

# Is the source–sink relationship in transplanted rice receiving deep-placed urea supergranules dependent upon the geometry of transplanting?

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**Abstract** Deep placement of urea supergranules in wetland rice (*Oryza sativa* L.) or correct urea band application enables to protect nitrogen (N) from various loss mechanisms, but recovering of fertilizer N by plants depends upon geometric and agronomic factors. The objective of this study was to characterize the diffusion of ammoniacal N from the two urea sources, point or line application, in a typical paddy soil. A model of ammonia diffusion was developed for the two geometries. The relation between the N application rate and the transplanting geometry was studied in two fields using probes attached to urea supergranule of different mass (2 and 4 g). The transplanting pattern was adapted for obtaining 58 or 116 kg N ha<sup>-1</sup> in the 4 g application. The ammoniacal nitrogen concentration was compared to the diffusion model prediction. The values of the diffusion coefficient were found to be 1.160 and 1.107 cm<sup>2</sup> d<sup>-1</sup>. Ammonia disappearance below 10 mmol L<sup>-1</sup> did not follow the same kinetics in the two treatments corresponding to 4 g application. Relative to the 2 g treatment, root ammonia uptake in the 4 g treatment was delayed and slowed in the classical geometry of 20 cm × 20 cm (116 kg N ha<sup>-1</sup>) when it was mainly delayed in the geometry provided with 58 kg N ha<sup>-1</sup>. This manipulation of the source–sink relationship enables to foresee possibilities for the development of new fertilizers adapted to wetland rice cultivation.

**Keywords** Urea supergranule · Urea deep placement · Diffusion · *Oryza sativa*

## Introduction

Urea is the main nitrogen fertilizer used by farmers cultivating wetland rice. In developing countries, its use is often limited by the fact that it must be imported and sometimes transported to distant areas of rice cultivation. It is, therefore, important that its utilization should be limited to situations where yield increases are certain.

Nitrogen fertilizer (urea or ammonium salt) is prone to important losses when it is broadcasted. Management of floodwater depth throughout the wet season (the rainfall season is considered here to be the main rice season) can eliminate runoff, but has little effect on ammonia volatilization (Li et al. 2008). Nitrogen deep placement can insure adequate distance from the ponded water (Cao et al. 1984; Kapoor et al. 2008) and consequently drive ammonia volatilization to an insignificant level. But placement is not simple task at a time when paddy soils are put in a muddy state (puddling) for rice transplantation (Mohanty et al. 1999). Two solutions are promoted by scientists and developers: either urea supergranules (USG) hand or mechanical placement (Dupuy et al. 1990a; Savant and Stangel 1990) or urea band (UB) mechanical injection (Schnier et al. 1993; Bautista et al. 2001). In this technique, an urea solution is delivered by discharge tubes placed behind furrowers. Pneumatic injection of urea prills was also tested for point positioning (Scholten 1992); recently, a light apparatus (6 kg) has been developed for USG application at adjustable row spacing (Hoque et al. 2013).

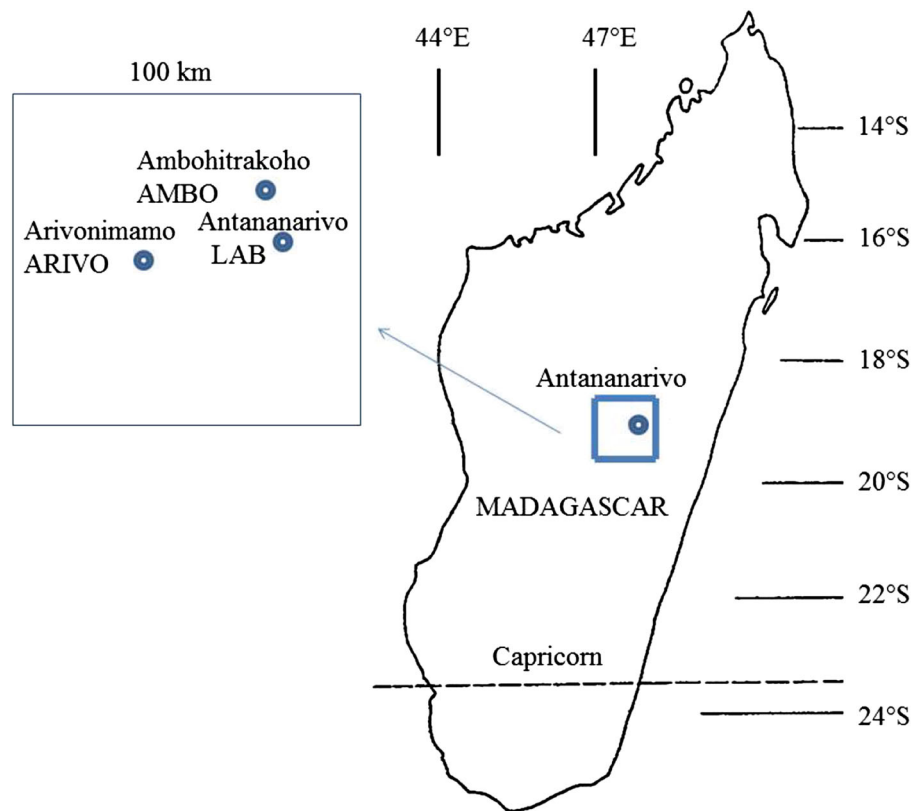
In this paper, we shall calculate how these alternatives, USG and UB, lead to differences in nitrogen source density

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**Fig. 1** Map of Madagascar and location of experiments



and consequently how ammonia diffusion can be different within the soil. Variation in ammonia distribution can influence ammonia uptake by rice roots. For the case of USG differing by mass, Gaudin and Dupuy (1999) have shown that ammonia uptake from 4 g-USG occurred too lately (for a large part at the end of the reproductive stage) in comparison with the pattern of ammonia uptake from lighter granules. The present paper will consider two geometrical patterns for 4 g-USG application and compare the ability of transplanting rice (sink function) to assimilate the fertilizer (source). Development of new fertilizers adapted to transplanted rice will be discussed.

## Materials and methods

### Experimental settings

The experiments were performed either in laboratory (LAB) or in two fields named ARIVO and AMBO (see geographical situation on map of Madagascar in Fig. 1). The characteristics of these experiments are given in Table 1. The principal aim of LAB experiments was characterization of ammoniacal nitrogen diffusion from 2 g-USG in a typical un-transplanted paddy soil; the ARIVO and AMBO experiments aimed at studying the transplanted situations, for 2 g- and 4 g-USG.

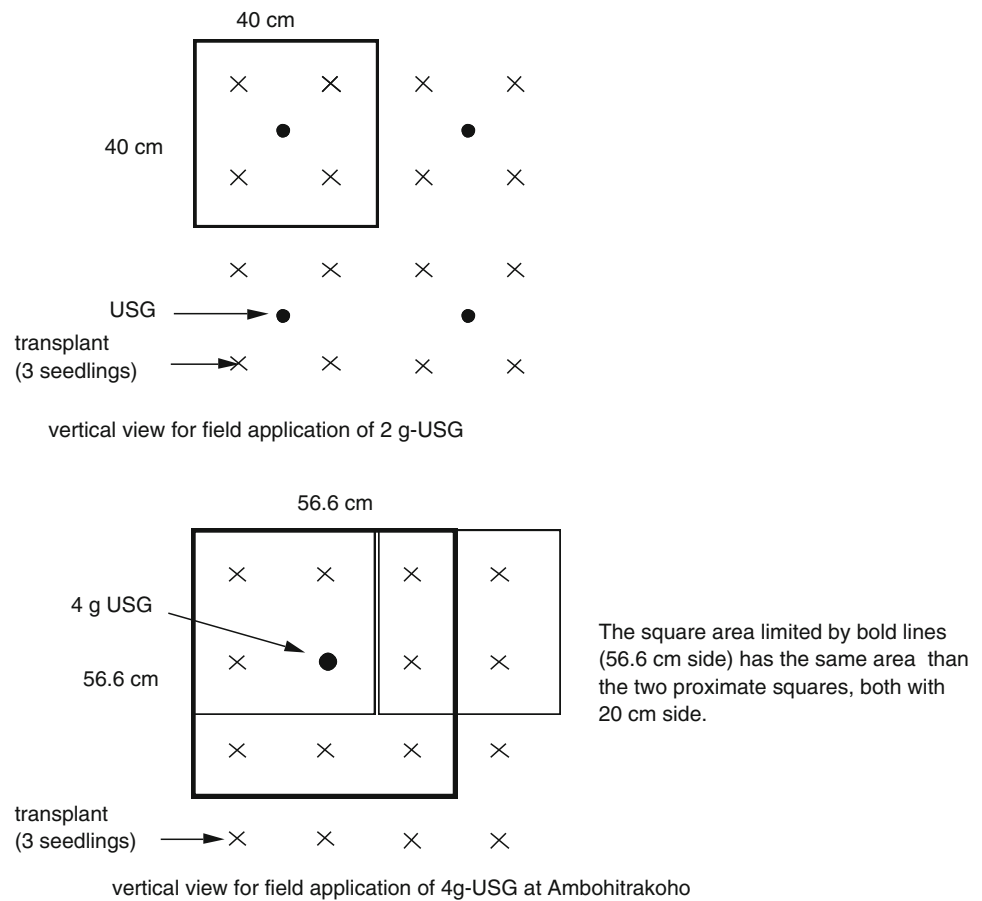
### Laboratory experiments

Ammoniacal nitrogen diffusion from deep-placed urea supergranules was monitored in tanks kept at 25 °C in a dark room of Laboratoire de Radio-Isotopes, a research unit of Antananarivo University located 18°53'57''S, 47°33'02''E, in the capital of Madagascar.

Four tanks were packed with earth coming from a paddy soil (Onibe bridge, Arivonimamo, Madagascar) with the following characteristics: 40 % clay, 27 % silt, 33 % sand, and 2.3 % organic matter. Water was added and mixed with the soil until a muddy condition of the soil was obtained. The soil was let to steady a few days. Flooding water was eliminated when 2 g urea supergranules and ceramic samplers were positioned. The soil water content was around 0.60 cm<sup>3</sup> cm<sup>-3</sup> at 10–20 cm depth in the tanks.

One tank was equipped with an array of samplers as follow. The 15 cm top layer was removed, and ceramic samplers were installed in the opened plane at 5, 10, or 15 cm from the central position according to the geometrical design of Fig. 3. Then, the top layer was brought over the plane in order to restore the initial volume. Flooding was practiced just after. The central sampler, noted O in Fig. 3, was placed 5 cm above the 2 g-USG when the top layer was restored. This sampler and its nylon tube were attached to a stick in order to permit descent for

**Fig. 2** Classical geometry for urea supergranule (USG) deep placement in transplanted rice and alternative geometrical pattern for doubled USG mass at the same N rate

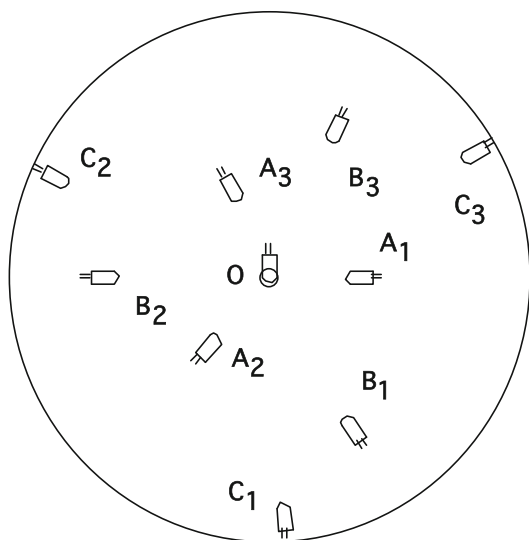


**Table 1** Location and description of experiments

Experiments	Localization	Description	Objectives
Lab	Laboratoire de Radio-Isotopes, Route d'Andraisoro, Antananarivo (Madagascar)	Diffusion in un-transplanted situation, soil from Arivo with array of samplers (Fig. 3) for observations at 8, 14, 28, and 56 days three replicates with one sampler attached to 2 g-USG	comparison of ammonia concentration with model prediction measurement of ammonia concentration at 4 days for calculation of D
Arivo	Field at Onibe bridge, 5 km West of Arivonimamo	Comparison of USG at 58 and 116 kg N ha <sup>-1</sup> in the same geometry: 20 cm per 20 cm (top of Fig. 2)	Kinetics of ammonia disappearance from 2 and 4 g-USG, both in classical transplanting geometry
Ambo	Field 17 km North of Antananarivo	Comparison of the two geometries for the same N level of 58 kg N ha <sup>-1</sup> (Fig. 2)	Kinetics of ammonia disappearance from 2 g-USG (classical geometry) and 4 g-USG (alternative geometry)

localization at the USG placement site at the first sampling time. The samplers had 13 mm diameter and 12 mm length. Their hemispheric ends were oriented toward the central position. A few mL of soil solution were withdrawn under the action of a manual vacuum pump. These volumes were collected in penicillin bottles at the following dates: 8, 14, 28, and 56 days.

The three other tanks were managed independently from the tank with the array of samplers. They were prepared in the same way (same soil, same temperature, and same soil water content). For each tank, a unique soil ceramic sampler (Gaudin 1991) was attached to a 2 g-USG and placed at 15 cm depth. Soil solution sampling was practiced 4 days later in order to obtain the ammonia concentration,



**Fig. 3** Experimental layout for studying diffusion from USG. Three samplers were installed at 5 cm (A serie), 10 cm (B serie), and 15 cm (C serie) from urea point position (USG). The central sampler (O) was descended in the point position at 8 d after USG placement

noted  $c_4$ . The mean value of  $c_4$  was used for calculation of  $D$ , the diffusion coefficient for ammonia (see data analysis below).

Ammonia was measured by an indophenol-blue method and urea by a diacetyl-thiosemicarbazide method.

#### Field experiments (Table 1)

The classical geometry of urea application was practiced in Arivo experiment: USG was placed at 7–10 cm depth in the center of a 0.16-m<sup>2</sup> square, between four rice transplants in 20 cm × 20 cm geometry. The N rates are 58 kg ha<sup>-1</sup> (2 g-USG) and 116 kg ha<sup>-1</sup> (4 g-USG). In Ambo, the classical geometry was also practiced in the 2 g-USG application, and the particularity was the N rate of 58 kg ha<sup>-1</sup> specially built for 4 g-USG application (Fig. 2). In comparison with the 20 cm × 20 cm geometry, the distance between transplants was 18.9 cm; the 4 g-USG was placed between 8 transplants (vs. 4 in the classical USG application).

The Arivo experiment was performed in a field (19°00'16''S, 47°07'24''E) situated near a bridge over the Onibe river, 5 km from Arivonimamo and 50 km west from Antananarivo. The variety was a local cultivar (1285). The 4 g-USG treatment was obtained by packing four 1 g-USG.

The Ambo experiment (alternative geometry for 4 g-USG) was performed in a field (18°46'40''S, 47°25'39''E) situated near the village of Ambohitrakoho, 17 km north of Antananarivo. The variety was also a local cultivar (1632).

The two cultivars were grown during the wet season. Phosphorus and potash were broadcasted prior to soil puddling. The rate of phosphorus and potash application was recommended by extension services: for P, 60 kg ha<sup>-1</sup> (Arivo) and 90 kg ha<sup>-1</sup> (Ambo); for K, 90 kg ha<sup>-1</sup> (Arivo) and 60 kg ha<sup>-1</sup> (Ambo). More P was applied at Ambo as the field was part of a lowland which was moderately drained during dry season and could exhibit a risk of phosphorus deficiency (Balasubramanian et al. 1995). The field of Arivo presented excellent drainage in dry season and good agronomic results in previous experiments (Dupuy et al. 1990b). More K was applied in this site to correct straw exportation.

In each plot (24 m<sup>2</sup>), one 2 g- or 4 g-USG was attached to one solution sampler as described in Gaudin (1991, 2012). The indophenol-blue method was used for ammonia determination. The pH of the soil solution extract was monitored on a mean sample obtained by adding the volumes left by ammonia determination.

#### Analytical solutions for ammonia diffusion from point and line sources

Because of the speed of USG dissolution and the speed of urea hydrolysis, USG is considered an instantaneous and point source of ammonia. Assuming diffusion in an infinite medium from this source, the analytical solution for the diffusion equation is in the case of spherical symmetry (Crank 1975):

$$c_g(r, t) = (Q/8\Theta)(\pi Dt)^{-3/2} \exp(-r^2/4Dt), \quad (1)$$

where  $c_g$  is the ammoniacal nitrogen concentration (mol L<sup>-1</sup>),  $t$  the time (d),  $r$  the distance to point of placement (cm),  $Q$  the USG mass (mmol),  $\Theta$  the soil moisture content (cm<sup>3</sup> cm<sup>-3</sup>), and  $D$  is the diffusion coefficient for ammonia (cm<sup>2</sup> d<sup>-1</sup>)

An interesting position for localization of samplers is the placement site because it is in this position that the ammonia concentration is the less varying relatively to distance ( $dc/dr = 0$ ):

$$c_g(0, t) = (Q/8\Theta)(\pi Dt)^{-3/2} \quad (2)$$

The analytical solution for the cylindrical diffusion from an instantaneous line source is (Crank 1975)

$$c_b(d, t) = (A/4\Theta)(\pi Dt)^{-1} \exp(-d^2/4Dt), \quad (3)$$

where  $c_b$  is the ammoniacal nitrogen concentration (mol L<sup>-1</sup>),  $t$  the time (d),  $d$  the distance to placement line (cm),  $A$  the amount of diffusing substance deposited initially per unit length of line source (mmol cm<sup>-1</sup>),  $\Theta$  the soil moisture content (cm<sup>3</sup> cm<sup>-3</sup>), and  $D$  is the diffusion coefficient for ammonia (cm<sup>2</sup> d<sup>-1</sup>)

## Data analysis

The diffusion coefficient for ammonia was calculated from the mean ammonia concentration measured at 4 days after USG deep placement (this concentration is noted  $c_4$ ) at the placement site. Its expression was derived from Eq. 2:

$$D = [1/(4\pi)][(Q/8\Theta c_4)]^{2/3} \quad (4)$$

In the lab, the mean value of  $c_4$  was used for calculation of  $D$  [Eq. 4], for prediction [with Eq. 1] of  $c_g(r, t)$  at  $r = 0-2.5-5-7.5$  cm and its comparison with the experimental values [ $c$  at  $(r, t) = (0,8)-(0,14)-(0,28)-(0,56)-(5,14)-(5,28)-(5,56)$ ]. In the fields, the  $c_4$  values (from measurements at four days) were used for calculation of the diffusion coefficient for each site [Eq. 4], and then for prediction [with Eq. 2] of  $c_g(0, t)$  corresponding to 2 or 4 g-USG, in situation without rice transplants. Root ammonia uptake was not noticed until the ammonia concentration attained a threshold of  $10 \text{ mmol L}^{-1}$ . It was documented by a transition in the log-linear representation of ammonia concentration versus time. The diffusion phase was described by a concave curve as for the theoretical prediction of Eq. 2. It was followed by a first-order disappearance of ammonia (Gaudin 1991), corresponding to root ammonia uptake and ammonia assimilation. The rate constant of ammonia uptake was obtained by linear regression of the Napierian logarithm of ammonia concentration with time. Its confidence interval (at the 95 % level) was visualized with a Statview software.

## Results and discussions

### Lab experiment

Urea hydrolysis was rapid after urea placement. At 8 days, 95 % of urea-N was hydrolysed in the placement site (Table 2). This percentage did not change very much in the following week, and it is possible that this percentage (or approaching level) was already attained when the peak of alkalinity had taken place (at 4 days). Organic compounds were formed by the attack of  $\text{NH}_3$  on organic matter (brown color of soil solution extract), and it is plausible that these compounds had an inhibitory role in hydrolysis of remnant urea (Rachhpal-Singh 1984) or that they were confounded with urea in analysis. The high speed of hydrolysis is in accordance with quick alkalisation in placement sites (Field experiment). In the previous section, we assumed USG to be an instantaneous source of ammonia. This is a simplification as far as ammonia concentration overpasses urea concentration at approximately 1 day after USG application (Savant et al. 1983), but it is very useful for graphical representation of the ammoniacal

**Table 2** Urea-N concentration in soil solution and percentage ratio of urea-N to the sum of ammoniacal N and urea-N at four sampling dates (time after urea application to soil). The USG mass was 2 g

Time after urea placement	Urea-N concentration in $\text{mmol L}^{-1}$ (and percentage ratio of urea-N to the sum of ammoniacal N and urea-N)				
	8 days	14 days	28 days	39 days	
Distance from USG	0 cm	5.5 (4.8)	3.1 (4.6)	0.8 (2.7)	0.4 (1.7)
	5 cm	0 (0)	0.3 (4.7)		

**Table 3** Ammoniacal N soil solution distribution. The distances are from point of USG application. Urea and samplers were placed at 15 cm depth in a cylindrical tank with 50 cm diameter and 50 cm depth

Time after placement	Ammonia concentration ( $\text{mmol L}^{-1}$ )				
	8 days	14 days	28 days	56 days	
Distance from USG	0	109.5	64.4	29.2	12.5
	5 cm		6.10	8.09	5.60
	10 cm		0.49	1.02	1.56
	15 cm		0.49	1.00	1.03
Control		0.19	0.17	0.46	0.71

nitrogen diffusion process (lasting several weeks), with a single parameter (diffusion coefficient for ammonia).

Ammonia diffusion (Table 3) was evident in USG treatment: in the placement site, ammonia concentration was approximately divided by 2 when time doubled; at 5 cm, concentration was greater than  $5 \text{ mmol L}^{-1}$  as soon as 14 days. Small amount of ammonia seems to have diffused as far as 10 cm, but 56 days were necessary to attain  $1.5 \text{ mmol L}^{-1}$ . This range of ammonia diffusion is in agreement with the ammonia distributions displayed 14, 28, and 56 days after 2 g-USG deep placement in an un-transplanted soil (Savant and Stangel 1990).

Calculation of the diffusion constant led to  $0.998 \text{ cm}^2 \text{ day}^{-1}$ .

The model of ammonia diffusion made good prediction in the placement position of USG for short duration of diffusion (Fig. 4) but underestimated the ammonia concentration at 14 days and after. The coefficient of correlation was 0.99 indicating a highly significant relationship. For the 5 cm distance, the observed concentration was less than the predicted one. Both data were consistent with a slowdown effect due to the exchange of ammonia between soil solution and soil matrix.

Mineralization was around  $1 \text{ mmol L}^{-1}$  for 56 days (0.71 for control, 1.0 for 15 cm distance, Table 3) in lab experiment. In the fields, N mineralization could have been

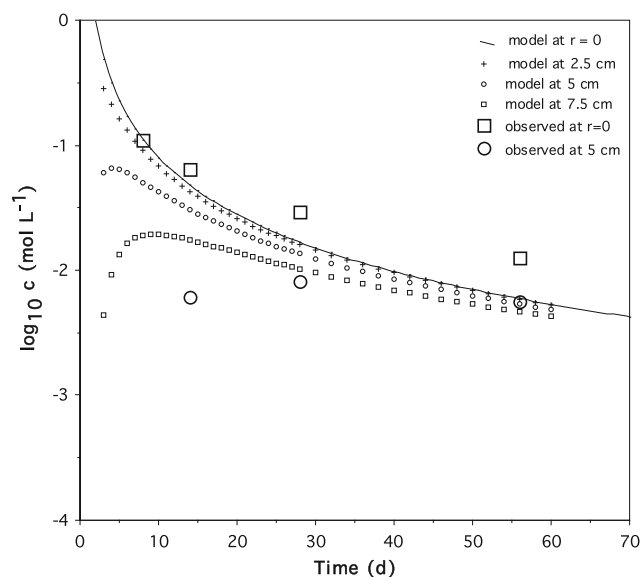
different because of differences in management of organic matter, notably roots of previous crop which were incorporated in lesser soil. Another important factor for future paddy yields is the initial exchangeable ammonium (Schön et al. 1985): in Madagascar, it is quite often low, except in regions of old volcanoes, deltas, and large alluvial plains with notable fertility. Note that the clay material is predominantly kaolinite, impeding ammonium fixation.

#### Field experiment

Urea hydrolysis generated alkalinity at and around the placement site (Table 4). This localized alkalinity attained its maximum within 3–4 days after urea placement: Savant et al. (1983) reported a maximum pH of 9.0 at 3 days for a 1-g-USG and Gaudin (1991) indicated a pH of 8.98 at 4 days for a 2 g-USG. The limit of attainable pH is set by the  $pK_a$  of ammonia (9.25 at 25 °C) as a consequence of the hydrolysis reaction:



The experimental values were in agreement with this prediction as the maximal value of pH was 9.20 in Ambo



**Fig. 4** Time course of ammonia concentration as predicted by the model for the positions: 0–2.5–5–7.5 cm, and lab measurement at positions: 0–5 cm, from placement point of a 2-g urea supergranule

**Table 4** Evolution of soil solution pH in the placement sites of 2 g- and 4 g-USG in Arivo and Ambo fields

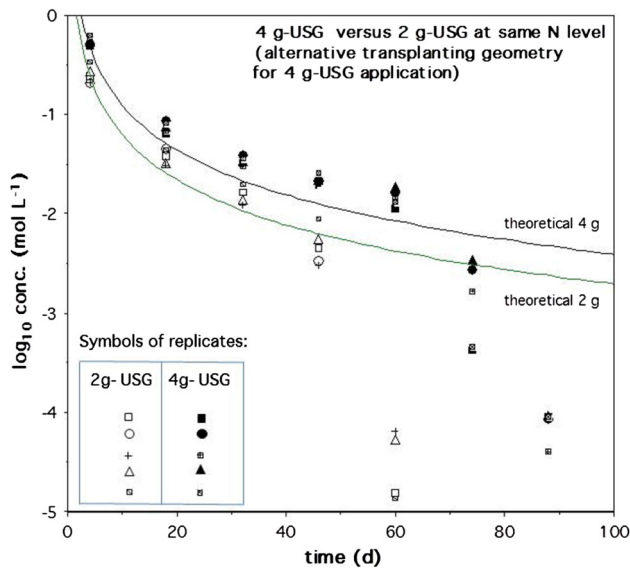
USG mass (g)	Field	Time (DAT)							
		4	13	18	24	31	46	60	74
2	Arivo	9.04	8.09		7.89	7.46			
	Ambo	8.95		8.03		7.69 <sup>a</sup>	6.98	6.00	5.85
4	Arivo	9.08	8.32		8.05	7.93			
	Ambo	9.20		8.43		8.31 <sup>a</sup>	8.21	8.02	6.14

<sup>a</sup> At 32 DAT for Ambo

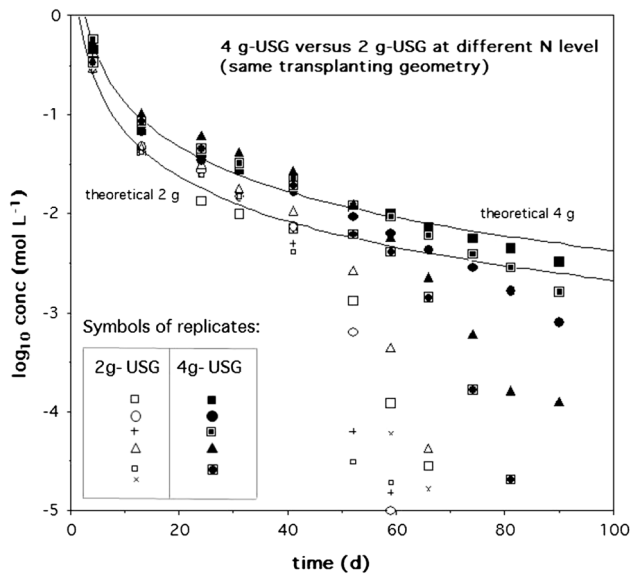
site, and the other values were between 8.95 and 9.08. Greater mass produced higher alkalinity. A consequence of this great alkalinity was an attack of organic matter attested by the brown color of all soil solution extracts at 4 DAT (days after transplanting). In the Arivo field, we also observed a light bubbling at the interface between the soil and the floodwater just at this time and at the place of 4 g-USG application, in approximately 25 % of all sites of application. Little dead worms were also noticed at the same place. It means that toxic ammonia was produced by the larger USG and that a part of ammonia was lost in the floodwater in some cases. We did not notice the same phenomenon in the Ambo field, but it does not mean that it did not occur a few hours before or after our visit on the field.

The mean ammonia concentration at 4 DAT (2 g-USG) was 0.249 mol L<sup>-1</sup> at Ambo and 0.268 mol L<sup>-1</sup> at Arivo. Assuming that the soil moisture content at saturation was 0.6 cm<sup>3</sup> cm<sup>-3</sup> in both situations, the diffusion constant for ammonia was 1.160 and 1.107 cm<sup>2</sup> d<sup>-1</sup>, respectively. For 4 g-USG, concentrations were enhanced (Figs. 5 and 6) yet they did not double the values attained in the 2 g-USG application. In the following month, the driving process of ammonia disappearance was diffusion as the experimental values were relatively close to the theoretical prediction. Diffusion was however less rapid than predicted: ammonia exchange between soil solution and soil matrix was plausibly involved in this moderation. At Ambo (Fig. 5), the diffusion phase was extended until 60 DAT for 4 g-USG when ammonia uptake was effective at 46 DAT for 2 g-USG. Local acidification was then associated with ammonia uptake (Table 4). The drop in ammonia concentration began around 10–12 mmol L<sup>-1</sup> as in previous experiments (Gaudin and Dupuy 1999). The first-order reaction of ammonia uptake had the following rate constants: 0.353 and 0.223 d<sup>-1</sup> (Fig. 7). For comparison, a rate constant of 0.356 d<sup>-1</sup> was associated with 90–135 PK level in an independent field experiment with a single 2 g-USG application. The greater this rate constant, the rapider the concerned roots are coping with the large quantity of ammonia at their disposal. The first-order mechanism is plausibly involving a mechanism (anaplerotic function of phospho-enol pyruvate carboxylase) activated in roots



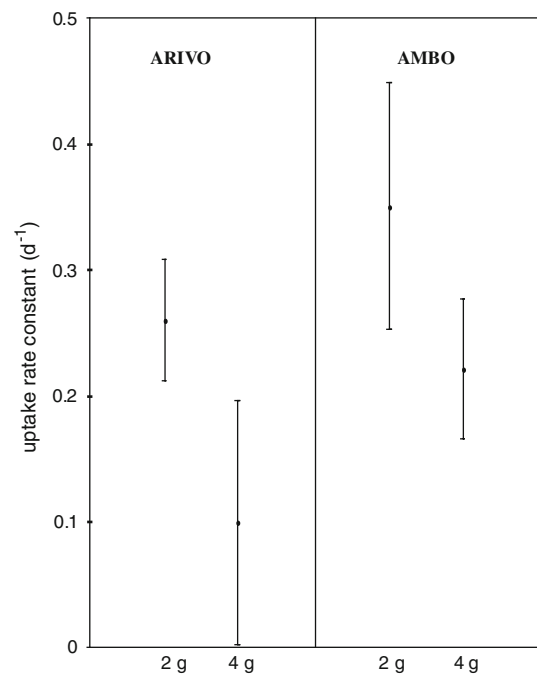


**Fig. 5** Time course of  $\log_{10}$  of ammonia concentration (c, molar) in the soil solution at the placement sites of 2 g- and 4 g-USG in Ambo experiment: the data are plotted against the theoretical curves corresponding to spherical diffusion from a point source with a diffusion coefficient of  $1.160 \text{ cm}^2 \text{ d}^{-1}$  (Eq. 2). From five replications out of five for 2 g-USG, and from five out of five replications for 4 g-USG



**Fig. 6** Time course of  $\log_{10}$  of ammonia concentration (c, molar) in the soil solution at the placement sites of 2 g- and 4 g-USG in Arivo experiment: the data are plotted against the theoretical curves corresponding to spherical diffusion from a point source with a diffusion coefficient of  $1.107 \text{ cm}^2 \text{ d}^{-1}$  (Eq. 2). From six replications out of six for 2 g-USG, and from five out of six replications for 4 g-USG (One replicate is missing, due to loss of contact between sampler and USG)

when ammonia is abundant in order to satisfy the priority of nitrogen assimilation over carbon metabolism (Gaudin 1993). The performance of this mechanism is known to be very dependent upon the energetic status of the plant.



**Fig. 7** Confidence intervals (at 95 %) for the mean rate constant of ammonia uptake in the USG rice systems studied at Arivo and Ambo

At Arivo, the data presented more dispersion (Fig. 6), notably with the 4 g-USG. The threshold indicating that ammonia uptake had started was identical to Ambo situation with 2 g-USG. It was not the case in the 4 g-USG treatment where each set of transplants displayed its kinetics. They shared however the characteristics of first-order reactions but with various rate constants. Contrarily, the 2 g-USG treatment presented more homogeneity (Fig. 7) in the speed of root ammonia uptake, with a mean rate constant of  $0.263 \text{ d}^{-1}$ .

The yield was  $3.9 \text{ Mg ha}^{-1}$  at Ambo for 2 g- and 4 g-USG treatments, at  $58 \text{ kg N ha}^{-1}$ . It was 3.9 and  $4.5 \text{ Mg ha}^{-1}$  for the 2 and 4 g-USG at Arivo, N rates being 58 and  $116 \text{ kg ha}^{-1}$ , respectively. Clearly, the timing of nitrogen uptake was not optimal in 4 g-USG application at Arivo, as nitrogen was available too late. At Ambo, it seems that source–sink relation remained constant although the 4 g-USG rice system had ammonia uptake lagging 4 weeks behind the 2 g-USG rice system. The main reason was that the ratio of USG mass to the number of transplants was constant yet this did not impede ammonia uptake to be delayed in the 4 g-USG treatment. It is plausible that the situation at Arivo could have been improved by elevation of PK application since the rate of ammonia consumption was largely determined by the number of tillers, itself dependent upon the PK rate (Gaudin 2012).

#### Guidance for the design of new fertilizer

All over the world, many scientists are testing new fertilizers, either to limit nitrogen (and PK) losses in difficult

environmental conditions (Islam et al. 2011) or to obtain the best kinetics of ammonia assimilation compatible with the highest yield (Sheehy et al. 2005). Substitutes for urea (urea modified material or coating) are sometimes considered the best solution, but long-term research has not yet attain this goal at a price affordable for farmers (Chien et al. 2009). Coated urea (controlled release urea: CRU) is promising, but its effect upon the assimilation rate is difficult to investigate in the field. As an example, Yang et al. (2012) have measured rice yield and CRU-nitrogen use efficiency together with the leaf enzymes activities of GS (glutamine synthetase) and GOGAT (glutamine oxoglutarate aminotransferase). For facility, the study was conducted on drainage lysimeters, and it was postulated that nitrogen assimilation occurred mainly in the leaves via the GS-GOGAT cycle. It is not certain that the reported values of GS-GOGAT activity represented the activity of the root enzymes (also GS and GOGAT) responsible for ammonia assimilation in most paddy soils (Tabuchi et al. 2007; Funayama et al. 2013) where ammonia predominates over nitrate (Yoshida 1981).

In anaerobic paddy soils, the device coupling one USG, and a ceramic soil solution sampler gives direct access to the kinetics of ammonia assimilation. The gained information are clarifying the limits of the positive effect of deep urea placement: USG application at  $116 \text{ kg ha}^{-1}$  or at higher N rates has no interest in the classical transplanting geometry ( $20 \text{ cm} \times 20 \text{ cm}$ ). One solution could be the split application of USG, using 2 g-USG, either placed at different times (Gaudin 2012) or at different places. But the required labor should be too much and consequently unacceptable by farmers: a single application has already

limited success in developing countries (Basak and Pandit 2011). It is worthwhile to mention that during the eighties, FAO's Fertilizer Program in Madagascar performed hundreds of demonstrative plots comparing USG versus prilled urea, in farmers' fields; the yield increase, due to USG, varied from 700 to 1,400 kg/ha; the final result was that, while recognizing the superiority of the USG versus prilled urea, the farmers, unanimously stated that the application of USG was too laborious and consequently expensive: it has practically the same cost as the labor of rice transplantation. This problem discouraged the majority of farmers led by the FAO mentioned program.

With the aim to overcome the problem, it is imperative to reduce the time of application or to increase the N application rate for the same time of application. To this end, we propose two alternative solutions.

The first application method uses normal prilled urea embedded in a resistant, supple, and biodegradable thin wire (of a few mm diameter, according to the N dosage required) enrolled on a spool, which will be incorporated into the flooded soil (muddy soil) by a manual rotating applicator (Fig. 8). This relatively simple tool is pushed at a quite normal walking pace; this greatly reduces the time of application.

Another solution should be the elaboration of 4 to 5 g urea "matches" about 5 to 10 cm long. These small sticks or "sticklets" should be placed 7–10 cm deep between four transplants. A cylindrical diffusion of ammonia should occur along the sticklet together with semi-spherical diffusion at its ends. The time at which the threshold level of  $10 \text{ mmol L}^{-1}$  ammonia in soil solution should be attained can be calculated from the urea distribution in the source;

**Fig. 8** Proposed employment of the application wheel in a paddy field





the distribution of ammonia should be optimized to correspond with the assimilating capacity of the plant (sink capacity). The root sink function should be manipulated through the root distribution invading the voluminous ammonia cylinder deriving from the source. In the USG-rice interaction, root uptake intervenes like a reverse process of ammonia diffusion. This is possible because the time derivative of  $c_g(r,t)$  at a given distance is equal to 0 for  $t = r^2/6D$  (see Appendix and curves at 2.5–5–7.5 cm in Fig. 4). This expression holds true for a pure diffusion process. One can suspect that the same property arises in the case of the diffusion-exchange process driving the ammonia concentration before root arrival. According to Table 3, the maximum concentration (corresponding to time derivative equal to 0) was attained at 5 cm at around 28 days. As the concentration at 28 days ( $8.09 \text{ mmol L}^{-1}$ ) was below  $10 \text{ mmol L}^{-1}$ , roots could have invaded this zone. For a distance of 3 cm, the concentration was probably above  $10 \text{ mmol L}^{-1}$  at this time, impeding any uptake (avoidance of ammonia toxicity). This concentration should still increase, then decrease. At a certain time, the  $10 \text{ mmol L}^{-1}$  threshold should be attained enabling root uptake. Though simplistic it seems, this dynamics must be studied with a numerical model to make predictions, first in the case of the USG problem, then in the case of a urea sticklet.

## Summary and conclusion

The objective of this study was to understand how different was ammonia diffusion under different placement geometries of urea in paddy soils and how the results of urea supergranules (in terms of paddy yields) in various geometries could reflect balance or imbalance in the source–sink relationship. A large part of these experiments were performed in farmers' fields where use of USG has been promoted by a FAO program. The collected data were interpreted with a model of ammonia diffusion. The following information were drawn from the kinetics of ammonia disappearance: time and rate of ammonia withdrawal under 2 g- and 4 g-USG treatments. A modified pattern of rice transplanting was used for one field situation in order to keep constant the N application rate ( $58 \text{ kg ha}^{-1}$ ) in the 4 g-USG treatment. This “artificial” transplanting geometry enabled the rice plants to make use of ammonia at approximately the same rate in the 2 g- and 4 g-USG treatments when it was not the case in the classical transplanting geometry ( $20 \text{ cm} \times 20 \text{ cm}$ ). These data were considered useful for the design of new fertilizers.

Two fertilizers are promising: either urea embedded in a flexible wire and applicable with a rotating wheel or urea sticklet in replacement of urea supergranules. In the first

case, the objective is to ensure a good placement of urea whatever the mud conditions at transplanting; the solution is altogether the proposed apparatus and a modified urea material sufficiently supple for safe storage (water free material) and easy passage in the trough of the wheel. The nature of this material was not discussed: some urea cellulose derivatives could probably satisfy this requirement. In the second case, there is no change in the placement technique (hand placement) and improved N availability for the roots of wetland rice should result from an adjustment in the diffusion process. However, the optimal geometry of the source has to be validated by a numerical model taking into account the exchange process affecting the ammoniacal nitrogen. As the cation exchange capacity is varying among soils, the optimal geometry of the fertilizer could present some variation in relation with the clay and organic matter contents of the paddy soils.

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## Appendix

In the case of spherical symmetry, the expression of the ammonia concentration is

$$c_g(r,t) = (Q/8\Theta)(\pi Dt)^{-3/2} \exp(-r^2/4Dt) \quad (1)$$

(symbol signification in the text).

Its time derivative is

$$dc_g/dt = (Q/8\Theta) [\exp(-r^2/4Dt)] (\pi Dt)^{-3/2} [r^2/4Dt^2 - 3/2t] \quad (6)$$

$$dc_g/dt = 0 \text{ when } r^2/4Dt^2 - 3/2t = 0 \text{ then for } t = r^2/6D$$

In the case of cylindrical symmetry, we shall use the italic letter,  $d$ , for distance to avoid confusion with the symbol of derivative  $d$ . The ammonia concentration is

$$c_b(d,t) = (A/4\Theta) (\pi Dt)^{-1} \exp(-d^2/4Dt) \quad (3)$$

Its time derivative is

$$dc_b/dt = (A/4\Theta) [\exp(-d^2/4Dt)] (1/\pi Dt^2) [d^2/4Dt - 1] \quad (7)$$

$$dc_b/dt = 0 \text{ when } d^2/4Dt - 1 = 0 \text{ then for } t = d^2/4D$$

The passage of the maximum concentration occurs earlier with point application. The main points are however: (1) what is the ammonia concentration at this time? (2) what is the corresponding distance  $r$  or  $d$ ? The calculus can be performed with the analytical expressions described before. The line application is much more dilute than the point application: it leads to a cylinder of small radius with

high concentration when the point application leads to a sphere of consequent radius with high concentration (data available on request). Numerical calculus is needed to take into account the effect of ammonia exchange on these important features (slowdown effect).

Another approach could be the deduction of the time course of ammoniacal nitrogen concentration for an urea sticklet from the central observations in USG case. Let us calculate the ratio of the two quantities in Eq. 1 and 3, for  $d = r = 0$

$$c_b(0, t) / c_g(0, t) = (2A/Q)(\pi Dt)^{1/2} \quad (8)$$

If we neglect nitrogen diffusion at the ends of the sticklet, it means that we can optimize the length (and quantity) of diffusing linear source to obtain an ammoniacal nitrogen concentration of  $10 \text{ mmol L}^{-1}$  at 40 DAT (for  $d = 0$ ). The result is certainly affected by the exchange term in the field conditions, but this approximation provides an interesting hint for future experiment.

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