the irrigation water (5,4 ± 0,7 ~ 6,2 ± 0,4 mg/L). An alternative explanation may be the nitrite can react chemically with suspended soil organic matter and become fixed, and at the same time nitrogenous gases can be evolved (Smith and Chalk, 1980). In this study, the levels of NO<sub>2</sub><sup>-</sup>-N were almost undetectable, where NO<sub>2</sub><sup>-</sup>-N concentrations were generally < 0,005 mg/L.

The average NH<sub>4</sub><sup>+</sup>-N runoff concentrations ranged from 1.17 ± 0,15 to 1.50 ± 0.50 mg/L (Table 1). These moderate NH<sub>4</sub><sup>+</sup>-N concentrations are due to nitrification and loss of NH<sub>4</sub><sup>+</sup>-N through volatilization as evidenced by neutral pH values (pH 7) observed over the experimental period. In a natural aquatic system, dissolved CO<sub>2</sub> can be consumed by algal cells during photosynthesis and result in increased pH, thus favoring NH<sub>3</sub> volatilization losses.

Under CO<sub>2</sub> limiting conditions, NH<sub>3</sub> volatilization was found to be the dominant process in NH<sub>4</sub><sup>+</sup>-N loss compared to nitrification process (Reddy and Sacco, 1981).

The application of 300 kg urea/ha significantly led to a greater increase in the surface water runoff than that of 200 kg urea/ha, indicating that the higher the dosages of N applied, the higher the N levels detected in surface water runoff or the increase in the runoff total N concentrations.

In general, N losses are caused mainly by denitrification, NH<sub>3</sub> volatilization, or mobilization into the organic N pool as plant residues or microorganisms. The size of this organic N pool is usually two orders of magnitude greater than the amount of inorganic N in the soil (Broadbent, 1981).

Most studies have reported similar findings (Diez et al., 1994 and Perez et al., 2003) that conventional fertilizer application (urea) affects a greater pollution. The conventional agricultural practices are one of the main causes of NO<sub>3</sub><sup>-</sup>-aquifer pollution, while excess nitrogenous fertilization occurs because of the lack of soil monitoring to rationalize the fertilizer dosages and because the flood irrigation system, used with the frequency and rates applied, accelerates NO<sub>3</sub><sup>-</sup> leaching (Diez et al., 1994).

In addition, the movement of  $\text{NO}_3^-$ -N from the root zone represents an economic loss since this N cannot be utilized by the growing plants (Timmons and Dylla, 1981). If the  $\text{NO}_3^-$ -N accumulates in underlying groundwater, it poses a potential environmental hazard if the water is used domestically. The Government Decree of the Republic Indonesia (No. 82 Year 2001 concerning "Water Quality Management and Water Pollution Control") stated 10 mg/L  $\text{NO}_3^-$ -N, 0,06 mg/L  $\text{NO}_2^-$ -N, and 0,5 mg/L  $\text{NH}_3$ -N as the upper limit criteria for drinking water. Thus, there is good incentive for farmers to use the most efficient farming practices in order to minimize N leaching losses.

One of the efforts for minimizing N leaching losses is creating a new policy to alleviate such nitrogen problems (van den Brandt and Smit, 1998). The management practices can also be undertaken in order to minimize N losses and to increase the efficiency of N utilization for rice such as: (1) the injection of fertilizers to the reduced soil layers, (2) the modified fertilizers, (3) the optimal and appropriate doses of fertilizers, and (4) the time of fertilizer application, as well as the suitable irrigation systems (Slak et al. 1998). In addition, the need of alternative strategies such as an integrated watershed management is very important for reducing N loading as well as solving eutrophication problems (Jensen and Skop, 1998).

#### 4. CONCLUSIONS

The present study has shown that the surface application of urea fertilizer at N levels of 200 and 300 kg urea/ha in paddy fields caused an increase in N concentrations (both inorganic and organic N) in surface water runoff. This will give the load on the receiving streams, further having a negative impact on the aquatic environments.

#### Acknowledgements

This paper is dedicated to Professor Dr. Ir. Soepangat Soemarto, M.Sc. (Department of Environmental Engineering, Faculty of Civil and Environmental Engineering, Bandung Institute of Technology) for his encouragement and helpful motivation.

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