

Nitrogen Fertilization and CaCO₃ Interaction on Corn (*Zea mays* L.) Grain and Dry Matter Yields and their Residual Effects on Al-Marj Soil, Libya

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Abstract: Two field trials were conducted at Al-Marj Research Center, north-east Libya, during the summers of 1996 and 1997 to examine the effects of nitrogen fertilizers on corn grain and dry matter yields grown in Al-Marj soil in Libya (fine mixed thermic, typic Xeroll) amended with different CaCO₃ levels. Two nitrogen fertilizer sources (urea and diammonium phosphate) were used at different rates (0, 80, 160 kg N ha⁻¹). The CaCO₃ treatments were 1, 6 and 12% based on the 15 cm furrow slice. A basal phosphorus dose of 46 kg P₂O₅ ha⁻¹ was applied to all experimental plots before planting. The experimental plots were arranged in a split-split plot design with three replications. The parameters measured included corn grain weight, shoot dry matter yield, soil contents of N, P, K, Ca and Mg. Urea was significantly superior over diammonium phosphate and increasing nitrogen levels significantly increased corn grain and dry matter yields. CaCO₃ significantly decreased the shoot dry matter and corn grain yields. Nitrogen fertilizer rates and their interactions with CaCO₃ significantly reduced shoot dry matter and corn grain yields. The CaCO₃, nitrogen source and nitrogen level interaction was significant on the grain and dry matter yield. The negative effect of CaCO₃ on yield was associated with concomitant significant reduction in soil N, P, and Mg contents, but a significant increase in the soil-Ca content was observed. The main nitrogen effect was significant on soil nitrogen and phosphorus, while it induced no significant effect on soil potassium. The interactions between CaCO₃, nitrogen source and levels were significant on the soil nitrogen, phosphorus, calcium and magnesium. However, the soil levels of these nutrients were considered insufficient for optimum corn growth. It is thus, concluded that the reduction of soil N by CaCO₃ in fertilized soils might have been the major cause of corn dry matter and grain yield reductions.

Key words: Crop nitrogen fertilizer, calcium carbonate.

Calcium carbonate which is thought to be precipitated from seawater, is the parent material for most arid and semi-arid soils (Skujins, 1991). Its concentration in these soils ranges between 1 to over 40%. Definitions of calcareous soils are variable, but soils can be considered calcareous when their CaCO₃ content exceeds 5% (Tisdale *et al.*, 1985). The soil profile in the study area is well-developed into A, B and C

horizon. CaCO₃ ranges from 1 to 5% in the A horizon and increases with depth to reach a maximum of 10% in the B horizon, and then decreases again to about 3% in the C horizon. It seems that the CaCO₃ is leached from A horizon and is accumulated in B horizon in a layer 10-20 cm thick as unconsolidated aggregates.

In calcareous soils, the pH is usually high; ranging between 7.5 to 8.2 and this

may cause an adverse effect on nutrient availability to plants. With respect to this, CaCO_3 particles often form strong absorbing sites for phosphorus and manganese, and thereby these nutrients may become unavailable to plants. Likewise, high pH in soils may cause loss of nitrogen from the soil through volatilization and denitrification (Green, 1994). Thus, there is a possible interaction between nitrogen fertilizers and CaCO_3 in calcareous soils of high pH.

The soils examined are mostly calcareous and nitrogen deficient. Fertilizers currently in use are urea and diammonium phosphate. The prevailing conditions are conducive to the loss of added nitrogen through ammonia volatilization and denitrification. Urea fertilizer coated with formaldehyde is locally produced and hence, may hold a promise of low ammonia volatilization because of delayed urea hydrolysis due to the low solubility of formaldehyde in water. Therefore, field experiment was designed to investigate the combined effect of CaCO_3 content in soil and nitrogen fertilization on grain and dry matter yields of corn to study the residual effect of CaCO_3 and nitrogen fertilization on soil nutrient contents at the end of the growing season.

Materials and Methods

The site selected was El-Marj (longitude 32° 34', 32° 36', and latitude 20° 61' 24° 61') 1200 km east of Tripoli, Libya. Two field experiments were conducted at the Agricultural Research Center (20 km south of Tolmitha town in the summers of 1996 and 1997. The soil belongs to the order Mollisols, and the suborder Rendzina, an association of red ferrisiallitic typical

leached clay soil classified as: fine mixed thermic, Typic Xeroll (sometimes called red earth). The soil is deep and calcareous (Ben Mahmoud, 1984). Selected soil characteristics and meteorological data are shown in Tables 1 and 2, respectively. The experimental area was one hectare divided equally between the two successive experiments. The soil was deeply ploughed by a moldboard, harrowed and leveled. The layout was a split-split plot design with nitrogen sources diammonium phosphate (DAP) and urea in the main plot and three nitrogen (0, 80, and 160 kg ha⁻¹) and CaCO_3 (0, 6 and 12%) levels in the sub-sub plots. Treatments were replicated thrice. The area of the main plot was 108 m². The fertilizer rates, CaCO_3 treatments and a basal dose of phosphorus fertilizers equivalent to 46 kg P₂O₅ ha⁻¹ were incorporated in the plough depth prior to planting.

Hybrid corn seeds (Egasead) were planted on 6th May at the rate of 37 kg ha⁻¹ and the spacing was 30 and 70 cm between holes and rows, respectively. Irrigation at the rate of 1 cm day⁻¹ was started immediately after seeding. Weeding and pest control measures were applied when necessary.

The grain and dry matter yields were recorded at the end of the season. Soil samples were collected, ground in stainless steel grinder and then analyzed for N, P, K, Ca and Mg.

Chemical analysis

Soil nitrogen, phosphorus, potassium, calcium, magnesium and particle size distribution were determined according to the methods of soil analysis (Page *et al.*, 1982; Klute, 1986). The concentrations of

Table 1. Some physical and chemical properties of Al-Marj soil

a) Physical

Horizon	Depth (cm)	Particle size distribution (%)			Bulk density (Mg/m ³)	Porosity (%)	Field capacity (%)	PWP (%)	Available water (%)
		Sand	Silt	Clay					
Ap	0-12	15.1	43.5	41.4	1.23	54.6	32.1	18.4	13.7
A1	12-32	11.0	44.3	44.7	1.34	51.1	32.3	19.9	12.4
B1	40-50	7.4	44.3	48.3	1.39	49.4	31.1	21.4	10.7

b) Chemical

Horizon	Depth (cm)	pH (paste)	EC (1:5) (dS m ⁻¹)	OC (%)	CEC (mmolc kg ⁻¹)	CaCO ₃ (%)	Exchangeable cations (mmolc kg ⁻¹)				Available (%)	
							Ca	Mg	K	Na	N	P
Ap	0-12	7.8	0.14	0.48	218	2.0	12.4	3.6	1.6	0.2	0.09	16
A1	12-32	8.0	0.15	0.29	242	1.8	12.4	5.5	1.2	0.4	0.07	16
B1	40-50	8.0	0.10	0.33	267	1.7	11.6	5.4	1.1	0.4	0.06	14

these elements were measured using atomic absorption spectrophotometer (model 2380, Perkin Elmer) adopting air acetylene flame. The pH of the soil paste was measured by Corning pH meter model 7. The electrical conductivity of the saturation extract was measured by conductivity TDS meter (model 44600, Hach). Statistical analysis was performed and the means were separated using Duncan Multiple Range Test.

Results and Discussion

Grain and dry matter yield

Corn grain and dry matter yields were significantly affected by the treatments. Urea significantly increased the yields compared to diammonium phosphate. Increasing the nitrogen fertilizer rate significantly increased grain and dry matter yields. This may be due to N deficiency in these soils (Manuel *et al.*, 2000). The responses of grain and dry matter yields were found to be linear ($r = 0.91$ and $r = 0.99$ for grain

and dry matter yields, respectively) indicating that the nutrients were mobile and readily available to the crop (Etilib *et al.*, 2003). It also indicated that the yield might be maximized by the application of more nitrogen. Increase in dry matter accumulation by nitrogen fertilization confirmed the findings of Drossopoulos *et al.* (1999). The effect of urea was more pronounced compared to diammonium phosphate, especially at higher application rate (160 kg ha⁻¹). Increasing the calcium carbonate level reduced mean grain and dry matter yields significantly compared to the control. Nitrogen and CaCO₃ interaction significantly reduced corn grain and dry matter yields irrespective of the nitrogen source (Tables 3, 4). These findings are in agreement with the findings of Fenn and Kessell (1975) and Bernal and Boig (1993).

Soil analysis

Statistical analysis showed that the soil nitrogen content increased significantly with

Table 2. Monthly averages of some meteorological data in Al-Marj City

Month	Temperature (°C)			Sunshine hours	Relative humidity (%)			Rainfall (mm)
	Max.	Min.	Mean		Max.	Min.	Mean	
Season 1996								
June	37	16	26	11.0	68	56	36	Nil
July	39	13	25	10.6	67	57	36	Nil
August	40	14	26	8.8	65	59	39	Nil
September	40	14	26	7.8	60	50	37	Nil
October	38	12	24	7.7	80	70	57	Nil
November	30	11	23	7.3	85	75	62	10
December	27	4	15	7.1	86	77	65	15
Season 1997								
June	38	13	25	10.1	65	59	35	Nil
July	37	12	24	9.9	66	55	34	Nil
August	38	13	25	8.5	65	57	37	Nil
September	39	13	25	7.5	60	50	35	Nil
October	36	11	23	7.8	80	68	55	Nil
November	29	12	22	7.4	89	73	61	11
December	25	4	14	7.0	84	75	64	17

increasing nitrogen levels compared to the control. Urea was superior in improving soil N over the diammonium phosphate. There is a positive relationship between microbial biomass and the N flushes (Diaz *et al.*, 1995). Increasing CaCO₃ level significantly reduced the soil nitrogen and the effect was more pronounced with diammonium phosphate (DAP) compared to urea. This is possibly due to the adverse effect of CaCO₃ on the availability of nitrogen by increasing ammonia volatilization as reported by Seddky and Rashide (1989). It could also be explained by the rapid urea hydrolysis in calcareous soils (Sullivan and Havlin, 1992) and the formation of ammonium ions which were then subjected to nitrification and leaching of nitrate ions (Tisdale *et al.*, 1985; Yadav and Singh, 1992). However, Marry *et al.* (1989) and Zhang *et al.* (1995) found that

volatilization of ammonia was the main reason of nitrogen losses in calcareous soils. The incubation experiment conducted in the laboratory reflected a drastic concomitant drop in NH₄-N compared to NO₃-N (data not shown). It is well established that CaCO₃ is an efficient soil cementing agent that improves soil aggregation and permeability to water and the leaching of nitrate dissolved therein. The soil-N was significantly affected by the nitrogen source. The interaction between nitrogen and CaCO₃ was significant. The interactive effects of nitrogen source, nitrogen rates and CaCO₃ levels were also significant (Table 5).

Most treatments and their interactions significantly affected the soil phosphorus content. The nitrogen sources significantly influenced the differences in soil-P content. Increasing the nitrogen rate to 80 kg ha⁻¹

Table 3. Average corn grain yield as affected by fertilizer nitrogen source, rates and CaCO₃ treatments in the two seasons

Nitrogen fertilizer source	N rate (kg ha ⁻¹)	Grain yield (Mg ha ⁻¹)			Nitrogen rate effect
		Calcium carbonate (%)			
		1	6	12	
DAP	0	3.96	4.67	3.43	4.02
	80	5.29	4.15	3.57	4.34
	160	5.19	4.11	3.64	4.31
DAP x CaCO ₃ rate effect		4.81	4.31	3.55	
Urea-N	0	3.95	4.27	3.51	3.91
	80	5.31	4.30	3.61	4.41
	160	5.44	4.94	4.80	5.06
Urea-N x CaCO ₃ rate effect		4.90	4.50	3.97	

LSD: DAP x CaCO₃ = 0.010; urea-N x CaCO₃ = 0.034; N-source x CaCO₃ x N-rate = 0.010.

significantly increased the soil phosphorus content with an average of 7 and 6.8 ($\mu\text{g g}^{-1}$ soil) for DAP and urea, respectively. Application of 160 kg N ha⁻¹ significantly reduced the soil-P content with an average of 6.1 and 5.9 ($\mu\text{g g}^{-1}$ soil) for DAP and urea, respectively. It is probable that application of 80 kg N ha⁻¹ affected phosphorus through slow release and less volatilization losses whereas, application of 160 kg N ha⁻¹ increased nitrogen losses markedly and hence, the reduction of soil-P.

Increasing the CaCO₃ levels (main effect) significantly reduced soil-P. The reduction was more pronounced with DAP compared to urea at the levels examined (Table 6). This is in agreement with the findings of Malhi and Nyborg (1985); Simard *et al.* (1988) and Jae and Jacobsen (1990) who observed decreased available phosphorus with increasing CaCO₃. The interaction between CaCO₃ and nitrogen had a significant effect on soil-P.

Table 4. Average corn dry matter yield as affected by fertilizer nitrogen source, rates and CaCO₃ treatments in the two seasons

Nitrogen fertilizer source	N rate (kg ha ⁻¹)	Grain yield (Mg ha ⁻¹)			Nitrogen rate effect
		Calcium carbonate (%)			
		1	6	12	
DAP	0	8.45	6.80	5.37	6.87
	80	10.19	7.68	6.86	8.24
	160	10.35	7.94	6.96	8.42
DAP x CaCO ₃ rate effect		9.66	7.47	6.40	
Urea-N	0	8.45	6.77	5.32	6.85
	80	10.82	9.93	7.46	9.40
	160	1.13a	10.69c	8.82g	10.21
Urea-N x CaCO ₃ rate effect		10.13	9.13	7.20	

LSD: DAP x CaCO₃ = 0.30; urea-N x CaCO₃ = 0.031; N-source x CaCO₃ x N-rate = 0.053.

Table 5. Soil nitrogen as affected by fertilizer nitrogen source, rates and CaCO₃ treatments in the two seasons

Nitrogen fertilizer source	N rate (kg ha ⁻¹)	Soil nitrogen (mg g ⁻¹)			Nitrogen rate effect
		Calcium carbonate (%)			
		1	6	12	
DAP	0	140	130	120	130
	80	160	140	120	140
	160	190	170	150	170
DAP x CaCO ₃ rate effect		163.3	146.7	130	6.11
Urea-N	0	140	140	130	136.7
	80	200	170	150	173.3
	160	250	200	180	210
Urea-N x CaCO ₃ rate effect		196.7	170	153.3	
Nitrogen rate	0	140	135	125	133.3
	80	180	155	135	156.7
	160	220	185	165	19.0
Main CaCO ₃ effect		180	158.3	141.7	

LSD: DAP x CaCO₃ = 8.58; urea-N x CaCO₃ = 15.59; N-source x CaCO₃ x N-rate = 14.86; main CaCO₃ effect = 6.07; main nitrogen effect = 11.02, nitrogen x CaCO₃ = 10.51.

The examined treatments and their interactions increased the soil-K content (Table 7). The response of soil-K to nitrogen

fertilization was linear ($r = 0.98$); increasing nitrogen rate can conceivably increase potassium in soil solution by ensuring

Table 6. Nitrogen source, rates and calcium carbonate effects on soil phosphorus in the two seasons

Nitrogen fertilizer source	N rate (kg ha ⁻¹)	Soil phosphorus (µg g ⁻¹)			Nitrogen rate effect
		Calcium carbonate (%)			
		1	6	12	
DAP	0	6.9	6.6	5.1	6.3
	80	8.6	6.9	5.5	7.0
	160	7.2	6.4	4.6	6.07
DAP x CaCO ₃ rate effect		7.57	6.63	5.17	6.11
Urea-N	0	6.8	6.4	5.13	6.83
	80	8.4	6.8	5.3	5.9
	160	7.1	6.0	4.6	
Urea-N x CaCO ₃ rate effect		7.43	6.4	5.01	
Nitrogen rate	0	140	135	125	133.3
	80	180	155	135	156.7
	160	220	185	165	19.0
Main CaCO ₃ effect		180	158.3	141.7	

LSD: DAP x CaCO₃ = 0.12; urea-N x CaCO₃ = 0.08; N-source x CaCO₃ x N-rate = 0.13; main CaCO₃ effect = 0.08, main nitrogen effect = 0.05; nitrogen x CaCO₃ = 0.141.

Table 7. Soil potassium content as affected by fertilizer nitrogen source, rates and CaCO₃ treatments in the two seasons

Nitrogen fertilizer source	N rate (kg ha ⁻¹)	Soil potassium (mg g ⁻¹)			Nitrogen rate effect
		Calcium carbonate (%)			
		1	6	12	
DAP	0	0.546	0.624	0.624	0.598
	80	0.858	0.585	0.663	0.702
	160	0.936	1.035	0.996	0.989
DAP x CaCO ₃ rate effect		7.78	0.748	0.761	
Urea-N	0	0.585	0.624	0.897	0.702
	80	0.988	0.95	0.819	0.919
	160	1.214	1.09	0.87	1.058
Urea-N x CaCO ₃ rate effect		0.929	0.888	0.862	
Nitrogen rate	0	0.565	0.624	0.76	0.65
	80	0.923	0.767	0.741	0.81
	160	1.075	1.062	0.933	1.023
Main CaCO ₃ effect		0.854	0.818	0.811	

LSD: DAP x CaCO₃ = 0.92; urea-N x CaCO₃ = 1.45; N-source x CaCO₃ x N-rate = 1.59;
main CaCO₃ effect = 0.65, main nitrogen effect = 1.03, nitrogen x CaCO₃ = 1.12.

appropriate balance of nutrients reduction in K content could possibly be (Uyovbisere, 1991; Diaz *et al.*, 1995). due to reduction in the rate of potassium CaCO₃ levels reduced soil potassium. This release in the soil solution by increasing

Table 8. Fertilizer nitrogen source, rates and CaCO₃ treatment effects on soil calcium in the two seasons

Nitrogen fertilizer source	N rate (kg ha ⁻¹)	Soil calcium (mg g ⁻¹)			Nitrogen rate effect
		Calcium carbonate (%)			
		1	6	12	
DAP	0	3.12	3.68	4.24	3.68
	80	3.76	5.28	5.28	4.773
	160	3.84	4.24	5.84	4.64
DAP x CaCO ₃ rate effect		3.573	4.4	5.12	
Urea-N	0	3.16	3.68	4.16	3.67
	80	3.44	5.44	5.76	4.88
	160	4.88	5.84	6.32	5.68
Urea-N x CaCO ₃ rate effect		3.827	4.987	5.417	
Nitrogen rate	0	3.14	3.68	4.205	3.675
	80	3.6	5.36	5.52	4.827
	160	4.36	5.04	0.08	5.16
Main CaCO ₃ effect		3.7	4.693	5.268	

LSD: DAP x CaCO₃ = 0.031; urea-N x CaCO₃ = 0.034; N-source x CaCO₃ x N-rate = 0.053;
main CaCO₃ effect = 0.022; main nitrogen effect = 0.024; nitrogen x CaCO₃ = 0.04.

Table 9. Soil magnesium content as affected by fertilizer nitrogen source, rates and CaCO₃ treatments in the two seasons

Nitrogen fertilizer source	N rate (kg ha ⁻¹)	Soil magnesium content (mg g ⁻¹)			Nitrogen rate effect
		Calcium carbonate (%)			
		1	6	12	
DAP	0	1.25	1.18	1.08	1.17
	80	1.20	1.15	1.03	1.127
	160	1.08	0.98	0.94	1.0
DAP x CaCO ₃ rate effect		1.18	1.103	1.017	
Urea-N	0	1.32	1.22	1.15	1.23
	80	1.27	1.18	1.13	1.193
	160	1.20	1.13	1.06	1.13
Urea-N x CaCO ₃ rate effect		1.263	1.177	1.113	
Nitrogen	0	1.285	1.2	1.115	1.2
	80	1.235	1.165	1.08	1.16
	160	1.14	1.055	1.0	1.065
Main CaCO ₃ effect		1.22	1.14	1.065	

LSD: DAP x CaCO₃ = 0.031; urea-N x CaCO₃ = 0.034; N-source x CaCO₃ x N-rate = 0.053; main CaCO₃ effect = 0.0024, main nitrogen effect = 0.024, nitrogen x CaCO₃ = 0.04.

the CaCO₃ levels (antagonistic effect). The depressive action of CaCO₃ on potassium availability was illustrated by Patel *et al.* (1986).

Increasing CaCO₃ levels significantly increased soil-Ca content relative to control by increasing the exchangeable calcium that consequently led to higher Ca availability in the soil solution. This is in agreement with the findings of Bailey (1995). Increasing nitrogen rates increased soil-Ca significantly in the two nitrogen sources (Table 8). This high correspondence between nitrogen and calcium could be due to the higher microbial activity which produced CO₂ and organic acids that increased the solubility of CaCO₃ and hence the available Ca.

Table 9 shows a significant reduction in soil-Mg content with increasing CaCO₃.

This may be due to antagonism between calcium and magnesium since increasing Ca supply as shown in Table 8 decreased Mg concentrations in the soil solution. Marcos *et al.* (1984) and Morard *et al.* (1996) have emphasized calcium magnesium antagonism. High CaCO₃ will also furnish higher CO₃ ions that may reduce the solubilities of any MgCO₃ or MgHCO₃ present in the soil due to common ion effect. Increasing nitrogen rates increased the concentrations of soil K, Ca, and total organic acids with increasing proportion of nitrogen (Huang *et al.*, 1990) therefore, reduced the soil-Mg significantly.

It can be concluded that CaCO₃ interferes seriously with N-fertilizer transformations and N uptake by corn crop in calcareous soils to the extent of reducing N to levels of deficiency. In Al-Marj soils the CaCO₃

content exceeds 30% thus, nitrogen fertilization therein should be practiced with caution. Increasing CaCO₃ levels especially at higher rates of N application caused severe N losses, therefore, N rate should not exceed 80 kg ha⁻¹ at a time, as higher rates were associated with higher losses. Soil nutrient concentrations P, K and Mg were adversely affected by increasing CaCO₃ level.

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