

Direct Measurement of N₂ Denitrified from Soil and Fertilizer in Paddy Fields Using ¹⁵N as a Tracer

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Introduction

It is pointed out that the efficiency of fertilizer nitrogen is notoriously low for rice in comparison with many upland crops.¹⁾ Greater efficiency in the use of fertilizer nitrogen is desirable not only for increasing rice yields with lower cost but also for decreasing environmental pollution.

Applied nitrogen other than its part absorbed by rice is presumed to be incorporated into organic substances namely microbial cells and plant residues in the soil, denitrified after being nitrified, or lost with percolating and runoff water. Of the loss of nitrogen from the soil-plant system in paddy fields, denitrification is the most important factor especially in the ill-drained soils. It is important to clarify the process and the amount of denitrification in order to increase the efficiency of nitrogen fertilizer and the nitrogen fertility of paddy fields.

Since the pioneer works of Shioiri²⁾ and Mitsui,⁴⁾ a number of works have been done about denitrification. However, very few workers have reported on the direct measurement of N₂ evolved from flooded paddy fields.³⁾ One of the reasons is the difficulty to cut off the contamination of atmospheric N₂ into measuring apparatus.

The authors developed the method for direct measurement of N₂ denitrified from soil and fertilizer nitrogen in paddy fields, using the fertilizer tagged with ¹⁵N.²⁾ The method consisted of the application of N-fertilizer tagged with high concentration of ¹⁵N, use of a gaschromatograph-mass spectrometer (GC-MS) and a new method to calculate denitrified N₂ from the soil and fertilizer in the presence of atmospheric nitrogen.

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Apparatus for gas sampling³⁾

In the ill-drained paddy fields (clayey gley soil) in the Hokuriku National Agricultural Experiment Station, two replicated chambers, i. e., polyacrylate resin cylinders (28.0 cm in diameter, and 40 cm in depth), one end of which was closed with a flat board, were inserted into the soil to a depth of about 25 cm. These chambers (Fig. 1) were fixed with the iron frames in order to prevent their upward shift caused by a rise of the inside gas pressure. Flooded water within the chamber was sucked by a pipette at first. Then 10–20 ml of solution containing 431 mg of N as NH₄Cl with 47.5 atom% ¹⁵N (equivalent to 70 kg/ha) was applied to the soil within the chamber with a pipette, and the soil and fertilizer were mixed thoroughly with a spatula. After leaving it for a night, the inside of the chamber was filled with tap water to remove the air. Then a mixture gas (80% He and 20% O₂) was introduced into the chamber through the stopcock A, to remove the water within the chamber through the stopcock B until the flooding water became 1 cm deep. The volume and ¹⁵N content of this exhausted water were determined.

Once a week, 20 ml of the gas within the chamber was sampled with a syringe, N₂ content of this gas was determined by gaschromatography, and the proportion of ²⁸N₂, ²⁹N₂ and ³⁰N₂ was determined by GC-MS.

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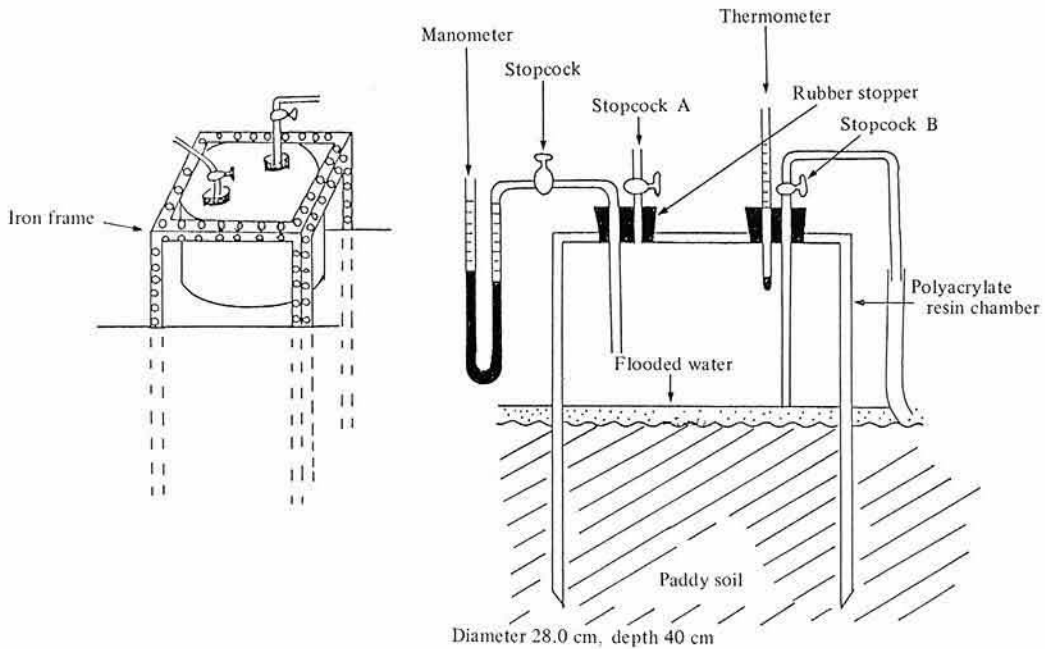


Fig. 1. Gas sampling apparatus

Calculation of denitrified N₂ by the new method

As N₂ concentration gradient between inside and outside the chamber was very steep, atmospheric N₂ contamination into the chamber might occur through the manometer, the stopcocks, the rubber stoppers, and the resin wall. Furthermore, N₂ gas inevitably remained in the chamber and in the soil. Nitrogen gas denitrified from the soil would exist in the chamber being mixed with these N₂ of atmospheric molecular composition. Consequently the proportion of ²⁸N₂, ²⁹N₂ and ³⁰N₂ would not be distributed statistically. So the authors developed the new method to discriminate denitrified N₂ from atmospheric N₂ using an iterative calculation. The outline of the calculation is given below.

Atom fraction of ¹⁵N in the sample gas (q₁) is given by the following equation,

$$q_1 = \frac{2I_{30} + I_{29}}{2(I_{28} + I_{29} + I_{30})} \dots\dots\dots (1)$$

where I₂₈, I₂₉ and I₃₀ are the peak intensities of ²⁸N₂, ²⁹N₂ and ³⁰N₂ respectively. There is no

assumption in the equation (1).

While ¹⁵N atom fraction in the sample gas is given by the following equation on the assumption that the isotopes are statistically distributed.

$$q_2 = 1 - \frac{1}{2(I_{30}/I_{29}) + 1} \dots\dots\dots (2)$$

When the atmospheric N₂ contamination into the chamber occurs, I₂₈ should be underestimated in the equation (2). Consequently q₂ should be larger than q₁. Expressing the total amount of N₂ in the chamber as T₁ and that assumed in the equation (2) as T₂, the equations (3) and (4) are obtained, because the total amount of ¹⁵N is equal in both equations (1) and (2).

$$T_1 q_1 = T_2 q_2 \dots\dots\dots (3)$$

or $T_1 - T_2 = (1 - q_1/q_2) T_1 \dots\dots\dots (4)$

In the equation (4), T₁-T₂ is an approximate value of the amount of the contaminated atmospheric N₂, and 1-q₁/q₂ is that of the ratio of contaminated atmospheric N₂ to total N₂ within the chamber.

Since the atmospheric N₂ contains an appreciable amount of ²⁹N₂, I₂₉ contains this component, (I₂₉)_a. Therefore we can obtain a more correct

value for I_{29} , or I_{29}' , instead of original I_{29} by subtracting $(I_{29})_a$ from I_{29} . The first approximation of $(I_{29})_a$ can be obtained by the use of Eq. (4). By substituting I_{29}' for I_{29} in Eq. (2), a more correct value for q_2 , or q_2' , is obtained, and by substituting this q_2' for q_2 in $(1 - q_1/q_2)$ in Eq. (4), a more correct value for the contamination rate of atmospheric N_2 can be obtained. Therefore calculating again the component $(I_{29})_a$ by the corrected contamination rate, we can correct I_{29} again. This iteration should be done until we get sufficient convergence.

Now, atom fraction of ^{15}N in the atmospheric nitrogen, q_a , is given as follows:

$$q_a = \frac{1}{2(I_{28})_a / (I_{29})_a + 1} = 0.00366 \dots\dots\dots (5)$$

Where $(I_{28})_a$ is the component of the peak intensity of contaminated atmospheric $^{28}N_2$. First approximation of $(I_{28})_a$ is given by,

$$(I_{28})_a = I_{28}(1 - q_1/q_2) \dots\dots\dots (6)$$

Solving the Eq. (5) and (6) for $(I_{29})_a$ we get,

$$(I_{29})_a = 2(I_{28})_a \frac{q_a}{1 - q_a} = 7.4369 \times 10^{-3} (I_{28})_a \\ = 7.4369 \times 10^{-3} I_{28}(1 - q_1/q_2) \dots\dots\dots (7)$$

and

$$I_{29}' = I_{29} - (I_{29})_a \dots\dots\dots (8)$$

where I_{29}' is a more correct peak intensity of denitrified $^{29}N_2$. Substituting I_{29}' for I_{29} in Eq. (2), and calculating q_2' by following equation,

$$q_2' = 1 - \frac{1}{2(I_{30}/I_{29}') + 1} \dots\dots\dots (2)'$$

we obtain $1 - q_1/q_2'$ for a more correct contamination rate of atmospheric N_2 .

$(I_{29})_a'$ and I_{29}'' are calculated again by Eq. (7) and (8) using q_2' instead of q_2 . When $I_{29}^{(n)}$ become nearly equal to $I_{29}^{(n-1)}$, the iteration can be ended. Finally q_3 for ^{15}N atom fraction and T_3 for the amount of denitrified N_2 are obtained as follows:

$$q_3 = 1 - \frac{1}{2(I_{30}/I_{29}^{(n)}) + 1} \dots\dots\dots (2)^{(n)}$$

$$T_3 = T_1(q_1 - q_a) / (q_3 - q_a) \dots\dots\dots (9)$$

The value d , namely the ratio of N_2 denitrified

from soil to N_2 from fertilizer nitrogen is obtained by,

$$d = \frac{q_0 - q_3}{q_3 - q_s} \dots\dots\dots (10)$$

where q_s is the ^{15}N atom fraction of soil nitrogen (equal to q_a) and q_0 is that of fertilizer nitrogen. Since the applied fertilizer ^{15}N is diluted to $(1 + d)$ fold, S_n , the denitrified N_2 from soil nitrogen is given by,

$$S_n = T_3 \frac{d}{1 + d} \dots\dots\dots (11)$$

The above calculation is based on two assumptions that (1) $(I_{30})_a$ is negligible and (2) fertilizer nitrogen mixes thoroughly with soil nitrogen.

Verification using a standard gas

To verify the validity of the above calculation method, a standard N_2 gas sample (^{15}N atom% = 41.95) was mixed with the air at various proportions in syringes, the gas mixture was injected into the GC-MS to determine three peak intensities, and the ^{15}N atom fraction of the injected standard gas was calculated. The result is shown in Fig. 2. Although the atom% shows the tendency to decrease with the increase of mixing rate of the air, no significant correlation between these values was observed, when a linear regression was assumed.

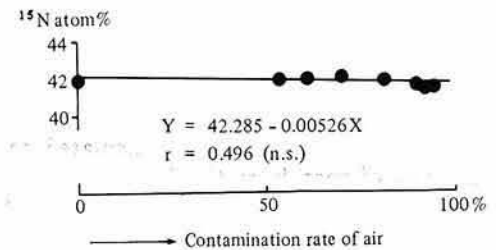


Fig. 2. Effect of contamination of air on isotopic composition of standard N_2 gas tagged with ^{15}N . Calculated by the proposed method.

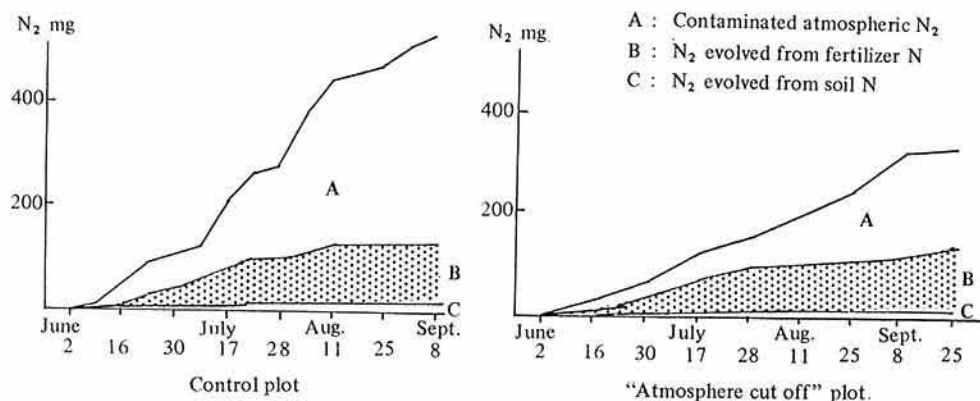


Fig. 3. Denitrification from soil and fertilizer nitrogen

Determination of denitrified N₂ in the chamber

Fig. 3 shows the result of the determination of gas in the chambers installed in the paddy field of Hokuriku National Agricultural Experiment Station. The gas within the chamber was sampled and analyzed periodically from June to September in 1981. In the "atmosphere cut off" plot the chamber was covered with a polyvinyl film bag, inside of which was ventilated with He gas. In the control plot the chamber was exposed to the atmosphere. The increase of N₂ was larger in the control plot than in the "atmosphere cut off" plot. By applying the above calculation method, the amount of N₂ gas denitrified from fertilizer nitrogen was found to be equal in both plots, and was calculated to be about 24% of the applied fertilizer nitrogen. This implies that the contaminated atmospheric N₂ does not affect the N₂ gas denitrified from the applied fertilizer nitrogen. Nitrogen gas denitrified from soil nitrogen was calculated to be about 20% of that from the fertilizer nitrogen. The assumption (2) described in the preceding section is questionable. It is probable that the calculated atmospheric N₂ includes N₂ from soil nitrogen.

The recovery of the applied nitrogen calculated from the N₂ gas evolved and the nitrogen remaining in the soil was about 100%.

A problem in many experiments dealing with denitrification is that the amount of denitrification is often measured indirectly as an unrecovered loss. In further researches, it is desirable to determine the denitrification occurring in fields by a direct method such as that proposed by the authors.

References

- 1) Craswell, T. & Vlek, P. L. G.: Fate of fertilizer nitrogen applied to wetland rice. In "Nitrogen and Rice," ed. IRRI, Los Baños, Philippines. 175-192 (1979).
- 2) Ito, J. & Iimura, K.: Direct measurement of N₂ gas denitrified from soil and fertilizer nitrogen in paddy field using GC-MS. *J. Sci. Soil and Manure, Jpn.*, **54**, 235-240 (1983) [In Japanese].
- 3) Kosuge, N. & Iimura, K.: Measurement of denitrification in paddy soils. *J. Sci. Soil and Manure, Jpn.*, **43**, 388-389 (1972) [In Japanese].
- 4) Mitsui, S.: Inorganic nutrition, fertilization and soil amelioration for lowland rice. Yokendo Ltd., Tokyo, 107 (1954).
- 5) Shioiri, M.: Denitrification in paddy soils. *Kagaku*, **11**, 1-24 (1941) [In Japanese].

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