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Tomato yield and soil chemical properties influenced by low–molecular–weight organic acids in calcareous soil

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ABSTRACT

Calcareous soils have restrictive characteristics that limit and pose a challenge for crop production; in this environment, plants can exude low-molecular-weight organic acids (LMWOAs). This study aimed to verify the influence of exogenously applied LMWOAs in calcareous soils on tomato yield and the chemical characteristics of soil and leachate. *Solanum lycopersicum* L. seedlings were grown in pots containing calcareous soil in a greenhouse, fertilized by drip irrigation with Steiner nutrient solution in which the treatments 0.1 mM citric acid (CA), 0.1 mM oxalic acid (OA), 0.01 mM salicylic acid (SA) and a control without LMWOAs (T0) were prepared, applied during the whole growth cycle. The experiment was repeated four times, with twenty replicates per treatment, under a completely randomized design. The yield per plant was quantified, while pH and microbial respiration (RMS) were measured in the soil. The pH, electrical conductivity (EC), oxidation-reduction potential (ORP), carbonate (CO_3^{2-}), and bicarbonate (HCO_3^-) contents were quantified in the leachates. SA application reduced the soil pH (8.75). SA and CA improved the fruit yield per plant by 11% and 33%, respectively ($p < 0.05$). CA induced a 1.7% reduction in leachate pH ($p < 0.05$) and a 15.9% increase in HCO_3^- content ($p < 0.05$). SA decreased EC and CO_3^{2-} concentrations by 8.9 and 23.1% ($p < 0.05$), but increased HCO_3^- content by 23.1 % ($p < 0.05$). The use of LMWOAs as a strategy in the management of calcareous soils can promote favorable conditions for tomato yield per plant.

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1. INTRODUCTION

Tomato (*Solanum lycopersicum* L.) is the second most economically valuable crop after *Solanum tuberosum* L., its production is distributed worldwide in Asia (61.1%), Europe (13.5%), America (13.4%) and Africa (11.8%) with high variability in yield (1.5 – 508 ton.ha^{-1}) (Quinet et al., 2019). This vegetable is highly consumed owing to its high content of carotenoids (lycopene and β-carotene), vitamins (A, B, and C), organic acids (citric and malic), phenolic compounds, sugars (sucrose, hexoses), metabolites, and good nutrient supply (Pramanik & Mohapatra, 2017). However, tomato production presents problems due to various stresses, such as stress due to calcareous soils, which limits its quality and production per plant. In this sense, calcareous soils covers more than 30% of the world's surface and are associated with semi–arid and arid climates; they are characterized by low organic matter content, presence of soluble salts such as sodium (Na^+) (some of them), magnesium (Mg^{2+}) and calcium (Ca^{2+}) and $CaCO_3$ and $MgCO_3$ layers (up to 95%), caused by a high concentration of carbonates (CO_3^{2-}) in the soil solution which in turn accumulated in the surface pores and, under precipitation and/or by excess irrigation, leach into the soil profile (Morad Wahba et al., 2019; Taalab et al., 2019). Likewise, the high release of OH^- ions as well as the dissolution of $CaCO_3$ induces a high concentration of HCO_3^- buffering the soil pH in the range of 7.5 – 8.5; these conditions lead to a low nutrient availability (nitrogen, phosphorus, potassium, magnesium, zinc, iron, copper, manganese and boron), volatilization of N, precipitation of soluble forms of phosphorus, imbalance in Ca:Mg:K ratios and loss of S-SO_4^{2-} by leaching (Ding et al., 2020; Morad Wahba et al., 2019;

Taalab et al., 2019). During leaching events some content of carbonates, bicarbonates and nutrients that have been mobilized to the surface of the aggregates (by a heterogeneous flow of water through the soil macropores and aggregates) are washed away by miscible displacement (Barnard et al., 2010). Ionic leaching (Ca^{2+}, Mg^{2+}, K^+ and Na^+ as well as H^+ or OH^-) and the release of low molecular weight organic compounds are mechanisms involved in soil pH (Neina, 2019); as leaching reduce the salt content in the topsoil and minimize total dissolved solids in the rhizosphere (Xiao et al., 2021), generating an optimal soil environment for root system development and promoting yield plant. In this context, the leaching rate seem to be conditioned by the environment related to calcareous soils and irrigation management. Therefore, quantification of some chemical characteristics of water leached from agricultural land (pH, electrical conductivity, oxidation-reduction potential, carbonates, and bicarbonates) can provide an idea of the edaphic and rhizospheric environment of the plant.

Crops growing on these soils may show reduced yields, mainly due to chlorosis and stunting (Taalab et al., 2019). However, some plants (i.e.: Lupin, tomato, maize, cotton, wheat, chickpea, soybean, pigeon pea, rice, Carrizo citrange, broad bean or faba bean) extrude of low–molecular–weight organic acids (LMWOAs) as a strategy to establish themselves in these conditions, and although the content of LMWOAs in the soil is low ≤ 50 µM), they play an active role in the soil by participating in carbon cycle, generating bioavailability of mineral nutrients, promotion of microbiological activity and signaling, chemotaxis and heavy metals detoxification (Adeleke et al., 2017; Panchal et al., 2021; Sokolova, 2020). In addition to being produced by the plant LMWOAs can be released during the decomposition or organic matter and by microbial metabolism (Adeleke et al., 2017). In plants, LMWOAs are synthesized mainly in mitochondria, through the glycolysis pathway and the glyoxylate cycle (Panchal et al., 2021). Several studies have detected LMWOAs such as benzoic, cinnamic, citric, maleic, malic, malonic, oxalic, shikimic, succinic, tartaric and valeric acids in soil solution (Panchal et al., 2021; Sokolova, 2020); however, their concentrations are strongly influenced by the C-fixation type of plants, microbial load, and soil type. Previous studies show that exogenously applied LMWOAs chelate heavy metals allowing their removal through leachates (Ren et al., 2023). Similarly, an increase in the availability and concentration of nutrients in leachates when applying LMWOAs is reported (Jalali & Jalali, 2022; Pérez-Labrada et al., 2016; Shen et al., 2023).

Several studies have shown a reduction in soil pH by applying LMWOAs, and the use of CA through the fertilizer solution significantly reduced the pH of the soil solution when applied at a rate of 0.1 mM in tomato grown in calcareous soil, in addition to increasing fruit yield per plant (Pérez-Labrada et al., 2016). Likewise, Al-balawna and Abu-Abdoun (2021) documented a reduction in pH from 13 to 7.5 by applying 2.5 g CA on calcareous soils in Jordan valley. Similarly, a soil incubation study (pH 7.25, 23% $CaCO_3$) found that CA (35 mM kg soil^{-1}) decreased the pH levels of calcareous soil to a value of 6.24 at 60 days (Mahdi et al., 2024). The studies cited contrast with the present study because they did not analyze leachates and some of them did not have constant applications during the entire crop cycle. However, there is insufficient research on the impact of LMWOAs on leachate characteristics and their relationship with crop yield in calcareous soils (Pérez-Labrada et al., 2016). In this sense, the analysis of soil and leachate chemical parameters should be a priority to understand the impact of organic compounds on plant growth and yield. Plants can significantly increase the concentration of LMWOAs in the cytosol of root cells (mainly malic, maleic, citric, and oxalic acid) (Panchal et al., 2021; Seregin & Kozhevnikova, 2021) generating a concentration gradient between root cells and soil solution leading to extrusion of these acids into the rhizosphere where they can modify pH (Panchal et al., 2021). Alteration of rhizosphere pH can be accompanied by changes in dissolved ions concentration and carbonate content in leachates. The exudation of LMWOAs involves a metabolic expense for the plant by increasing the rate of anaplerotic reactions to replenish its extrusion (Panchal et al., 2021). In this sense and taking into account the productive potential of calcareous soils (Morad Wahba et al., 2019), the natural distribution of LMWOAs in the soil (Sokolova, 2020) and the promotion of nutrient bioavailability (Al-balawna & Abu-Abdoun, 2021), as well as the great importance of tomato cultivation in Mexico, due to the area planted, the economic value it represents and its consumption in fresh or processed products, the present work was established with the aim of verify the influence of exogenously applied LMWOAs via fertilizer solution on tomato yield and calcareous soil and leachate chemical characteristics. Therefore, because calcareous soils are closely related to arid and semi-arid zones, this knowledge can serve as a strategy for tomato production under calcareous soil stress, reducing salinization, and favoring plant yield.

2. MATERIAL AND METHODS

2.1. Experimental site and design

The experiment was conducted at the greenhouse of the Horticulture Department of Universidad Autónoma Agraria Narro (México) during four season. In the first experiment (spring season, February-May 2015), 2 kg of soil was used; in the second (summer season, June-September 2015), third (autumn season, October 2015-January 2016), and fourth (spring season, March-June 2016) experiments, 9 kg of soil was used. For each experiment, new soil from the same location was used. Some soil samples were collected at 0-30 cm depth from an area with rosetophilous desert scrub vegetation (25°21'14.5''–101°2'25'') (Table 1). In each season, new soil was used.

The experiment was conducted using tomato (*Solanum lycopersicum* L.) seedlings of determine growth. Transplanting was performed 30–days after sowing in pots containing calcareous soil, and the plants were grown to a single stem under greenhouse conditions. Pots with one plant were used as the experimental unit and were arranged in a completely randomized design with 20 replicates per treatment. Immediately after transplant and until the end of the each experiment, the plants were fertilized with a Steiner-

Table 1. Chemical properties of calcareous soil used in the study.

Texture	pH	TC	OM	$N\text{-}NO_3^-$ (mg.kg^{-1})	P (mg.kg^{-1})	K (mg.kg^{-1})	Mg (mg.kg^{-1})	Ca (mg.kg^{-1})	Na (mg.kg^{-1})	S (mg.kg^{-1})	Zn (mg.kg^{-1})	Mn (mg.kg^{-1})	Cu (mg.kg^{-1})	B (mg.kg^{-1})	Fe (mg.kg^{-1})
Loamy soil	8.5	7.34	0.2	5	9	285	546	3253	42	10	0.1	2	0.6	0.8	5

TC= total carbonates (%), OM= organic matter (%).

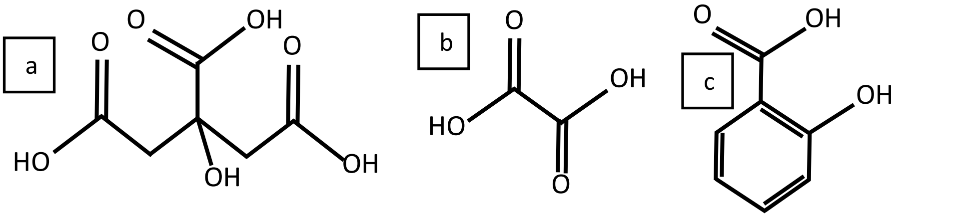

Figure 1. Molecular structure and functional groups of LMWOAs used in this study, citric acid (CA; $C_6H_8O_7$), (a) oxalic acid (OA; $C_2H_2O_4$) (b) and salicylic acid (SA; $C_7H_6O_3$) (c).

nutrient solution (Steiner, 1961) [4.5 mmol $Ca(NO_3)_2{\cdot}4H_2O$, 2.0 mmol $MgSO_4$, 0.7 mmol KNO_3, 2.0 mmol K_2SO_4, and 1.6 mmol KH_2PO_4, micronutrients were applied in the form of chelates] at 100%, through drip irrigation system and depending on the water demand of the plant. pH of nutrient solution was stabilized at 6.3 with H_2SO_4, the electrical conductivity (EC) was 2.0 dS m^{-1}. Four doses of LMWOAs (Figure 1) were applied in each season as follows: 0.1 mM citric acid (CA), 0.1 mM oxalic acid (OA), 0.01 mM salicylic acid (SA) as well as a control (T0) without LMWOAs. For accessibility and purity, we used food-grade CA and OA, while SA was reagent grade. Each treatment was performed by completely dissolving the corresponding LMWOAs in Steiner solution in a total of four containers of fertilizer solution. Treatments were applied immediately after transplanting and until the end of the crop (in each season) using the drip irrigation system. Daily irrigation per pot was performed using a localized system according to crop demand by applying the volume of solution necessary to maintain 20% drainage.

2.2. Soil and leachates chemical traits

At the end of each experiment, soil samples were collected at a depth of 10 cm from the pot, dried at room temperature, ground in a mortar, and sieved (2 mm mesh). The pH was determined using a 1:10 suspension of solid/distilled water (Cayuela et al., 2013). 1 g of dry and sieved soil was taken and dissolved in 10 mL of distilled water, shaking for 1 hr, then allowed to stand 10 min. Subsequently the pH was measured in the soil + water suspension with a potentiometer Hanna HI98130 (Hanna Instruments, Woonsocket, R.I., USA). Soil microbial respiration (SMR) was determined by the CO_2 released over time using the titration method described by Stotzky (1965). Briefly, 25 g dry and sieved soil firs taken and brought to 55% field capacity with distilled water and placed in a flask containing a vial with 5 mL of NaOH (1 N) and a filter paper strip, incubated at 28 °C for 24 h. Vial content was poured into a flask, 2 mL of $BaCl_2$ (2%) and phenolphthalein (1%) was added and titrated with HCl (0.1 N). The SMR was calculated according to Equation 1 (Stotzky, 1965).

$$SMR = (C - V)\, N\, x\, E \quad \text{..........} [1]$$

where: C = volume of HCl spent in the control titration; V = volume of HCl spent in the sample with soil; N = normality of HCl; E = equivalent weight of CO_2.

The leachates were collected during the second irrigation of the day in the phases of vegetative development, flowering, and physiological maturity of the 2nd cluster; for this purpose, a container was placed under the pot (first experiment 11 cm x 15 cm x 12 cm with a capacity of 2 kg of soil and 17.5 cm x 24 cm x 16.5 cm with a capacity of 9 kg of soil for the rest of the experiments) and the leachate was collected approximately 30 min after irrigation. In the leachates, pH, EC, and Oxidation-Reduction Potential (ORP) were quantified in situ; pH and EC were determined using an HI98130 potentiometer and ORP with an ORP-200 potentiometer (HM Digital Inc. Los Angeles, CA, USA). Some of the leachate was stored at 4°C and carbonate (CO_3^{2-}) and bicarbonate (HCO_3^-) content was determined using the methodology cited by Nag and Joshi (2014). Briefly, on a 1:6 mixture of leachate and distilled water, five drops of phenolphthalein (1%) were added and titrated with HCl (0.02 N) until the pink solution became colorless, and the quantification of CO_3^{2-} was determined using Equation 2. Then, five drops of methyl orange were added to the solution and titrated with HCl (0.02 N) until the solution turned yellow to orange, and the quantification of HCO_3^- was determined using Equation 3. CO_3^{2-} and HCO_3^- were expressed as meq L^{-1}.

$$CO_3^{2-} = \frac{[(2\text{ x mL HCl})\text{ x Normality HCl x }1000]}{\text{mL sample}} \quad \text{..........}[2]$$

$$HCO_3^- = \frac{[(\text{mL HCl of 2 titrations - 2 x mL of 1st titration})\text{ x Normality HCl x }1000]}{\text{mL sample}} \quad \text{..........}[3]$$

2.3. Production per plant

To determine yield, all fruits harvested per plant were counted, as well as the total weight of fruit per plant; five bunches per plant were harvested (semi-vertical whole and ripe clusters with thick peduncles and a standard number of fruits arranged in a regular plane with similar orientation, size, and uniform distribution).

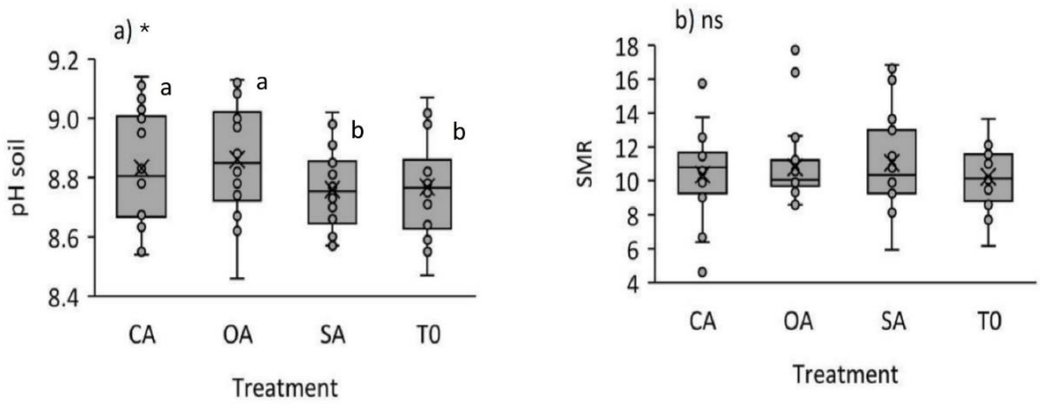

Figure 2. Box plot for the pH soil (a) and soil microbial respiration, SMR (b) where tomato was developed with the application of nutrient solution supplemented with LMWOAs (data correspond to the average of all values of the four production seasons). The different letters on the bars indicate differences at the 0.05 significance level. CA=citric acid at 0.1 mM; OA=oxalic acid at 0.1 mM; SA=salicylic acid at 0.01 mM; T0=without organic acids. SMR = mg C–CO_2 g^{-1} soil.

2.4. Statistical analysis

The experiment was replicated for four production cycles, using twenty biological replicates in each cycle. All parameters were analyzed by two–way analysis of variance under a completely randomized design. Leachates and soil data were presented as a boxplot; 25 and 75% quartile, median, minimum and maximum values as well as outliers. Differences were separated by Fisher's Least Squares Difference (LSD, $p < 0.05$). A Spearman correlation test ($p < 0.05$) was applied to the leachates and soil characteristics data. All analyses were performed with IBM SPPS v19.

3. RESULTS

3.1. Effect of the LMWOAs on soil chemical traits

Figure 2 shows the overall effect (mean of the total data from the four-production season) of the LMWOAs treatments on pH and SMR parameters. The average soil pH was 8.81, representing an increase of 3.65% with respect to the initial pH value (8.5). The addition of SA had a very similar behavior to T0 (8.76), while the application of CA and OA increased the pH value in the calcareous soil (0.06 and 0.09 units, respectively) ($p < 0.05$). There were no significant differences in SMR ($p > 0.05$); however, an 8% increase was found under the SA treatment with respect to T0. The OA treatment increased this variable by 5.5%, and the addition of CA induced a 1.2% increase in mean data with respect to T0 (Figure 2b). Soil pH differed between samples ($p < 0.05$), with the highest values in seasons three and four (≈ 8.9), whereas in the first and second experiments, general average of 8.73 and 8.60, respectively, were documented. The SMR did not show differences in the different experiments ($p > 0.05$); however, it was observed that in the fourth experiment, the highest average was presented (10.92 mg C–CO_2 g^{-1} soil) while the lowest value was 10.31 mg C–CO_2 g^{-1} soil in the first experiment.

3.2. Effect of the LMWOAs on leachates chemical traits

The pH, EC, ORP, CO_3^{2-}, and HCO_3^- levels differed significantly between the experiments ($p < 0.05$). In this regard, the pH of the leachates showed the lowest average value during the fourth experiment, particularly under CA treatment (7.23). In the case of EC, the highest average values (4.05 dS m^{-1}) were observed during the third season, particularly under T0 (4.56 dS m^{-1}), while the lowest average was documented in the first experiment (3.24 dS m^{-1}) with the AO treatment (2.83 dS m^{-1}). Regarding ORP, the most reduced values were documented in season one with SA treatment (125 mV), whereas in season two, T0 showed the most oxidized values (213 mV). Concerning CO_3^{2-} seasons one and two showed high concentrations mainly with OA (5.66 and 3.80 meq L^{-1}, respectively), while in seasons three and four there was a lower concentration when SA was applied (1.75 meq L^{-1}). Finally, the highest HCO_3^- content in leachates was documented in seasons three (7.79 meq L^{-1}) and two (7.66 meq L^{-1}) to a greater extent with CA treatment (9.68 meq L^{-1}). On the other hand, in season one, the lowest concentration was documented in OA treatment (3.55 meq L^{-1}). Figure 3 presents trends of the pH, CE, ORP, CO_3^{2-} and HCO_3^- of leachates from calcareous soil as response to LMWOAs addition. The pH shows a 1.7% reduction with CA addition, in the case of SA and OA treatments, the opposite behavior was observed since these increased pH values by 0.9 and 1.2% with respect to T0 ($p = 0.0455$, Figure 3a). In the case of the EC (Figure 3b) presented changes among treatments induced a consistent reduction ($p = 0.0373$), OA treatment reduced this parameter by 12%, followed by SA (8.9%) and CA (6.5%), compared to the T0 treatment (3.82 dS m^{-1}). For the ORP no differences among treatments ($p > 0.05$); however, a reduction in the values was found with SA, CA, and OA application (5.2, 4.7 and 2.6%, respectively, Figure 3c). CO_3^{2-} content showed a differences among treatments ($p = 0.0175$), application of OA presented a higher concentration (22.1% compared to T0), while SA and CA showed a reduction of 23.1 and 3% (Figure 3d). Finally, HCO_3^- content showed differences among treatments ($p = 0.0125$), adding CA increased the concentration by 15.9%, while SA treatment induced an increase of 23.3% when compared to T0 (Figure 3e).

3.3. Spearman correlation

The variables studied presented low correlation coefficients, among which the positive relationship between pH soil with the ORP and HCO_3^- of leachates stands out.

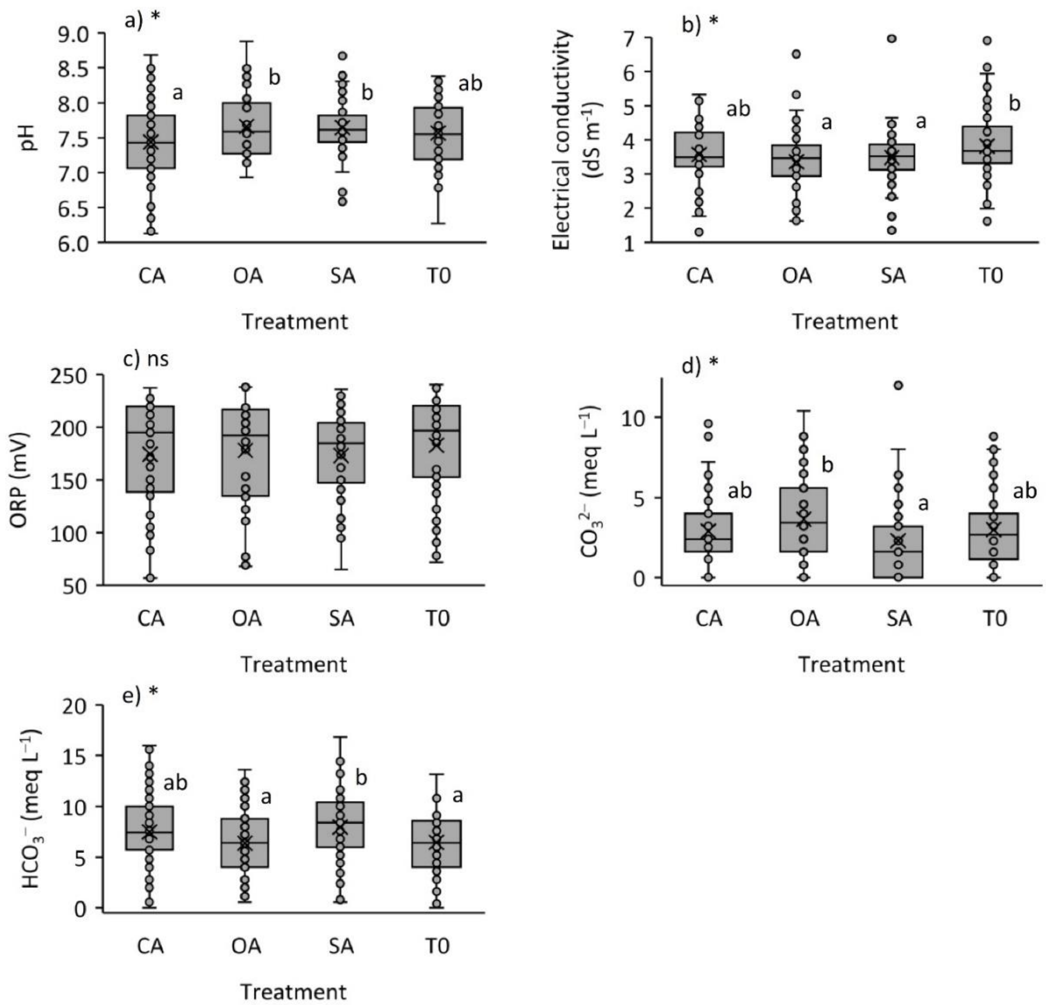

Figure 3. Box plot for chemical traits of soil leachates where tomato was developed with the application of nutrient solution supplemented with LMWOAs (data correspond to the average of all values of the four production seasons). The different letters on the bars indicate differences at the 0.05 significance level. CA=citric acid at 0.1 mM; OA=oxalic acid at 0.1 mM; SA=salicylic acid at 0.01 mM; T0=without organic acids.

SMR showed a positive correlation with HCO_3^- leachates (R=0.12) and a negative correlation with pH leachates and ORP leachates (R=–0.15). In leachates, pH was significantly correlated with ORP, EC and CO_3^{2-} (R= –0.14, –0.39 and 0.24, respectively). While ORP showed significant positive correlation with EC and HCO_3^- (R=0.19 and 0.22, respectively) (Table 2).

3.4. Production per plant

The addition of different LMWOAs modified the number of harvested fruits as well as the production per plant (Table 3). Differences between seasons ($p < 0.05$) were documented in the number of fruits harvested, and production per plant was higher in seasons 2 and 4 with SA application. An increase in the average fruit production was observed with the application of SA and CA ($p < 0.05$), while OA presented values very similar to T0. The CA and SA treatments increased the harvested fruit compared to the tomato plants without the addition of any organic acid (10.7 and 12%, respectively). Although OA presented the same average production as T0, it was possible to appreciate a greater number of fruits (8.6% greater than T0); however, these fruits were smaller in size.

4. DISCUSSION

The high buffering capacity (generated by carbonates) can limit fluctuations in the pH of calcareous soils (de Soto et al., 2022; Poschenrieder et al., 2018). LMWOAs can induce a hormetic response in plants (Zhao et al., 2023), and when applied exogenously to the soil, they generate an acidifying reaction in the soil and in the rhizospheric zone owing to the contribution of H^+ (Al-balawna & Abu-Abdoun, 2021; Panchal et al., 2021), which can alter soil pH in a "microlocalized" manner along the profile by converging with the root respiration process and differential nutrient uptake mechanisms (Husson, 2013; Panchal et al., 2021). In this sense, SA can promote a signaling response and has the ability to acidify the medium by deprotonating the soil and reducing the high pH of calcareous soil. This environment generates a suitable zone for plant development in this type of soil, where microbiological activity can proliferate as LMWOAs contribute to carbonate groups (Macias-Benitez et al., 2020; Panchal et al., 2021). In our study, there was no statistically significant difference between treatments, probably because of the low fertility level of the soil, but the application of SA seems to exert a biostimulating action on the microbiome (16 mg C–CO_2 g^{-1} soil).

Table 2. Spearman's (R) correlation matrix of soil and leachates chemical traits where tomato was developed with application of nutrient solution supplemented with LMWOAs (four production seasons).

	Parameter	Soil		Leachate				
		pH	SMR	pH	ORP	EC	CO_3^{2-}	HCO_3^-
Soil	pH	1	0.09 ns	–0.01 ns	0.19 *	–0.01 ns	0.10 ns	0.14 *
	SMR		1	–0.15 *	–0.15 *	–0.01 ns	–0.06 ns	0.12 *
Leachate	pH			1	–0.14 *	–0.39 *	0.24 *	–0.09 ns
	ORP				1	0.19 *	0.02 ns	0.22 *
	EC					1	–0.18 *	0.27 *
	CO_3^{2-}						1	–0.58 *
	HCO_3^-							1

Notes: Value corresponds to Spearman's correlation coefficient (Rho). SMR=microbial respiration of soil (mg C–CO_2 g^{-1} soil; ORP= oxidation–reduction potential (mV); EC=electrical conductivity (dS m^{-1}); CO_3^{2-}=carbonates content (meq L^{-1}); HCO_3^- =bicarbonates content (meq L^{-1}); ns=no significant differences; * significant deferences at $p < 0.05$.

Table 3. Average behavior of harvested fruits and yield of tomato plants developed on calcareous soil and with the application of a nutrient solution supplemented with LMWOAs (four production seasons).

Treatment	Total number of fruits harvested per plant	Production per plant (kg $plant^{-1}$)
	Season 1	
CA	57.8±2.9 ab¥	2.8±0.13 b
OA	57.9±2.5 ab	2.9±0.06 ab
SA	62.2±2.2 a	3.0±0.08 a
T0	53.4±2.0 b	2.7±0.04 b
	Season 2	
CA	30.9±4.8 a	1.4±0.29 ab
OA	23.2±4.0 a	1.1±0.22 ab
SA	19.9±3.3 a	0.9±0.20 b
T0	28.8±3.3 a	1.6±0.21 a
	Season 3	
CA	38.5±3.9 ab	2.4±0.17 ab
OA	42.4±1.9 a	2.2±0.08 bc
SA	42.6±2.0 a	2.7±0.20 a
T0	31.1±2.0 b	1.8±0.14 c
	Season 4	
CA	57.8±2.7 ab	2.8±0.10 b
OA	57.9±2.0 ab	2.9±0.11 ab
SA	62.2±2.7 a	3.0±0.08 a
T0	53.4±2.1 b	2.7±0.08 b
Season	*<0.0001*	*<0.0001*
LMWOAs	*0.0658*	*0.1932*
Interaction	*0.0654*	*0.0015*

Notes: Mean ± standard deviation. ¥=different letters on the numerical values indicate significant differences ($p < 0.05$) along the columns. CA=citric acid at 0.1 mM; OA=oxalic acid at 0.1 mM; SA=salicylic acid at 0.01 mM; T0=without organic acids.

LMWOAs did modify the chemical characteristics of leachates (liquid resulting from water percolation through the soil) (Naik et al., 2021). When fertilizer solution (treatments) is constantly applied on the soil it mixes and displaces the soil solution mobilizing ions (Sadeghizadeh & Jalali, 2017) towards the surface of the aggregates or from micropores to macropores where they can be leached by miscible displacement (Naik et al., 2021). This loss of soil ions alters parameters such as pH, EC, ORP, $CaCO_3$ and HCO_3^- of the leachates (Geng et al., 2020); our data suggest that the inclusion of LMWOAs in the fertilizer solution can enhance such changes depending on the degree of dissociation of the applied acids.

Here we found that the pH of the leachates showed the lowest values when applying the CA treatment (Figure 3a), which could be due to the fact that this is a tricarboxylic acid that can provide a greater amount of H^+ to the soil system. In the case of EC, the significant reduction under the OA treatment followed by SA and CA (Figure 3b), may be due to the permanence in the soil of exogenous LMWOAs that promote the dissolution of carbonates (Macias-Benitez et al., 2020; Panchal et al., 2021) induce bioavailability and retention of nutrients such as Ca^{2+}, Mg^{2+}, K^{+}, Na^{+}, NH_4^{+}, SO_4^{2-}, Cl^{-} and NO_3^{-} (Brindhavani et al., 2022; Mihoub et al., 2017) modifying the amount of washed ions (Alam et al., 2020; Hosseininia et al., 2019). However, the constant leaching of ions causes an equilibrium between the soil solution and the exchangeable sites generating a constant EC, in our report the average EC values found in leachates were below the salinity threshold (4.0 dS m^{-1}) for tomato crop (Chourasia et al., 2022). The ORP variable is strongly associated with soil water status (Husson, 2013), we a constant and uniform irrigation was maintained in all treatments, so the alterations cannot be due to this factor. The ORP exhibits a "redox kinetic cycle" by oxidation and reduction reactions of its redox couple (Zhang & Furman, 2021), in agricultural soils its value ranges from –300 to +900 mV and affects the concentration and behavior of LMWOAs (Hassanpour & Aristilde, 2021). The ORP data in leachates obtained represent a moderately reducing environment; the exogenous addition of LMWOAs seems to promote more reducing conditions with respect to the control treatment due to the deprotonation of these compounds.

In the case of CO_3^{2-} and HCO_3^{-} values in leachates can reveal the degree of $CaCO_3$ dissolution from the soil (Bahnasawy, 2013) driven by the oxidation of the LMWOAs. The increase in CO_3^{2-} concentration in leachates with OA treatment suggests a greater capacity of this compound to react with soil carbonates. In contrast, SA and CA treatments appear to dissolve soil carbonates by increasing the HCO_3^{-} content of leachates (Macias-Benitez et al., 2020; Panchal et al., 2021). The high reactivity of CO_3^{2-} and HCO_3^{-} (Taalab et al., 2019) with CO_2 and Ca^{2+} (Bahnasawy, 2013; Poschenrieder et al., 2018) affect rhizospheric processes, so a favorable environment for crop development in calcareous soils would suggest low soil and high leachate values of these two compounds. Interestingly CO_3^{2-} and HCO_3^{-} can be metabolized in the root (via phosphoenolpyruvate carboxylase) causing an increase in the concentration of organic acids (Ding et al., 2020; Poschenrieder et al., 2018; Sun et al., 2021).

Recalling the permanence of LMWOAs in soil the modifications in leachate variables could be intrinsically related to phenomena triggered by these anionic compounds as well as by the interaction between the parameters themselves. For example, ORP is closely related to pH by the flow of protons and electrons (Husson, 2013) and changes in redox potential are accompanied by alterations in pH according to the Nernst equation (Rinklebe et al., 2020). Likewise, SMR is influenced by plant metabolism and with drying-wetting cycles, soil pH and ORP (Zhang et al., 2019; Zhang & Furman, 2021). The EC represents the content of dissolved salts in the medium (Alam et al., 2020), the variables CO_3^{2-} and HCO_3^{-} will show an eventual relationship with it. The high pH values of calcareous soils generate restrictive conditions for plants (Taalab et al., 2019), exogenous applications of LMWOAs through the irrigation system could acidify the rhizospheric medium, induce favorable EC and ORP values and dissolve and leach CO_3^{2-} and HCO_3^{-} allowing good tomato growth and development (Husson, 2013). Likewise, tomato plants would have a lower metabolic expenditure due to the supply of carbonaceous skeletons in the soil from LMWOAs, as evidenced by an improvement in fruit yield per plant under the CA and SA treatments.

5. CONCLUSION

The addition of low molecular weight organic acids through the nutrient solution to the calcareous soil where tomato was grown did not modify soil pH and soil microbial respiration, but significantly reduced pH, EC and CO_3^{2-} content, increasing the HCO_3^{-} of the leachate. There was an 11 and 33% increase in production per plant when SA and CA applied, respectively. The quantification of these parameters represents a quick, simple and low-cost way to monitor and know the state of the soil. The response of low-molecular-weight compounds to calcareous soil is complex, and further field studies are required. The implementation of this practice should be accompanied by economic analysis to verify its feasibility at the field level.

Declaration of Competing Interest

The authors declare that no competing financial or personal interests that may appear and influence the work reported in this paper.

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