Nitrate (NO$_3^-$) and ammonium (NH$_4^+$), mineral nitrogen forms uptaken by plant roots, are susceptible to soil losses in the processes of nitrification, denitrification, ammonia (NH$_3$) volatilization and NO$_3^-$ leaching, under variable magnitudes as a function of environmental conditions, especially humidity, aeration and temperature (CAMERON et al., 2013). In soils cultivated with irrigated rice, N losses are associated, mainly, to the increase of its concentration in soil solution in response to nitrogen fertilizer application and to alternate wetting and drying soil conditions that lead to nitrification/denitrification processes (PONNAMPERUMA, 1972).

The application of nitrogen fertilizers aims to increase the N mineral soil amount that, in general, does not supply the crop demands. However, the efficiency of conventional N sources for irrigated rice rarely exceeds 50% due to losses. The most practical management measure adopted to minimize N soil losses is the adjustment of fertilizer application to the crop needs. For irrigated rice, the N management measures recommended includes the partitioning of doses in such a way that the nutrient will be available to the plants in the higher demand periods, i.e., at both the beginning of tillering and reproductive phase (SOSBAI, 2014).

The technology of increased efficiency fertilizers, such as those with controlled and slow release, stabilized with enzymatic inhibitors provides a potential alternative to reduce N losses and to improve N use efficiency and, consequently, crop yields. The controlled release fertilizers (CRF)
are conventional fertilizers coated with material having low solubility in water, slowly releasing this nutrient to the soil (LINQUIST et al., 2013; CAMERON et al., 2013).

The performance of CRF in flooded soils is still barely known, especially under irrigated rice conditions in Rio Grande do Sul State, Brazil, requiring better understanding in order to verify the economical and environmental viability of adopting this technology. Therefore, the present study had the objective of evaluating the solubilization and the N use efficiency of CRF for the irrigated rice crop, when compared to urea.

The experiment was performed in greenhouse, at the Universidade Federal de Pelotas (UFPel), Capão do Leão-RS. The treatments were: 1. Control - without N; 2. Urea split in pre-sowing (10kg N ha\(^{-1}\)) and topdress, at 12 days after emergence (DAE), four leaf stage – V4 (55kg N ha\(^{-1}\)) and at 34 DAE, eight leaf stage – V8 (55kg N ha\(^{-1}\)); 3. Urea at pre-sowing incorporated into soil; 4. PCU 60 - polymer coated urea (39.6% N, CRF presenting 30% and 100% N with release at 15 and 60 days after application, respectively) at pre-sowing, incorporated into soil; 5. PCU 90 - polymer coated urea (39.4% N, CRF presenting 20%, 80% and 100% N with release at 15, 60 and 90 days after application, respectively) at pre-sowing, incorporated into soil. The recommended N dose was 120kg ha\(^{-1}\), established as a function of soil chemical analyses results for predicted high fertilizer response (SOSBAI, 2014).

Treatments were disposed in random block design with four replications. The experimental units consisted of 8dm\(^3\) pots, containing 7.2kg of soil originating from a superficial layer sample (0-20cm) of a Albaquef previously sieved in 10mm mesh. Results from the soil chemical analyses were the following: clay = 24.7%; pH\(_{\text{cal}}\) (1:1) = 5.1; P = 5.4 mg dm\(^{-3}\); K = 32.3 mg dm\(^{-3}\); O.M. = 0.9%; Ca = 2.0 mol dm\(^{-3}\); Mg = 1.1 mol dm\(^{-3}\); Al = 0.6 mol dm\(^{-3}\); CEC\(_{\text{eff}}\) = 3.9 mol dm\(^{-3}\); CEC\(_{\text{pH7}}\) = 7.5 mol dm\(^{-3}\) and base saturation = 45% (TEDESCO et al., 1995).

At pre-sowing, the N sources were applied at 5cm depth, at amounts corresponding to the calculated doses for each treatment. The soil received, also, phosphate (triple superphosphate - 100kg ha\(^{-1}\) P\(_2\)O\(_5\)) and potassium (potassium chloride - 120kg ha\(^{-1}\) K\(_2\)O) sources. These fertilizers were uniformly mixed to the soil of each pot. Soil solution extractors were installed at 5 and 10cm depth during pot filling, according to Sousa et al. (2002). Four rice plants of cv. Puitá Inta CL were cultivated per pot. Rice irrigation by flooding started 13 DAE.

Soil solution sampling was performed at 2, 9, 15, 23, 30, 37 and 44 days after soil flooding. The pH and redox potential values (Eh) of the collected soil solution at 10cm were determined by combined specific electrodes, according to Sousa et al. (2002). Also, 30mL of soil solution were collected at 5 and 10cm depths for determining ammonium (NH\(_4^+\)) and nitrate (NO\(_3^-\)) concentrations by steam distillation, with the help of a Kjeldahl distiller (TEDESCO et al., 1995). At 57 DAE, plants were harvested and shoot dry matter (SDM) and N content were determined. From this data, the N accumulated in the rice plants was calculated. The nitrogen use efficiency (NUE) was obtained by the difference between N accumulated in treatments and the control, divided by the used N dose.

Results obtained for NH\(_4^+\) and NO\(_3^-\) concentrations in the soil solution and the evaluated plant parameters were subjected to analysis of variance and, when significant, the treatment means were compared by Tukey test (P<0.05), using the software Assistat®.

The soil solution pH and Eh values during the evaluation period presented a typical behavior of flooded soils, i.e., reflected the usual variations for these electrochemical parameters observed for irrigated rice fields (Figures 1A and 1B). At the initial flooding period, the Eh values were higher than 400mV and pH values lower than 5.0, still characteristic of an oxidized environment. As the time of flooding increased, Eh decreased and pH increased, stabilizing around 200mV and 6.2, respectively, which are characteristic of a reduced environment (PONNAMPERUMA, 1972).

Independent from treatment, NH\(_4^+\) concentration in the soil solution was higher at two days of soil flooding. At 5cm depth, treatments with full N dose at pre-sowing showed higher NH\(_4^+\) concentrations. One week later, the PCUs provided higher NH\(_4^+\) concentrations (Figure 1C). At this moment, pre-sowing urea provided higher concentrations of NH\(_4^+\) at 10cm (Figure 1D). From the 15th day of flooding, NH\(_4^+\) concentrations in the solution were close to null for the treatments with N application, being equivalent to the control. There was not an increase in NH\(_4^+\) concentration after the second cover application for the split urea treatment, probably because of high demand by the plants during this period.

The highest NO\(_3^-\) concentrations in the soil solution were observed for the sampling performed two days after flooding. At 5cm depth, the magnitude and variation in NO\(_3^-\) concentrations was similar.
between treatments, with exception of urea applied at pre-sowing, which presented higher concentration than the remaining treatments (13 mg L$^{-1}$) at the ninth day after flooding (Figure 1E). This treatment, as well as the other treatments receiving full N at pre-sowing, provided higher NO$_3^-$ concentrations in solution at 10 cm depth (Figure 1F). At both depths, NO$_3^-$ concentrations reached values close to zero at the 23$^{rd}$ day after flooding (Figures 1E and 1F). Decrease in NO$_3^-$ values is faster than those of NH$_4^+$ as a function of nitrate reduction by flooding and consequent depletion of O$_2$ in the soil (PONNAMPERUMA, 1972). Mineral N concentration in the solution decreased with soil flooding, due to plant uptake and system losses, particularly in the nitrification/denitrification processes (CAMERON et al., 2013).

The CRFs did not maintain NO$_3^-$ and NH$_4^+$ concentration values in the soil solution that were higher than urea for longer times. Therefore, these sources did not comply with their specifications regarding the N release period in soil flooded for rice cultivation. Similar results

Figure 1 - pH (A) and Eh (B) values; NH$_4^+$ concentration in the soil solution (mg L$^{-1}$) at 5 cm (C) and 10 cm (D) depth and NO$_3^-$ concentration in the soil solution (mg L$^{-1}$) at 5 cm (E) and 10 cm (F) depth during irrigated rice cultivation as a function of N fertilizer management. 1. Control: control without N application; 2. Split urea: urea split into pre-sowing and cover applications; 3. Pre-sowing urea: full urea application at pre-sowing; 4. PCU 60: polymer coated urea with predicted 60 day release time; 5. PCU 90: polymer coated urea with predicted 90 day release time. Vertical bars represent the least significant difference (LSD) by Tukey’s test ($P<0.05$). ns = not significant.
were obtained by JI et al. (2007) also working with irrigated rice. These authors reported that total N and NH$_4^+$ concentrations in soils fertilized with CRF were higher than those receiving urea only at the first 15 days after application. Conversely, RANSOM (2014) reported that some controlled release sources make N available at faster rates than predicted, an effect that seems associated with variations in daily temperatures.

Treatments with N application did not differ regarding to N content in the rice shoots and, except for the splitted urea application, they were similar to the control without N (Table 1). This result indicated that the irrigated rice management recommendations for south Brazil, where soluble N sources should be partitioned to reach the stages of higher demand by the plants, optimizes the use of this nutrient by the crop (SOSBAI, 2014). Regarding the variables dry matter, N accumulated in shoots and NUE by rice, higher values were detected for the treatments with N application, only when compared to the control, displaying non-significant differences between the various N sources. (Table 1). This indicated that native N was not enough to meet the crop demands.

The initial N demand for rice plants is relatively low due to the short plant stature. From the beginning of tillering on (between 20-30 DAE), this demand is increased, with little variations between cultivars (SOSBAI, 2014). In the present study, the maximum concentrations of N mineral forms in the soil solution occurred earlier than the high demanding plant stage, indicating a possible nutrient limitation during the highest crop demand period.

Results obtained agree with reports regarding N management for irrigated rice, where benefits from replacing soluble N sources by CRF were not seen (SLATON et al., 2009; MIAO et al., 2016). Unfavorable results regarding the use of covered sources can be explained by the reduction of its efficiency by soil flooding in the cultivation of irrigated rice. In this environment, fertilizer recover is subjected to a higher water dilatation and penetration, speeding the nutrient release rate.

There are studies, however, in which the use of controlled release fertilizers is very advantageous to the crop. In this sense, YANG et al. (2013) reported that a reduced (125kg ha$^{-1}$) and full (187.50kg N ha$^{-1}$) dose of CRF, when compared to the full urea dose, lead to grain yield and NUE increases. Recently, TAO et al. (2014) reported an increase in grain yield and NUE by irrigated rice, when using CRF compared to urea and urea treated with nitrification inhibitor. Such reports indicate that some increased efficiency sources can be beneficial to the rice crop. However, in order for them to be economically viable it is necessary that the increase in efficiency result in yield gains that compensate the investment on a higher cost product, therefore enabling the replacement of conventional sources.

The polymer coated ureas (PCUs) made the N more readily available than predicted in the cultivation of irrigated rice, not maintaining high N mineral contents in the solution for longer time than urea. The NUE of PCUs was similar to the plain urea, not resulting in a longer time for nutrient release to the rice crop.

Table 1 - N content, dry matter production (DM), shoot accumulated N (AN) and nitrogen use efficiency (NUE) as a function of nitrogen fertilizer management.

| Treatments         | N content | DM       | AN        | NUE  |
|--------------------|-----------|----------|-----------|------|
|                    | g kg$^{-1}$ | g       | mg/pot   | %    |
| 1. Control         | 13.3b     | 3.6b     | 48.0b     | -    |
| 2. Split urea      | 20.7a     | 12.7a    | 262.0a    | 50.9a|
| 3. Pre-sowing urea | 18.5ab    | 12.9a    | 238.8a    | 45.4a|
| 4. PCU 60          | 17.1ab    | 12.2a    | 208.7a    | 38.2a|
| 5. PCU 90          | 18.2ab    | 11.6a    | 211.2a    | 38.8a|
| CV(%)              | 18.43     | 7.79     | 12.93     | 13.58|

1. Control: control without N application; 2. Split urea: urea split into pre-sowing and cover applications; 3. Pre-sowing urea: full urea application at pre-sowing; 4. PCU 60: polymer covered urea with predicted 60 day release time; 5. PCU 90: polymer coated urea with predicted 90 day release time.

Means followed by the same letter, in columns, do not differ by the Tukey test (P<0.05).
Soil solution and plant nitrogen on irrigated rice under controlled release nitrogen fertilizers.

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