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RESEARCH ARTICLE

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Phosphogypsum amendments and irrigation with acidulated water affect tomato nutrition in reclaimed marsh soils from SW Spain

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Abstract

Phosphogypsum (PG) is a by-product of the P fertilizer industry usually valorised as amendment for acidic and sodic soils. This work was aimed to study the effects of PG on nutrient uptake by industrial tomato plants in an originally sodic soil. A completely randomized experiment was performed involving two factors: (i) acidification with nitric acid (mimics cleaning techniques in drip irrigation), and (ii) PG rate (equivalents to 0, 20, 60, and 200 Mg ha^{-1}). The highest PG rate resulted in an increased dry matter yield, which can be ascribed at least in part to an increased water use efficiency. PG decreased K, Mg and P concentrations in shoots, and P and Cu concentrations in fruits. At the highest rate, PG increased B concentration in shoots and total B content in the aerial parts of plants when acid was applied. The highest PG rate also increased Ca concentration in fruits, which can be considered positive in view of reducing the incidence of blossom end rot. The total content of Ni and Mo in aerial parts increased with PG, probably related to a decreased adsorption of these nutrients in soils. Acid application increased the concentration of all micronutrients in shoots and the concentration of Fe, Cu and B in fruits. In conclusion, PG promoted positive effects on B, Ni, Mo, and Ca nutrition, and some negative nutritional effects through antagonisms or affecting nutrient cycling in the soils, which however did not result in decreasing yields, even at a large dose which mimics the cumulative application during 20-30 years. Acid treatments resulted in improved micronutrient nutrition of tomato plants.

Additional key words: calcium; magnesium; phosphorus; potassium; *Solanum lycopersicum*; tomato micronutrient nutrition.

Introduction

Phosphogypsum (PG) is the main by-product of the industrial production of phosphoric acid. Large quantities of PG are produced worldwide (about 170 million tons in 2006; Enamorado *et al.*, 2009), most of it being stockpiled. It is composed mainly by $CaSO_4 \cdot 2H_2O$; this means that it can be a source of Ca for agricultural soils, which in fact are one of the main worldwide sinks for this material (Soratto & Crusciol, 2008). Beneficial uses of PG have been demonstrated, among others, for improving soil structure and the yield of some crops in sodic soils, and reducing soil erosion as a result of an increased Ca saturation in soil (May & Mortvedt, 1986; Mullins & Mitchell, 1990; Zhang *et al.*, 1998; Shah *et al.*, 2013). An adequate S supply, which can be achieved with PG, can protect plants from adverse effects of salinity stress (Astolfi & Zuchi, 2013). In marsh soils from SW Spain, where it was usual to apply 20-25 Mg ha^{-1} (wet weight after being sun-dried and with typical residual water content of 20%), PG has been effective in reducing Na saturation (Delgado *et al.*, 2006; Abril *et al.*, 2008; Hurtado *et al.*, 2011a,b), which has resulted in improved physical and chemical properties of these soils (Domínguez *et al.*, 2001; Hurtado *et al.*, 2011b).

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Abbreviations used: CEC (cation exchange capacity); DM (dry matter); EC (electrical conductivity); FM (fresh matter); PG (phosphogypsum); WC (water consumption); WUE (water use efficiency).

The PG content in S and Ca contribute to enhance plant uptake of these nutrients (Soratto & Crusciol, 2008). Also, its application as soil amendment or sodic water treatment can contribute to increase the plant uptake of K (Favaretto *et al.*, 2008; Rani & Khetarpaul, 2009; Shah *et al.*, 2013). In acidic soils, it has been shown that PG improves Ca, Mg, K, Na and S accumulation in plants as a consequence of the intrinsic richness in these elements of the amendment. Also, the effects of PG on the geochemistry of nutrients in soil can affect their uptake by plants (Mariscal-Sancho *et al.*, 2009). The high Ca content of PG is expected to affect Mg, K and Na accumulation in plants not only as a result of cation exchange in soil, but also through antagonisms in plant uptake (Marschner, 1995). Also, Ca is expected to interact with P by enhancing the precipitation of Ca phosphates which can negatively affect P uptake by plants (Favaretto *et al.*, 2008). However, the use of PG in reclaimed marsh soils from SW Spain has been shown to increase P availability index in soils (Domínguez *et al.*, 2001). Beside this, fluoride, transition metals, boron and trace elements are present in PG (Enamorado *et al.*, 2009). These elements can affect plant nutrition, not only by the supply, but also by the dissolution of some silicates by fluoride which can result in the potential release of toxic elements such as Al (Mariscal-Sancho *et al.*, 2009). Moreover, PG has shown to reduce the potential leachability of As, Cd, Tl, Pb, Zn and Ni in acid soils (Aguilar-Carrillo *et al.*, 2009; Rodríguez-Jordá *et al.*, 2010).

Studies on the effect of PG in sodic soils have been traditionally focused on physical soil properties related to a decreased Na saturation. However, beside this, the above mentioned evidences reveal that PG amendments can affect plant nutrition both directly (nutrient supply) and indirectly (by affecting the geochemistry of nutrients and their interactions in soil or plant). This reveals the need of a deeper knowledge about the effects of PG amendments on nutrient uptake by plants, particularly in originally sodic soils, such as those of the irrigated marshland area from SW Spain, where the application of this amendment is being usual since late the 1970's. Traditional furrow or sprinkler irrigation in this area is being progressively substituted by drip irrigation, particularly in tomato crop. The clean-up of drips and pipes, to avoid clogging, is usually performed through with the application of acidified water. Thus, it is also interesting to study the potential interference effects of this acidification, which can also affect nutrient cycling in soil, with the use of PG. The main objectives of this work were to study the effects of different PG rates on the concentration and total content of nutrients in industrial tomato (*Solanum lycopersicum* L.) in an originally sodic soil from the reclaimed marshland area from SW Spain and how this potential effect can be affected by the application of nitric acid (simulating the method for cleaning the irrigation system). Industrial tomato was selected due to its economical relevance in the area.

Material and methods

Soil characteristics

The study was performed using a representative soil of the reclaimed marsh area from the estuarine region of Guadalquivir River, SW Spain (36°56'N, 6°7'W). Information about the area and about the soils is available elsewhere (Delgado *et al.*, 2006; Hurtado *et al.*, 2011a,b). Although a sizeable portion of these soils currently has a low Na saturation, the application of phosphogypsum continues to be a common practice in the region. It is usually added at a rate of 20-25 Mg ha^{-1} every two-three years. After reclamation, the soils can be classified as Aeric Endoaquepts (Soil Survey Staff, 2010).

Surface soil was collected from a farm in the area (37°1.2' N, 6°7.4' W) for a pot experiment (ca 0-30 cm soil from 10 points randomly collected from a 6 ha area). The general properties of this soil can be found in Delgado *et al.* (2006) and Hurtado *et al.* (2011b). The soil was clayish (85, 372 and 543 g kg^{-1} of sand, silt and clay, respectively); with 6.4 and 235 g kg^{-1} of organic carbon and calcium carbonate equivalent concentration, respectively; 32 cmol$_c$ kg^{-1} of cation exchange capacity (CEC); and a pH of 8.1. The Na adsorption ratio in the saturated extract of the soil was 3 in the surface horizon, 8 at 30-60 cm depth and 18 at 60-90 cm depth. Based on the $^{226}Ra/^{238}U$ activities ratios, Abril *et al.* (2008) found that the soils of this farm had already received six typical PG applications, roughly distributed in the 0-40 cm soil horizon.

Plant material and cultivation conditions

A completely randomized experiment was performed with six replications involving two factors, namely: (i) nitric acid application/no application (a single initial irrigation) to mimic the usual maintenance of drip irrigation systems, and (ii) PG rate with four rates, equivalent to 0, 20, 60 and 200 Mg ha^{-1}, corresponding to zero, one, three, and ten typical phosphogypsum amendment rates (20 Mg ha^{-1}), respectively. The highest rate mimics the cumulative effect of a typical application during 20-30 years in the area. Phosphogypsum (from a non-active stack in Huelva, Spain, disposal site) properties are described elsewhere (Enamorado *et al.*, 2009; Hurtado *et al.*, 2011a). Total nutrient contents of PG were (all in g kg^{-1}): P (3.5), S (150), Ca (229), B (3.1), Fe (0.4), Cu (0.0052), Mn (0.0003), Zn (0.011), Ni (0.012) and Mo (0.0009); beside this, its content in Na was 0.3 g kg^{-1}; the content of N, K and Mg was not detectable. The experiment was carried out growing one plant of tomato in a 15-L pot containing 11.6 kg of soil, each pot corresponding to one replication. Plants were transplanted to pot after 1.5 months in seedbed. Fertilization was done by applying 0.06 kg of Osmocote® fertilizer (18% N, 10% P_2O_5, 11% K_2O) per pot. Besides this slow release fertilizer, Ca was applied by foliar spraying 1% $Ca(NO_3)_2$ in order to avoid the blossom end rot, an usual nutritional disorder in soils of the area. Addition of perlite (at a 1:3 perlite:soil volume ratio) was necessary in order to favour soil structure in pots for plant growth. Phosphogypsum and soils were air-dried and ground to pass a 2 mm screen. The same irrigation sequence was applied to all the pots, being the total water volume 54 L. Drainage (1% to 5% of the applied water) was monitored for each pot throughout the experiment. The nitric acid application was done by applying a first irrigation with 1 L of 6 mM HNO_3; in the control pots (without nitric application) only water was supplied in the same irrigation event. The volume of acid or water applied in this first irrigation did not produce any drainage. In any case, the amount of N applied with the acid cannot justify a significant change in N supply in order to explain potential differences ascribed to the treatment.

Plant sampling and analysis

The aerial parts of plants were collected 111 days after transplanting, and separated in shoots (stems + leaves) and fruits. Fresh and dry matter in shoots and fruits were measured; fresh plant material was washed and dry matter determined after drying in a forced-air oven at 65°C until constant weight. The number of fruits and the percentage of ripe (red) fruits were determined for each treatment. For nutrient analysis in plant, dried plant material (aerial part) was ground to pass a 1-mm sieve.

Nitrogen (Dumas) and S were determined using a LECO CNS analyzer (Leco Instrumentos S.L., Madrid, Spain). For other macronutrients (P, Ca, Mg and K) and Na, an aliquot of 0.5 g was allowed to homogenize with 5 mL of concentrated HNO_3 (Merck, Suprapure® grade) for 12 h. After that, the samples were acid-digested on a digestion block at 120°C for 4 h and filtered through 20-25 mm pore size filters. For micronutrients analysis, another aliquot of 0.5 g of sample was digested with 10 mL of concentrated HNO_3 of Suprapure grade using a Multiwave 3000 (Anton Paar, Graz, Austria).

In the digests, P was determined colorimetrically (Murphy & Rilley, 1962), Ca and Mg by atomic absorption spectrometry, K and Na by atomic emission spectrometry and Fe, Cu, Mn, Zn, Ni, Mo and B were measured by mass spectrometry with inductively coupled plasma (ICP-MS) using a Thermo X7-Series (Thermo Fisher Scientific, S.L.U., Madrid, Spain) with tuning conditions described by Enamorado *et al.* (2013).

Soil sampling and analysis

After plant harvest, soil samples were recovered from each pot and carefully separated from roots and the inert material. After that, the samples were dried and ground to pass a 2-mm screen. Electrical conductivity (EC) and pH were determined in 1:2.5 soil to water extract and concentrations of B, Mn, Fe, Ni, Cu, Zn and Mo determined as described for plant material (after microwave assisted digestion with concentrated HNO_3 of Suprapure grade following the same procedure than for plants). This digestion method applied to soil samples provides a reasonable estimation of the soil enrichment in the elements mentioned above, eliminating bias introduced by the variable amount of non-reactive residual material (Enamorado *et al.,* 2013).The effect of PG on other nutrients (P, Ca, Mg and K) and Na in the soil was not studied here since it is well-known from previous works using the same soil (Delgado *et al.*, 2006; Hurtado *et al.*, 2011b).

Water consumption estimation

Water consumption (WC) was estimated as the difference between applied and drained volume and water use

Table 1. Effect of different phosphogypsum (PG) rates and acid treatments on the soil pH and electrical conductivity (EC) and on the concentration of micronutrients in soil. Means, n = 12 for PG rate and n = 24 for acid treatment

PG rate	EC ($dS\ m^{-1}$)	pH	Fe ($g\ kg^{-1}$)	Mn	Cu	Zn	Ni	B	Mo
				($mg\ kg^{-1}$)					
0 $Mg\ ha^{-1}$	1.73	8.05	32.3	846	26	72	34	54	1
20 $Mg\ ha^{-1}$	2.36	7.79	32.8	832	26	72	34	54	0.8
60 $Mg\ ha^{-1}$	2.42	7.77	31.4	827	25	69	33	51	0.6
200 $Mg\ ha^{-1}$	2.46	7.77	31.3	872	27	73	33	44	0.8
Acid	2.23	7.84	31.6	843	26	68	33	49	0.9
No acid	2.31	7.82	32.4	844	27	74	34	53	0.7
ANOVA[1]				***p* values**					
Acid	0.5428	0.4690	0.1715	0.4341	0.0741	0.0033	0.2280	0.1534	0.5181
PG rate L	0.0277	0.0049	0.1237	0.2196	0.5325	0.6937	0.4133	0.0186	0.9000
PG rate Q	0.0115	0.0002	NI	NI	NI	NI	NI	NI	NI

[1] Significance levels of the ANOVA factors: Dilute acid treatment, PG rate, and their significant interactions. PG rate was analysed using orthogonal polynomial contrasts. L = linear response; Q = quadratic response. NI = not included in the final model of analysis of variance, but initially considered. In preliminary analyses, all terms (factors and interactions) were included in the model. If PG rate (Q) or interactions were found to be non-significant, they were removed from final models. Interactions were not shown because they were not significant in any case.

efficiency (WUE) as the grams of biomass produced per L of consumed water during the whole grow cycle.

Statistical analysis

An analysis of variance was performed to identify the effects of the two factors on: fresh (FM) and dry matter (DM) production (shoots and fruits), nutrient concentration and content in shoots and fruits, fruit per plants, % of red fruits, WC and WUE. To this end, the General Linear Model procedure in Statgraphics Plus 5.1 (StatPoint, 2000) was used. Linear and quadratic responses (L and Q) to PG rate were considered in the model. In a preliminary analysis, all terms (factors and interactions) were included. When PG rate (Q) or interactions were found to be non-significant, they were removed from the final models, as described by Borrero *et al.* (2012). Homogeneity of variance was assessed by means of the Cochran, Levene and Bartlett tests; the last of which is sensitive to departures from normality (Snedecor & Cochran, 1989). In all the cases, the three tests were non-significant (at $p < 0.05$) and, thus homogeneity of the variance and a normal distribution of the dataset were assumed. Means were compared via Tukey's test, except when the interaction between factors was significant; in this case, the main effects could not be evaluated in a combined analysis.

Results

Electrical conductivity (EC) increased with increasing PG rates, meanwhile soil pH decreased with increasing PG rates (Table 1). Phosphogypsum only significantly affected Boron concentration in soil, which decreased with increasing PG rates. Concerning the effect of acid treatment, no statistically significant differences were found in element concentrations in soil, except for Zn.

Shoots FM and DM, fruit DM yield, water consumption and water use efficiency increased with increasing PG rates, results being evident at the highest rate (Table 2). The number of fruits per plant increased with increasing PG rates, meanwhile the FM and DM per fruit decreased (Table 2).

The concentrations of P, K, Mg, Cu and Mo in plant shoots and the concentrations of P, K, Cu, Zn and B in fruits decreased with increasing PG rates (in all the cases linear response to PG was significant, Tables 3 and 4). On the contrary, the application of this amendment increased Na and B concentration in shoots and Ca, Na, Fe, Ni and Mo concentrations in fruits (linear response to PG significant, Tables 3 and 4). Total content in the whole aerial part (shoots + fruits) of P and Cu decreased with increasing PG rates, meanwhile Na, Ni and Mo increased with increasing PG rates (Table 5). The total Ca content was increased when com-

Table 2. Effect of the different phosphogypsum (PG) rates and acid treatments on plant production variables, water consumption, and water efficiency use. Means, n = 12 for PG rate and n = 24 for acid treatment

PG rate (Mg ha^{-1})	FM shoots (g plant^{-1})	DM shoots	FM fruits	DM fruits	FM fruit (g fruit^{-1})	DM fruit	Fruits (units plant^{-1})	Red fruits (%)	WC (L plant^{-1})	WUE (g DW L^{-1})
0	227	49	650	90	24	3.3	27	64.9	51.9	2.70
20	227	51	635	89	23	3.3	27	63.5	51.0	2.68
60	214	49	601	87	20	2.9	31	62.7	51.4	2.54
200	257	59	650	95	18	2.6	38	58.1	53.0	2.92
ANOVA [1]	***p* value**									
Acid	0.5387	0.5189	0.7224	0.8501	0.6025	0.5194	0.4149	0.8885		
PG rate L	0.1930	0.0001	0.6930	0.0179	0.0000	0.0001	0	0.0459	0.0001	0.0042
PG rate Q	0.0444	0.0446	NI	NI	NI	NI	NI	NI	0.0193	0.0125

[1] Significance levels of the ANOVA factors: Dilute acid treatment, PG rate, and their significant interactions. PG rate was analysed using orthogonal polynomial contrasts. L = linear response; Q = quadratic response. NI = not included in the final model of analysis of variance, but initially considered. In preliminary analyses, all terms (factors and interactions) were included in the model. If PG rate (Q) or interactions were found to be non-significant, they were removed from final models. Interactions were not shown because they were not significant in any case. Acid was not significant in any case and means were not shown. FM, fresh matter; DM, dry matter; WC, water consumption in each pot; WUE, water use efficiency as g of aboveground biomass per L of water

Table 3. Effect of different phosphogypsum (PG) rates and acid treatments on the concentration of nutrients and Na in the shoots tomato plants. Means, n = 12 for PG rate and n = 24 for acid treatment

PG rate	N (g kg^{-1})	P	K	Ca	Mg	S	Na	Fe	Mn (mg kg^{-1})	Cu	Zn	Ni	B	Mo
0 Mg ha^{-1}	26	0.67	5.2	46	12	2.1	3.1	3.2	103	16	39	9	74	2.9
20 Mg ha^{-1}	23	0.60	5.8	45	11	1.6	3.3	2.6	86	14	31	10	66	2.7
60 Mg ha^{-1}	25	0.54	4.2	45	10	1.5	3.9	3.1	92	13	34	10	79	2.7
200 Mg ha^{-1}	24	0.53	4.6	45	9	1.9	4.0	2.7	95	12	32	10	94	2.7
Acid	24	0.59	5.3	45	10	2.0	3.5	4.6	126	18	42	15	126	4.1
No acid	25	0.58	5	45	10	2.0	3.5	1.2	60	10	27	5	28	1.1
ANOVA[1]	***p* values**													
Acid	0.5196	0.1765	0.3705	0.9815	0.8133	0.8109	0.8514	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
PG rate L	0.8378	0.0000	0.0222	0.7757	0.0000	0.7828	0.0001	0.0876	0.4066	0.0000	0.1017	0.2221	0.0005	0.0005
PG rate Q	NI	NI	0.0232	NI	0.0013	0.0328	0.0082	NI	NI	0.0022	NI	NI	NI	NI

[1]Significance levels of the ANOVA factors: Dilute acid treatment, PG rate, and their significant interactions. PG rate was analysed using orthogonal polynomial contrasts. L = linear response; Q = quadratic response. NI = not included in the final model of analysis of variance, but initially considered. In preliminary analyses, all terms (factors and interactions) were included in the model. If PG rate (Q) or interactions were found to be non-significant, they were removed from final models. Interactions were not shown because they were not significant in any case.

pared with control without PG only at the highest amendment rate (Table 5). Quadratic response revealed that, in the case of K, Mg and Zn, the rate of 60 Mg PG ha^{-1} promoted a decrease in the accumulation of these nutrients in the whole aerial part when compared with the other PG rates (Table 5).

Overall, acid application increased the concentration of all micronutrients in shoots (Table 3), meanwhile it only increased the concentration of Fe, Cu and B in fruits (Table 4). Acid treatment also increased the total content of all micronutrients in the aerial parts (Table 5). Ni was not detectable in fruits of plants not sub-

Table 4. Effect of different phosphogypsum (PG) rates and acid treatments on the concentration of nutrients and Na in the fruits of tomato plants. Means, n = 12 for PG rate and n = 24 for acid treatment

PG rate	N	P	K	Ca	Mg	S	Na	Fe	Mn	Cu	Zn	Ni	B	Mo
	(g kg^{-1})							(mg kg^{-1})						
0 Mg ha^{-1}	27	1.7	5.1	0.64	1.1	1.0	1.5	79	19	10	30	0.9	23	1.7
20 Mg ha^{-1}	29	1.5	4.6	0.66	1.1	0.9	1.8	72	19	10	32	0.7	20	3.2
60 Mg ha^{-1}	28	1.4	4.5	0.58	1.0	0.9	1.8	82	16	9	27	0.9	21	3.5
200 Mg ha^{-1}	29	1.3	4.4	0.81	1.0	1.0	1.8	99	18	7	26	1.2	20	2.8
Acid	29	1.4	4.5	0.72	1.1	1.0	1.7	97	17	11	27	0.9	25	3.4
No acid	28	1.5	4.8	0.62	1.0	0.9	1.7	70	18	9	29	nd	16	2.2
ANOVA[1]	***p* value**													
Acid	0.4065	0.2974	0.0276	0.9488	0.8721	0.6250	0.6208	0.0001	0.0511	0.0000	0.0595	NI	0.0000	0.0000
PG rate L	0.2735	0.0001	0.0157	0.0064	0.2533	0.1613	0.0363	0.0042	0.1591	0.0000	0.0021	0.0077	0.0180	0.0000
PG rate Q	NI	0.0168	NI	NI	NI	NI	NI	NI	NI	NI	NI	0.2922	NI	0.0000

[1]Significance levels of the ANOVA factors: Dilute acid treatment, PG rate, and their significant interactions. PG rate was analysed using orthogonal polynomial contrasts. L = linear response; Q = quadratic response. NI = not included in the final analysis of variance, but initially considered. In preliminary analyses, all terms (factors and interactions) were included in the model. If PG rate (Q) or interactions were found to be non-significant, they were removed from final models. Interactions were not shown because they were not significant in any case. nd = not detectable.

Table 5. Effect of different phosphogypsum (PG) treatments on the total content of nutrients in the aerial parts (shoots + fruits) of tomato plants. Means, n = 12 for PG rate and n = 24 for acid treatment

PG rate	N	P	K	Ca	Mg	S	Na	Fe	Mn	Cu	Zn	Ni	Mo
	(g plant^{-1})								(µg plant^{-1})				
0 Mg ha^{-1}	3.7	0.18	0.72	2.4	0.70	0.19	0.24	0.14	6.5	1.6	4.7	0.8	0.27
20 Mg ha^{-1}	3.8	0.17	0.69	2.3	0.63	0.16	0.27	0.12	5.9	1.6	4.4	0.7	0.40
60 Mg ha^{-1}	3.6	0.15	0.60	2.3	0.56	0.15	0.27	0.15	5.7	1.4	3.9	0.8	0.43
200 Mg ha^{-1}	4.2	0.15	0.69	2.7	0.61	0.21	0.33	0.17	7.3	1.3	4.5	1.1	0.39
Acid	3.8	0.16	0.64	2.4	0.62	0.17	0.28	0.22	8.0	1.8	4.7		0.50
No acid	3.8	0.17	0.70	2.4	0.64	0.18	0.28	0.07	4.9	1.2	4.1		0.25
ANOVA[1]	***p* value**												
Acid	0.5276	0.1916	0.0375	0.5723	0.3117	0.8109	0.6604	0.0000	0.0000	0.0000	0.0016	NI	0.0000
PG rate L	0.0001	0.0317	0.7916	0.0012	0.6915	0.7828	0.0000	0.2969	0.4460	0.0030	0.6482	0.0000	0.0397
PG rate Q	NI	0.0076	0.0031	NI	0.0002	0.0328	NI	NI	0.0168	NI	0.0024	NI	0.0000

[1]Significance levels of the ANOVA factors: Dilute acid treatment, PG rate, and their significant interactions. PG rate was analysed using orthogonal polynomial contrasts. L = linear response; Q = quadratic response. NI = not included in the final analysis of variance, but initially considered. In preliminary analyses, all terms (factors and interactions) were included in the model. If PG rate (Q) or interactions were found to be non-significant, they were removed from final models. Only the interaction Acid × PG rate L was significant, and shown in Figure 1; the other interactions were not shown because they were not significant. The element Ni was not detectable in fruits of plants without acid treatment; thus the statistical analysis for it could not be performed.

jected to the acid treatment; thus a positive effect on the concentration in fruits and total content of Ni in aerial parts can be assumed, although the corresponding statistical analysis could not be performed. The acid treatment did not significantly affect FM or DM yield in shoots or fruits, fruit production, % of red fruits or water consumption or water use efficiency (data not shown).

The only significant interaction between both factors was observed for total B in the whole aerial parts

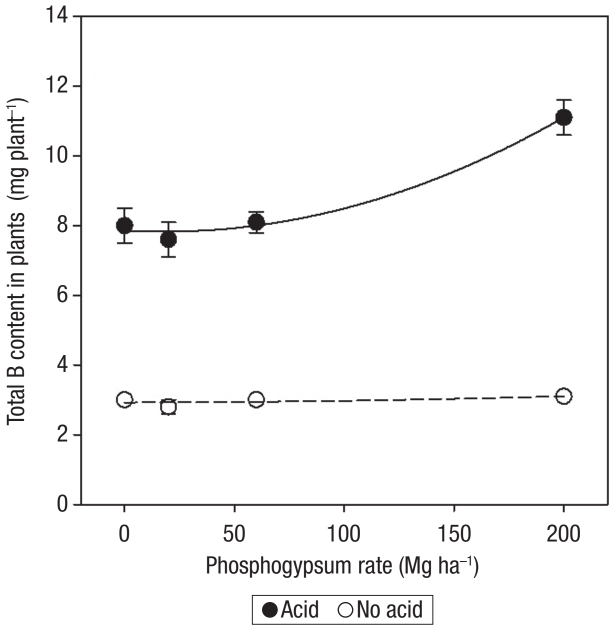

Figure 1. Total content of B in the aerial parts of tomato plants as affected by PG rate and acidulated water treatment; interaction between both factors was significant at $p < 0.001$.

of plants, which increased with increasing PG rates (only significant at the highest rate) only when acid was applied (Fig. 1).

Discussion

Although the linear contrast revealed that DM in shoots and fruits increased with increasing PG rates (Table 2), the application of the two lowest PG rates (20 and 60 Mg ha^{-1}) did not affect significantly these variables when compared with the control without PG and only the highest PG rate (200 Mg ha^{-1}) resulted in an increased DM yield in shoots and fruits (Table 2). Also, FM in shoots was only significantly greater than the control at the highest PG rate (Table 2). This response to PG rate observed for mentioned variables could be related, at least in part, to the increased water consumption (WC) and water use efficiency (WUE) observed with this PG rate (Table 2). The increased WC and WUE could be the result of a decreased water drainage fraction as the result of the PG application. In field experiments, an increased WUE has been observed due to an increased infiltration rate in gypsum amended soils (Amezketa *et al.*, 2005; Tang *et al.*, 2006), which in this pot experiment cannot be the explanation since all the irrigation water infiltrated. The increased WUE can be the result of the effect of Ca sulphate decreasing bulk density and consequently increasing porosity (Courtney *et al.*, 2009). Nutritional effects of PG do not seem to explain differences in fresh or dry matter yield in plants because the highest PG usually resulted in a decreased concentration of some nutrients in plants, which in none of the cases were above toxicity limits in the control. On the other hand, the effect of PG increasing the concentration of Na or B in shoots does not seem to explain the increased FM and DM yield at the highest PG rate, since Na is not essential and B concentrations were in all the cases above the threshold of deficiency (Huett *et al.*, 1997).

Although the fruit production (DM and number of fruits) increased at the highest PG rate, the DM and FM per unit of fruit and the portion of red fruits decreased (Table 2). This does not imply a negative effect on the quality of industrial tomato. The decreased size of fruits has been observed as a consequence of salinity (Magán *et al.*, 2008) which in this case could be the consequence of the solubilisation of Ca sulphate. This may promote an increase in Na salts in the soil solution after the displacement of Na from exchange sites by Ca as described previously in the same soil by Hurtado *et al.* (2011b). The increased EC in the soil extract (Table 1) due to PG supports the hypothesis of an increase in soluble salts in soil solution. The increased Na salts in solution also explains the increased Na concentration in shoots and fruits and the increased total content of this element in the aerial parts of plants (Tables 3 to 5). This increased Na availability could promote a toxicity effect in sodic soils if leaching is not sufficiently applied to remove Na salts from the soil, which is not the case in reclaimed marsh soils from the Guadalquivir Valley with low Na saturation in the exchange complex. On the other hand, the increased Ca activity in the solution of this soil by PG application (Hurtado *et al.,* 2011b) can explain the decreased K and Mg concentration in shoots (Table 3), the decreased K concentration in fruits (Table 4) and the negative effect of PG rates applied at 60 Mg ha^{-1} on the total content of K and Mg in aerial parts (Table 5). This is the likely consequence of a decreased content of exchangeable Mg and K (Peregrina *et al.*, 2008) or an antagonism between Ca and the other nutrients (Marschner, 1995) and contrasts with previous works in acidic soils, where the application of gypsum or phosphogypsum did not result in a negative effect on K or Mg nutrition of tomato plants (Favaretto *et al.*, 2008; Rani & Khetarpaul, 2009). In this soil, the application of PG at usual rates (20 Mg ha^{-1}) was found to significantly decrease the content of exchangeable Mg, but not that of exchangeable K (Hurtado *et al.*, 2011b).

It is surprising that the concentration of elements supplied in significant amount by PG amendment, such as Ca, P, or S, did not increase significantly in shoots (Table 3). The lack of significant effects on Ca concentration could be the likely result of foliar spraying of Ca fertilizer and the immobility of this nutrient in phloem since its concentration in solution and exchange complex is significantly increased by PG as stated above. The total content of Ca in the whole aerial part was only increased at the highest PG rate (Table 5), which can be explained by the increased Ca concentrations in fruits at increased PG rates. This latest is a positive effect because it contributes to reduce the incidence of the blossom end rot, which is the main physiological disorder contributing to decrease the fruit quality of tomato (Tabatabaie *et al.*, 2004).

Increased EC in soil when PG is applied may be partially related to an increased sulphate salts (*e.g.* Na sulphate) concentration in soil solution. However, S concentration in shoots and total content in the whole aerial part showed a quadratic response to PG rates (Table 3), revealing that lowest rates (20 and 60 Mg ha^{-1}) decreased its concentration and content when compared with control while the highest PG rate did not (Tables 3 and 5). The complex geochemistry of sulphate in soil, which is the form in which the nutrient is absorbed by plants, can contribute to explain this effect. Addition of sulphate as phosphogypsum can enhance formation of ionic pairs (Domínguez *et al.*, 2001) which can affect its uptake; nevertheless, very high rates can overcome this effect, in part due to the increase in more soluble sulphates (*e.g.* Na sulphate) in solution.

The decreased P concentration in shoots with increasing PG rates (Table 3) may be the consequence of an enhanced precipitation of poorly soluble Ca phosphates —hydroxyapatite type— as a result of the increased Ca activity in soil solution (Delgado *et al.*, 2002a,b). The slight pH decrease due to PG is not enough to affect the dominant thermodynamically stable phosphate —hydroxyapatite— formed in the soil. Under acidic conditions, hydroxyapatite is not a thermodynamically stable phase; this might explain why PG did not affect negatively P uptake by plants grown in acidic soils (Mariscal-Sancho *et al.*, 2009).

Gypsum-like by-products can decrease the proportion of micronutrients in the exchange complex as a result of the increased exchangeable Ca (Illera *et al.*, 2004; Garrido *et al.*, 2005) increasing their losses through leaching. However, there is not a decrease in micronutrients concentration in soil due to PG, except for B. Thus, transformation into less phytoavailable forms or antagonistic effects must explain the negative effect of PG on Cu concentration and its total content and on Zn concentration in fruits (Tables 3 to 5) and also the negative effect of intermediate PG rates on total contents of Mn and Zn in the whole aerial part (Table 5). At the highest PG rate, Mn and Zn contents were not decreased when compared with control pots, probably due to the increased plant development at this PG rate which may increase the nutrient uptake capacity of plants (Table 2). Sulphate present in PG can also enhance the adsorption of Cu on Fe oxides, thus contributing to a decreased availability to plants; this effect however, seems to be more significant at pH lower than 7 (Beattie *et al.*, 2008). In soils amended with gypsum-like by-products, Zn has been shown to be bound to Fe oxides (Rodríguez-Jordá *et al.*, 2010) thus revealing an increased sorption on these soil components. Beside this, sulphate can promote the formation of Zn and Cu complexes (Mesquita & Viera e Silva, 1996; Gunton *et al.*, 2006; Rodríguez-Jordá *et al.*, 2010) which can negatively affect its absorption by plants. Also, Cu can precipitate with phosphate present in PG decreasing its solubility and uptake by plants (Garrido *et al.*, 2005). Beside these effects on the geochemistry of metals, Ca from PG can decrease the uptake capacity of metals by plants (Min *et al.*, 2013). Fe concentration in fruits increased with increasing PG rates (Table 4) likely due to an increased transport to fruits, more than to an increased availability of this nutrient since its concentration in soil (Table 1) and shoots (Table 3) was not increased by PG.

In spite of the non-significant effect of PG on Ni concentration in soil, the total content of this nutrient in the whole aerial part of tomato plant increased with PG. This can be explained by an increased Ni desorption from sorbent surfaces due to Ca (Mamindy-Pajany *et al.,* 2013). The total content of Mo in the whole aerial part of tomato was increased with the application of this amendment (Table 5) due to the increased concentration in fruits (Table 4). An increased availability of Mo can not be explained by an increased concentration of this nutrient in soil (Table 1) and must be related to an increased sorption of a part of the P applied with PG on Fe oxides, displacing adsorbed Mo (as molibdate) from them (Xu *et al.*, 2006) and thus, enhancing the uptake of this element by plants. This increased Mo availability can contribute to explain a negative effect of PG on S accumulation in plants because sulphate transport in plant is decreased by Mo (Fitzpatrick *et al.*, 2008).

In spite of the significant amounts of B supplied with PG, the concentration of this nutrient in soil decreased with increasing PG rates. This can be explained by the displacement of B adsorbed on Fe oxides by P supplied with PG which may lead to an increased loss through leaching. The increased B desorption contributes to explain the increased B concentration in shoots observed with PG as the likely result of an increased B concentration in soil solution (Table 3). The effect of PG on the total B content was only significant when the acid treatment was applied (Fig. 1). This can be probably explained because B adsorption to soil particles, which is critical affecting the availability to plants of this nutrient, decreases with decreasing pH (Goldberg & Glaubig, 1986).

Overall, the application of nitric acid improved the accumulation of all micronutrients in plant, the effect being particularly evident with Fe, whose total content in the aerial parts of plants was increased three times (Table 5). This is particularly relevant for calcareous and sodic soils where the pH buffered at high values restricts the availability in soil and the uptake by plants of all these nutrients, except Mo.

Acidification of the rhizosphere increases the mobilization of micronutrients from soil particles, being this strategy one of the main acquisition mechanisms of nutrients by plants and microorganisms in soil (Marschner *et al.*, 2011). In spite of only one application, which resulted in no significant decrease of soil pH at the end of the experiment (Table 1), the effect was observed at the end of the crop cycle. This reveals additional mechanisms besides a transient acidification of the rhizosphere which can only increase micronutrient uptake by plants at the beginning of the cycle. Nitric acid can dissolve partially Fe oxides in soil, which can recrystallize after acid neutralization as less crystalline forms which are sources of Fe more easily mobilizable by plants (de Santiago & Delgado, 2006). This can also contribute to increase the absorption by plants of other micronutrients adsorbed on Fe oxides, such as Zn (Montilla *et al.*, 2003), Cu (Bibak, 1997), or B (Goldberg & Glaubig, 1986). Also, the nitric acid treatment can oxidize soil organic matter thus releasing metal bound to it (Tessier *et al.*, 1979) or can alter the structure of organic matter (Liu *et al.*, 2011) increasing its complexing capacity, which can positively affect the availability of metallic elements to plants (de Santiago & Delgado, 2007). The decreased concentration in fruits and the decreased total content in aerial parts of K with the nitric acid application could be the result of an antagonism with Ca because the application of acid promotes the dissolution of Ca-carbonates and thus increases Ca activity in soil solution.

In conclusion, application of phosphogypsum amendments at usual rates in reclaimed marsh soils from SW Spain (20 Mg ha^{-1}) can negatively affect the uptake by tomato plants of some nutrients, including K, Mg and Cu, and positively others such as Ca, B, Ni and Mo, without negative effects on plant yield (shoot or fruit dry matter). The simulation with 10 times the usual rate (equivalent to the amendment applied in a 20 to 30 years period in the area) resulted in less nutritional concerns and improved yields, at least partly related to an improved water use efficiency. Application of a first irrigation with acidulated water, which mimics the typical self-cleaning techniques in drop irrigation, resulted in overall improvement in micronutrient nutrition of tomato plants.

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