The side effects of nitrification inhibitors on leaching water and soil salinization in a field experiment

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Abstract

In experiments carried out in greenhouses, some authors have shown that ammonium sulphate induces greater soil acidity and salinity than other sources of N. Moreover, nitrification inhibitors (NI) tend to cause ammonium to accumulate in soil by retarding its oxidation to nitrate. This accumulated ammonium would also have an effect on soil salinity. Consequently, the aim of this paper was to evaluate the soil and leaching water salinization effects associated with adding NI, dicyandiamide (DCD) and dimethylpyrazole-phosphate (DMPP) to ammonium sulphate nitrate (ASN) fertilizer. This experiment was carried out in the field with an irrigated maize crop. Drainage and Na concentration were measured during both seasons (2006 and 2007) and leached Na was determined. The treatments with NI (DCD and DMPP) were associated with greater Na concentrations in soil solutions and consequently higher rates of Na leaching (in 2007, ASN-DCD 1,292 kg Na ha⁻¹, ASN-DMPP 1,019 kg Na ha⁻¹). A treatment involving only ASN also increased the Na concentration in soil and the amount of Na leached in relation to the Control (in 2007, ASN 928 kg Na ha⁻¹ and Control 587 kg Na ha⁻¹). The increase in the ammonium concentration in the soil due to the NI treatments could have been the result of the displacement of Na ions from the soil exchange complex through a process which finally led to an increase in soil salinity. Treatments including ammonium fertilizer formulated with NI produced a greater degree of soil salinization due to the presence of ammonium from the fertilizer and accumulated ammonium from the nitrification inhibition.

Additional key words: ammonium, N fertilization, sodium.

Resumen

Efectos secundarios de los inhibidores de la nitrificación sobre la salinización del suelo y agua de drenaje en un experimento de campo

En experimentos realizados en invernadero, algunos autores han mostrado que el sulfato amónico origina mayor acidez y salinidad que otras fuentes de nitrógeno. Los inhibidores de la nitrificación (NI) tienden a acumular amonio en los suelos al retardar la oxidación a nitratos. Este amonio acumulado también tendría un efecto sobre la salinidad del suelo. Consecuentemente, el objetivo de este trabajo fue evaluar la salinización del suelo y agua de drenaje, debido al efecto asociado a la adición de NI, dimetilpirazolfosfato (DMPP) y diciandiamida (DCD), al fertilizante nitro-sulfato amónico (ASN). Este experimento fue realizado en condiciones de campo con un cultivo de maíz irrigado. Se midieron el drenaje y la concentración de Na durante dos periodos de cultivo (2006 y 2007) y también se determinó el sodio lixiviado. Los tratamientos con NI (DCD y DMPP) dieron lugar a mayores concentraciones de Na en la solución del suelo y consecuentemente mayores cantidades de Na lixiviado (en 2007, ASN-DCD 1.292 kg Na ha⁻¹, ASN-DMPP 1.019 kg Na ha⁻¹). Con el tratamiento de ASN sin inhibidor, también aumentó la concentración en el suelo y el Na lixiviado (en 2007, 928 y 597 kg Na ha-1 para ASN y el Control, respectivamente). El aumento de la concentración de amonio en el suelo, debido a los tratamientos con NI, podría deberse al desplazamiento de los iones Na del complejo de cambio, mediante un proceso que finalmente conduce a un aumento de la salinidad. Los tratamientos que incluyen amonio en la formulación del fertilizante junto a un NI originaron un mayor grado de salinización debido al amonio procedente del fertilizante y al amonio acumulado procedente de la inhibición de la nitrificación.

Palabras clave adicionales: amonio, fertilización nitrogenada, sodio.

Received: 26-05-09; Accepted: 23-01-10.

Introduction

Various authors have reported that ammonium fertilizer increases electrical conductivity (EC) in soils (Gonçalves et al., 2000; Wei et al., 2007). Due to their particular environments and management systems, surface soils in controlled environments are often subject to secondary salinization. Fertilizers provide necessary nutritional elements for the growth of crops, but at the same time, increase the type and quantity of soluble salt ions in the soil. As a result, selecting fertilizer types and determining appropriate dosages and ratios when combining them is key to preventing the salinization of soils in greenhouse cultivation (Tong and Chen, 1991; Li et al., 1995).

The results obtained by Wei et al. (2007) revealed that continuous cropping increased soil salinity and reduced pH. The increase in the nitrogen rate gradually raised the EC of the soil, especially when ammonium sulphate was used as the nitrogen source and compared with urea. Adding a large amount of nitrogen markedly reduced the pH value of the soil, particularly when ammonium sulphate was used as the nitrogen source and applied to soils with pHs between 6.5 and 7.5. Costa et al. (1986) also observed that fertilization may induce problems such as the salinization and acidification of soils. These problems may be increased by localized irrigation. Among nitrogen fertilizers, ammonium sulphate induces greater increases in soil acidity and salinity than other N sources such as urea. Gonçalves et al. (2000), working with drip irrigation, concluded that in the growing season, the EC of saturated extracts of soil remained practically unchanged in the soil of a non-fertilized treatment. However, when this soil was subjected to fertilizer treatments with nitrogen, EC values increased because the salt concentration in the soil increased during the crop growing season. Even so, the EC values obtained with these treatments were below 1,300 µS cm⁻¹ and consequently did not affect lettuce (Lactuca sativa L.) yield; lettuce is a crop which is moderately sensitive to soil salinity (Ayres and Westcot, 1985). All of these experiments were carried out in controlled environments: in solar greenhouses with drip irrigation. Maize also has a low tolerance to salinity, especially when plants are young; 1,700 μS cm⁻¹ values of EC could therefore cause a reduction in maize production (Quemada et al., 2006).

On the other hand, nitrification inhibitors (NI) have been frequently applied at low concentrations to reduce nitrate leaching (Amberger, 1981; Ashword *et al.*, 1982). An accumulation of ammonium in the soil was obtained after fertilizer-NI application, with its oxidation to nitrate being retarded as a result of its bacteriostatic action on *Nitrosomonas*. However, this increase in soil ammonium could have had a secondary effect on the soil by displacing other cations present in the exchange complex such as Na. This could finally have led to soil and aquifer salinization. This effect would be similar to that originated by applying ammonium fertilizer to the soils observed by several other authors (Gonçalves *et al.*, 2000; Wei *et al.*, 2007).

The aim of the present work was to evaluate the effect on soil and leaching water salinization of adding the nitrification inhibitors (NI) dimethylpyrazole-phosphate (DMPP) and dicyandiamide (DCD) to ammonium sulphate nitrate (ASN) fertilizer in a field experiment with irrigated maize crop, under Mediterranean conditions. A control was carried out to monitor the effects of the treatment on EC, Na concentration in subsoil water and leached Na.

Material and methods

Experimental site

The experimental site was located at the La Poveda Field Station in Arganda del Rey (Madrid) (40°19'N, 3°19'W), in the middle of the Jarama river basin. The soil, a *Typic Xerofluvent* (Soil Survey Staff, 1993), was a sandy-loam that became progressively sandier with depth and had a gravel layer at a depth of 1.5-2.2 m. There was an aquifer below the test plot, at a depth of 4 m. Some of the physicochemical characteristics of the top 0-50 cm are presented in Table 1. Soil samples (an average of 25 sub-samples were taken from each plot) were analyzed for pH, organic matter (Walkley and Black, 1934), and carbonate (ISO 10693, 1995). Soil N, P, K and Ca levels were extracted using the electroultrafiltration (EUF) technique (Nemeth, 1979). The phosphorus concentration was colourimetrically deter-

Descriptor		EUF (mg kg ⁻¹)		
pH _{H2O}	8.1 ± 0.1	P 20°Ca	0.14 ± 0.02	
OM (g kg ⁻¹)	14.0 ± 0.2	K 20°C	1.22 ± 0.21	
CaCO ₃ (g kg ⁻¹)	34.0 ± 0.8	Ca 20°C	3.90 ± 0.24	
Texture	Sandy loam	$N (20^{\circ}C + 80^{\circ}C)^{b}$	0.83 ± 0.15	
Bulk density (Mg m ⁻³)	1.47	,		

Table 1. Psysicochemical properties of the soil before sowing

mined using ammonium molybdate as a reagent (AOAC, 1990). Potassium and Ca levels were determined by flame emission photometry. Levels of Na in subsoil water were also determined by the same method. Texture (ISO 11277, 1998) and bulk density (ISO 11272, 1998) were also determined.

Experimental design, field instrumentation and crops

Twelve 100 m² experimental plots were selected and four treatments with three randomized replications were applied in the first year. In the second year, the plots received the same treatments with the reviewed dose of nitrogen. The treatments applied were: an optimal rate of ammonium sulphate nitrate (ASN); the same N dose plus 0.8% DMPP (DMPP); the same N dose plus 12% DCD (DCD); and a control containing no N fertilizer (C). DCD and DMPP were used as nitrification inhibitors.

The 12% DCD-ASN fertilizer (% N relative to ASN-N) was prepared by mixing the two components and adding liquid vaseline as an adhesive 10 days before application. In the case of DMPP-ASN, Entec, a commercial product manufactured by Compo, was used. The treatments were applied only once, as top-dress after sowing, when plants had four leaves. Available soil N was calculated by soil analysis (EUF) before sowing (Sánchez *et al.*, 1998). Optimal N rates were calculated using the expression:

where N uptake is the foreseeable aboveground biomass and N efficiency is the % of N fertilizer used by plant. The doses of N applied depended on soil available N, which was determined by EUF before cultivation. The doses applied were 220 and 180 kg N ha^{-1} , in 2006 and 2007, respectively. These N rates were lower than those

traditionally applied by farmers in this area (300 kg N ha⁻¹ for maize).

Maize (*Zea mays* L. cv Helen) was sown at the start of April in both years. The crop rows were 75 cm apart and plant density was 90,000 plants ha $^{\!-1}$. During seedbed preparation, super-phosphate (18% P_2O_5) and K_2SO_4 (50% K_2O) were applied at 22 kg P ha $^{\!-1}$ and 111 kg K ha $^{\!-1}$. Maize was grown following traditional farm practices for the area and it was harvested in October, when the grain was mature.

Monitoring soil water content and drainage

Throughout the experiment, all of the water used was taken from an irrigation channel fed by the River Jarama. An overhead mobile-line sprinkler system was used to irrigate the maize. Irrigation started on June and continued until the end of August. The maize was watered every 7-10 days, following the schedule traditionally used by most growers in the local area. The respective amounts of irrigation water applied to the maize crops in 2006 and 2007, based on soil water reserves, were 788 and 778 mm.

A year before the experiment began, a system was installed for monitoring soil water content in real time which involved the use of semi-permanent multisensor capacitance probes (EnviroSCAN, Sentek Pty Ltd, South Australia) (Buss, 1993). Drainage was calculated as follows:

$$D = R + I - ET \pm \Delta S$$
 [2]

where D is drainage (mm), R is rainfall (mm), I is irrigation (mm), ET is evapotranspiration (mm) and ΔS is the change observed in the soil water reserve (mm) from depths of 0 to 50 cm. Four of the 12 plots, corresponding to different treatments, were monitored using EnviroSCAN probes (Sentek Pty Ltd, South Australia) located at a depth of 150 cm. Each probe

^a Fraction I EUF: 20°C, 30 min, 15 mA. ^b Fraction I+II EUF: 20°C, 30 min, 15 mA + 80°C, 5 min, 150 mA. EUF: electroultrafiltration method. OM: organic matter.

contained five capacitance sensors which took measures of frequency domain reflectometry (FDR) (Fares and Alva, 2000) at depths of 10, 40, 70, 120 and 150 cm. The frequency signal (FS) from the device was converted into a percentage of volumetric moisture (θv) . The measuring equipment was specifically calibrated for the soil in question, using the calibration equation proposed by Paltineanu and Starr (1997). EnviroSCAN probes were programmed to take one reading per hour throughout the cultivation period, in both years. A data logger recorded the data. Water drainage was calculated from descent curves for water reserves obtained from EnviroSCAN data corresponding to sensors situated near the drainage zone (150 cm depth) and from the water balance between different soil layers (Arauzo et al., 2005). The depth of the water table fluctuated from 4-4.5 m below the soil surface, depending on rainfall and river discharge. The average rainfall in this area is 460 mm yr⁻¹.

Sampling

Treatments were randomized across the experimental area and analyzed individually. After N application, soil samples (obtained from 25 sub-samples per plot) were taken on a weekly basis, over a period of two months. They were taken at depths of 0 to 0.20 m in both 2006 and 2007 to determine the ammonium and nitrate contents. Samples were air dried, ground, and extracted using 1M KCl at a ratio of 1:5. NH₄⁺ contents in the supernatant liquid were determined directly from extracted aliquots.

Samples of the soil solution were collected in ceramic cups at a depth of 1.4 m and extracted 18 times during the course of the experiment. A vacuum of -80 kPa was applied to the tubes and maintained for a period of 7 to 10 days. After this period, water samples were extracted using air pressure. Na+concentration and EC were subsequently determined. For the Na leaching study, two ceramic cups were used to obtain soil solution samples from each plot at a depth of 1.4 m (Díez et al., 2001). It was considered that any water reaching this depth, near the gravel layer, would be leached into the groundwater (at an average depth of 4 m) because of the high hydraulic conductivity (Smith and Mullins, 1991). During drainage periods, Na leaching was calculated on a weekly basis by multiplying the weekly drainage by the corresponding Na concentration at 1.4 m for each sampling event (Diez et al.,

1997). Na⁺ concentration was determined using an atomic absorption spectrophotometer (Perkin-Elmer 403, Perkin-Elmer Hispania) and by EC with a Crison 525 conductivity meter.

Maize plants were harvested from the central five metres of the rows in each plot and aboveground biomass was determined. Ten of the harvested plants were randomly selected before their different parts (stalk, leaves, bracts, cob and grain) were separated, weighed, oven-dried for 24 h at 60°C, and then kept for a further 2 h at 80°C before reweighing to determine their dry matter (DM) content. The harvest index (HI) was calculated as grain weight over aboveground biomass (percentage). Grain yield (kg ha⁻¹) was determined as described in Díez *et al.* (2001).

Statistical analysis

Statistical analysis was performed using STAT-GRAPHICS plus 5.1 software (Manugistics, 2000). Analysis of variance (ANOVA), according to multivariate models, was used to study differences between datasets, agronomic data (plant DM at harvest and grain yield) and soil solution data (EC and Na $^+$ concentrations). These datasets passed the normality test. Differences between seasons and treatments were analyzed and compared using the Duncan test. Significance was set at P < 0.05.

Results

Drainage was greater in 2007 (161 mm) than in 2006 (71 mm). The average quality components (\pm standard deviation) of the irrigation water were: NO $_3^-$, 5.1 \pm 0.5 mg N L $^{-1}$; Na, 90 \pm 16 mg L $^{-1}$; total solids, 650 \pm 50 mg L $^{-1}$; EC, 1,000 \pm 90 μ S cm $^{-1}$; Na adsorption ratio (SAR), 1.55; and pH, 7.6 \pm 0.2. The Na contributions to soil from irrigation water were 688 and 663 kg Na ha $^{-1}$, in 2006 and 2007, respectively, after taking into account water dose and Na concentration.

NH₄ content in soil after fertilization

The changes in ammonium content over time, which were determined from soil extracted with 1M KCl in the 2006 and 2007 seasons, are shown in Figure 1. In both years, higher ammonium values were observed

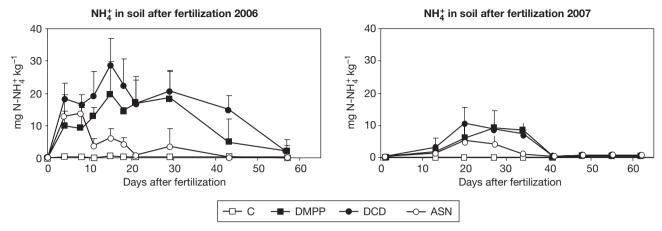


Figure 1. NH₄⁺ extracted from the soil by 1M KCl in 2006 and 2007, shown in days after N fertilisation. Values are means of three replicates. Treatments: C, DCD, DMPP and ASN, respectively refer to the unfertilized control, 12% ASN-DCD, 0.8% ASN-DMPP and ammonium sulphate nitrate. Vertical lines indicate standard deviation bars.

after fertilization in the treatments that included a nitrification inhibitor. Soil NH $_4^+$ concentrations respectively reached their highest values 15 and 19 days after N application, in 2006 and 2007. In 2006, the treatments with DCD and DMPP reached values of 29 and 20 mg NH $_4^+$ -N kg $^{-1}$, respectively. In 2007, the highest values for the DCD and DMPP treatments were 10 and 9.3 mg NH $_4^+$ -N kg $^{-1}$, respectively. These higher values in 2006 could be attributed to milder May and June temperatures in 2007. ANOVA (Table 2) showed significant differences between the control and the rest of the treatments (P < 0.01) and among different samplings after fertilization. Significant differences were also observed between ASN and the NI treatments.

Sodium concentration in soil solution

Regardless of the N source, in soil solutions collected from a depth of 140 cm, Na concentrations and EC

Table 2. Mean NH₄⁺ (mg NH₄⁺ kg⁻¹) extracted from top soil samples by 1M KCl, after fertilization and multifactor ANOVA between treatments in 2006 and 2007. Data based on three replicates per treatment (10 samplings in 2006 and 9 samplings in 2007)

Year		C	ASN	DMPP	DCD
2006 2007	P < 0.01 P < 0.01			10.90c 3.11c	10.014

Means followed by different letters in each row indicate significant differences between treatments. C: control. DCD: ASN+12%DCD. DMPP: ASN+0.8%DMPP. ASN: ammonium sulphate nitrate, at the optimal N application rate.

were affected by the fertilizer treatments. In both years, the highest Na concentration corresponded to the DCD treatment. DMPP and ASN produced similar values, which were both lower than those for DCD (Fig. 2). The mean values and standard deviations for Na concentration (mg Na L⁻¹) for the two years were: DCD 691 ± 132 ; DMPP 556 ± 113 ; ASN 553 ± 120 and C 353 ± 40 . The mean values and standard deviations for EC (μ S cm⁻¹) were: DCD 5,780 ± 1431; DMPP $5,245 \pm 1,170$; ASN $5,548 \pm 1,380$ and C $3,654 \pm 355$. The ANOVA (Table 3) presents the mean values for Na concentrations (mg Na L-1) in the soil solution at a depth of 1.40 m in 2006 and 2007. Significant differences (P < 0.01) were found between C and the other treatments. In 2007, significant differences were also observed between DMPP and DCD.

Sodium leached

In order to improve the poor results obtained in 2006 for Na leached as a result of low drainage (71 mm), in 2007, the drainage were increased by modifying the frequency of irrigation (leaving one day between two consecutive watering events) and thereby obtained greater drainage (161 mm) with similar irrigation doses. The water lost due to drainage represented an average equivalent of 10% of the total irrigation water applied in 2006 and 20% in 2007.

The curves for Na leached in 2006 and 2007 are shown in Figure 3. The amount of Na leached in 2006 was lower than in 2007, as shown by the corresponding drainage values. The amount of Na lost in 2006 ranged

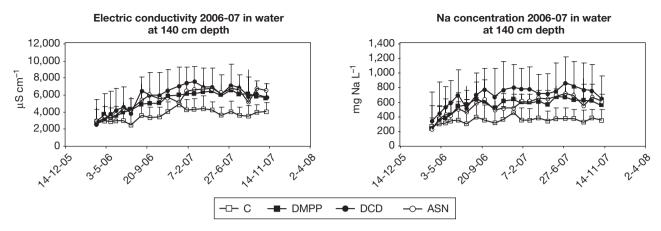


Figure 2. Evolution of EC and Na concentration in relation to the DCD, DMPP and ASN treatments in 2006 and 2007 with a maize crop. Vertical lines indicate standard deviation bars.

from 250 to 439 kg Na ha⁻¹, while in 2007 losses ranged from 587 to 1292 kg Na ha⁻¹. According to the results for 2007, the DCD treatment showed the greatest loss of Na (1,292 kg Na ha⁻¹) as a consequence of Na being displaced from the soil exchange complex. This effect was associated with a greater account of ammonium and Na being contributed by irrigation water. The DMPP treatment also produced high losses of Na (1,019 kg Na ha⁻¹). The ASN treatment also produced an increase in leached Na (928 kg Na ha⁻¹) with respect to the Control (587 kg Na ha⁻¹) due to its ammonium content, although the ASN treatment consequently produced lower values than the NI treatments.

Sodium balance

The Na balance was calculated with the data obtained for 2006 and 2007 (Table 4). In 2006, leached the amount of Na was less than that provided by irrigation

Table 3. Mean Na concentration (mg Na L^{-1}) of the soil solution at a depth of 1.40 m and multifactor ANOVA between treatments in 2006 and 2007. Data based on six replicate ceramic candle extractions taken at a depth of 1.4 m (8 samplings per growing season)

Year		C	ASN	DMPP	DCD
2006	P < 0.01	336.3a	411.6b	503.2c	503.2d
2007	P < 0.01	343.5a	659.9b	595.9c	738.8c

Means followed by different letters in each row indicate significant differences between treatments. C: control. DCD: ASN+12%DCD. DMPP: ASN+0.8%DMPP. ASN: ammonium sulphate nitrate, at the optimal N application rate.

water for all treatments as a result of low drainage (71 mm). As a consequence, a significant fraction of Na (438 kg Na ha⁻¹) was retained by the soil and the amount of Na displaced by the ASN fertilizer (N applied at a dose of 220 kg N ha⁻¹) was 111 kg Na ha⁻¹, while the induced effect of NI was 78 kg Na ha⁻¹ with DMPP and 39 kg Na ha⁻¹ with DCD. However, in 2007, the drainage was greater (161 mm) and the amount of leached Na was greater than that provided by irrigation water; Na retention by the soil was consequently lower. Independently of the residual effect of the treatments applied in the previous year, Na retention by the soil was reduced to 76 kg Na ha⁻¹ during crop growth and the application of ASN fertilizer (applied at 180 kg N ha⁻¹), which represented a net contribution of 189 kg Na ha⁻¹. The induced effect of NI was more pronounced with the DCD treatment, whose contribution was of 364 kg Na ha-1, which was followed by DMPP, with 91 kg Na ha⁻¹. This table shows the differential effect of low and high drainage on the Na balance and also differences between applying ammonium fertilizer on one hand and NI on the other.

Effect of nitrification inhibitors on dry matter and grain yield

The effects of different fertilizer treatments, both with and without nitrification inhibitors, on maize DM and grain yield in the two growing seasons: 2006 and 2007, are shown in Figure 4. In 2006, more accused differences between replications were observed than in 2007. Grain production was higher in 2007 than in 2006 (P<0.05) because the climatic conditions were

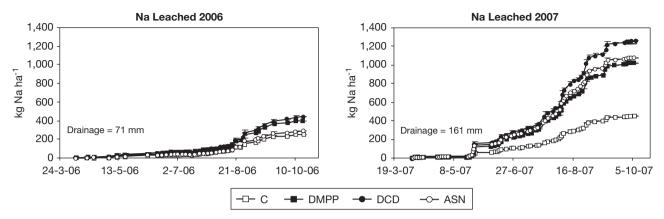


Figure 3. Cumulated curves of leached Na, originated by the DCD, DMPP and ASN treatments in 2006 and 2007 with a maize crop. Vertical lines indicate standard deviation bars.

Table 4. Na balance in the plant-soil-leached system in 2006 and 2007 (kg Na ha⁻¹)

Seasons	Na	Ca	ASN	DCD	DMPP
2006	Water irrigation	688 (a) ^b	688 (a)	688 (a)	688 (a)
Na water > Na leached	Retained in soil	438 (b)	438 (b)	438 (b)	438 (b)
	Displaced by ASN		111 (d)	111 (d)	111 (d)
	Displaced by NI	_		$39(e_2)$	$78(e_1)$
	Leached	250 (c)	$361(c_1)$	$400(c_3)$	$439 (c_2)$
2007	Water irrigation	663 (a)	663 (a)	663 (a)	663 (a)
Na water < Na leached	Retained in soil	76 (b)	76 (b)	76 (b)	76 (b)
	Displaced by ASN		189 (f)	189 (f)	189 (f)
	Displaced by NI	_		$364 (g_2)$	$91(g_1)$
	Leached	587 (c)	$928 (c_1)$	$1,292 (c_3)$	$1,019(c_2)$

^a Treatments: C = control, ASN = ammonium sulphate nitrate, DCD = ASN+12%DCD, DMPP = ASN+0.8%DMPP. ^b Letters in brackets indicate the parameters used for calculation in each year. When Na water irrigation > leached Na, Na retention takes place in soil due to low drainage (year 2006). Estimation of parameters: b = a - c; $d = c_1 - c$; $e_1 = c_2 - c_1$; $e_2 = c_3 - c_1$. When leached Na > Na water irrigation, there were low levels of Na retention in the soil and high levels of leached Na (year 2007). Estimation of parameters: b = a - c; $f = c_1 - a - b$; $g_1 = c_2 - a - b - f$; $g_2 = c_3 - a - b - f$.

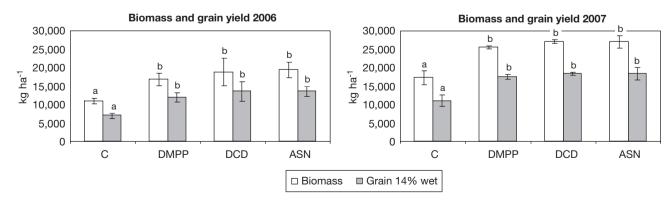


Figure 4. Biomass and grain yield with the C, DCD, DMPP and ASN treatments in 2006 and 2007 with a maize crop. Vertical lines indicate standard deviation bars. Different letters in a given column for a given year indicate significant differences between treatments (P < 0.05, Duncan Test).

more favourable. With respect to the two reference parameters (DM biomass, and grain yield), significant differences (P < 0.05) between the two experimental seasons (2006 and 2007) were detected. In both experimental seasons significant differences between C and the rest of the treatments were observed. No significant differences were found between the fertilized treatments.

Discussion

DCD is less widely used than DMPP because it is not yet protected by patents and also because the concentration of DCD in the fertilizer formulation is higher (12%), which increases the price of the product. In contrast, DMPP is applied to a greater extent because it contains patent-protected molecules that offer improved competitiveness and also smaller doses are required (0.8%). DCD is produced in various countries (Germany, Japan, Norway and China) and has a wide industrial use (Odda, 1995). DCD in soil is decomposed (partly abiotically and partly biotically, by specific enzymes) and converted to urea, a conventional fertilizer, via guanyle urea and guanidine (Hauser and Haselwandter, 1990).

The results shown in Figure 2 demonstrate that when there was an increase in soil ammonium associated with NI or ammonium fertilization, greater values of Na and EC were observed. There may therefore be a relationship between ammonium concentration and salinization, associated with higher Na concentrations and EC values. These results confirm those obtained by other researches in greenhouse experiments (Costa et al., 1986; Gonçalves et al., 2000; Wei et al., 2007). It is evident that the treatments with NI generated greater soil salinization due to ammonium from the fertilizer and accumulated ammonium from the nitrification inhibitor. The curves in Figure 2 show an increase in Na concentration during the first year associated with the fertilized treatments, with this level being maintained throughout the second year. The cumulative effect has not taken place over time. Nevertheless, a long term experiment with NI should be carried out in the future in order to check this hypothesis.

The results obtained with respect to grain yield and biomass production in this experiment showed that NI treatments did not increase the production values but nor did they have a depressive effect on maize yields. No evidence of toxicity was registered in relation to the use of either DCD or DMPP. In this regard, Reddy

(1964) emphasizes that maize, wheat and oats moderately tolerate DCD at rates of between 6 and 17 mg kg⁻¹ of N-DCD. The results obtained in this experiment were similar to those obtained by Reeves and Touchton (1986) who reported that commercial N fertilizers formulated with DCD contain between 5 and 15% DCD-N and produced no observable signs of toxicity. On the other hand, Roll (1999) showed that DMPP passed all of the toxicological and ecotoxicological tests to which it was subjected and Zerulla *et al.* (2001) proved that DMPP is highly plant compatible.

These results also show that the increase in soil ammonium from fertilizers, and especially the application of fertilizer in combination with NI, increased soil salinity and that this was induced by the high ammonium content. However, this salinity did not have a negative effect on either grain yield or the DM content of the biomass. Similar effects were obtained by Gonçalves *et al.* (2000). This was due to the fact that EC values were below 1,300 µS cm⁻¹: the value established by Ayres and Westcot (1985) for lettuce crops. Maize also has a low tolerance to salinity, especially when plants are young. EC values of 1,700 µS cm⁻¹ could cause a decline in maize production (Quemada *et al.*, 2006).

On the other hand, in light textured soils, as in our case, this salinization effect has few consequences because any leached Na finally goes to the aquifers, which are the true receptors of the salts. However, it is possible that the continued use of NI in successive crops may result in more pronounced soil salinity, consequently generating negative effects on crops. Long term research is recommended to monitor the effect of NI over a longer period.

Acknowledgements

The authors are grateful to the *Comunidad de Madrid* and *Fertiberia S.A.* for funding this research and proving us with the fertilisers and nitrification inhibitors.

References

AMBERGER A., 1981. Dicyandiamide as a nitrification inhibitor. Proc Technical Workshop on Dicyandiamide (Hauck R.D., Behnke H., eds). SKW Trostberg, Germany. pp. 3-17.

- AOAC, 1990. Official method of analysis. Association of Official Analytical Chemists. 13th ed, Arlington, VA, USA.
- ARAUZO M., DÍEZ J.A., HERNAIZ P.J., 2005. Utilidad de las sondas de capacitancia en el estudio de los procesos de lixiviación de nitratos en agrosistemas. Edafología 12, 43-52. [In Spanish].
- ASHWORD J., WIDDOWSON F.V., PENNY A., GIBBS A.J., HODGKINSON R.A., HEWIT M.V., 1982. Results from an experiment on permanent grass evaluating the cumulative effects of aqueous urea, injected alone or with a nitrification inhibitor, within those of «Nitro-Chalk». J Agric Sci, 98, 141-154.
- AYRES D.R.B., WESTCOT D.W., 1985. Water quality for agriculture. FAO Irrigation and Drainage paper 29 (Rev 1), Rome, 174 pp.
- BUSS P., 1993. The use of capacitance based measurements of real time soil water profile dynamics for irrigation scheduling. Under Pressure Irrig 93, Proc Natl Conf Irrig Assoc Australia and the Ntl Committee of Irrig and Drainage, Launceston, Tasmania. 17-19 May, Irrig Assoc Australia, Homebush, NSW.
- COSTA E.F., FRANÇA G.E., ALVES V.M.C., 1986. Aplicação de fertilizantes via água de irrigação. Informe Agropec 139, 63-68. [In Portuguese].
- DÍEZ J.A., ROMÁN R., CABALLERO R., CABALLERO A., 1997. Nitrate leaching from soils under a maize-wheat-maize sequence, two irrigation schedules and three types of fertilizers. Agr Ecosyst Environ, 65, 189-199.
- DÍEZ J.A., DE LA TORRE A.I., CARTAGENA M.C., CARBALLO M., VALLEJO A., MUÑOZ M.J., 2001. Evaluation of the application of pig slurry to an experimental crop using agronomic and ecotoxicological approaches. J Environ Qual 30, 2165-2172.
- FARES A., ALVA A.K., 2000. Soil water components based on capacitance probes in a sandy soil. Soil Sci Soc Amer J 64, 311-318.
- GONÇALVES A.C.A., REZENDE R., FRIZZONE J.A., FOLEGATTI M.V., 2000. Water and nutrient management effects on soil variables and on lettuce (*Lactuca sativa* L.) yield. II Int Symp on Irrigation of Horticultural Crops. ISHS Acta Hortic 537, 799-804.
- HAUSER M., HASELWANDTER K., 1990. Degradation of dicyandiamide by soil bacteria. Soil Biol Biochem 22, 113-114.
- ISO 10693, 1995. Soil quality. Determination of carbonate content. Volumetric method. Int Org Stand, Switzerland. pp. 1-7.
- ISO 11272, 1998. Soil quality. Determination of dry bulk density. Int Org Stand, Switzerland.
- ISO 11277, 1998. Soil quality. Determination of particle size distribution in mineral soil material. Method by sieving and sedimentation. Int Org Stand, Switzerland.
- LI W.Q., LI G.D., LUO H.Y., 1995. Effect of plastic greenhouse usage on soil salt. J Shandong Agric Univ 2, 165-169. [In Chinese].
- MANUGISTICS, 2000. Statgraphic Plus Version 5.1 Manugistics, Rockville, USA.

- NEMETH K., 1979. The availability of nutrients in the soil as determined by electroultrafiltration (EUF). Adv Agron 31, 155-187.
- ODDA, 1995. Dicyandiamide general data/product. Range/ Applications Publisher: Odda Smelteverk AS. Odda, Norway.
- PALTINEANU C., STARR J.L., 1997. Real-time soil water dynamics using multisensor capacitance probes: Laboratory calibration. Soil Sci Soc Amer J 61, 1576-1585.
- QUEMADA M. (ed), 2006. Balance de nitrógeno en sistemas de cultivo de cereal de invierno y de maíz en varias regiones españolas. Monografías INIA: Serie Agrícola nº 22, 138 pp. [In Spanish].
- REDDY G.R., 1964. Effect of varying quantities of dicyandiamide on the utilization of nitrogen by several crops from sodium nitrate and ammonium sulphate. J Agric Sci 62, 35-38.
- REEVES D.W., TOUCHTON J.T., 1986. Relative phytotoxicity of dicyandiamide and availability of its nitrogen to cotton, corn and grain sorghum. Soil Sci Soc Amer J 50, 1353-1357.
- ROLL R., 1999. Toxicology of DMPP. In: Fertilizer with a new technology innovation in the fertilization ENTEC (BASF A.G., ed). Proc Scientific Colloquium, 17-18 May. BASF Agricultural Centre, Limburgerhof Scientific. pp. 39-44. [In German].
- SÁNCHEZ L., DÍEZ J.A., VALLEJO A., CARTAGENA M.C., POLO A., 1998. Estimate of mineralised N organic in soils, using N balances and determining available N by EUF technique. Application to Mediterranean climate soils. J Agric Food Chem 46, 2036-2043.
- SMITH K.A., MULLINS C.E. (eds), 1991. Soil analysis. Physical methods. Marcel Dekker, NY, USA.
- SOIL SURVEY STAFF, 1993. Soil survey manual. Soil Conservation Service. US Department Agriculture, Handbook 18.
- TONG Y.W., CHEN D.F., 1991. Study on the cause and control of soil secondary salinization in greenhouses. Acta Hortic Sinica 18, 159-162. [In Chinese].
- WALKLEY A., BLACK A.I., 1934. An examination of the Degtjareff method for determining soil organic matter, and proposed modification of the chromic acid titration method. Soil Sci 37, 29-38.
- WEI M., LI T.L., XU H., WANG X.F., YIN Y.D., 2007. Electrical conductivity and pH of root zone soil as affected by continuous and combined application of chemical fertilizers to cucumber cultured in solar greenhouses. XXVII Int Hort Cong Int Symp Advances in Environmental Control, Automation and Cultivation Systems for Sustainable, High-Quality Crop Production under Protected Cultivation. ISHS Acta Hortic 761, 457-462.
- ZERULLA W., BARTH T., DRESSEL J., ERHARDT K., HORCHLER VON LOCQUENGHIEN K., PASDA G., RÄDLE M., WISSEMEIER A.H., 2001. 3,4-dimethylpyrazole phosphate (DMPP) a new nitrification inhibitor for agriculture and horticulture. Biol Fertil Soil 34, 70-84.