Title page

Slow release N fertilisers are not an alternative to urea for fertilisation of autumn-grown tall cabbage.

M. Ângelo Rodrigues[1]*, Helga Santos, Sérgio Ruivo, Margarida Arrobas*

Mountain Research Centre (CIMO) – Escola Superior Agrária, I. P. Bragança, 5301-855
Bragança, Portugal

[1]Corresponding author

Manuel Ângelo Rodrigues

Tel.: +351 273303260; fax: + 351 273325405. E-mail address: angelor@ipb.pt

Mountain Research Centre (CIMO) – Escola Superior Agrária, I. P. Bragança, 5301-855
Bragança, Portugal

Abstract

Tall cabbage (*Brassica oleracea* var. *costata*, cv. Penca de Mirandela) is grown in Portugal during autumn and winter months when heavy rains can be expected. In this agrosystem the management of N is a considerable challenge due to the risk of nitrate leaching. Field experiments with tall cabbage and rye were carried out during the growing seasons of 2007/08 and 2008/09. The experimental design included three fertilisers that delay N availability by different mechanisms [Floranid permanent, containing isobutylidene diurea (IBDU); Basacote, a polymer-coated fertiliser; and Entec 26, containing 3,4-dimethylpyrazole phosphate (DMPP) as nitrification inhibitor], two urea treatments (total N applied basally; and divided into two equal rates in preplant and topdress application), and a zero N control. The fertilisers were applied at a rate of 120 kg N ha^{-1}. A pot experiment with tall cabbage followed by ryegrass grown in the same pots was carried out in 2007/08. The fertiliser treatments were essentially the same and a rate of 2.94 g N/pot was applied. Dry matter yield, plant N concentration, plant N recovery and indices of N-use efficiency were compared among the fertiliser treatments. In the pot experiment, soil nitrate concentration was also monitored by using anion exchange membranes inserted directly into the soil. Urea produced mean DM yields statistically higher than control in all crops and in both field and pot experiments and years. No significant differences in DM yield were usually found among fertilised treatments. Basacote produced DM yields often not significantly different from that of control. In the field experiment of tall cabbage, plants recovered 20 and 50% of the amount of N applied, respectively in Basacote and in the other fertilised plots. In the pot experiment, tall cabbage + ryegrass recovered 49.6 and ≈100% of N applied, respectively in Basacote and in the other fertilised plots. From the strictly agronomic point of view, none of the slow-release N materials provided advantages over urea to be advised for this agrosystem, considering also their high cost.

Key words: slow-release fertilisers; controlled-release fertilisers; stabilized fertilisers; isobutylidene diurea (IBDU/Isodur); 3,4-dimethylpyrazole phosphate (DMPP)

1. Introduction

Tall cabbage (*Brassica oleracea*, var. *costata*) is very popular in Portugal. In the northernmost part of the country, a regional form of tall cabbage known as Penca de Mirandela, forms part of the traditional Christmas Eve dinner every year, and was recently included as a new cultivar in the National catalogue of varieties. The cultivation of tall cabbage begins in the middle of summer with the preparation of seedlings, usually being transplanted late in August. The growing season includes an initial warm and dry period (August-September), where the crop is usually irrigated. However, the higher growth rates of this vegetable, as well as the expected higher demands for N, occur later, in the middle of the autumn, during a period where there is a high risk of nitrate leaching. Consequently, N management must be carefully carried out to maximize N use efficiency and to reduce environmental pollution. Recently, the use of slow and controlled-release fertilisers and stabilized fertilisers has become of interest to tall cabbage producers.

Slow and controlled-release fertilisers are those that delay of initial availability, or extended the time of continued availability, achievable by a variety of mechanisms. The microbially degradable N products, such as urea-formaldehydes and other urea-aldehyde compositions are commonly referred to in the trade as slow-release fertilisers, and coated or encapsulated products (sulphur coatings, polymer coating ...) as controlled-release fertilisers (Trenkel, 2007). Stabilized fertilisers refers only to those which are modified during production with a nitrification inhibitor. In all other cases, fertilisers and nitrification and urease inhibitors are sold separately (Trenkel, 2007).

Several studies have shown beneficial effects of the use of slow and controlled-release fertilisers, stabilized fertilisers and/or nitrification and urease inhibitors to enhance crop productivity. Pasda et al. (2001) reported positive effects of the use of the nitrification inhibitor DMPP on yield of various agricultural and horticultural crops under various soil-climatic conditions. An increase in rice yield and N-use efficiency through the use of slow-release fertilisers and nitrification inhibitors was reported by Carreres et al. (2003). Studies involving the use of slow- and controlled-release fertilisers and/or nitrification inhibitors in containerized nursery tree plants showed suitable performances of seedlings treated with those fertilisers in comparison with traditional water-soluble formulations (Walker and Huntt, 1999; Fernández-Escobar, 2004; Oliet et al., 2004; Girardi et al., 2005). Nitrification inhibitors have also been widely used as a means of mitigating environmental pollution. It is well documented that dicyandiamide (DCD), DMPP and other nitrification inhibitors can reduce nitrous oxide (N_2O) emissions from grazed pastures (Macadam et al., 2003; Zaman et al., 2009), irrigated rice (Majumdar et al., 2000) and many other irrigated field crops (Delgado and Mosier, 1996; Linzmeier et al., 2001; Shoji et al., 2001; Majumdar et al., 2002). A reduction in CH_4 emission from a rice-wheat cropping system in India with the use of DCD was reported by Pathak et al. (2003). Nitrification inhibitors may also reduce NH_3 emissions from grazed pastures (Zaman et al., 2009).

In other studies, however, no positive results have been reported following the application of fertilisers that delay nutrient availability (Cartagena et al., 1995; Diez et al., 1997; Guertal, 2000). Inconsistencies in results may appear since nutrient-release rates could vary depending on fertilisers' characteristics, soil properties and/or climatic conditions. Nitrogen of IBDU, for instance, is released by hydrolysis, which is affected by soil moisture and temperature. IBDU is also unstable in acid media. Thus, it tends to release its N more rapidly in strongly acidic soils (Trenkel, 2007). Nutrient release from polymer-coated fertilisers is also temperature dependent. Kochba et al. (1990) found a doubling of the release rate in three coated controlled-release fertilisers for every 10ºC rise in temperature. Huett and Gogel (2000) reported an increase in the nutrient release rate of around 20% for a temperature increase of 30 to 40ºC for various controlled-release fertilisers. Stabilised N fertilisers contain a nitrification inhibitor which delays the oxidation of NH_4^+ to NO_3^- for a certain period of time. Both NH_4^+ and NO_3^- ions are already available to plants. Furthermore, NH_4-N in soil is protected from leaching and denitrification, but is easily immobilized through biotic and abiotic processes. Giocchini et al. (2006) reported that the interlayer NH_4^+ immobilization from the use of Entec26 (with DMPP as nitrification inhibitor) contributed to 78% of the decrease in availability of NH_4^+ in a clay loam soil, whereas no significant amounts of NH_4^+ were immobilized in a sandy loam soil.

The objective of this research was to examine the effect of three fertilisers with different mechanisms of delaying N availability in the soil to be used in tall cabbage fertilisation, in a growing cycle that includes a period where both crop demand for N and risk of nitrate leaching are high. The time and rate of N released from fertilisers were evaluated in a field experiment with tall cabbage. In order to obtain supplemental data on the N release pattern of fertilisers, a field trial with rye, and a pot experiment with tall cabbage followed by ryegrass, were also carried out. Thus, the field trials consisted of the cultivation of tall cabbage in the autumn (Aug. to Dec.) as the main crop, and rye (Sep. to May) as a test crop, included to monitor the soil N availability after winter rains. Tall cabbage absorbs N mainly in the autumn whereas rye absorbs N mainly after March, associated with stem elongation. The pot experiment was conducted to determine nitrogen availability from the fertilisers in conditions of reduced risks of nitrate leaching and denitrification. The pot experiment also allows the monitoring of soil nitrate levels over time, by using anion exchange membranes, an aspect not considered in the field experiments. The pot experiment started with the cultivation of tall cabbage followed by the cultivation of ryegrass in the same soil.

2. Materials and methods

Data reported on this work were obtained from three different experiments carried out in Bragança, NE Portugal (41º 48' N; 6º 44' W), from August 2007 to May 2009. They consisted of: (i) cultivation of tall cabbage, cv. Penca de Mirandela in the field; (ii) rye (*Secale cereale*) also cultivated in the field; (iii) and tall cabbage followed by ryegrass (*Lolium multiflorium*) grown in a pot experiment.

The region benefits from a Mediterranean climate with some Atlantic influence. The summer is warm and dry and the winter somewhat cold and rainy. The mean annual temperature and annual precipitation are 11.9ºC and 741 mm, respectively. Weather data registered during the experimental period are presented in figure 1. The soil of the field where the experiments were carried out is a Eutric regosol of silty-loam texture. Soil organic carbon (Walkley-Black) was 11.4 g kg^{-1}; pH (soil/water, 1:2.5) 5.9; extractable P and K (Egner-Rhiem) 27 and 119 mg kg^{-1}, respectively; exchangeable Ca, Mg and K (ammonium acetate, pH 7) 3.11, 0.51 and 0.41 cmol$_c$ kg^{-1}; and soluble B (boiling-water and azomethine-H procedure) 1.36 mg kg^{-1}. The soil in the pot experiment was collected from the upper 0-20 cm layer in the lot where the field experiments were carried out. The soil has been cultivated over a two years rotation that included rye for silage in one year and tall cabbage in the second year. The field experiments were laid out using rye for silage as the preceding crop in both years and for both crops.

2.1. Field experiment with tall cabbage

During two consecutive years (Aug.-Dec. 2007; and Aug.-Dec. 2008) tall cabbage was subjected to six different fertiliser treatments arranged in a completely randomized design with three replicates. The fertiliser treatments were: Urea, applied in a rate of 120 kg N ha^{-1} at preplant; Urea, applied at half the rate (60 kg N ha^{-1}) at preplant, supplemented with Ammonium Nitrate (60 kg N ha^{-1}) as topdressing (Urea/AN); Floranid Permanent 16-7-15 (slow-release fertiliser, containing 6% N as IBDU); Basacote plus 9M 16-8-12 (controlled-release fertiliser, copolymer ethylene acrilic); and Entec 26 (stabilized fertiliser, with DMPP as nitrification inhibitor), all these three fertilisers were applied at preplant and in a rate of 120 kg N ha^{-1}; and a zero N control. Phosphorus and potassium rates were balanced among experimental plots by using singular-granular superphosphate and potassium chloride. Each experimental unit consisted of plots of 14.7 m^2 with a population of $\approx$ 2 pl m^{-2}. The young plants were hand-hoe transplanted on 21 and 26 Aug., respectively in 2007 and 2008. The preplant fertilisers were broadcasted in the respective plot and incorporated by soil tillage. Ammonium nitrate applied as topdress was distributed in the respective plots on 11 Oct. 2007 and 8 Oct. 2008.

In 2007, three plants per plot were randomly selected to obtain final harvest. Tall cabbage plants were cut at the ground level on 14 Dec. 2007. In 2008, two plants were cut three times during the growing season. The first cut occurred on 8 Oct., the second on 31 Oct. and the last harvest on 5 December. The plants were weighed in the field, and a representative subsample was oven-dried at 70ºC to estimate DM yield. Dried samples were ground and analysed for total N. These data allow also the estimation of above ground crop N recovery.

2.2. Field experiments with rye

Rye was included in this study as a supplemental test crop to provide information on soil N availability in spring, after the winter rains. Taking into account that it is not feasible to sow the rye crop following the harvest of tall cabbage, in late December, due to unfavourable climatic conditions, rye was sown in September in an adjacent field to that of the tall cabbage. Thus, From Sep. 2007 to May 2008 and Sep. 2008 to May 2009 a similar experiment was carried out with rye, including the experimental design, the preceding crop, the fertiliser treatments and nutrient rates. Rye was sown on 28 and 27 Sep., respectively in 2007 and 2008. Topdress N of the Urea/AN treatment was applied on 19 and 12 March, respectively in 2008 and 2009. The harvests occurred on 2 May and 23 April in 2008 and 2009. Random samples of 1 m^2 were cut at 5 cm above ground level and weighed. To reduce the volume of biomass to dry, a subsample of $\approx$ 500 g was weighed, oven-dried at 70ºC and weighed again to estimate DM yield. The dry material was ground and analysed for total N. The greenness of the leaves was determined with a SPAD-502 chlorophyll meter to be used as an N nutritional index. In 2008, SPAD readings were recorded on 19 March, shortly before topdress N application, and on 16 April, 28 days after. In 2009, the SPAD readings were only recorded before topdress N application on 12 March.

2.3. Pot experiment

Young plants of tall cabbage were planted on 21 Aug. 2007 in pots filled with 15 kg of screened (6-mm mesh) and air dried soil mixed with the respective fertilisers. The treatments were practically the same that were reported for field experiments and the fertilisers were applied at a rate of 2.94 g N per pot. The treatment Urea/AN was substituted by a treatment with half the N rate (1.47 g/pot) applied at preplant (Urea1/2), the most adequate for the pot experiment. Otherwise, in the pot experiment Urea and Urea/AN treatments would be practically the same, since the growing conditions do not favour N losses from the soil, reducing the practical importance of the Urea/AN treatment. Each treatment had five replicates (5 pots). A single plant was grown in each pot. The pots were placed in a well aerated wire netting structure of 3.5 m eight, covered with a corrugated PVC sheet, which protected the pots from rainfall, reducing the possibility of nitrate leaching and denitrification. The plants were regularly irrigated with distilled water. Tall cabbage plants were cut at the ground level on 14 Dec. 2007 and weighed. Approximately half of the plant was dried (70ºC) and weighed to allow the estimation of total DM yield. Dried samples were ground and analysed for total N. From the remaining fresh half of the plant two young fully expanded leaves were separated between petioles and blades and the petioles dried and ground for nitrate concentration determination.

After cutting the tall cabbages on 14 Dec. 2007, the soil was kept moist to maintain high levels of microbial activity in the pots. On 4 Apr. 2008, 1 g/pot of seed of Italian ryegrass was sown to evaluate the residual effect of the fertiliser treatments. Two cuts of Italian ryegrass were performed on 17 May and 12 June 2008. Dry matter yield and plant N concentration were recorded from ryegrass biomass which also allowed the estimation of plant N recovery.

Nitrogen released from applied fertilisers and soil organic matter was monitored by recovering nitrate ions in 1x2 cm strips of an anion exchange membrane inserted 7 cm into the soil and kept there for a week, as described by Rodrigues et al. (2006). Soil nitrate concentration was determined on 29 Sep., 24 Oct. and 5 Dec. 2007 and on 4 Apr. 2008.

2.4. Laboratory analysis

Nitrogen concentration in tissues was determined by steam distillation and acid titration in a Kjeltec Autoanalyser 1030. Nitrate ions adsorbed in the anion exchange membranes were eluted with 20 mL of 0.5 *M* HCl and analysed in the extracts by UV-vis. spectrophotometry. The strips of the anion exchange membrane were regenerated in $NaHCO_3$ before being reused as reported by Qian and Schoenau (1995). Nitrate concentration in tall cabbage petioles was determined by adding 50 mL of distilled water to 1 g of petiole and shaking for 1 hour. Nitrate concentration in the extracts was determined by UV-vis. spectrophotometry.

2.5. Data analysis

Data analysis was carried out using JMP software. After ANOVA examination, the means with significant differences ($\alpha < 0.05$) were separated by the Tukey HSD test. The interpretation of the results of the field trials and pot experiment was also based on two indices of N use efficiency estimated as following:

- Apparent N Recovery (PNR, %) = 100 x (plant N uptake in fertilised plots – plant N uptake in the control) / amount of N applied as fertiliser; and

- Physiological Efficiency (PE, kg kg^{-1}) = (dry matter yield in fertilised plots – dry matter yield in the control) / (plant N uptake in fertilised plots – plant N uptake in the control).

3. Results

3.1. Field experiments

In the growing season of 2007, the tall cabbage DM yield was significantly higher in the Urea treatment (307.0 g/plant) in comparison with the Control (172.7 g/plant). No significant differences in DM yield were found among fertilised treatments (table 1). Plant N concentration (PNC) was statistically different among treatments. Urea/AN and Floranid showed the highest mean values (25.4 and 24.8 g kg^{-1}), whereas Basacote and Control the lowest ones (18.9 and 17.5 g kg^{-1}). Plant N recovery (PNR) was not statistically different among fertilised treatments. Control showed a significant lower mean value than Urea/AN, Urea, Entec and Floranid treatments. Plant N recovery from Basacote was not statistically different from that of Control. Apparent N recovery was 19.6% for Basacote and varied between 47.8 and 56.2% for the other fertilised treatments. Physiological efficiency values were higher in Basacote and Urea (43.1 and 42.8 kg kg^{-1}) and lower in Urea/AN and Floranid (24.0 and 23.9 kg kg^{-1}).

In 2008, the response of tall cabbage to the different fertiliser treatments was not greatly dissimilar to that of 2007 though slightly lower DM yields were obtained (table 2). Similar results were also recorded for PNC and PNR. Apparent N recovery varied from 21.2 and 57.1% from Basacote and Urea fertilisers. The slight differences found in DM yield and PNR between 2007 and 2008 produced a cumulative effect that stressed the differences in PE observed among the fertilised treatments in 2008. However, Urea/AN and Floranid registered again the lower PE, whereas Urea registered the higher value. Basacote presented in 2008 a low PE value contrary to that which had been registered in 2007. The DM yields in the 31 Oct. sampling varied from 56.9 to 73.2% (table 2). The relative values of PNR on 31 Oct. were comparatively higher, varying from 64.7 to 85.8%. This means that in the first part of the growing season, plants absorbed proportionally more N comparatively to the increase in DM yield. This observation is also reflected in the higher PNC in the younger than in the older plants (data not shown).

Rye DM yield varied from 7.0 and 11.1 Mg ha^{-1}, respectively in the Control and Urea/AN treatment, in the field experiment of 2007. Control and Basacote produced significantly lower DM than the other treatments (table 3). PNC and PNR were significantly higher in the Urea/AN than in any of the other treatments, reflecting the application of 60 kg N ha^{-1} as topdressing. Apparent N recovery varied from 8.9% in Basacote and 78.9% in the Urea/AN treatment. Apparent N recovery from Urea, Floranid and Entec was 35.8, 30.6 and 27.2%, respectively. As observed for tall cabbage, Urea/AN showed the lowest PE among fertilised treatments. SPAD readings were significantly higher in Urea, Entec and Floranid than in Urea/AN, Basacote and Control treatments before topdress N application in Urea/AN plots, reflecting the lower soil N availability in the former treatments. After topdress N application, Urea/AN registered the higher SPAD values as a direct response to the increase in soil available N.

No significant differences were found in DM yield, PNC, PNR and SPAD readings among fertilised treatments in the rye field experiment of 2008 (table 4). The control, however, showed significantly lower DM yield than the fertilised treatments. Rye DM yields were lower in 2008 than in 2007. In 2008, the spring (March, April and May) was particularly dry (figure 1), which limited N uptake and crop growth. Even N applied as a topdress, in the Urea/AN treatment, did not produce any significant positive effect on DM yield, PNC and PNR over the other fertilised treatments. Apparent N recovery was low for all the fertilised treatments, varying from 32.6 to 49.4%, respectively for Basacote and Urea/AN.

3.2. Pot experiment

In the pot experiment there were observed significant differences in tall cabbage DM yield among the treatments (table 5). The control produced the lowest mean value (32.8 g/plant) and Urea treatment the highest (82.9 g/plant). Mean values of PNC, PNR and petiole nitrate concentration were also significantly different among treatments. Control, followed by Basacote and Urea(1/2) presented the lower values, whereas Urea, Entec and Floranid produced higher values than the former treatments but quite similar among them. ANR from Basacote was 33% and varied between 86.4 and 90.1% from the other fertilized treatments.

Basacote produced the highest ryegrass DM yields among all the treatments and in both cuts, whereas the lowest values were registered in the Control (table 6). Plant N recovery was also significantly higher in Basacote than in any of the other treatments, whereas the Control showed the lowest values. Apparent N recovery is directly dependent on DM yield and PNC, showing the highest values for Basacote (16.6%) and the lowest for Urea(1/2) (9.7%). Physiological efficiency varied from 20.0 and 35.3 kg kg^{-1}, respectively in Urea(1/2) and Basacote treatments. Apparent N recovery was very close to 100% for Urea, Urea(1/2) and Entec, which mean that an amount of N similar to that was applied was recovered by the plants. In Floranid pots ANR was even higher than 100%. Apparent N recovery in Basacote pots was only 49.6%.

Nitrate concentration in the anion exchange membrane extracts on 29 Sep, 39 days after fertilisers' application, was significantly lower in control than in any of the fertilised treatments (table 7). Basacote pots showed the lower soil nitrate levels among the fertilised treatments. The higher values were recorded in Floranid and Urea followed by Urea(1/2) and Entec treatments. On the sampling dates of 24 Oct. and 5 Dec. 2007 soil nitrate levels suffered a pronounced decrease mainly due to the absorption by plants. On 5 Dec. 2007, no significant differences among treatments were found. On 4 April 2008, 120 days after tall cabbage plants had been cut, soil nitrate levels increased in all pots, and significant differences among treatments were once again registered. The mean soil nitrate concentrations in the anion exchange membrane extracts were 341.4, 339.0, 322.4, 371.3, 201.7 and 184.0 mg L^{-1}, respectively in Floranid Basacote, Urea, Entec, Urea(1/2) and Control pots.

4. Discussion

In the field experiments of tall cabbage, Floranid treatment produced DM values not statistically lower than Urea. Plant N concentration in the Floranid treatment was significantly higher in comparison with the Urea treatment in the experiment of 2008. The combination of the effect of DM yield and PNC led to similar ANR from Floranid and Urea. Plant N concentration in Floranid plots was similar to that observed for Urea/AN, where half the N rate was applied as topdress. This similarity in the results of Floranid and Urea/AN treatments indicated that, as in the Urea/AN treatment, a fraction of N released from Floranid was only available later in the growing season, contributing to the increase in PNC but to a much lesser extent for DM yield. As a consequence, PE was lower for Floranid and Urea/AN than for the other fertilised treatments. Nitrogen in Floranid is 2.1% NO_3-N, 7.9% NH_4-N and 6% IBDU-N. It would be N from IBDU that was released later in the growing season which acted as a topdressing fertilisation. As a final remark, the short growing season of tall cabbage and the higher PE of N use if the nutrient is available early in the season, as observed in Urea and Entec treatments, may justify the absence of advantages found in delaying N availability by means of using a slow release N fertiliser or even by splitting the N dose.

In rye the demand for N increased greatly in early spring with stem elongation. However, the delay in N availability from Floranid did not benefit rye crop. It seems that the delayed period was not long enough to reduce N losses during the winter. Rye DM yield, ANR and N nutritional indices were the highest in Urea/AN plots which benefited from the topdress N applied in March. IBDU hydrolysis is affected by soil moisture and temperature (Trenkel, 2007). In September and October the temperature would be favourable for IBDU hydrolysis (figure 1) and, as shown for tall cabbage, N from IBDU would be available from the middle of the autumn. Thus, during the winter, N from Floranid would not better protect than N from urea from leaching and denitrification. In other field studies with wheat and maize the use of fertilisers containing IBDU (Floranid 32) did not increase crop yields in comparison with other commercial fertilisers (Cartagena et al., 1995) nor even with unfertilised check plots (Diez et al., 1997). Guertal (2000) also reported results with bell pepper were slow-release fertilisers had no consistent advantages over a soluble N source.

In the pot experiment, Floranid produced similar DM yields and N nutritional indices to Urea. Soil nitrate concentrations at 39 days after fertilisers' application were also similar in the pots fertilised with Urea and Floranid. It seems that the hydrolysis of IBDU occurred faster in the pots than in the field. The frequent irrigation and the probably higher daily fluctuation in the soil temperature in the pots than in the field may have enhanced IBDU hydrolysis. The ANR from Floranid (tall cabbage + ryegrass) was higher than 100%. This may mean that a positive priming effect occurred; having also in mind that the N recovered in the root system was not included in the estimation of ANR. A positive priming effect associated to the application of IBDU was already mentioned by Gioacchini et al. (2006).

Entec did not yield statistically different DM values, N nutritional indices and N-use efficiency parameters to Urea in both field and pot experiments. Plants can readily absorb NO_3^- and NH_4^+, and may benefit from the presence of both forms in soil solution (Cao and Tibbitts, 1993). Entec contains 7.5% NO_3-N, 18.5% NH_4-N and 0.8% DMPP. In aerated soils urea is rapidly hydrolyzed to NH_4^+ which is thereafter converted in NO_3^- (Rodrigues, 2004). Thus, in both Entec and Urea plots, NH_4^+ and/or NO_3^- was available for plant uptake. In the tall cabbage experiment of 2008, 86% of PNR at harvest was absorbed by 31 October, before any relevant rainfall events had occurred (figure 1). Hence, the probable higher persistence of NH_4^+ in soil in Entec than in Urea plots, due to the effect of DMPP, had not any advantage for crop growth since the weather conditions during the first half of the growing seasons did not promote NO_3^- leaching and denitrification. In addition, part of NH_4^+ may be fixed in clay minerals (Gioacchini et al., 2006) reducing N availability to plants.

Nitrate concentration in the anion exchange membrane extracts at 39 days after fertilisers' application was lower in Entec than in Urea pots. This means that DMPP effectively delayed NH_4^+ nitrification. The long-term analysis provided from rye results showed that DMPP would not be able to stabilize NH_4^+ for such a long period to reduce, for instance, N losses during the winter. Consequently, ANR in Entec plots varied from 50.5 and 38.6% in tall cabbage and 27.2 and 46.5% in rye and these results were not better than that obtained in Urea treatment. It seems that the growing season of tall cabbage did not favour Entec performance, since more than 80% of N absorption occurred before autumn rains. On the other hand, rye did not benefit from the inhibitory effects of DMPP on NH_4^+ nitrification, since the demand for N is low until April, 6 months after fertiliser application. Thus, as occurred with Floranid, the delayed effect of DMPP on NH_4^+ nitrification did not benefit tall cabbage growth over Urea. In other studies, however, positive effects of the use of DMPP on yield and quality of various agricultural and horticultural crops were reported (Pasda et al., 2001). DMPP has also been linked with positive environmental effects such as the reduction of nitrate leaching (Serna et al., 2000; Zerulla et al., 2001; Roco and Blu, 2006) and N_2O emissions (Linzmeier et al., 2001; Macadam et al., 2003; Hatch et al., 2005) from soils.

Basacote gave the lowest tall cabbage DM yield in the field trial among fertilised treatments. ANR and N nutritional indices were also low. The results of Basacote were often not statistically higher than that of Control. ANR from Basacote was close to 20%, whereas in the Urea and the other fertilised treatments a value close to 50% was recorded. In the rye experiments DM yield and ANR were also lower for Basacote than for any of the other fertilised treatments. In the pot experiment, total ANR from Basacote was 49.6%, whereas in the other fertilised treatments was close to 100%. Ryegrass DM yield was higher in Basacote pots as a result of inorganic N accumulation in soil from the cut of tall cabbage in December. The results of Basacote were attributed to the higher longevity of this fertiliser beyond the labelled rates provided by the manufacturer. The reason for this is that the release pattern of the polymer-coated fertilisers is determined in a water-leach test at 25 ºC (Trenkel, 2007). This is a higher temperature than that registered during the growing seasons reported in this study. The mean monthly air temperatures during the experimental periods varied from 4.0 and 16.8ºC, respectively in December and September 2007 and 3.8 and 16.0ºC, respectively in January 2009 and September 2008. Temperature has been reported as an important parameter in controlling nutrient release of polymer-coated controlled-release fertilisers in other studies. From a laboratory leaching study where the fertilisers were subjected to high temperature (30 and 40ºC), Huett and Gogel (2000) observed that longevities of 17 controlled-release fertilisers were considerably shorter than the release periods set by their manufacturers. Dai et al. (2008) also showed that as the temperature increased, nutrient release of the controlled-release fertilisers increased. Based on a study with four controlled-release fertilisers with different labelled release periods, Haase et al. (2007) concluded that new refinements are needed in controlled-release fertilisers' technology in order to optimize nutrient availability under realistic field conditions.

5. Conclusions

There was no clear evidence of any advantage of the use of Floranid, Entec or Basacote over Urea in DM yield of tall cabbage and ANR from fertilisers in the weather conditions of the autumns of 2007 and 2008 in NE Portugal. Basacote showed a very slow release pattern. Nutrient release from Basacote was prolonged beyond the labelled rates (9 months) probably because of the low temperatures which characterized the growing season. Floranid effect seemed to be similar to a basal plus topdress N fertilisation, with IBDU-N fraction being released after the period of highest demand for N of tall cabbage. DMPP delayed NH_4^+ nitrification from Entec although this had not been an advantage for tall cabbage DM yield, probably because both NH_4^+ and NO_3^- forms can be absorbed by the crop. In this study the three slow-release materials did not enhance rye growth in comparison with urea. It seems that the formulations Entec and Floranic were not able to protect N from leaching during winter and Basacote maintained a very slow release pattern even after April. According to the literature published on the subject, one of the significant advantages of the use of slow release fertilisers is related to the reduction in green house gaseous emissions, not determined in this work. From the strictly agronomic point of view, it seems that the theoretical advantages of the use of slow release fertilisers need to be demonstrated for each agro-environmental condition before being recommended to farmers.

Acknowledgment

The authors would like to thank Rita Diz and Ana Pinto for laboratory assistance. Financial support was provided by Mountain Research Centre, ESA, Polytechnic Institute of Bragança.

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Table 1. Tall cabbage dry matter yield (DM), plant N concentration (PNC), plant N recovery in above-ground biomass (PNR), apparent N recovery (ANR) and physiological efficiency (PE) in the growing season of 2007.

Treatment	DM (g/plant)	PNC (g kg^{-1})	PNR (kg ha^{-1})	ANR (%)	PE (kg kg^{-1})
Urea	307.0 a[1]	20.2 bc	123.6 a	52.2	42.8
Urea/AN	253.7 ab	25.4 a	128.5 a	56.2	24.0
Entec	269.6 ab	22.3 abc	121.6 a	50.5	32.0
Floranid	241.1 ab	24.8 ab	118.4 a	47.8	23.9
Basacote	223.3 ab	18.9 c	84.5 ab	19.6	43.1
Control	172.7 b	17.5 c	61.0 b	---	---

[1] Mean separation within columns by Tukey's test, $P < 0.05$.

Table 2. Tall cabbage dry matter yield (DM), plant N concentration (PNC), plant N recovery of above-ground biomass (PNR), apparent N recovery (ANR) and physiological efficiency (PE) in the growing season of 2008.

Treatment	DM^2 (g/plant)	PNC (g kg^{-1})	PNR^4 (kg ha^{-1})	ANR (%)	PE (kg kg^{-1})	DM^1 (%)	PNR^3 (%)
Urea	271.8 a[5]	22.6 b	121.6 a	57.1	28.9	65.5	85.8
Urea/AN	194.3 b	27.4 a	107.7 ab	43.7	8.2	68.7	73.3
Entec	227.2 ab	22.1 b	100.5 ab	38.6	23.5	73.2	85.5
Floranid	220.4 ab	27.0 a	119.1 a	54.2	14.6	65.1	64.7
Basacote	193.9 b	20.5 b	79.7 bc	21.2	16.6	65.0	69.9
Control	172.8 b	15.7 c	53.9 c	---	---	56.9	92.3

[1,2] Tall cabbage DM yield on (1)31 October presented as the percentage of DM yield on (2)5 December.

[3,4] Plant N recovery on (3)31 October as the percentage of PNR on (4)5 December.

[5] Mean separation within columns by Tukey’s test, *P* < 0.05.

Table 3. Rye dry matter yield (DM), Plant N concentration (PNC), plant N recovery of above-ground biomass (PNR), apparent N recovery (ANR), physiological efficiency (PE) and SPAD readings in the growing season of 2007.

Treatment	DM (Mg ha^{-1})	PNC (g kg^{-1})	PNR (kg ha^{-1})	ANR (%)	PE (kg kg^{-1})	SPAD^{d1}	SPAD^{d2}
Urea	10.4 a[1]	9.7 b	100.2 b	35.8	78.8	44.2 a	40.7 b
Urea/AN	11.1 a	13.7 a	151.9 a	78.9	42.8	40.0 b	50.1 a
Entec	10.0 a	9.0 b	89.9 bc	27.2	89.7	43.9 a	41.1 b
Floranid	10.5 a	8.9 b	93.9 b	30.6	95.4	42.8 a	42.1 b
Basacote	7.9 b	8.6 b	67.9 cd	8.9	81.1	39.0 b	37.7 c
Control	7.0 b	8.2 b	57.2 d	---	---	38.4 b	37.2 c

^{d1,d2} - 19 March and 16 April, shortly before and 28 d after topdress N application in Urea/AN treatment.

[1] Mean separation within columns by Tukey's test, $P < 0.05$.

Table 4. Rye dry matter yield (DM), plant N concentration (PNC), plant N recovery in above-ground biomass (PNR), apparent N recovery (ANR), physiological efficiency (PE) and SPAD readings in the growing season of 2008.

Treatment	DM ($Mg\ ha^{-1}$)	PNC ($g\ kg^{-1}$)	PNR ($kg\ ha^{-1}$)	ANR (%)	PE ($kg\ kg^{-1}$)	SPAD[1]
Urea	8.8 a[2]	12.4 ab	108.3 a	35.0	64.5	46.3 a
Urea/AN	8.7 a	14.6 a	127.4 a	50.9	43.0	44.0 a
Entec	9.7 a	12.6 ab	122.1 a	46.5	65.8	43.3 a
Floranid	8.6 a	13.5 ab	121.6 a	46.1	46.1	46.6 a
Basacote	7.9 a	13.2 ab	105.4 ab	32.6	48.5	45.3 a
Control	6.1 b	11.0 b	66.3 b	---	---	42.9 a

[1] SPAD readings on 12 March before topdress N application in Urea/AN treatment.

[2] Mean separation within columns by Tukey's test, $P < 0.05$.

Table 5. Tall cabbage dry matter yield (DM), plant N concentration (PNC), plant N recovery in above-ground biomass (PNR), petiole nitrate concentration (PNO_3C), apparent N recovery (ANR) and physiological efficiency (PE) in the pot experiment.

Treatment	DM (g/plant)	PNC (g kg^{-1})	PNR (g/pot)	PNO_3C (g kg^{-1})	ANR (%)	PE (kg kg^{-1})
Urea	82.9 a[1]	40.0 ab	3.21 a	107.0 a	87.3	19.5
Urea(1/2)	62.5 ab	30.6 bc	1.92 b	47.0 b	87.2	23.2
Entec	68.5 a	47.0 a	3.18 a	111.8 a	86.4	14.1
Floranid	78.5 a	42.1 a	3.29 a	102.7 a	90.1	17.2
Basacote	66.5 a	24.5 c	1.61 bc	36.7 b	33.0	34.8
Control	32.8 b	19.7 c	0.64 c	22.9 b	---	---

[1] Mean separation within columns by Tukey's test, $P < 0.05$.

Table 6. Ryegrass dry matter yield (DM), total (cut 1 + cut 2) plant N recovery in above-ground biomass (PNRt), apparent N recovery (ANR), physiological efficiency (PE) and total (tall cabbage + ryegrass) apparent N recovery (ANRt) in the pot experiment.

Treatment	DM[1] (g/pot)	DM[2] (g/pot)	PNRt (g/pot)	ANR (%)	PE (kg kg^{-1})	ANRt (%)
Urea	10.8 b[3]	15.7 b	0.63 b	10.8	31.2	98.1
Urea(1/2)	9.1 cd	10.3 c	0.45 c	9.7	20.0	96.9
Entec	10.3 bc	16.2 b	0.62 b	10.4	32.3	96.8
Floranid	10.5 bc	18.0 ab	0.65 b	11.9	34.4	102.0
Basacote	12.9 a	20.8 a	0.80 a	16.6	35.3	49.6
Control	8.8 d	7.7 c	0.31 d	---	---	---

[1,2] cuts on 17 May and 12 June, respectively.

[3] Mean separation within columns by Tukey's test, $P < 0.05$.

Table 7. Nitrate concentration (mg/L) in soils of the pot experiment during the growing seasons of tall cabbage and ryegrass. Nitrate ion was extracted through anion exchange membranes inserted directly into the soil.

	Days after fertilisers' application			
Treatment	39	64	106	226
Urea	424.1 a[1]	66.7 ab	30.0 a	322.4 a
Urea(1/2)	309.9 b	50.1 b	24.6 a	201.7 c
Entec	303.9 b	80.3 a	40.2 a	271.3 b
Floranid	468.4 a	84.3 a	31.4 a	341.4 a
Basacote	122.6 c	41.7 bc	24.8 a	339.0 a
Control	51.4 d	29.9 c	19.8 a	184.0 c

[1] Mean separation within columns by Tukey's test, $P < 0.05$.

Figure captions

Figure 1. Mean monthly temperature (line) and precipitation (bars) during the growing seasons of 2007/08 and 2008/09.