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Reclaimed wastewater: Impact on soil–plant system under tropical conditions

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ABSTRACT

This study investigated the ionic speciation of reclaimed urban wastewater (RWW), and the impact of increasing RWW irrigation rates on soil properties and plant nutrition under field conditions. Most RWW elements (>66%) are readily available as NH_4^+, Ca^{2+}, Mg^{2+}, K^+, SO_4^{2-}, Cl^-, H_3BO_3, Mn^{2+} and Zn^{2+}, but in imbalanced proportion for plant nutrition. Lead, Cd, Cr and Al in RWW are mostly bounded with DOM or OH^-. Irrigation with RWW decreased soil acidity, which is beneficial to the acidic tropical soil. Although RWW irrigation builds exchangeable Na^+ up, the excessive Na^+ was leached out of the soil profile after a rainy summer season (>400 mm). Benefits of the disposal of RWW to the soil under tropical conditions were discussed, however, the over irrigation with RWW (>100% of crop evapotranspiration) led to a nutritional imbalance, accumulating S and leading to a plant deficiency of P and K.

1. Introduction

Agriculture is estimated to withdraw two thirds of the worlds' fresh water, thus accounting for 90% of the total water consumption [1] Within this context, increasing attention has been directed to the reuse of reclaimed urban wastewater (RWW) [2,3] for agricultural proposes. Besides saving fresh water, the irrigation with RWW has economical advantages and environmental benefits which help promote sustainability and include: (i) reduce water withdrawals from pristine sources [2] (ii) recycling nutrients; (iii) saving energy used for production, transport and application of mineral fertilizers; (iv) increasing water availability for crop irrigation all year long; (v) reducing or eliminating the discharge of nutrients in water bodies and subsequently preventing eutrophication of surface waters; and (vi) promoting small but steady supply of nutrients to crop plants, like slow-release fertilizers.

Most studies regarding RWW irrigation focused on contamination with heavy metals [4,5] and xenobiotic organic compounds [5,6] in soil–plant systems. However, many questions remain unanswered with regard to RWW speciation and to the adverse impact of the disposal of high amounts of RWW on soil properties and plant nutrition, specially under tropical conditions. In Brazil, RWW irrigation on sunflower (*Helianthus annuus* L.) and maize (*Zea mays* L.) for two years increased soil pH by 0.5–1.0 unit, and reduced total acidity by more than 50% [6]. Irrigating sugarcane (*Saccharum* spp.) with RWW resulted in temporary accumulation of sodium (Na), but exchangeable sodium (Na^+) was leached out of the soil profile after a rainy season (90 mm) [7]. Researches [8] reported that RWW irrigation makes it possible to save ~32 to ~81% of mineral N in the production of Tifton 85 bermuda grass (*Cynodon dactylon* Pers. x *C. nlemfuensis* Vanderyst) under tropical conditions. Other studies [9] reported that nitrogen (N) and phosphorus (P) contents in a pasture soil irrigated with RWW (2300 mm $year^{-1}$) for two years increased by 700 and 280 kg ha^{-1} $year^{-1}$ respectively. After irrigation with RWW during three years, coffee (*Coffea arabica* L.) plant contents of P, N and S dropped to deficient values [10].

The disposal of RWW to the soil seems to be economically feasible. However, researches [11] evaluated three irrigation rates – 1100, 1500 and 1850 mm $year^{-1}$ –, and observed that plants irrigated with the highest rate displayed smaller trunk diameter and lower height. These results suggest possible negative impacts of RWW overirrigation rates on soil–plant systems. Regarding the nutrition of plants cultivated in soil receiving RWW after three years of irrigation, differences in N and P concentrations were found at the 0–15-cm layer of an Entisol in Florida [12]. Calcium (Ca) and boron (B) amounts found in RWW could meet

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the requirements of orchard trees [13]. Leaf tissue of mature citrus trees in Florida showed optimal concentration range of N (2.2–2.5%), P (0.12–0.16%) and K (1.2–1.7%) when irrigated with RWW [14]. After four years of RWW irrigation, the level of P in the soil increased by 25% and plant growth improved; no additional P from fertilizers was required [15].

Adverse impacts of RWW disposal to the soil is dependent on RWW quality. Consequently, it is fundamental to determine the nutrients and heavy metals ionic species in RWW to predict their bioavailability, as previously investigated for sewage sludge and industrial wastewater [16,17]. However, minimal information is available regarding ionic speciation of nutrients and contaminants, which is essential for environmental management and balanced supply of nutrients to crops.

Due to the increasing availability of RWW and the costs of disposal, overirrigation with RWW is often an attractive alternative. However, the impacts of overirrigation rates on soil quality and plant nutrition have not been well addressed. In this context, this work investigated: (i) the chemical characterization of RWW regarding the ionic speciation of nutrients and toxic elements; and (ii) the impacts of increasing RWW irrigation rates on soil properties and plant nutrition under tropical conditions.

2. Materials and methods

2.1. Study area

The field experiments were carried out in Piracicaba, São Paulo State, Brazil (22°43′04″ S; 47°37′10″ W, 554 m), on a Rhodic Paleudult soil, close to the SEMAE (Municipal Service for Water and Wastewater) Wastewater Treatment Plant (WWTP). The region has humid subtropical climate with a mean temperature ranging from 17 °C to 38 °C, and annual rainfall of 1253 mm.

Untreated surface soil layer (0–20 cm) displayed the following chemical properties: active acidity (pH_{CaCl2}) = 5.3; labile P = 11.8 mg dm^{-3} [18]; labile K^+, Ca^{2+} and Mg^{2+} = 1.5, 11.0 and 5.1 mmol$_c$ dm^{-3} respectively [18]; total acidity (H + Al) = 19.8 mmol$_c$ dm^{-3}; aluminum saturation = 5.3%; sodium (Na) [19] = 0.1 mmol$_c$ kg^{-1}; cation exchange capacity (CEC) at pH 7.0 = 37.6 mmol$_c$ kg^{-1}; and base saturation (V) = 46%; sulphur (S) = 7.1 mg kg^{-1}; boron (B) = 0.3 mg kg^{-1} [18]; copper (Cu), iron (Fe), manganese (Mn) and zinc (Zn) = 1.0, 41.4, 62.1 and 1.0 mg kg^{-1} respectively [20]. Soil granulometric fractions were of 73.0%, 10.8% and 16.2% for sand, silt and clay, respectively. Based on soil analysis, in November 2006 the soil was limed to 70% base saturation.

2.2. Crop and irrigation application and experimental design

In February 2007, 500 g $CaCO_3$ m^{-1} and ~26 g P m^{-1} were applied to the furrow before transplanting 300 citrus 'Valência' [*Citrus sinensis* (L.) Osbeck] nursery trees on citrumelo 'Swingle' (*Citrus paradisi* Macf. x *Poncirus trifoliata* Raf.) with a 6 x 4-m spacing.

It has been reported that RWW irrigation could provide 65% of the total N need for citrus [21]. Based on this reference, only 50% of the recommended N was applied as NH_4NO_3 – 50 and 110 g N plant^{-1} in the first and second year, respectively. A full amount of K needed was applied as KCl – 22 and 110 g K plant^{-1} in the first and second year, respectively [22]. Prior to application, KCl and NH_4NO_3 were homogenized and then distributed at a 50-cm distance from the tree center. The application was performed three times per year (September–October, December–January, March–April), from 2007 to 2009.

The experimental design comprised three randomized blocks with five treatments. Each of the fifteen plots contained twenty plants, six of them located centrally and fourteen at the border. Four RWW irrigation rates were applied based on the crop evapotranspiration (ETc) [23]: 100% ETc, 125% ETc, 150% ETc and 200% ETc, plus the control treatment (CT) (without irrigation). These irrigation rates with RWW, based on the ETc, were equivalent to 350, 437, 525, 700 and 0 mm RWW year^{-1}, respectively. The need for irrigation was determined every three days. Citrus plants were irrigated with RWW from September 2007 to July 2009.

The RWW was collected from the SEMAE-WWTP and previously treated by an upflow anaerobic sludge blanket (UASB) system, filtered through a sand filter (Hidrosolo^{TM}, model FA7 super) and disinfected using a 45-W ultraviolet (UV) reactor.

A self-compensating drip irrigation system (Netafim^{TM}, model RAM) with ten emitters per plant (23 L h^{-1} plant^{-1}) was built. Two lines of drippers were installed, one for each side of the trees, at a 20-cm spacing from the trunk.

2.3. Soil sampling and analysis

Soils samples were collected at two times using a dutch auger: in September 2008, after the winter season (12 months of treatment), and in March 2009, after the summer season (18 months of treatment). Six subsamples were collected at a 30 cm distance from each of the six central trees in each plot to form a composite sample. They were collected from soil layers 0–10, 10–20, 20–40, 40–60, 60–80, and 80–100 cm.

Air-dried soil samples were used for determining active acidity – pH using a $CaCl_2$ (0.01 mol L^{-1}) solution at a 1:2.5 soil:solution ratio. Total acidity was determined using a pH 7.0 SMP buffer solution [18]. Sodium and K^+ were extracted using Mehlich-1 solution [19] (1:10) and analyzed by flame-emission photometry (FEP) (Corning model 400, Corning Scientific Ltd., England). Magnesium, Ca and P were extracted using the exchangeable resin method (1:10) [18]. Calcium and Mg concentrations in the extracts were determined using flame atomic absorption spectrophotometry (F-AAS) (Perkin-Elmer, model AAS-700, Norwalk, CT, USA) and P concentration was determined using a spectrophotometer (λ = 720 nm) (Klett Summerson photoelectric colorimeter, model 900-3, NY, USA). Sulfate was extracted from the soil using a $Ca(H_2PO_4)_2{\cdot}H_2O$ (0.01 mol L^{-1}) solution (1:12,5), and sulfate concentration in the extract was determined turbidimetrically using a spectrophotometer (λ = 420 nm) [18]. Total N was determined using a CN analyzer (Carlo Erba, model EA 1110, Milan, Italy). Aluminun, Cu, Fe, Ni, Zn, Cr, Pb in soil were extracted using DTPA solution at pH 7.2 [20] and determined by inductively coupled plasma optical emission spectrometry (ICP-OES, Ultima II, JY Horiba Group, Edison, NJ, USA). Available B in soil was extracted with hot water [24] and the extracts were analyzed for B using the ICP-OES.

2.4. Reclaimed wastewater sampling and analysis

Treated RWW was collected from the drippers monthly from August 2007 to June 2009. RWW electrical conductivity (EC) and pH were determined using a pH/conductivity meter (model 220, Denver Instrument Inc., Denver, USA). Alkalinity was determined by titration using H_2SO_4 (0.02 mol L^{-1}). For other analyses, RWW subsamples were prepared separated and analyzed in three groups: (i) for dissolved organic carbon (DOC), an aliquot of RWW was filtered through a 0.45-μm GF/F glass fiber filter (Whatman^{TM}) and preserved using $HgCl_2$ at 5 °C, and dissolved organic carbon was analyzed using high-temperature catalytic combustion (Shimadzu TOC-500-A, Kyoto, Japan); (ii) for the analysis of macronutrients and micronutrients and heavy metals, an aliquot of subsamples was filtered through a 0.22-μm acetate cellulose membrane filter (Millipore^{TM}), and the filtrate was analyzed for the concentrations of P, K, Ca, Mg, S, Na, B, Cu, Fe, Mn, Ni, Zn, Al, Cd, Cr and Pb by inductively coupled plasma optical emission spectrometry (ICP-

OES, Jobin Yvon – JY ULTIMA 2000 – Longjumeau, France); and (iii) for measurement of dissolved inorganic carbon (DIC), Cl^-, NO_3^- and NH_4^+, an aliquot of the subsamples was filtered through a 0.22-μm acetate cellulose membrane filter and preserved with thymol (2-isopropyl-5-methylphenol) at 5 °C prior to analysis. Dissolved inorganic carbon was determined by high-temperature catalytic combustion. The concentrations of Cl^-, NO_3^- and NH_4^+ were analyzed by spectrophotometry (FIAstar model 5000 – FOSS – Höganäs, Sweden). The ionic speciation of nutrients and heavy metals in the RWW was performed using the *visual Minteq* software version 2.61 [25].

2.5. Leaf sampling and analysis

Leaves of the six central trees in each plot were sampled in May 2009. Four leaves of each tree were collected from four to six month-old spring flush nonfruiting twig. The leaves were rinsed in tap water to remove solid particles and then washed in a low-concentration detergent solution (phosphorus free), rinsed in deionized water, soaked in HCl solution (1%) for 1 min and rinsed four times in deionized water. Then, the leaves were dried in a forced-air oven at 70 °C for three days and ground in a ball mill (4 canister, model 4200, Kleco-Garcia Machine, Visalia, CA, USA).

A portion of the oven-dried leaf samples (0.4 g) was digested using nitric and perchloric acid on a block digester (AIM 500-c, AI Scientific, Brisbane, Australia) [26]. The concentrations of P, K, Ca, Mg, S, B, Cu, Fe, Zn, Al, Cd, Cr, Ni, Pb and Na were determined using ICP-OES. Total N in plant samples was determined using a CN analyzer (Carlo Erba, model EA 1110, Milan, Italy).

2.6. Statistical analysis

For RWW variables the mean and the standard error (±SE) were calculated. Response surfaces were used for soil analyses. Reclaimed wastewater irrigation rates (I) and the soil depth (D) were considered as independent variables in correlation with each of the dependent ($\hat{Y}$) variables (pH_{CaCl2}, H + Al, N, P, K, Ca, Mg, S, B, Cu, Al, Fe, Ni, Zn, Cr, Pb and Na) according to the $\hat{Y} = b_0 + b_1 I + b_2 D + b_3 I^2 + b_4 I \times D + b_5 D^2$ model. The maximum and minimum points were calculated as $\partial\hat{f}/\partial X$ when necessary.

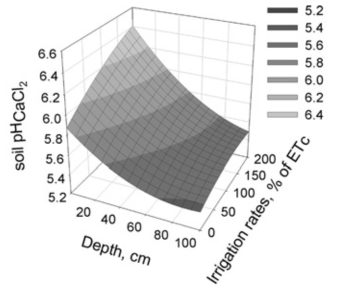
Quadratic and linear regression were performed to examine the relationships between the elements determined in leaf tissue (P, K, Ca, Mg, S, B, Cu, Fe, Zn, Al, Cd, Cr, Ni, Pb) and RWW irrigation rates. The best models for soil and plant analysis were chosen based on statistical significance ($p < 0.05$) and coefficient of determination (R^2). Only the dependent variables with significant differences were discussed. Time's effect was discussed according to the model when necessary. Prior to statistical analysis of soil and plant variables, the normality of the data was tested using histograms and the Kolmogorov–Smirnov test [27]. All statistical analyses were made using the SAS program version 9.1.2 [28].

3. Results

3.1. Reclaimed wastewater chemical properties

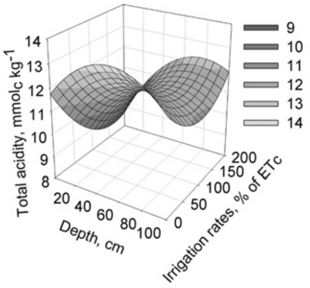
Generally speaking, RWW had decent quality for agricultural use. All the measured parameters were adequate according to the standards established by USEPA and previous studies [29–34] (Table 1). Reclaimed wastewater pH, EC, macronutrients (NO_3^-, NH_4^+, PO_4^{3-}, K, Ca, Mg and SO_4^{2-}), micronutrients (B, Cu, Fe, Mn, Ni, Zn) and toxic elements (Al, Cd, Cr and Pb) concentrations were all at the acceptable levels according to the reference limits (Table 1).

More than 66% of their total concentration in both the macronutrients and micronutrients were in the form(s) of readily available for plant uptake as NO_3^- (99%), NH_4^+ (98%), HPO_4^{2-} and/or H_2PO^{4-} (91%), H_3BO_3 (99%), Cl^- (99%), Zn^{2+} (66%). However, a variable proportion of metals was bound to dissolved organic matter (DOM): Cu-DOM (65%), Zn-DOM (20%), Cd-DOM (12%) and Pb-DOM (82%) (Table 1); or bound with OH^-: $Al(OH)_4^-$ (87%) and $CrOH^+$ (99%),



$$\widehat{pH} = 5.87E{+}00 + 3.92E{-}04 \times I - 1.11E{-}02 \times D - 5.63E{-}06 \times I^2 - 2.13E{-}05 \times I \times D + 6.20E{-}05 \times D^2;\quad R^2 = 0.493^{***}$$

Fig. 1. Response of soil pH at different depths to increasing rates of RWW irrigation for 12 months. The irrigation rates of 100% ETc, 125% ETc, 150% Etc, 200% ETc, and the control treatment (CT) (without irrigation) were equivalent to 350, 437, 525, 700 and 0 mm $year^{-1}$ of irrigation with RWW. (***) significant at $P < 0.0001$.



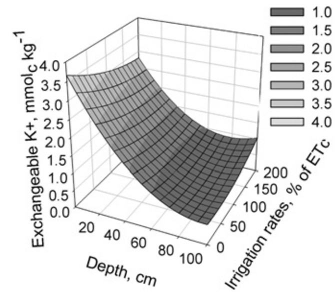
$$\widehat{H+Al} = 1.17E{+}01 - 3.91E{-}02 \times I + 6.66E{-}02 \times D + 1.20E{-}04 \times I^2 + 1.39E{-}04 \times D \times I - 6.22E{-}04 \times D^2;\quad R^2 = 0.193^{*}$$

Fig. 2. Response of soil total acidity (H + Al) at different depths to increasing rates of RWW irrigation for 12 months. The irrigation rates of 100% ETc, 125% ETc, 150% Etc, 200% ETc, and the control treatment (CT) (without irrigation) were equivalent to 350, 437, 525, 700 and 0 mm $year^{-1}$ of irrigation with RWW. (*) significant at $P < 0.05$.

3.2. Reclaimed wastewater effects on soil properties

Compared with CT, plants irrigated with RWW at 200% of ETc generally decreased the active (−8.5%) (Fig. 1) and total acidity (−25%) (Fig. 2) as well as the concentration of K (−7.5%) (Fig. 3), but increased Na (+500%) (Fig. 4) in soil at the 20 cm depth.

The pH, or the active acidity, of the entire soil profile was raised in response to increasing RWW irrigation rates. This effect was pro-



$$\hat{K} = 3.66E{+}00 - 7.81E{-}03 \times I - 6.33E{-}02 \times D + 1.74E{-}05 \times I^2 + 6.68E{-}05 \times D \times I + 3.23E{-}04 \times D^2;\quad R^2 = 0.736^{*}$$

Fig. 3. Response of exchangeable K^+ concentration in soil at different depths to increasing rates of RWW irrigation for 12 months. The irrigation rates of 100% ETc, 125% ETc, 150% Etc, 200% ETc, and the control treatment (CT) (without irrigation) were equivalent to 350, 437, 525, 700 and 0 mm $year^{-1}$ of irrigation with RWW. (*) significant at $P < 0.05$

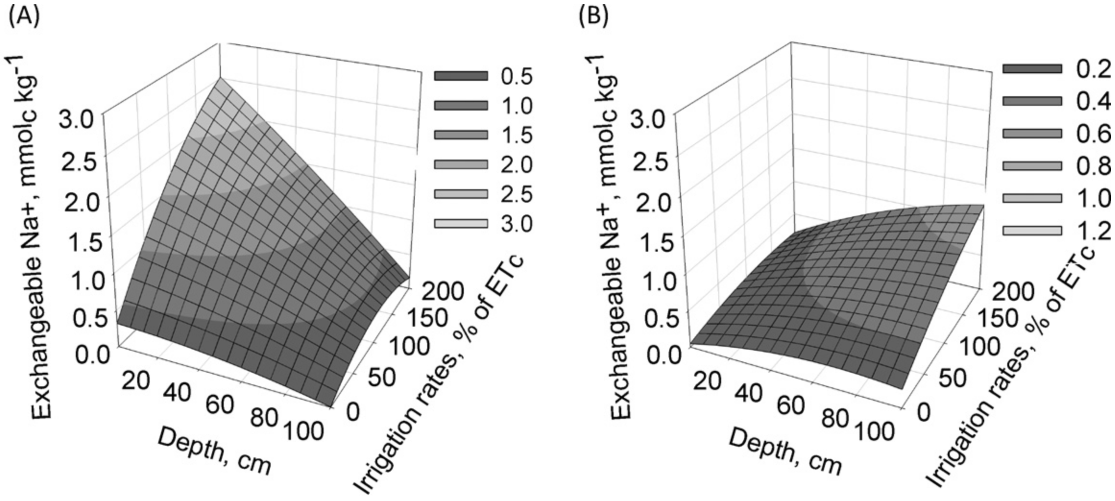
Table 1
Mean values (±standard error) of quality parameters and ionic speciation of reclaimed wastewater (RWW) from the wastewater treatment plant (SEMAE) at Piracicaba, SP, Brazil.

Parameters	Units	Average ± SE	Limits	Distribution of main ionic species (e)
pH	–	7.17 ± 0.03	8.1 [29]	–
EC[a]	μS cm^{-1}	599.90 ± 15.19	2000 [32]	–
DIC[b]	mg L^{-1}	132.70 ± 10.63	–	–
DOC[c]	mg L^{-1}	11.43 ± 1.74	200 [28]	[f]DOM (69%), Ca-DOM (27%)
RAS[d]	(mmol$_c$/L)$^{1/2}$	2.06 ± 0.20	7.9 [31]	–
Na:Ca	–	3.10 ± 0.48	–	–
Alkalinity $CaCO_3^-$	mg L^{-1}	93.87 ± 3.76	150 [31]	HCO_3^- (87%); $H_2CO_{3(aq)}$ (12%)
N-NO_3^-	mg L^{-1}	0.12 ± 0.04	50 [33]	NO_3^- (99%); $CaNO_3^+$ (0.06%)
N-NO_2^-	mg L^{-1}	0.01 ± 0.003	10 [31]	NO_2^- (99%)
N-NH_4^+	mg L^{-1}	19.75 ± 1.20	40 [31]	NH_4^+ (98%); $NH_4SO_4^-$ (0,87%)
P-PO_4^-	mg L^{-1}	4.44 ± 0.59	30 [33]	HPO_4^{2-} (49%); $H_2PO_4^-$ (42%)
Cl	mg L^{-1}	43.76 ± 5.12	360 [31]	Cl^- (99%); NaCl (0.06%)
Ca	mg L^{-1}	14.12 ± 1.76	120 [31]	Ca^{2+} (81%); $CaSO_{4(aq)}$ (11%)
Mg	mg L^{-1}	6.00 ± 0.45	50 [31]	Mg^{2+} (88%); $MgSO_{4(aq)}$ (10%)
Na	mg L^{-1}	34.70 ± 2.82	200 [29]	Na^+ (99%); $NaSO_4^-$ (0.4%)
K	mg L^{-1}	10.06 ± 0.96	40 [31]	K^+ (99%); KSO_4^- (0.5%)
S-SO_4^{2-}	mg L^{-1}	38.35 ± 6.26	500 [29]	SO_4^{2-} (93%); $CaSO_{4(aq)}$ (3%)
Al	mg L^{-1}	0.081 ± 0.024	5 [26–28]	$Al(OH)_4^-$(87%); $Al(OH)_{3(aq)}$ (11%)
B	mg L^{-1}	0.258 ± 0.073	0.75 [33]	H_3BO_3 (99%)
Cd	mg L^{-1}	0.003 ± 0.001	0.01 [27,30]	Cd^{2+} (66%); Cd-DOM (12%)
Cr	mg L^{-1}	0.020 ± 0.005	0.1 [30]	$CrOH^+$ (99%)
Cu	mg L^{-1}	0.047 ± 0.015	0.2 [26,27]	Cu-DOM (65%); Cu^{2+} (9%)
Fe	mg L^{-1}	0.391 ± 0.118	5 [29]	$Fe(OH)^{2+}$(99%); $Fe(OH)_{3(aq)}$(0.7%)
Mn	mg L^{-1}	0.050 ± 0.125	0.1 [26,27,30]	Mn^{2+}(86%); $MnSO_{4(aq)}$(9%)
Ni	mg L^{-1}	<0.001 ± <0.001	0.2 [26,27,30]	–
Pb	mg L^{-1}	0.048 ± 0.0130	5 [30]	Pb-DOM(82%); Pb^{2+} (5%)
Zn	mg L^{-1}	0.099 ± 0.0360	2 [26,30]	Zn^{2+} (66%); Zn-DOM (20%)

[a] Electrical conductivity.
[b] Dissolved inorganic carbon.
[c] Dissolved organic carbon.
[d] Sodium adsorption ratio: SAR = $[Na^{2+}]/([Ca^{2+}]+[Mg^{2+}])^{1/2}$.
[e] Charge difference of 3.53% estimated by visual Minteq ver 2.61.
[f] Dissolved organic matter.

nounced at the surface layer (0–20 cm) and became less in deeper soil layers (>30 cm) (Fig. 1). After one year of irrigation with RWW at 100% ETc, soil pH_{CaCl2} at the surface layer increased by 0.5 unit as compared with CT.

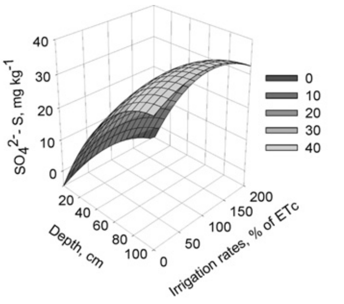
The total acidity ($H^+ + Al^{3+}$) at the surface layer (0–20 cm) decreased from 12 mmol$_c$ kg^{-1} at CT to 9 mmol$_c$ kg^{-1} at 200% ETc after RWW irrigation. According to the response function at the surface soil, the irrigation with RWW at 150% ETc for 12 months



(A) $\widehat{Na}$ = 3.23E-01 + 1.66E-02 x I - 6.64E-04 x D - 2.81E-05 x I^2 – 1.02E-04 x D x I - 2.52E-05 x D^2; R^2 = 0.852***

(B) $\widehat{Na}$ = 4.72E-02 + 2.58E-03 x I + 6.86E-03 x D - 8.87E-06 x I^2 + 4.08E-05 x D x I - 4.08E-05 x D^2; R^2 = 0.685***

Fig. 4. Response of exchangeable Na^+ concentration in soil at different depths to increasing rates of RWW irrigation for 12 months (A) and 18 months (B). The irrigation rates of 100% ETc, 125% ETc, 150% Etc, 200% ETc, and the control treatment (CT) (without irrigation) were equivalent to 350, 437, 525, 700 and 0 mm year^{-1} of irrigation with RWW. (***) significant at $P < 0.0001$.



$$\hat{S} = -5.25E{+}00 + 1.09E{-}01 \times I + 7.51E{-}01 \times D - 5.63E{-}04 \times I^2 + 6.74E{-}06 \times D \times I - 3.75E{-}03 \times D^2,\ R^2 = 0.731^{***}$$

Fig. 5. Response of exchangeable SO_4^{2-} -S concentration in soil at different depths to increasing rates of RWW irrigation for 18 months. The irrigation rates of 100% ETc, 125% ETc, 150% Etc, 200% ETc, and the control treatment (CT) (without irrigation) were equivalent to 350, 437, 525, 700 and 0 mm year^{-1} of irrigation with RWW. (***) significant at $P < 0.0001$.

could eliminate total acidity (assumed soil depth $D = 20$ cm; total acidity $\partial\widehat{\mathbf{H}+\mathbf{Al}}/\partial I = 0$) (Fig. 2).

A slight decrease in exchangeable K^+ was observed with increasing rates of RWW irrigation (Fig. 3). The maximum K^+ concentration at the surface soil (0–20 cm) was found at CT, ~2.5 mmol$_c$ kg^{-1}, and the minimum, ~1.9 mmol$_c$ kg^{-1}, at 200% ETc. The greatest difference between the treatments was of only 0.5 mmol$_c$ kg^{-1}.

After the winter season, exchangeable Na^+ amount increased in proportion to the irrigation rates mainly at the surface (0–20 cm) and subsurface layers (20–40 cm). Maximum Na concentration was found at the 200% ETc treatment (Fig. 4A). The irrigation with RWW at 200% ETc resulted in a buildup of exchangeable Na^+ of up to 500% in comparison to CT. After the summer season, irrigation with RWW had almost no influence on exchangeable Na^+ at the 0–40-cm layer (Fig. 4B). However, major changes were detected at the layers deeper than 60 cm. The irrigation with RWW at higher rates slightly enhanced the buildup of exchangeable Na^+ at the deeper layers (60–100 cm). Exchangeable Na^+ concentrations at a 100 cm depth were of ~0.3 and ~1.3 mmol$_c$ kg^{-1}, respectively for the CT and 200% ETc treatments (Fig. 4B).

No significant influences of RWW irrigation were observed on N, P, Ca, Mg, B, Cu, Al, Fe, Ni, Zn, Cr and Pb concentrations in the soil.

After summer season, the concentrations of SO_4^{2-}-S in the surface soil (0–20 cm depth) were 13.8, 8.2 and 8.8 mg kg^{-1}, respectively for the irrigation rates of 98%, CT and 200% of ETc (Fig. 5). The maximum SO_4^{2-}-S concentration occurred at the irrigation rate of 98% ETc (assumed soil depth $D = 20$ cm; $\partial\widehat{SO_4^{2-}}/\partial I = 0$), whereas the minimum concentration was obsereved in the CT and 200% ETc treatments.

3.3. Reclaimed wastewater effects on citrus leaf composition

Irrigation with RWW for 20 months generally affected N, P, K, S, Mn, Zn, Cr, Al and Na concentrations in leaf tissue (Fig. 6), but had no significant influence on Ca, Mg, B, Cu, Fe, Cd and Pb concentrations

The highest N concentration ($\partial\widehat{N}/\partial I = 0$) in leaf tissue was found at 100% ETc treatment. The difference between CT and 100% ETc was of 7.53% or ~2 g N kg^{-1} (Fig. 6). Citrus leaf P concentration tended to decrease with increasing RWW irrigation rates (Fig. 6): by ~22%, i.e. from 1.47 g kg^{-1} to 1.15 g kg^{-1}, in the plots irrigated with RWW at 100% ETc in comparison to the CT plot (Fig. 6). Leaf K concentration also decreased with increasing RWW irrigation rates: a ~7.5% reduction occurred at the 100% ETc irrigation rate (Fig. 6). Irrigation with RWW at 100% ETc added ~26 kg SO_4^{2-}-S ha^{-1} year^{-1} to the soil. Consequently, citrus leaf S concentration increased by 41% (Fig. 6). Leaf tissue Na concentration was most affected by RWW irrigation rates, and ranged from ~40 mg kg^{-1} at the CT to ~80 mg kg^{-1} for the plants treated with 100% ETc, a 100% increase (Fig. 6). The concentrations of Al, Mn, Zn and Cr in citrus leaves decreased by 23%, 30%, 13% and 7%, respectively at the treatment of 100% of ETc as compared to CT (Fig. 6).

4. Discussion

4.1. Reclaimed wastewater chemical properties

The concentrations of macronutrients (N, P, K, Ca, Mg and S), micronutrients (B, Cl, Cu, Fe, Mn, Ni and Zn), and toxic elements (Al, Cd, Cr and Pb) in the RWW were within adequate ranges for agricultural use according to the standards established by USEPA [34]. The order of total concentration of macronutrients in the RWW was: $S > NH_4^+ = Ca > K > Mg > P > NO_3^-$; for micronutrients, the order was: $Cl > Fe > B > Zn > Mn > Cu > Ni$ (Table 1). This shows the imbalanced proportion of nutrients in the RWW when compared with the Hoagland nutrition solution [35] used for growing many species, for which the macronutrient order is $N > K > Ca > P > S > Mg$, and the micronutrient order is $Fe > Cl > B > Mn > Zn > Cu = Ni$.

There is minimal information available on ionic speciation of nutrients and heavy metals in RWW. The charge difference between cations and anions in RWW ionic speciation was of ~3.5%, which reveals an appropriate distribution of charges. The predominant nutrients species found in the RWW as NO_3^-, NH_4^+, HPO_4^{2-}, H_2PO^{4-}, Cl^-, Ca^{2+}, Mg^{2+}, K^+, SO_4^{2-}, H_3BO_3, Mn^{2+} and Zn^{2+} are in the preferential form for plant uptake [36].

More than 95% of the N in the RWW is in the NH_4^+-N form. This corroborates results reporting that NH^{4+} represents 65–95% of the total N in RWW. Sixty-six percent of the Cd content in RWW was in the Cd^{2+} form, and 9% of the copper was in the Cu^{2+} form. These results are also similar to those of Sterrit and Lester [37], who reported that nearly 88% of the total cadmium found was in the Cd^{2+} form and 3.2% of the total copper found was in the free Cu^{2+} form.

Macronutrients in the RWW are mostly present as free ionic species which are readily available, whereas metallic micronutrients (Cu, Fe and Zn), heavy metals (Cd, Cr and Pb) and Al are less available because they are more or less bound with organic and inorganic ligands such as OH^- and DOM. These findings confirm that RWW has potential for providing nutrients in available ionic forms and as a steady supply to crop plants similar slow-release fertilizer.

4.2. Reclaimed wastewater effects on soil properties

Irrigation with RWW raised soil pH at the surface layer to the range of 5.0–7.0, which is optimal for the availability of most nutrients to crop plants [35]. The decrease in soil active acidity may be attributed to: (i) RWW's natural alkalinity (HCO_3^-), which neutralizes the Al^{3+} commonly found in tropical soils; and (ii) the addition of exchangeable bases from RWW, which replace the Al^{3+} and H^+ from soil colloids. Despite our findings, there are conflicting results in literature regarding RWW effects on soil pH. There are reports of soil alkalinization, from pH 7.4 to pH 7.8 [38,39]; soil acidification, from pH 8.2 to pH 7.1 [40]; or no effects [41]. Thus, we hypothesized that RWW might behave as an amphoteric solution once the RWW ionic speciation (Table 1) showed considerable concentration of compounds such as DOM, metal hydroxides – $M(OH)_3$, $M(OH)$ – (Table 1) that have amphoteric properties in aqueous media [42,43]. Moreover this amphoteric property may is related with the characteristics of the waste and the type of treatment adopted in the wastewater treatment plant.

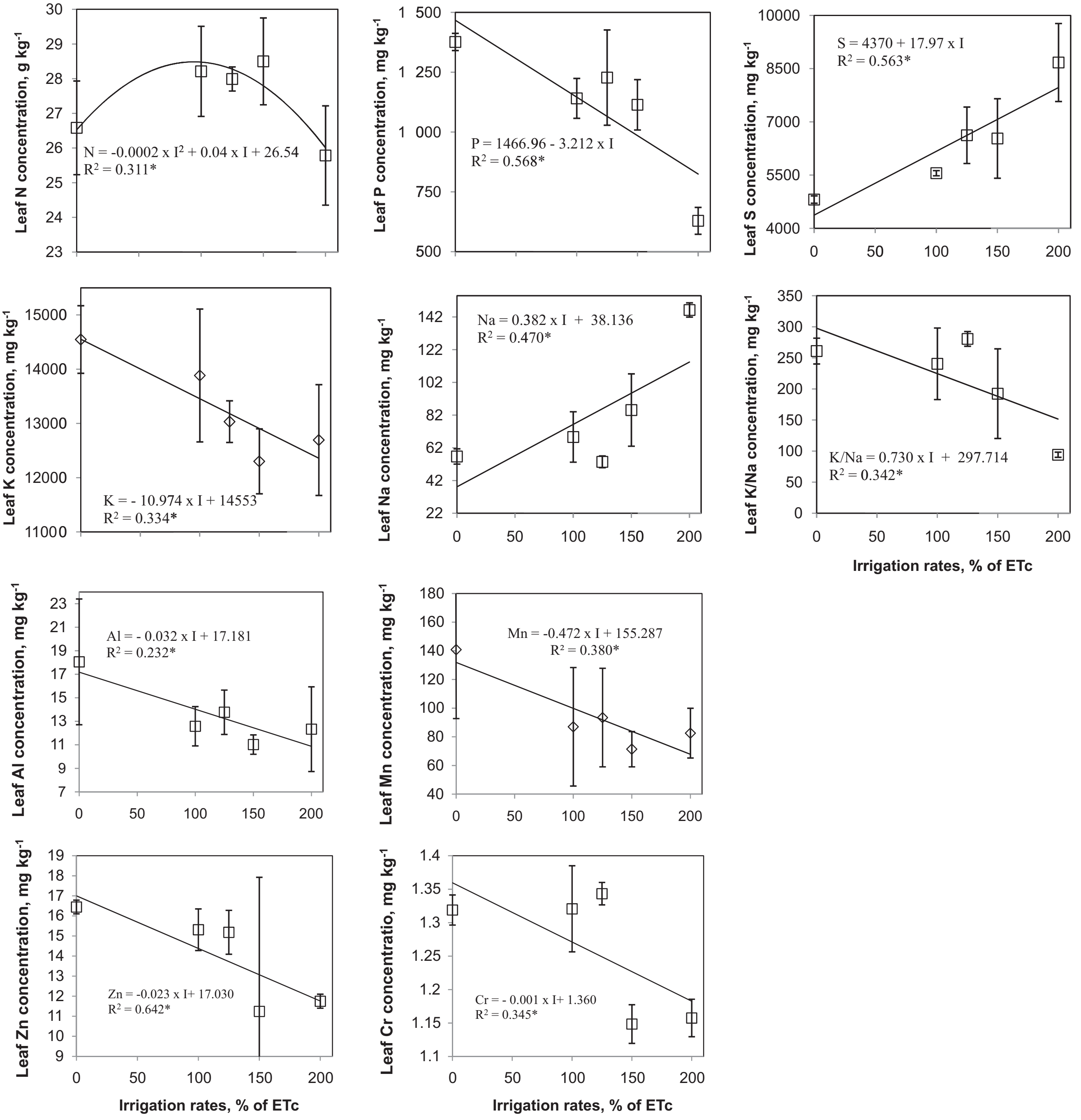


Fig. 6. Influence of irrigation rates of RWW on the concentration of N, P, S, K, Na, K/Na, Al, Mn, Zn and Cr in leaf tissue. The irrigation rates of 100% ETc, 125% ETc, 150% Etc, 200% ETc, and the control treatment (CT) (without irrigation) were equivalent to 350, 437, 525, 700 and 0 mm year^{-1} of irrigation with RWW. (*) significant at $P < 0.05$.

The total acidity represents the amount of H^+ and Al^{3+} adsorbed on soil colloids, which is in balance with active acidity in soil solution. After 12 months of irrigation at 150% ETc, RWW could completely eliminate soil acidity. Similar results were also reported by Gloaguen et al. [6]. The decreased total and active acidity indicate the beneficial effects of RWW irrigation on acidic soils in tropical regions. Soil acidity is one of the most severe problems, affecting 580 million ha of potentially arable land in the humid tropics [44]. Apparently the irrigation with RWW can minimize costs by eliminating [45] or reducing the need for lime in the correction of soil acidity.

A decrease in exchangeable K^+ in the soil receiving RWW irrigation may be related to the input of Na^+ from the RWW, which partially replaced K^+ on the soil colloids. Furthermore, the irrigation with RWW at high rates (>100% ETc) may enhance the leaching of exchangeable K^+ from the soil, as also pointed out by Morgan et al. [13]. However, available K^+ concentration in the soil was still considered high according to the guidelines (> 3.0 mmol$_c$ dm^{-3}) [22].

The concentration of $SO_4{}^{2-}$ increased in the entire soil profile at 98% of ETc as compared to CT (Fig. 5) due to the input of $SO_4{}^{2-}$ via RWW, but the increase was diminished at higher irrigation rates (>100% of Etc), likely because of enhanced $SO_4{}^{2-}$leaching. Moreover, the higher soil pH at the rates of >100% of ETc may increase negative charges of the tropical soils, thus decreasing soil's adsorption capacity for $SO_4{}^{2-}$.

After the winter season we observed an apparent influence of RWW on Na^+ concentration at the 0–40-cm soil layer. The winter season in this region has low precipitation, which increases the need for irrigation, and consequently the addition of Na to the soil. Sodium accumulation is one of the major concerns regarding RWW reuse in agriculture [46]. It causes degradation of the soil structure due to clay dispersion. Leal et al. [7] observed that clay dispersion occurred when the soil was irrigated with RWW containing up to 120 mg L^{-1} of Na^+. In the present study the Na^+ concentration in RWW was of 34.70 ± 2.82 mg L^{-1}, almost fourfold lower, presenting much less risk to the soil structure. Moreover, during the summer season Na^+ was leached down to deeper layers (>40 cm) due to increased rainfall (Fig. 4). Several factors may have contributed to the leaching, including: (i) exchangeable Na^+ was readily replaced by other cations, as it is the weakest cation in the cation exchange order ($Al^{3+} = H^+ > Ca^{2+} > Mg^{2+} > K^+ = NH_4^+ > Na^+$) [35], (ii) the rainfall during the summer was intense (430.6 mm), and according to Chesworth [47] 400 mm of precipitation can leach 80% of the salts out of the surface in a loamy sand soil.

4.3. Reclaimed wastewater effects on citrus leaf composition

The optimal range (25–27 g kg^{-1}) of N in the leaf tissue was found for CT plots and 200% ETc RWW irrigation (Fig. 6). RWW irrigation at the rates of 100%, 125% or 150% ETc resulted in higher leaf N concentrations (28–30 g kg^{-1}), even though they received only 50% of the N needed from regular fertilizers in the form of NH_4NO_3. These values are still below excessive N levels (>30 g kg^{-1}) according to Obreza and Morgan [48]. Nevertheless, it is important that the amount of N from RWW be calculated and included in the fertilization program for the citrus crop.

According to the interpretation of guidelines for nutritional state of citrus [48], the optimal range of leaf P concentration is 1.2–1.6 g kg^{-1}. Based on this standard, RWW irrigation appears to reduce leaf P concentration to a relatively low range (0.9–1.1 g kg^{-1}) (Fig. 6). Herpin et al. [10] also found P deficiency in coffee leaves after RWW irrigation in tropical soil. Kalavrouziotis et al. [39] reported decreasing concentrations of N, P and K in leaf tissue of broccoli and brussels sprout after irrigation with RWW as compared with the control treatment. The mechanisms responsible for decreased P availability after RWW irrigation are not well understood. There may be an antagonistic interaction between phosphate and sulfate. Aulakh and Parischa [49] reported a decreased leaf P concentration with increasing doses of S applied to the soil. Besides, the high concentration of sulfate (SO_4^{2-}-S 38.4 mg L^{-1}) relative to phosphate (PO_4-P 4.4 mg L^{-1}) in RWW might have enhanced phosphate leaching, thus reducing P availability to the plants.

The increased concentration of S in the leaf tissue of plants irrigated with RWW may be attributed to: (i) the addition of SO_4^{2-} provided by the RWW (38.35 ± 6.26 mg L^{-1}); (ii) increased soil pH from RWW irrigation (Fig. 1), which may enhance the desorption of sulfate from Fe and Al oxyhydroxides, thus increasing SO_4^{2-} concentration in soil solution. Leaf S concentrations were at a high range (4–5 g kg^{-1} S) for CT plants and RWW irrigation with 100% ETc and became excessive (>5 g kg^{-1} S) [50] when irrigated with RWW >100% ETc. These results highlight that overirrigation with RWW may cause excessive S and nutrient imbalance in the soil–plant production system.

The decreased K concentration in the leaf tissue of plants irrigated with RWW may be related to: (i) decreased availability of soil K^+ due to enhanced leaching by added Na^+ from the RWW (Fig. 3); (ii) the antagonistic effect of NH_4^+ from the RWW on K^+ uptake; (iii) high Na^+ concentration in soil solution, which inhibits the passive absorption of K^+ through the proteic channels [35]. The replacement of K^+ by Na^+ in low proportion has no harmful effects on plant nutrition, as Na^+ can substitute for K^+ in the non-specific functions of osmotic homeostasis [35]. Regardless of RWW irrigation rate, the concentrations of K in the leaf tissue were within the optimal range (12–17 g kg^{-1}) [48]. Therefore, the negative effects of RWW irrigation on plant nutrition of K should be minimal.

The increased Na concentration in soil as a consequence of RWW irrigation is responsible for plant Na accumulation. However, this level of increase may be beneficial to crop plants, as adequate levels (40–80 mg kg^{-1}) of Na can enhance plant growth by improving water balance and substitution of K in the plant [51]. The toxic level of Na for citrus plant is around 2700 mg kg^{-1}, and the leaves start to drop at 8000 mg Na kg^{-1} [52], which may occur only in some saline soils. The concerns of Na input from RWW irrigation are more related to its effect on soil quality, particularly soil structure. However, in tropical and subtropical regions like São Paulo – Brazil, the high annual rainfall (>1200 mm $year^{-1}$) leaches almost all Na out of the soil profile (Fig. 4B), and the irrigation with RWW with low concentrations of Na ($\sim 34.7 \pm 2.82$ mg L^{-1}) is unlikely to cause Na accumulation, as evidenced by the relatively low concentration of Na (<3 $mmol_c$ kg^{-1}) in the soil. Therefore, the potential of negative impacts of Na input from RWW irrigation on soil fertility and plant nutrition should be minimal.

Higher irrigation rates of RWW decreased K/Na ratios in plant tissue (Fig. 6), which can be attributed to the input of Na from the RWW irrigation. The lower K/Na ratios in plants may indicate the sensitivity of the plants to soil salinity as a high cystolic K/Na ratio in plants usually implies its high tolerance to salinity [53,54]. Moreover, there was a strong correlation of K/Na in leaves with the yield of crop plants. Most susceptible rice genotypes had lower K/Na ratios [55]. Hence, RWW irrigation rates >100% of ETc decreases K/Na ratio in plants (Fig. 6) highlighting the sensitivity of citrus to soil salinity.

The decrease of Al in plant tissue is apparently related to the increased soil pH (Figs. 1 and 2) and declined Al^{3+} concentration in soil solution. This result highlights an important benefit of RWW irrigation, since Al^{3+} toxicity is the most severe growth-limiting factor in acid soils such as Oxisols and Ultisols [56]. Moreover, many plant species are sensitive to Al toxicity [57].

The decrease in Mn, Zn and Cr concentrations in leaves (Fig. 6) tissue is also related to the increased soil pH from RWW irrigation. In the acidic Ultisol, water soluble and exchangeable forms of Mn are converted into less available oxide fractions, as pH increased [58]. The transformation of Cr to less available species is related to increased pH and humic substances in the soil [59]. At pH >5.2, Zn was predominately as organic complexes, and, at pH >6.9, bonded with amorphous and crystalline iron oxide [58]. In the tropical soils, usually rich in iron oxides, the availability of metallic ions is strongly associated with pH-dependent charge. Hence, pH increases from RWW irrigation plays an essencial role in the availability of metallic ions in the tropical acidic soils.

5. Conclusions

The major forms of macronutrients and micronutrients in RWW are NH_4^+, Ca^{2+}, Mg^{2+}, K^+, SO_4^{2-}, Cl^-, H_3BO_3 and Zn^{2+}, which are readily available to plants, despite being in an imbalanced proportion for plant nutrition. Non essential heavy metals in RWW are mostly bounded with DOM or OH^- (Pb-DOM, Cd-DOM, Cd-OH^+, $Al(OH)_4^-$, $CrOH^+$). The irrigation with RWW decreases soil acidity, which is desirable for the acidic tropical soil. It tends to decrease exchangeable K^+ in the soil and leaf K concentration as a result of increased exchangeable Na^+ and leaf Na concentration. However, the levels of both available K^+ in the soil and leaf K concentration are still within the optimal range. RWW irrigation can provide a significant amount of available N and S to the plants and decrease leaf Al concentration. However, overirrigation with RWW (>100%

ETc) is not recommended, since it has potential to cause nutritional imbalance of plants due to the excess of S, which may enhance P deficiency.

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