

## Nitrogen Fertilization of Flooded Rice Through Mud Balls. Laboratory experiments on transformation in soil and N loss during preparation

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The mud balls prepared from an admixture of soil and urea or ammonium sulphate, with and without carbonaceous material, were tested for loss of N through ammonia volatilization during sun-drying and transformation in flooded soil. During sun-drying, the mud balls, particularly those prepared from powdered rice straw and urea, lost as much as 26% of the fertilizer N through ammonia volatilization. Addition of small quantities of super phosphate or neem oil-extract effectively reduced this loss. The average dissolution rate of mud balls in soil was about 5% in 10 weeks. Laboratory incubation of <sup>15</sup>N-labelled mud balls revealed initial immobilization of fertilizer N which varied depending upon the presence and decomposibility of added carbonaceous residue. It is suggested that subsequent remineralization may result in an overall slow-release effect.

The common method of surface application of fertilizer N in flooded rice culture usually results in higher losses and poor utilization by the crop. In split application, with the prevailing practice of field to field irrigation with hardly any control over water, only the basal pre-planting dose can be incorporated into the soil. Placement in the reduced zone, on the other hand, is the most satisfactory method (Mitsui, 1954; De and Digar, 1955; Patrick *et al.*, 1967; Broeshart and Middleboe, 1968). One of the ways to facilitate deep placement is the use of mud balls (Mitsui, 1954; De Datta *et al.*, 1968; Shiga *et al.* 1977). In the mud balls prepared in this study, carbonaceous materials were included in addition to soil and

fertilizer N to promote biological immobilization. Remineralization of immobilized N, it was hoped, may confer the advantage of slow-release character on these mud balls. A study of the mud ball technique was conducted at the Central Rice Research Institute, Cuttack during 1974-75 using <sup>15</sup>N-labelled and unlabelled fertilizers. The results of these studies are reported in this paper.

### MATERIALS AND METHODS

#### A. *Materials:*

1. Soil: The alluvial, sandy loam, kaolinitic soil of the Central Rice Research Institute, Cuttack, (pH 5.5, organic C 0.49%, total N 0.05% and CEC 8.9 me/100 g) was used.

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## 2. Carbonaceous materials (20 mesh):

(a) Rice straw: Total N 0.4-0.6% and, organic C 40.0%

(b) Rice husk: Total N 0.4% and organic C 36.0%

## 3. Non-edible oil cakes (20 mesh):

(a) Neem (*Azadirachta indica*): Total N 1.86% organic C 26.92% and oil content 4.16%

(b) Kokum (*Garcinia indica*): Total N 0.75%, organic C 30.37% and, oil content 6.70%

## 4. Neem oil-extract (Sp. gr. 0.99) obtained by treating the crude neem oil by spirit denatured with 5% methanol, distillation and separation.

## 5. Sulphur-coated urea (SCU) (TVA):

(a)  $^{15}\text{N}$ -labelled: Total N 39.1%,  $^{15}\text{N}$ -atom excess 9.9%, dissolution rate in water (38°C) 28% in 7 days, total coating 16%, conditioner 2%, wax 3% and sulphur 11%.

(b) Unlabelled: Total N 36.8%, dissolution rate in water (38°C) 30.3% in 7 days and total coating 19.9%

## 6. Urea and ammonium sulphate :

(a)  $^{15}\text{N}$ -labelled: 10.0% atom-excess materials manufactured by prochem/BOC Ltd., England.

(b) Unlabelled: Ordinary, fertilizer grade materials.

## 7. Shellac-coated urea (LCU) of

Indian Lac Research Institute, Ranchi Total N 32.0%, dissolution rate in water (38°C) 7% in 5 days, total shellac coating 25.9%.

8. Superphosphate: Fertilizer grade single super phosphate, Total  $\text{P}_2\text{O}_5$  16.0%.

## B. Preparation of mud balls:

Depending upon the N rate in kg/ha, the entire urea or ammonium sulphate was dissolved in minimum water. Carbonaceous materials to give 12 parts of carbon to 1 part of fertilizer N was weighed and mixed with sufficient soil. Single superphosphate to provide  $\text{P}_2\text{O}_5$  equivalent to 50% of the fertilizer N or neem oil-extract at the rate of 20% of the fertilizer N was also added to the soil and mixed. Urea or ammonium sulphate solution was added to this mixture and intimately mixed. The mixture was kneaded using additional dry soil or water as required and then shaped into ball form of about 4 cm diameter. The mud balls were then dried in the sun. Mud balls without any added carbonaceous material or with non-edible oil cakes were also prepared. For the latter, the cakes were used @ 100 kg/ha.

## C. Estimation of ammonia volatilization loss during the drying process :

The  $\text{NH}_3$  volatilization loss during the process of sun-drying was estimated using static ammonia traps (dil.  $\text{H}_2\text{SO}_4$  solution in a petridish) and a sealed atmosphere of 30°C enclosed within an inverted jar of clear glass. The ammonia absorbed in the trap was estimated by Nesslerization.

D. Estimation of mineral  $\text{NH}_4 + \text{NO}_3 - \text{N}$  in mud balls :

A few selected mud balls were ground to pass a 20-mesh screen. The

mineral  $\text{NH}_4 + \text{NO}_3 - \text{N}$  was estimated in a sub-sample by extraction with 2 M KCl followed by distillation with  $\text{MgO}$ -Devarda's alloy mixture.

**E. Measurement of dissolution rate of mud balls in flooded soil:**

The rate of release of mineral N from mud balls placed 5 cm deep in soil was evaluated by analyzing the leachate drawn from porcelain pots fitted with individual drainage lines. A flood level of 5 cm was maintained and no crop was grown. No algal growth was allowed to occur. The drainage line was kept open to collect the leachate @  $100 \pm 5$  ml/day into a closed, 1-litre glass bottle to which a few drops of conc.  $\text{H}_2\text{SO}_4$  had been added to prevent algal and bacterial growth. The samples pooled over 7 days were measured and analyzed for  $\text{NH}_4 + \text{NO}_3 - \text{N}$ .

**F. Transformation of labelled N in mud balls:**

A laboratory incubation experiment was conducted to study the transformation of 100 ppm labelled N in mud balls. The mud balls were prepared using urea or ammonium sulphate of 10% atom excess  $^{15}\text{N}$  by the procedure described earlier. Single superphosphate to provide  $\text{P}_2\text{O}_5$  equivalent to 50% of the fertilizer N was also included. Air-dry, 2-mm surface soil was placed in tall glass jars flooded with 5 cm depth of water and initially incubated for 7 days in the dark at 30°C. Then the mud balls were

pushed to a depth of 5 cm, the jars were covered with muslin cloth and incubated at 30°C in the dark for 30, 60 and 90 days. SCU was incubated in soil after incorporating it with top 5 cm layer. Distilled water was added from time to time to keep the flood water constantly at 5 cm level. The experiment was run in duplicate for each treatment and incubation period. At the end of each incubation period, duplicate jars were quickly air-dried and the contents were ground to 2-mm size. The total and labelled N in Kjeldahl and other fractions were determined. Labelled N incorporated into mineral and organic fractions was used to calculate 'biomass N' using the equation of Jansson (1971).

**G. Analytic procedures:**

Kjeldahl N was determined in air-dry 100-mesh soil samples using the salicylic acid modification to include  $\text{NO}_3 - \text{N}$  (Bremner, 1965a). Mineral  $\text{NH}_4 + \text{NO}_3 - \text{N}$  was determined in air-dry, 2-mm soil samples by extraction with 2M KCl and distillation with  $\text{MgO}$ -Devarda's alloy mixture (Bremner, 1965b). Mineralizable N in soil was determined in air-dry, 2mm samples by the 14-day anaerobic incubation method of Waring and Bremner (1964). Organic N in soil was determined as difference between Kjeldahl and mineral fractions. No correction was made for clay-fixed  $\text{NH}_4 - \text{N}$  which was expected to be negligible on account of the predominant kaolinitic nature of the soil. The volatilized  $\text{NH}_3$  trapped in dil.  $\text{H}_2\text{SO}_4$  was determined by Nessler-

rization. The colour intensity was read at 420 m $\mu$  in a Bausch and Lomb spectrophotometer. Acid-hydrolyzable organic N and its fractions were determined by refluxing air-dry, 100-mesh soil samples with boiling 6 N HCl (Bremner, 1965c).  $^{15}\text{N}/^{14}\text{N}$  isotopic ratio of soil extracts was determined in acidified samples after titration following standard procedures (Bremner, 1965d) and that of plant samples according to the modified Dumas method (Fieldler and Proksch, 1972). The isotopic ratio analysis was performed by the Seibersdorf Laboratory of the International Atomic Energy Agency, Vienna using mass spectrometry.

## RESULTS AND DISCUSSION

### *Ammonia volatilization during sun-drying:*

Among carbonaceous materials, straw when combined with urea caused the highest loss of about 26% (Table I). The straw, an energy material, is known to enhance microbial activity (Meo, 1967; Lloyd and Sheaffe, 1973) and consequent loss of Ammonia by volatilization. Inclusion of superphosphate to provide  $\text{P}_2\text{O}_5$  equivalent to 50% of the fertilizer N in the mixture reduced the loss from 26 to 1.3%. The neem oil-extract also proved effective, but to a lesser extent. With ammonium sulphate the volatilization losses were quite small, and therefore, superphosphate or neem-oil extract did not provide any substantial benefit. This fact and relative losses with carbonaceous materials other than rice straw indicated that although energy source was a factor, the pH effect (Overrein

and Moe, 1967) was probably more important. The losses could be much higher in the case of neutral or alkaline soils.

### *Immobilization of fertilizer N during preparation and sun-drying:*

The mineral N content of a few selected type of mud balls (Table II) showed that even during the short span of time (about 7 days) required to dry them, substantial immobilization had occurred. It was greater with the use of urea than with ammonium sulphate, and with straw than husk. During preparation and early stages of sun-drying, the moisture conditions were quite favourable for microbial immobilization. The mud balls without any added carbonaceous material also showed some immobilization, particularly with urea. Broadbent and Nakashima (1970) have reported about 20% of the added urea-N may be immobilized in soil even in the absence of added rice straw.

**Dissolution rate of mud balls in flooded soil:** The release of N from mud balls, as revealed by leachate concentration, is shown in Table III. upto 4 weeks the release from urea mud balls was more or less similar to that of LCU, but there after N release from the former tended to be higher. Inclusion of straw depressed the release upto 3 weeks as compared to urea mud balls without any added carbonaceous material. But latter, straw + urea mud balls released N at a faster rate which was also higher than the

from SCU or LCU. The carbonaceous materials depressed the release from mud balls prepared from ammonium sulphate only upto 2 weeks. The per cent dissolution in 10 weeks, corrected for the control values and volatilization loss, showed that the mud balls, on average, released about 5% of its N as compared to 2 and 0.4% from LCU and SCU, respectively.

*Transformation of  $^{15}\text{N}$  labelled N in mud balls:*

The distribution of labelled fertilizer N in various fractions is shown in Table IV. Averaged over 30, 60 and 90 days of incubation, the labelled N in the Kjeldahl fraction was only about 27% with SCU as compared to 50 to 53% in straw mud balls, 45 to 47% in husk mud balls, and 44% in urea mud balls without added carbonaceous material. The fertilizer N incorporated into organic N also showed that straw was able to immobilize more of the added N as compared to husk or non-carbonaceous urea mud balls. As per cent of the labelled N in the Kjeldahl fraction, transformation of  $^{15}\text{N}$  into organic form averaged 79 to 84% in straw mud balls and 75 to 77% in husk or non-carbonaceous mud balls.

In the case of straw or husk mud balls the acid-hydrolyzable organic N did not show much variation and incorporation of added labelled N ranged from 30 to 35%. However, the incorporation decreased to an average of about 28% when no carbonaceous material was included. The lowest in-

corporation of about 19% was found in the case of SCU.

The consequences of adding carbonaceous energy materials through mud balls on microbial turnover were evident from the change in 'biomass N' (Table IV). According to Jansson (1971), 'biomass N' corresponds to the tagged N incorporated in active heterotrophic organisms and fresh debris originating from such organisms. The 'biomass N' on an average, constituted about 115 to 129 ppm or 22 or 24% of the total soil N in the case of straw mud balls. For husk mud balls it was 15 to 16%, almost on par with urea mud balls without any added carbonaceous material. It is quite understandable that straw, a more easily decomposable and, therefore, a better energy source than husk, generated greater microbial turnover.

Fractionation of the acid hydrolyzate is shown in Table V. Labelled N in these fractions could not be determined. But the distribution of total (soil+fertilizer) N showed that the ammonium and amino acid fractions, which are important source of 'plant-available' N, were, on an average, about 27 and 15% of the total Kjeldahl N, respectively, in soil treated with husk+urea mud balls. Other mud balls, particularly those prepared from urea without any carbonaceous material showed much lower values.

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TABLE I Loss of  $\text{NH}_3\text{-N}$  through volatilization from mud balls during sun drying (%)

N rate=250 mg/mud ball

Mud balls prepared from	N source	
	Urea	Amm. sulphate
Soil	0.80	0.61
Soil+NE	0.13	0.41
Soil+SP	0.04	0.42
Soil+Rice straw	26.43	1.60
Soil+Rice straw+NE	23.95	1.61
Soil+Rice straw+SP	1.30	1.21
Soil+Rice husk	4.04	1.40
Soil+Rice husk+NE	0.85	0.95
Soil+Rice husk+SP	0.01	1.00
Soil+Neem cake	0.19	0.00
Soil+Kokum cake	0.00	0.00

NE=Neem extract; SP=Single superphosphate.

TABLE II Mineral  $\text{NH}_4+\text{NO}_3\text{-N}$  in dried mud balls.

N rate=250 mg/mud ball.

Mud balls prepared from	% Mineral N
Urea+SP	46.71
AS+SP	93.66
Straw+Urea+SP	24.25
Straw+AS+SP	86.26
Husk+Urea+SP	32.75
Husk+AS+SP	90.00

AS=Ammonium sulphate.

Values expressed as percentage of added N after correcting for volatilization losses during drying and mineral N in the soil.

TABLE III.—Release of N from mud balls in flooded soil.  $\text{NH}_4 + \text{NO}_3$  — N in leachate (mg per pot) and per cent dissolution

(Mean of duplicate values)

N rate = 250 mg per pot.

Treatment	$\text{NH}_4 + \text{NO}_3$ — N in leachate, mg per pot at week										Total for 10 weeks	Percent dissolution	% dissolution corrected for volatilization loss
	1	2	3	4	5	6	7	8	9	10			
Control, no N	1.42	0.71	0.95	0.71	0.85	1.85	0.75	0.88	1.13	2.00	11.15	—	—
LCU	1.37	1.13	0.57	1.28	1.28	1.42	1.88	2.13	2.36	2.75	16.17	2.01	—
SCU (unlabelled)	0.99	0.85	0.99	0.99	1.28	1.42	1.13	1.38	1.25	1.88	12.16	0.40	—
<i>Mud balls prepared from</i>													
Urea	1.62	2.14	1.71	1.23	2.28	2.98	2.25	2.37	3.50	2.75	22.83	4.67	4.67
AS	1.28	1.42	0.99	1.14	1.71	3.27	2.50	3.75	3.12	4.75	23.93	5.11	5.13
Straw + urea	0.85	0.99	1.34	1.71	2.84	4.55	3.75	2.00	4.87	5.25	28.15	6.80	6.89
Straw + AS	0.43	0.85	1.28	1.71	1.85	2.98	3.12	3.63	3.75	5.25	24.85	5.48	5.55
Husk + urea	1.43	1.29	1.85	0.99	0.85	1.85	1.75	2.25	3.13	4.50	19.89	3.50	3.50
Husk + AS	0.91	1.28	1.28	1.28	1.99	2.28	3.37	3.75	4.50	5.28	25.69	5.90	5.96

AS = Ammonium sulphate; All mud balls contained superphosphate.



TABLE IV Distribution of labelled fertilizer N in different N fractions and biomass N.

(Average values over 30, 60 and 90 days of incubation)

	Mud balls prepared from					SCU (labelled)
	Straw + urea	Straw + AS	Husk + urea	Husk + AS	Urea	
(a) N fractions	<i>% of added labelled N</i>					
Kjeldahl N(including NO <sub>3</sub> -N)	52.51	49.96	47.07	44.93	44.06	27.05
Mineral NH <sub>4</sub> +NO <sub>3</sub> -N	10.78	7.89	10.95	11.12	10.15	5.88
Mineralizable NH <sub>4</sub> +NO <sub>3</sub> -N	0.6	1.22	—	0.29	0.27	0.05
Total organic N	41.72	42.07	36.12	33.80	33.91	21.17
Acid hydrolyzable organic N	33.90	35.24	30.63	29.70	27.89	18.97
(b) Biomass N	<i>ppm</i>					
	114.92	129.26	78.92	80.29	81.82	77.94
	<i>% of soil + fertilizer Kjeldahl-N</i>					
	21.76	24.48	15.49	15.95	16.61	15.87

TABLE V Distribution of soil+fertilizer N in various fractions of the acid-hydrolyzate as per cent of total Kjeldahl-N.

(Average values over 30, 60 and 90 days incubation)

N fractions	Mud balls prepared from					SCU
	Straw + urea	Straw + AS	Husk + Urea	Husk + AS	Urea	
Ammonium N	21.9	20.1	27.3	21.1	19.1	24.7
Hexosamine N	6.3	10.4	3.1	10.8	13.0	5.4
Amino acid N	13.3	6.0	15.1	9.9	6.9	11.3
Unidentified N	25.9	29.9	24.2	27.6	29.8	30.9
Total	67.5	66.4	69.7	69.4	68.8	72.4

AS ± Ammonium Sulphate