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EFFECT OF WATER ACIDIFICATION ON BEHAVIOR OF SOME ELEMENTS IN SOIL IRRIGATED WITH TREATED INDUSTRIAL WASTEWATER

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ABSTRACT

The main objective of this investigation was to study the effect of injection of citric and phosphoric acids with drip irrigation on behavior of some nutrients and heavy metals in soil irrigated with wastewater; the field experiment was conducted in EL-Sadat City, Minufiya Governorate, Egypt situated 31° 51´N latitude and 30° 36´E longitude which irrigated with treated industrials wastewater. Behavior of some elements in the soil, its concentrations in the shoots, roots and in the grains of red radish and celery vegetables as well as yield of vegetables were determined. Application of citric acid with treated industrial wastewater decreased soil pH value suddenly in the emitting point in the zero time after irrigation, below the emitter and within 0-10 cm depth compared to phosphoric acid. After that, the peak of pH value increased gradually with time, get way horizontally from the emitter and increasing soil depth. Concentration of N and K, were found mostly in the upper 0-40 cm soil layer. Such increases in the ryhizospher (0-40 cm depth) are 3.0 and 1.5 % for N and 13.8 and 0.6 % for K with injection of citric acid or phosphoric acid, respectively as compared with the control treatment. On the other hand, chemically available P trend is highly increased with application of phosphoric acid compared with application of citric acid. Such increases in the ryhizospher (0-40 cm depth) reach 0.37 and 1.2% in the treatments of citric acid and phosphoric acid, respectively, as compared with the control treatment. The concentrations of Fe, Mn, Zn and Cu in the upper layer (0-40 cm) were 30.6, 19.7, 14.3 and 7.8 fold for Fe, Mn, Zn and Cu respectively as compared with control treatment. Where as, the increases of such elements with injection of phosphoric acid was 22.5, 10.0, 10.8 and 7.0 fold, respectively. The concentration of Co and Ni in the soil treated with citric acid recorded 67 and 27% more than the control, respectively. Where as, the increases of such elements with injection of phosphoric acid reached 58 and 22 % more than the control, respectively. Whereas, Pb-DTPA-extractable was increased with injection of citric acid compared to the control or phosphoric acid treatment. Data indicate an increase in NPK concentrations in red radish and celery shoots and grains with injection of citric or phosphoric acid with irrigation water as compared to the control treatment. The amounts of grain yield of both radish and celery vegetables crops increased due to the injection of two acids as compared with the control treatment. Such increases record 40 and 20% for radish with the injection of citric acid and phosphoric acid, respectively. Whereas, grain yield of celery increases were 2.3 and 1.2 fold with the injection of citric acid and phosphoric acid compared to the control, respectively. Heavy metals in the grains increased resulted injection of citric acid with irrigation water for cultivated red radish, which recorded 0.7, 1.4, 2.3, 1.6, 4.5, 1.7 and 1.8 fold over the control for Fe, Mn, Zn, Cu, Co, Ni and Pb, respectively.

Key words: Citric acid- phosphoric acid- industrial wastewater- red radish - celery - sandy soil- macro nutrients- micro nutrients- heavy metals.

INTRODUCTION

Values of pH for optimal availability of all the nutrients are in the rank of 6-6.5. The main factor affecting pH in the ryhizospher is NH_4/NO_3 ratio in the irrigation water especially in sandy soils and inert substrates with low buffer capacity such as rockwool. Ryhizospheric pH determines the phosphorus availability since it affects the processes of precipitation/solubilization and adsorption/desorption of phosphates pH also influences the availability of micronutrients (Fe, Zn, Mn) and the toxicity of some of them (Al, Mn).

The transfer of heavy metals from soils to plants is dependent on three factors: the total amount of potentially available elements (quantity factor), the activity as well as the ionic ratios of elements in the soil solution (intensity factor), and the rate of element transfer from solid to liquid phases and to plant roots (reaction kinetics)

(Marschner, 1995). The leaching of metals into the ground water must be minimized. Because acid functional groups are deprotonated with increasing pH, the solubility of organic substances increases, as does the stability of metal–organic complexes (Harter and Naidu, 1995). Thus, especially at higher pH, organic substances can contribute to heavy metal mobilization and accumulation Heavy metal solubility in soils is mainly controlled by the soil reaction (pH), the amount and kind of sorption sites, and the total amount of heavy metals in the soil (Brümmer et al., 1986 and Gray et al., 1999). Hornburg and Brümmer (1993) found that the proportions of the soluble content of Cd and Zn increased strongly as pH decreased below 6.5 and 5.3, respectively. While, the Cu and Pb solubilities increased strongly as pH decreases below 4.5 and 3.5, respectively; above these values, solubilities are mainly controlled by organic and inorganic metal complexes. According to McKenzie (1980), mobilization decreases in the order Cd > Ni > Zn > Cu > Pb. The mobility of As, however, decreases with decreasing pH. Nigam et al. (2001) found that the Cd accumulation by corn after applying the carboxylic acids citric and malic acid to a Cd-spiked soil (3.5 µM kg-1 or 0.39 mg kg-1) was enhanced; it was also higher than with the amino acid aspartic acid or glycine. The organic acids were applied in the same molar concentrations as Cd to the soil, and the Cd concentrations in corn shoots were more than doubled with citric acid (to 19 mg kg-1) and also significantly increased with malic acid (to 15 mg kg-1). A dominant pH effect can be excluded here because, in all treatments, pH was adjusted to 5.5 with 0.1 M HCl. This study therefore showed that organic acids, which are commonly exudated by the roots of corn plants, also effectively enhance phytoextraction when added to the soil.

The objective of this study was to examine the influence of citric and phosphoric acids on soil pH, status of different nutrients in soil and plants. Also, the relationship between enhancing metal solubility in soils and plants, and applying strategies to minimize the risk of heavy metal leaching, will be discussed.

MATERIALS AND METHODS

The study was carried out on the experimental farm of EL-Sadat City, Minufiya Governorate, Egypt situated 31° 51´N latitude and 30° 36´E longitude. Red radish and celery vegetables crops were chosen to evaluate the effect of application of citric and phosphoric acids with treated wastewater to irrigation sandy soil, El-Sadat City, on pH and behavior of some nutrients of such soil along with crop yield, and nutrient concentration of such plants. Some physical and chemical properties of this soil are shown in table, 1a, and characteristics of irrigation water are shown in table, 1b. In a field experiment, red radish and celery vegetables crops were planted. Compost was added to the soil at the rate of 25 ton/ fed. The following three treatments, replicated three times, were adopted for the study:

a- Control (drip irrigation with treated industrial wastewater).
b- Citric acid injected to reduce the soil pH value to 6.0-6.5 (365g/m^3 water).
c- Phosphoric acid injected to reduce the soil pH value to 6.0-6.5 (200ml/m^3 water).

The acids were injected at vegetative stage one time for week.

Representative shoots samples were taken at the flowering stage from red radish and celery plants, red radish and celery grains being taken at harvest stage. The plant samples were washed with tap water and 10^{-4} M HCl, and then oven dried at 65°C for 48 hours. Plant materials were ground, mixed well and kept for N, P, K and micronutrients determination.

Table 1a: Some physical and chemical characteristics of the selected soils.

Parameter		Soil
pH (1:2.5) (soil : water suspen.		8.66
EC_e	dS.m^{-1}	0.92
$CaCO_3$	%	2.08
Sand	%	91.00
Silt	%	8.00
Clay	%	1.00
Textural class		Sand
N	ppm	20.5
P	ppm	5.32
K	ppm	90.6
Fe	ppm	12.4
Mn	ppm	8.34
Zn	ppm	5.34
Cu	ppm	3.80
Ni	ppm	0.97
CO	ppm	0.82
Pb	ppm	0.86

Soil samples were taken from 0-10, 10-20, 20-40, 40-60 and 60-90 cm soil depth at the emitting point, 20- 40- and 60 cm horizontally away from the emitting point and 0-2-4 and 6 hours after end irrigation with acid at the emitting point to determined soil pH. Also, the soil samples were collected from the same depths at flowering stage to determine chemically available different elements. The samples were air dried, crushed, sieved through a 2-mm sieve and stored for different determination.

Soil characteristics were determined using standard methods outlined by Jackson (1958), Sauter and Stoub (1990), Watanabe and Olsen (1965) and Baruah and Barthakur (1997). Heavy metals content of DTPA extract as well as digestion solutions of plant samples were analyzed using Atomic absorption spectroscopy.

Table 1b: Some chemical composition of the treated industrial wastewater in Sadat area*.

Parameter		FAO ,WHO guidelines	Wetland
pH		6.5-8.4	7.12
EC	$dS.m^{-1}$	<3	4.04
TDS	ppm	<450	212
COD	ppm		150
BOD_5	ppm		95.2
Ca^{2+}	ppm		215
Mg^{2+}	ppm		54.9
Na^+	ppm	<70	549
K^+	ppm		34.2
Total N	ppm	<30.0	65.2
NO_3^-	ppm	10	19.51
PO_4^-	ppm	8.6	3.23
B	ppm	<1.0	0.16
Cl^-	ppm	<140	903
HCO_3^-	ppm	<90	628.8
Fe	ppm	5.0	2.48
Mn	ppm	0.2	0.95
Zn	ppm	2.0	0.72
Cu	ppm	0.2	0.31
Ni	ppm	0.2	0.27
CO	ppm	0.05	0.08
Cd	ppm	0.01	0.06
Pb	ppm	5.0	1.28
SAR	ppm	<9.0	8.62

* C.F El-Arby and Elbordiny (2006)

RESULTS AND DISCUSSION

Effect of citric and phosphoric acids on soil pH value.

Data in figures (1a, b and c) show change in soil pH value thought profile varied with time, horizontally and vertically from the emitting point as affected by the applied citric or phosphoric acid with irrigation treatments. Generally, injection of citric acid with industrial wastewater for irrigated radish or cereal vegetables decreased soil pH value suddenly in the emitting point in the zero time after irrigation, below the emitter and within 0-10 cm depth. After that, the peak of pH value increased gradually with time, get way horizontally from the emitter and with increasing soil depth. For example, soil pH value reached 7.09, 7.06 and 7.06 in the zero time after irrigation, below the emitter and within 0-10 cm depth, respectively. The change in the soil pH value between the first time after irrigation and after six hours from irrigation was 0.62 units. Whereas, the change in the soil pH value between below the emitter and 60 cm horizontally from the emitter was 1.12 units. While, the change in the soil pH value between soil surface layer (0-10 cm) and 90 cm soil depth was 1.36 unit. Also, application of citric acid with irrigation water decreased soil pH value in the ryhizospher (0-40 cm depth) from 8.66 to 7.17. Whereas, with injection phosphoric acid soil pH value take the same trend such as citric acid within 10 cm soil depth. After that the beak of pH value increased quickly after tow hours from irrigation, at 20-40 cm soil depth and 20 cm horizontal distance from the emitter. After that the soil pH value decreased steadily up to six hours from irrigation, up to 90 cm depth and 60 cm horizontal distance from the emitter. Beyond four hours from irrigation, 40 cm horizontally far from the emitter and 40 cm soil depth the soil pH value found to be uniform through the time, horizontally distance and soil depth. Application of phosphoric acid with irrigation water changed the soil pH value form 8.66 in control treatment (without acid) to 6.81, 6.73 and 6.77 at the first time after irrigation, at 20 cm horizontal distance from the emitter and at 0-10 cm soil depth, respectively. The soil pH value changed from 6.81after irrigation to 7.94 after tow hours from irrigation. The change in the soil pH value between the first time after irrigation and after six hours from irrigation was 1.73 units. Whereas, the change in the soil pH value between below the emitter and 60 cm horizontally from the emitter was 1.95 units. While, the change in the soil pH value between soils surface layer (0-10 cm) and 90 cm soil depth was 1.79 units. Also, injection of phosphoric acid with irrigation water decreased soil pH value in the ryhizospher (0-40 cm depth) from 8.66 to 7.66. The lower pH in the ryhizospher zone is causally related to the enhanced H^+ secretion from roots in concentration with cell extension, (Weisenseel, et al., 1979) or to the net excretion of HCO_3^- and OH^- due to imbalance between cation and anion uptake, (Nye, 1986). Also, the evaluation of CO_2 by root respiration and release of low molecular weight root exudates (e.g. organic acids and amino acids especially citrate) are responsible.

Effect of citric or phosphoric acids on chemically available N, P and K in soil.

Data in table, 2 show that injection of either citric acid or phosphoric acid with drip irrigation to the sandy soil leads to a significant increase in the amount of chemically available nitrogen in the soil for both red radish and celery plants. The N concentration, at flowering stage was found mostly in the upper 0-40 cm soil layer. Such increases in the ryhizospher (0-40 cm depth) were 3.0 and 1.5 % in the soils treated with citric acid and phosphoric acid, respectively as compared with control treatment. The concentration of N below 0-10 cm depth decreased with increasing soil depth with application of any acid acid.

Also, results show that the available P increased with injected acid with irrigation water. Chemically available P trend to highly increase with injection of phosphoric acid compared with application of citric acid. Such increases in the ryhizospher (0-40 cm depth) reach 0.37 and 1.2% in the treatments of citric acid and phosphoric acid, respectively as compared with control. Such results could be explained according to release of organic acids which enhance the solubility and availability of P. Other possibilities could be: (a) Effect of organic acid on lowering the fixation of phosphorus through several mechanisms such as chelation and formation of organic complexes relatively available for plants (b) Effect of organic acid through coating the $CaCO_3$ particles as protective mechanism against precipitation and adsorption of various elements, (ELgala and Amberger, 1982., and El-Leboudi et al., 1988). On the other hand, the increase of available P with injection of acid with irrigation water treatment may be also due to the production of CO_2, thus formation of H_2CO_3, which contributes to phosphate solubility (Barsoom, 1998).

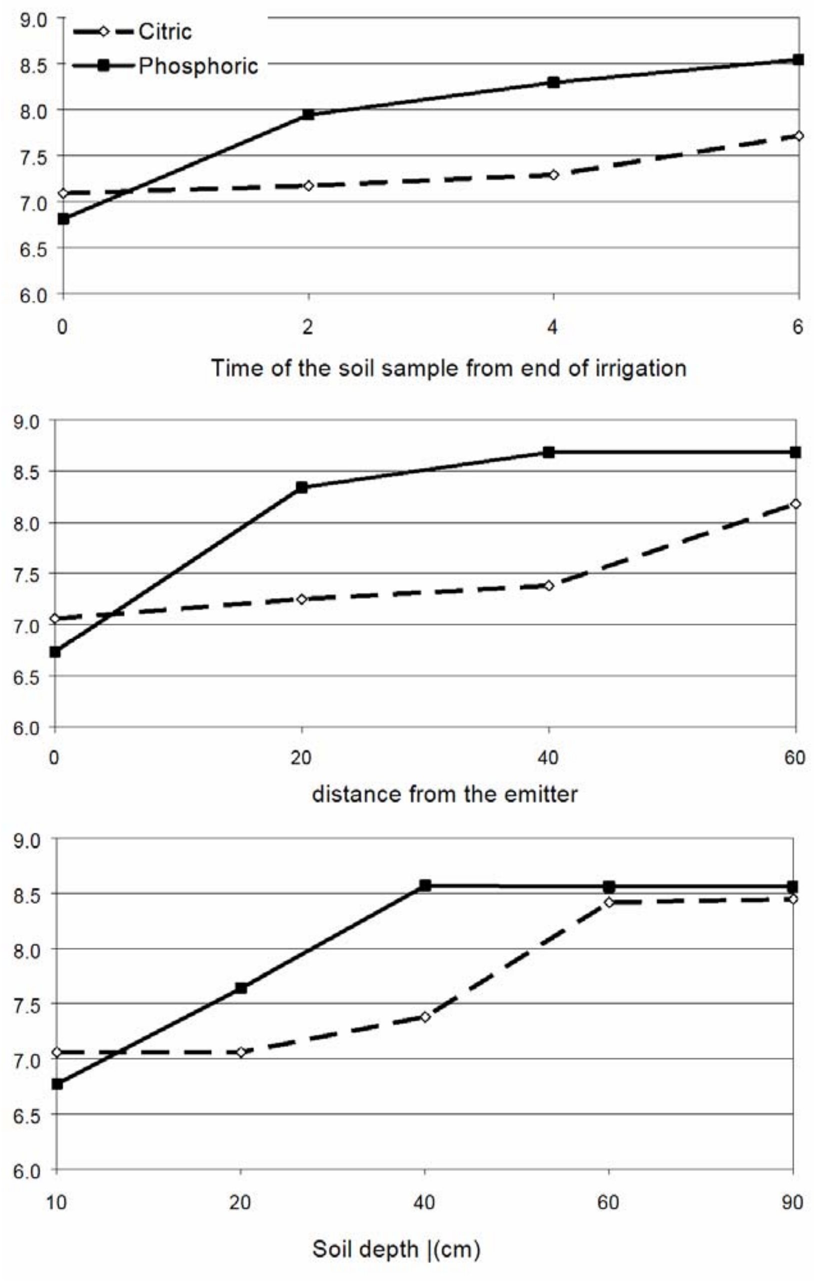

Fig. 1: Effect of time of sampling, destance horzontally from the emitter, soil depth and kinde ofacid on change of soil pH value.

The distribution of available P in the soil profile was almost similar to that of available N. The P concentration decreased towards the deeper layers up to 40 cm depth and then mentioned approximately a constant value till 60-90 cm depth. This may be due to the consistently wet and acidified condition around the emitter ensures that the conversion of complicated elements form such as organic and adsorption on colloidal to available form occurs in relatively drier zone, where more oxygen is available (Laher and Avnicmelech, 1980).

Table 2: Effect of acidification irrigation water by citric or phosphoric acids on chemically available some nutriments in the soil.

Soil depth (cm)	N	P	K	Fe	Mn	Zn	Cu	Co	Ni	Pb
	ppm									
	Citric acid									
0-10	139	11.4	139	27.7	17.78	11.4	8.51	1.16	0.99	1.16
10-20	121	8.46	131	30.6	24.52	16.9	9.04	1.68	1.11	1.81
20-40	79.7	4.77	118	36.4	19.85	17.6	8.82	2.17	1.71	2.63
40-60	31.6	3.27	109	19.9	9.89	6.82	4.35	1.05	0.78	1.15
60-90	24.4	1.95	104	15.3	6.02	4.08	2.13	0.88	0.63	0.86
	Phosphoric acid									
0-10	97.6	18.2	127	25.4	18.97	13.6	8.40	1.68	1.39	0.96
10-20	88.2	13.4	122	25.8	15.35	13.0	8.91	1.43	1.24	1.03
20-40	24.1	8.22	114	19.3	13.76	8.82	6.58	1.63	0.92	1.06
40-60	23.5	3.51	101	17.5	4.95	5.28	3.36	1.03	0.73	1.01
60-90	22.0	2.12	101	12.70	4.61	3.46	2.51	0.92	0.59	0.81
	Control									
0-10	33.4	8.82	118	17.7	11.9	8.53	7.53	1.83	1.47	2.28
10-20	28.3	6.52	116	17.9	9.63	8.18	7.48	1.55	1.23	2.13
20-40	22.2	2.68	107	13.4	8.63	5.53	4.13	1.08	0.96	1.05
40-60	20.7	2.17	98.9	14.9	4.81	3.31	2.11	0.98	0.76	0.96
60-90	18.1	1.86	91.5	12.1	4.29	3.23	1.73	0.62	0.67	0.78

Concerning the values of available K, data show similar trend to that obtained previously for N. Generally, the injection of citric or phosphoric acid increased the amounts of available K in the soil. Table, 2 shows that the amount of available K increased in the soil after injection of citric acid compared with injection of phosphoric acid with irrigation water. Such increases in the ryhizospher (0-40 cm depth) reach 13.8 and 0.6% in the treatments of citric acid and phosphoric acid, respectively as compared with the control. This could be due to citric acid supplies H^+ as well as citrate anion, which serves as a ligand. The citrate ligand may form an inner-sphere complex with surface most of elements, thereby facilitating its detachment and enhancing dissolution; in addition to complex formation in solution that enhances solubility. Moreover, surface colloidal may be exchanged by citrate, ligand exchange. As mentioned above citric acid treatment gave the highest extractable-elements from soil.

Chemically available Fe, Mn, Zn and Cu in the soil.

Data in table, 2 show that generally, the injection of citric acid or phosphoric acid increases the availability of Fe, Mn, Zn, and Cu as compared with control. This could be due to reducing of soil pH as well as increasing Fe solubility as a result to application of such organic group. Lindsay and Norvell (1972) reported that Fe availability in soil was controlled largely by soil pH increases and the redox potential, i.e., every unit decrease in soil pH increases the concentration of Fe^{3+}1000 times and the concentration of Fe^{2+} increases 100 times. The obtained results show that the amounts of DTPA- extractable Fe, Mn, Zn and Cu resulted from injection of phosphoric acid with irrigation water was less than citric acid. This may be due to the citrate anion can influence the solubility of such elements in soils in different ways causing an increase in the solubility of micronutrient cations by forming relatively stable organic complexes. However, the ability of the citric acid supplies H^+ which decreased soil pH value has also been reported. The mobilization or immobilization effect of organic materials is dependent on the soil reaction which influences the behavior of organic form of these nutrients, (Abou-Seeda et al., 1992). The micronutrients concentrations, at flowering stage were found mostly in the upper 0-40 cm soil layer. Such increases in the ryhizospher (0-40 cm depth) with injection of citric acid were 30.6, 19.7, 14.3 and 7.8 fold for Fe, Mn, Zn and Cu respectively as compared with control treatment. Where as, the increases of such elements with injection of phosphoric acid was 22.5, 10.0, 10.8 and 7.0 fold, respectively. The concentration of different micronutrients below 0-10 cm depth was found to increase with increase in soil depth up to 40 cm layer and then mentioned constant value till 90 cm depth. Kabata-Pendias and Pendias (1992) reported that both mineral and organic compounds of Fe are easily transformed in soils. Wasay et al., (1998) found that salts of citrate, tartarate and oxalate effectively removed Cu, Zn, Pb and Cd from the soil; citrate salts removed 80-99.9 % of all four metals within 24h at pH 2.3 to 7.5. McBride and Blasiak (1979) stated that the adsorption of Zn^{2+} can be reduced at lower pH by competing cations and these results in easy mobilization and leaching of Zn from light acid soils. At higher pH values, while an increase of organic compounds in soil solution become more evident, Zn-organic complexes may also account for solubility of this metal.

Solubility of Co, Ni and Pb in soil.

The behavior of heavy metals in soil depends not only on the level of contamination as expressed by the total content, but also on the form of the metal. Concerning chemically available Co, Ni and Pb in the studied soil as affected by injection of citric acid or phosphoric acid with irrigation water, tables, 2 show that DTPA-extractable of different heavy metals in the upper layer (0-10 cm) treated with citric acid were markedly decreased by about 42.6, 32.7 and 49.1% for Co, Ni and Pb, respectively compared with control treatment. Whereas, the same elements in the same layer decreased by about 2.0, 5.4 and 57.9 respectively with injected phosphoric acid with irrigation water. The concentrations of Co and Ni at lower depth (60-90 cm) remained almost similar and equal to the heavy metals concentrations in the control treatment. Bloomfield (1981) reported that soluble Ni may be quite mobile in soils with high complexation ability. Also, values of DTPA-extractable of Co and Ni in the ryhizospher (0-40 cm depth) generally increased with injection of citric acid compared with phosphoric acid. The concentration of Co and Ni in the soil treated with citric acid recorded 67 and 27% more than the control, respectively. Where as, the increases of such elements with injection of phosphoric acid reached 58 and 22 % more than the control, respectively. Whereas, Pb-DTPA-extractable was increased with injection of citric acid compared to the control or phosphoric acid treatment. This agrees with the findings of Petrovic et al., (1999) who reported that solid and aqueous phases is controlled by properties such as surface area, surface charge (induced by the formation of organic coatings on the surface), pH, ionic strength, and concentration of complexing ligands. Metal mobilization through precipitation and adsorption is also considered a common mechanism to decrease the hazards of heavy metal in contaminated soils (Malakul et al., 1998; Ma et al., 1993).

Concentration of studied elements in shoots and roots of red radish and celery vegetables crops.

Concentrations of NPK in shoots and roots of red radish and celery plants as affected by type of injected acid are shown in table, 3. Data indicate an increase in NPK concentrations in red radish and celery shoots with injection of acid with irrigation water as compared to the control treatment. The obtained results indicate also, the superiority of citric acid treatment relative to phosphoric acid especially with N ad K. Generally the N concentration increased in shoots of red radish and celery plants with injection of citric acid by about 2.1 and 0.9 fold that of control treatment.

In general, heavy metals concentrations in red radish and celery shoots and roots reflect the amounts of the chemically available metals present in the cultivated soil, which in turn are highly affected by type of acid injected with irrigation water. However, the applied acids tended to increase concentration of heavy metals in shoots and roots of red radish and celery plants compared to the control treatment. Data show also that concentrations of various heavy metals in shoots of red radish and celery plants were markedly lower compared with those in roots. Several authors have shown that heavy metals tend to accumulate in roots of plants, among them Zhang and Wang (1991), Wang *et al.,* (1997) and Elbordiny (2001). Generally injection of citric acid with irrigation water was more effective than phosphoric acid on concentration micronutrients and heavy metals in red radish and celery shoots and roots. Pulford (1982) reported that the affinity between Fe^{3+} and H_2PO^{-4} ions is known to be great and therefore the precipitation of $FePO^4$. $2H_2O$ can easily occur under favorable conditions. Furthermore, P anions compete with the plant roots for Fe and thus P interferes with Fe uptake and with the internal Fe transport. Abbas (1993) reported that alkalinity of soil reaction, retention of elements by mineral and organic colloids, competition between heavy metals for the same site of adsorption and limited translocation of these elements to plant tops are all factors contributing to reducing uptake of the heavy metals and eliminating plant toxicities.

Table 3: Effect of citric acid and phosphoric acid injected with irrigation water on the macro, micronutrients and heavy metals concentrations in the shoots and roots of red radish and celery plants

Treatment	N		P		K		Fe		Mn		Zn		Cu		Co		Ni		Pb	
	Shoots	Roots	Shoots	Roots	Shoots	Roots	Shoots	Roots	Shoots	Roots	Shoots	Roots	Shoots	Roots	Shoots	Roots	Shoots	Roots	Shoots	Roots
	ppm																			
	Red radish																			
Citric	2.67	1.31	0.50	0.96	1.82	2.35	192	285	16.8	27.9	21.3	38.7	10.1	21.1	2.54	3.30	2.15	3.79	1.96	5.22
Phosphoric	1.31	0.54	0.96	1.26	1.32	1.66	169	232	12.5	19.4	19.7	32.8	8.5	19.0	1.38	1.71	1.64	2.92	1.01	3.65
Control	0.87	0.29	0.25	0.74	0.52	0.88	109	166	6.7	13.1	12.6	26.2	6.1	13.8	0.32	1.57	0.83	1.29	0.53	0.87
	Celery																			
Citric	1.83	0.80	0.65	1.02	1.89	1.48	354	418	25.5	48.8	19.8	33.9	14.0	18.9	2.39	3.89	1.92	2.87	1.74	1.88
Phosphoric	1.42	0.79	0.87	1.04	1.81	1.50	236	292	20.4	36.1	17.6	26.4	11.4	14.5	0.97	1.61	1.14	2.26	1.13	1.34
Control	0.96	0.54	0.48	0.61	0.98	0.78	194	250	16.9	29.4	15	19.3	7.3	11.2	0.73	0.91	0.42	1.24	023	0.65

Grain yield and concentration of studied elements in red radish and celery vegetables crops:

Data presented in table, 4 indicate that the amounts of grain yield of both radish and celery vegetables crops increased due to the injection of citric acid and phosphoric acid as compared with the control. Such increases record 40 and 20% for radish with the injection of citric acid and phosphoric acid, respectively. Whereas, grain yield of celery increases were 2.3 and 1.2 fold with the injection of citric acid and phosphoric acid compared to the control, respectively. Such increases could be due to the positive effect of injection acid with irrigation water on improving nutritional status and nutrients release and hence their availability to the growing plants. The injection of citric acid was generally superior as compared with that of phosphoric acid.

Concentration of Fe, Mn, Zn, Cu, Co, Ni and Pb in both red radish and celery vegetables crops as affected by injected two acids with irrigation water were shown in table 4. Data illustrate that the injection of two acids increased concentrations of different heavy metals in the grains, compared to the control treatment. The highest increase resulted from injection of citric acid with irrigation water for cultivated red radish, which recorded 0.7, 1.4, 2.3, 1.6, 4.5, 1.7 and 1.8 fold over the control for Fe, Mn, Zn, Cu, Co, Ni and Pb, respectively. The increases in concentration of different heavy metals in red radish due to injection of citric acid may be related to reducing soil pH, consequently increasing solubility and availability of some nutrients via plant roots absorption.

Regarding the ability of two plants on accumulation of different heavy metals in grains yield, celery plants were more efficiency on accumulation heavy metals compared to red radish plants. This may be due to the celery plants were more efficiency on transfer different heavy metals from the soil solution to shoots and other organs than the red radish plants. Such increases in the Fe, Mn, Zn, Cu, Co, Ni and Pb reach 20.4, 22.7, 86.1, 43.6, 85.8,50.7 and 85.8 in the grains yield of celery crop, respectively, as compared with grains yield of red radish crop. Kabata-Pendias and Pendias (1992) who reported that different micronutrients uptake and transport between plant organs are highly affected by several plant and environmental factors, of which soil pH, concentration of Ca and P and ratio of several heavy metals are most pronounced. Norvell *et al.,* (1987) who reported that the specific effects of P on the concentration of Zn^{2+} in the solution were small and observed only when the Zn^{2+}content was raised previously by Zn fertilizers. However, the addition of P also caused small decreases in the concentrations of other divalent cations in the solution. Das (2000) observed that application of phosphate precipitated Cu as its phosphates, beside the Cu-P antagonisms effect that occur in root media as phosphates have a strong tendency to adsorb Cu.

Table 4: Effect of citric acid and phosphoric acid injected with irrigation water on the grain yield and nutrients concentrations in grains of red radish and celery plants

Treatment	Grain yield,	Fe	Mn	Zn	Cu	Co	Ni	Pb
	kg/fed	ppm						
	Red radish							
Citric	19.7	10.14	1.50	1.94	2.36	1.20	1.42	1.69
Phosphoric	17.4	8.36	1.23	1.86	2.10	0.93	0.98	1.32
Control	14.2	6.07	0.62	0.59	0.91	0.22	0.53	0.61
	Celery							
Citric	37.1	12.21	1.84	3.61	3.39	2.23	2.14	3.14
Phosphoric	25.2	8.43	1.34	2.84	3.21	1.42	1.50	2.02
Control	11.3	6.81	0.80	0.73	0.79	0.22	0.64	0.78

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تأثير تحميض المياه على سلوك بعض العناصر فى الاراضى التى تروى بمياه صرف صناعى معالج

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الهدف من هذا البحث هو دراسة تأثير حقن اى من الستريك او الفسفوريك من خلال شبكة الرى بالتنقيط على سلوك بعض العناصر فى الارض التى تروى بمياه صرف صناعى معالج . ولانجاز ذلك اقيمت تجربة حقلية فى مدينة السادات التابعة لمحافظة المنوفية بمصر حث تم دراسة سلوك بعض المغذيات الكبرى والصغرى وبعض العناصر الثقيلة فى التربة وكذلك تركيز تلك العناصر فى المجموع الخضرى ومحصول الحبوب لنباتى الفجل الاحمر والكرفس نتيجة حقن حمض الستريك او الفوسفوريك خلال شبكة الرى بالتنقيط . وكانت اهم النتائج المتحصل عليها مايلى:

أدى استخدام حمض الستريك الى انخفاض قيم درجة حموضة الارض بشكل واضح بعد الحقن مباشرة مقارنة باستخدام حمض الفوسفوريك واسفل النقاط ولعمق 10 سم ثم بدات قيم درجة الحموضة فى الزيادة تدريجيا مع مرور الوقت وبالبعد عن النقاط او بزيادة عمق العينة. أدى استخدام اى من حمض الستريك او الفوسفوريك الى زيادة تركيز كل من النيتروجين والبوتاسيوم خاصة فى منطقة انتشار الجذور (صفر-40 سم) وكان مقدار الزيادة فى النيتروجين والبوتاسيوم عند الحقن بالستريك او الفوسفوريك هى 3 و % 1.5 للنيتروجين و 13.8 و 0.6 % للبوتاسيوم على الترتيب مقارنة بمعاملة الكنترول. على الجانب الاخر فان استخدام حمض الفوسفوريك فى الحقن ادى الى زيادة تركيز الفوسفور فى منطقة انتشار الجذور مقارنة بحمض الستريك حيث وصل مقدار الزيادة فى تركيز الفوسفور فى منطقة انتشار الجذور الى 0.37 و 1.2 % مع استخدام الستريك والفوسفوريك على الترتيب مقارنة بمعاملة الكنترول. أدى استخدام حمض الستريك الى زيادة تركيز العناصر الغذائية الصغرى فى منطقة انتشار الجذور حيث وصل تركيز كل من الحديد والمنجنيز والزنك والنحاس الى 30.6و 19.7و 24.3و 7.8 ضعف الموجود فى معملة الكنترول على الترتيب. فى حين ادى استخدام حمض الفوسفوريك الى زيادة تلك العناصر بمقدار 22.5و 10.0و 10.8و 7.0 ضعف الموجود بعاملة الكنترول. كذلك فان استخدام حمض الستريك ادى الى زيادة تركيز الكوبالت والنيكل بمقدار 67و 27% مقارنة بالكنترول فى حين ان استخدام الفوسفوريك ادى الى زيادة تلك العنصرين بمقدار 58 و 22 % مقارنة باكنترول على الترتيب. اما بخصوص الرصاص فقد زادت كميتة عند الحقن بالستريك مقارنة بالكنترول والفوسفوريك. ادى استخدام اى من الحمضين الى زيادة تركيز المغذيات فى المجموع الخضرى للفجل الاحمر والكرفس مقارنة بالكنترول.مما ادى الى زيادة محصول التقاوى حيث وصلت الزيادة فى محصول التقاوى للفجل الاحمر الى 40 و 20 % عند الحقن بالستريك او الفوسفوريك على الترتيب. فى حين كانت الزيادة فى تقاوى الكرفس 2.3 و 1.2 % عند الحقن بالستريك او الفوسفوريك على الترتيب. ادى استخدام الستريك الى زيادة تركيز العناصر الثقيلة فى الحبوب لكلا النباتين حيث وصل تركيزها الى 0.7و 1.4و 2.3و 1.6و 4.5و 1.7و 1.8 من عناصر الحديد والمنجنيز والزنك والنحاس والكوبالت والنيكل والرصاص مرة قدر الموجود بالكنترول على الترتيب.