Egypt. J. Chem. **Vol. 64,** No. 1 pp. 165 - 176 (2021)

Egyptian Journal of Chemistry

http://ejchem.journals.ekb.eg/

Heavy Metals in Citrus Fruits as Affected by Primary Treated Sewage Irrigation

Hussein I. Abdel-Shafy*, Mohamed A. El-Khateeb*

Water Pollution Research Department, National Research Centre, Dokki, Cairo, Egypt

Abstract

This work aims to investigate the distribution pattern of heavy metals in the different parts of citrus trees. Monthly samples of different types of irrigation water (treated wastewater, groundwater, and fresh canal water) were collected. Both physicochemical characteristics and heavy metal concentration were evaluated. Different citrus plant samples and fruits from three different species of citrus trees were collected from the sewage farm as well as the farms irrigated with groundwater and canal water. All citrus tree samples were partitioned into: leaves, stem and citrus fruit. The fruits were divided to the outer crust, and squeezed juice. The results showed that the level of metals in treated wastewater was within the permissible limits; while the citrus trees irrigated by this water contains higher levels due to metals accumulation. One important notice is that the toxic metals including Cd, Pb, Ni, Cr in all cases were at the lowest and/or below detection limit, particularly, in the citrus juice. The outer crust of the citrus fruits contained the second lowest level of all metal. Thus, the citrus fruits showed no accumulation of heavy metals. This could be explained by the fact that heavy metals were up taken by the roots and only smaller fractions were trans-located to the other parts of the tree. The essential nutrient metals including Fe, Mn, and Zn were accumulated mostly by leaves and stems. It was concluded that heavy metal accumulated differently according to the plant species, the part of the tree and fruit. Such fluctuations are governed by the irrigating water, pH of the soil, plant uptake and/or water-soil-to-plant transfer factors. Other factors include temperature, moisture, organic matter, phosphorous content and the availability of the other nutrient elements. The present experimental study showed that the primary treated wastewater should not be used for irrigating any edible plant.

Keywords: citrus trees; sewage farm; water reuse; accumulation of metals

1. Introduction

Despite growing constraints on the production of conventional water supplies and wastewater discharges. The reuse has become an important way in many countries for meeting the needs for water supply and disposal of wastewater. This increasing reliance on reuse means incorporating reuse programs into wider planning initiatives is crucial.

There is a widespread international concern over the lack of food in the developing countries, particularly these countries that suffer from deficiency of water resources for irrigation and/or cultivation [1; 2]. Egypt, as a developing country is among these countries due to the limited water resources and fertile land for cultivation [3; 4]. One additional problem is the fast growing population that will reach about 150 million by the year 2025 [5; -7]. In Egypt, Nile water is the major water resource for irrigating the agriculture area that represents about 3.8% of the total land [1; 8; 9]. The rest, 96.2% of the Egyptian land, is an arid and semi-arid land without almost any cultivation [6]. Therefore, land reclamation is the most stressing problems for cultivation and food production [5]. Meanwhile, the reclamation of the sandy soil nature of the desert consumes large amount of water. Such sandy soil usually suffers from lack of fertility, micro-and macro-nutrient elements as well as very poor water holding capacity [6]. Water recycling and the reuse of

*Corresponding author e-mail: *hshafywater@yahoo.com*, *el-khateebcairo@yahoo.com*.
Receive Date: 14 June 2020, Revise Date: 08 July 2020, Accept Date: 26 July 2020
DOI: 10.21608/EJCHEM.2020.32685.2693

properly treated wastewater may be viewed as water resource for irrigation in arid and semi-arid countries that improves the fertility of poor soils [8; 10; 11].

The use of treated wastewater provides a reliable alternative source of nutrient source for plants in arid and semi-arid regions [8]. The purpose is to close the gap between demands and supply of water, eliminate the pollution of freshwater resources and providing sound solution to water scarcity to fulfill the development strategies [12; 13].

The planned water projects in Egypt aim to achieve effective and healthy reuse of water by using biotechnology as an efficient treatment of wastewater. As a renewable source of irrigation water, rich in nutrients and organic matter in addition to being cost-effective, alternative to traditional irrigation water, it had been of interest to both environmentalists and agronomists over the last decades. However, it is always associated with various adverse impacts on soil ecosystem and farming due to the presence of heavy metals [12; 14-18.

Currently, there are more than 230 municipal wastewater treatment plants in Egypt. The total volume of treated sewage effluent produced in Egypt is expected to rise from 6,348 million m3 daily in 2004 to 9,684 million m3 daily in 2021 [19]. While, a total annual generated amount of sewage effluent in Egypt is estimated at 2020 at 2.54 billion m3/yr. The daily rate of sewage generation is estimated at 120 and 80 liter/capita/d in urban and rural areas, respectively. There are 83 sewer plants in Egypt, most of them carry out secondary treatment and few apply only primary treatment [20; 21].

Urban coverage of improved sanitation is gradually increased from 45% in 1993, to 56% in 2004, and estimated to reach 81.3% in 2021 [22; 23]. Conversely, sanitation progress still slow in rural areas. It is worth mentioning that huge amounts of sewage effluent were disposed to the environment, hence reached the soil and caused severe adverse impacts. Moreover, the industrial wastewaters were discharged along with the sewage [11; 21; 24; 25]. As a result sewage contained mixed industrial contamination including heavy metals [26-28]. The use of adequately treated wastewater in agriculture proved to be an alternative solution of freshwater in several countries [29; 30]. In Egypt, sewage irrigation farms are not common and are not officially allowed unless for woody trees [31; 32].

Generally, the Citrus fruit trees are irrigated by fresh Nile water in the Delta area. The Citrus fruits are considered one of the major fruit crops in Egypt. The total cultivated area is about 29% (204,095 hectare), of the total fruit area (700,854 ha). The total fruitful area of Citrus reached (175734 ha), which produce about 4,272,886 metric tons all are planted in the Delta area using Nile River freshwater for irrigation. Out of this amount, around 1.8 million tons are exported according to Ministry of Agriculture (2017-2018) [32]. Egypt is ranking as the 1st biggest producer of fresh orange throughout the world in year 2019 followed by Brazil, China, US, EU, and Mexico, where it was the sixth world producer [8].

This work aims to investigate the level of heavy metals in the different parts of citrus fruit plants that was irrigated with treated wastewater in the experimental area of Abu-Rawash, Egypt. The distribution pattern of heavy metals in the different parts of the orange fruits is among the aim of the present study. Does it represent any health hazard to Man? How far is the level of metals in the studied plant correlated with the national and international permissible limits?

2. Materials and Methods

2.1. Abu-rawash sewage experimental farm (ASF)

The total area of this experimental Farm was 250 fedan which was expanded to 500 fedan. The experimental Farm receives between 4500 to 5500 m3/d secondary treated sewage water from both Zenien and Abu-Rawash Sewage Treatment Plants. The ASF has been established in 1936 and became fully operated in 1944. The ASF consists of essentially planting hardwood trees, besides some experimental fields of flower plants beside a very small experimental area on irrigating citrus trees. Research experiments for the use of digested sludge were conducted for land reclamation. The ASF is surrounded by the Eucalyptus trees as environmental protection to the surrounding desert area.

2.2. Abu-rawash sewage treatment plant

The plant receives about 500 x10^3 m^3/d raw sewage water from the Giza area. The plant receives also 30,000 m^3/d liquid sludge at a concentration of 0.4-0.6% from the Zenien sewage plant. The plant is a primary treatment consists of the following: Screening, Grit champers, Primary Aeration Tanks, Primary Sedimentation Tank, and Sludge Concentration Basins. This sludge is pumped from Zenien sewage plant to Abu-Rawash plant, to be concentrated in the "Sludge Concentration Basins", mixed with the sludge produced from the Abu-Rawash plant. The final mixed liquid sludge is then pumped to the great lagoon in the Western Desert. The amount of this sludge is about 42,000 to 45,000 tds/y.

However, extensive sewage irrigation for citrus trees was conducted in a very limited area, namely “Abu-Rawash” as a long term study. It is the second-largest sewage experimental farm in Egypt after “Gabal El-Asfar” S.F. which is irrigated by the treated municipal effluent from Abu-Rawash Sewage Treatment Plant (STP). The present total capacity of this STP is 1.6 million m3/d as one of the largest STP. The first part of this plant was implemented in 1992 with a capacity of 400,000 m^3/d. It was preliminary upgraded and funded by US aid to increase the capacity to 800,000 m^3/day and was put into service on 15 February 2010, bringing the plant's initial treatment capacity up to 1.2 million m3/day. It serves about 9.5 million people. Abu-Rawash Sewage Experimental Farm was designed to irrigate woody trees only. However, a very limited area of the experimental farm was planted with Citrus fruits as an experiment for a short period [8].

2.3. Treated wastewater samples

This study was carried out during the period from January to October 2019. Monthly samples of the treated wastewater were collected for the determination of the physicochemical characteristics. The level of heavy metals in these samples was also determined monthly according to APHA [33]. For correlation, samples from the nearby groundwater and Nile water were collected for the determination of the physico-chemical characteristics and the level of heavy metals of these waters for correlation with the corresponding metals in the treated wastewater according to APHA [33].

2.4. Plant samples

Different citrus plant samples and fruits from three different species of citrus trees were collected from the sewage farm. Similar samples were collected from other filed of citrus trees that were irrigated by Nile water and/or groundwater. The fruits were divided into the outer crust and squeezed juice. The plant parts namely stem and leaves and the outer crust of the citrus fruit were oven-dried at 105°C for 24 hrs until a constant weight was obtained. The dried plants were grinded to a fine powder then acid digested with nitric acid followed by H_2O_2 according to APHA [33]. The acidic treatment releases the metals in the digested samples.

2.5. Citrus juice samples

The citrus fruit samples were squeezed to extract the juice out of the fruit cells. The liquid juice samples were then acid digested using nitric acid followed by H_2O_2. The digested juice samples were filtered and brought back to its original volume.

2.6. Metal Determination

Metals were determined in all samples using atomic absorption spectroscopy. The determined metals were Cd, Pb, Cu, Cr, Zn, Ni, Mn, and Fe. Flame Photometer was used for the determination of Na, K, Mg, and Ca.

Table 1 :The investigated *Citrus* Species

Species	The given symbol
Citrus senensis (variety Washington Navel orange)	A
Citrus senensis (variety Laring orange)	B
Citrus (Lime orange)	C

3. Results

3.1. Physico-chemical characteristics of irrigation water

Physico-chemical characteristics of groundwater, fresh canal water, and the treated sewage water that were used for irrigation at Abu-Rawash experimental farm during the experimental period from January to October 2019 are given in Tables (2, 3, and 4). By correlating the studied parameters in groundwater and the canal water (Tables 2, and 3) the results indicate that the levels of studied parameters in the groundwater are higher than the corresponding parameters in canal water with the exception that the pH of the later is slightly higher than the former. The origins of the heavy metals in the groundwater can be due to the release of chemical weathering of some rocks, and soil leaching processes in the environment, as well as anthropogenic activities. Those anthropogenic causes include industrial and household effluent, landfill leachate, and mining [22; 32; 34]. Meanwhile, the presence of some algae in the canal water can be responsible for the slightly higher pH [35]. However, the pH in three types of water was generally around the neutral or slightly alkaline level.

Table 2 :Physico-chemical characteristics of groundwater that used for irrigation at Abu-Rawash Experimental Farm (from Jan. to Oct. 2019)

Month	pH	EC *u*mohs/cm at 2S°C	Cations (mg/l)				Anions (mg/l)		
			Na^+	K^+	Mg^{++}	Ca^{++}	HCO_3^-	Cl^-	SO_4^{2-}
Jan.	7.3	0.98	6.22	0.66	2.35	11.0	6.22	5.4	1.79
Feb.	7.2	0.98	7.18	0.78	2.55	12.0	6.23	5.38	1.58
March	7.5	1.01	8.79	0.89	2.71	12.5	6.27	5.28	1.82
April	7.2	1.27	7.82	0.93	2.41	11.2	6.01	5.19	0.42
May	7.3	1.28	7.93	0.99	2.53	12.3	6.04	5.2	.0.45
June	7.1	1.31	8.45	1.11	2.55	12.1	6.02	5.22	0.44
July	7.4	1.32	8.56	l.l8	2.63	12.6	6.05	5.23	0.46
Aug.	7.6	1.41	8.65	1.26	2.74	13.2	6.06	5.26	0.47
Sept	7.4	0.97	3.54	0.48	1.88	10.5	6.07	5.24	1.40
Oct.	7.5	0.95	5.12	0.57	1.95	11.0	6.11	5.2	1.8
Min	7.10	0.95	3.54	0.48	1.88	10.50	6.01	5.19	0.42
Max	7.60	1.41	8.79	1.26	2.74	13.20	6.27	5.40	1.82
Av		1.15	7.23	0.85	2.43	11.84	6.11	5.26	1.13
St.dev	0.16	0.18	1.75	0.25	0.30	0.87	0.10	0.07	0.66

Min. = Minimum, Max. =Maximum, Ave = average, St.dev. = standard deviation

Table 3:Physico-chemical characteristics of canal water in the area of Abu-Rawash during the period of study (from Jan. to Oct. 2019)

Month	pH	EC *u*mohs/cm at 2S°C	Cations (mg/l)				Anions (mg/l)		
			Na^+	K^+	Mg^{++}	Ca^{++}	HCO_3^-	Cl^-	SO_4^{2-}
Jan.	8.1	0.53	3.01	0.11	0.73	4.0	3.13	2.42	0.84
Feb.	7.8	0.6	3.4	0.18	0.89	4.3	3.11	2.5	0.92
March	8.2	0.61	3.54	0.29	0.92	4.7	3.27	3.08	0.88
April	7.5	0.58	1.48	0.37	1.13	5.0	3.22	3.99	0.9
May	7.9	0.59	2.72	0.4	1.18	5.1	2.2	3.95	1.02
June	7.8	0.62	2.89	0.38	1.25	5.4	2.29	4.01	1.5
July	8.3	0.57	3.05	0.45	1.05	5.0	2.42	2.8	1.59
Aug.	8.4	0.6	3.45	0.35	0.99	4.7	2.49	0.89	0.99
Sep.	8.0	0.62	4.77	0.29	1.02	4.9	3.62	0.77	0.23
Oct.	8.2	0.58	2.53	0.21	0.75	4.0	3.79	2.52	0.18
Min	7.50	0.53	2.53	0.11	0.73	4.00	2.20	0.77	0.18
Max	8.40	0.62	4.77	0.45	1.25	5.40	3.79	4.01	1.59
Ave	7.8	0.59	3.26	0.30	0.99	4.71	2.95	2.69	0.91
St. dev	0.27	0.03	0.66	0.11	0.17	0.47	0.57	1.17	0.45

Min. = Minimum, Max. =Maximum, Ave = average, St.dev. = standard deviation

Table 4:Physico-chemical characteristics of the primary treated sewage water that is used for irrigation at Abu-Rawash Experimental Farm (from Jan. to Oct. 2019)

Month	pH	COD (*mg*/l)	BOD (mg/l)	TSS (mg/l)	TKN (*mg*/l)	TP (*mg*/l)
Jan.	6.8	135	75	38	27	4.3
Feb.	7.2	151	78	40	28	4.2
March	7.5	146	75	42	27	4.3
April	6.5	145	72	40	26	4.0
May	7.8	142	70	38	25	3.9
June	8.0	139	69	37	25	4.0
July	8.3	135	65	30	25	3.8
Aug.	8.7	133	63	31	26	3.7
Sept.	6.8	135	65	32	26	3.8
Oct.	6.5	136	68	33	28	4.0
Min	6.5	133	63	30	25	3.7
Max	8.7	151	78	42	28	4.3
Ave	7.5	140	70	36	26	4.0
St. dev	0.8	6.0	5.0	4.3	1.2	0.2
Permissible level [35]		600	300	350		

Min. = Minimum, Max. =Maximum, Ave = average, St.dev. = standard deviation

On the other hand, the physicochemical characteristics of Abu-Rawash's primary treated effluent during Jan. to Dec. 2019 period are set out in Table (4). These characteristics are within the permissible limits of the Egyptian Law [36] as primary treated wastewater which is allowed to be reused for irrigating lumber trees only. Meanwhile, the level of heavy metals in the treated sewage water, raw canal water, and groundwater during the studied period is given in Table (5). By correlating the permissible limits of the international regulation including the FAO (long term, and short term) [37], and the USEPA [38] it is apparent that the level of metals in wastewater and the other two types of water studied are within the permissible level. However, sewage water contains higher values than canal water or groundwater (Table 5). It is worth mentioning here that the industrial wastewater was discharged; in former times; to the sewer system without adequate treatment. According to the local Standards of the Egyptian Manual Guidelines for Treated Wastewater Reuse in Agriculture [37-39], it is enforced that all kinds of wastewater should be primarily treated at least before discharging to the environment. Therefore, better quality of sewage water, particularly level of heavy metals is; presently; expected.

Table 5 :Level of heavy metals in the primary treated sewage water, canal water and ground water at Abu-Rawash area during the period from Jan. to Oct. 2019 (as mg/l)

Water resource type		Cu	Zn	Fe	Mn	Pb	Cr	Cd	Ni
Sewage Water	Min	0.1	0.49	0.35	0.13	0.02	0.004	0.01	0.04
	Max	0.2	1.89	0.69	0.19	0.04	0.01	0.01	0.12
	Ave	0.14	1.11	0.53	0.17	0.04	0.007	0.01	0.07
	St.dev	0.04	0.59	0.1	0.02	0.01	0.004	0.002	0.03
Ground Water	Min	0.04	0.12	0.13	0.1	0.01	<0.001	0	0.01
	Max	0.09	0.41	0.57	0.18	0.03	0.003	0.01	0.06
	Ave	0.05	0.22	0.33	0.14	0.02	0.002	0.003	0.03
	St.dev	0.01	0.1	0.13	0.03	0.01	0.001	0.001	0.01
Canal Water	Min	0.01	0.03	0.22	0.08	0.003	<0.001	0.001	0.01

Max	0.03	0.24	0.44	0.16	0.01	0.004	0.002	0.02
Ave	0.02	0.12	0.24	0.11	0.01	0.002	0.001	0.01
St.dev	0.01	0.06	0.07	0.03	0.002	0.001	0	0
Long term use, Maximum concentration level* [37-38]	0.2	5	5	0.2	5	0.1	0.01	0.2
Short term use, Maximum concentration mg/l** [37-38]	5	10	20	10	10	1.0	0.05	2

* Water can be constantly used in all types of soil.

** Water can be used for up to 20 years in types of soft soil textures, whether neutral or alkaline..

3.2. Heavy Metals in Citrus Trees Irrigated by Treated Sewage Water

***Citrus senensis* (variety Washington Navel), Species A**

The results in Table (6) present the level of heavy metals in different parts of these citrus plants, namely: stems, leaves of the citrus tree and the fruits (outer crust and the juice). It can be noticed that the pattern of heavy metals accumulation in this plant can be arranged as follow:

Fe > Mn > Zn > Cu > Cr > Ni > Pb > Cd

The Pb was higher than the Ni, only for the crust. The level of heavy metals in all cases was at the lowest in the juice of the citrus orange than in the other parts and was the highest in the stem of the tree according to the following pattern:

S > L > C > J

The lowest level among all the studied metals was exhibited by Cr, Ni, Pb, and Cd. The order of heavy metals showed some fluctuations but the levels of iron, manganese, zinc, and copper were much higher than lead and cadmium (Table 6).

Table 6: Level of macro, micro-nutrient elements, and heavy metals in Citrus trees irrigated by treated sewage water at Abu-Rawash Sewage Experimental Farm [Species A *Citrus senensis* (variety Washington Navel)] (as mg/kg dry weight) (during 2019).

Table 6

Level of macro, micro-nutrient elements and heavy metals in Citrus trees irrigated by treated sewage water at Abu-Rawash Sewage Farm [Species A *Citrus senensis* (variety Washington Navel)] (as mg/kg dry weight) (during 2019)

Part of plant		Fe	Mn	Zn	Cu	Cr	Ni	Pb	Cd
	Min	92.92	21.83	20.35	8.95	1.13	1.30	0.30	0.10
	Max	767.07	51.52	42.22	19.78	18.76	16.88	5.52	1.07
	Ave	303.34	34.20	27.52	15.55	14.06	8.72	4.50	0.81
S	Stdev	99.48	9.60	13.09	4.50	5.66	2.56	1.91	0.17
	Min	72.10	14.03	12.34	6.57	4.08	0.50	0.35	0.01
	Max	154.83	45.91	38.53	14.60	7.65	4.39	2.29	0.85
	Ave	112.70	30.03	24.30	11.73	5.17	2.28	1.23	0.70
L	Stdev	36.30	3.14	14.85	5.40	2.59	0.54	0.64	11.63
	Min	10.48	10.25	6.04	4.22	3.00	0.20	0.10	0.14
	Max	64.94	26.10	15.83	13.79	7.34	0.63	1.20	1.10
	Ave	48.62	17.63	13.90	7.69	5.11	0.160	1.09	0.62
C	Stdev	13.55	6.98	4.76	2.86	1.50	0.261	0.91	0.317
	Min	8.04	6.02	4.10	2.50	2.00	0.200	0.05	0.030
	Max	37.69	20.20	8.10	6.10	4.46	0.500	0.40	0.300
	Ave	23.25	10.09	6.50	4.50	0.45	0.300	0.25	0.200
J	Stdev	5.25	2.60	2.80	1.60	1.00	0.040	0.03	0.300

S = Stem of the tree, L=leaves of the tree1, C = Outer peel of the Citrus Fruit, J= Juice of the Citrus fruit

***Citrus senensis* (variety Laring), Species (B)**

The results are given in Table (7). These results indicated that the level of metals in the different parts of Species (B) is as follow:

S > L > C > J

Meanwhile, it can be noticed that the Fe, Mn, and Zn are the highest among all metals. The concentration of metals in the stem, leaves, and juice only can be arranged as follow:

Fe > Mn > Zn > Cu > Cr > Ni > Pb > Cd

Only, the outer crust of the orange fruit has different arranging as follow:

Fe > Mn > Zn > Cu > Pb > Cd > Cr >Ni

Level of Pb and Cd were higher than Cr and Ni. It is worth mentioning that the steam accumulated Cd less than leaves and crust but higher than the juice. Therefore, the level of Cd in the different studied parts according to the following decreasing order:

L > C > S > J

Table 7: Level of macro, micro-nutrient elements, and heavy metals in citrus trees irrigated by treated sewage water at Abu-Rawash Sewage Experimental Farm (during 2019 *Citrus senensis* (variety Laring) (species B) as (mg/kg dry weight).

Table 7

Level of macro, micro-nutrient elements and heavy metals in citrus trees irrigated by treated sewage water at Abu-Rawash Sewage Farm (during 2019 *Citrus senensis (variety Laring)* (species B) as (mg/kg dry weight)

Part of plant		Fe	Mn	Zn	Cu	Cr	Ni	Pb	Cd
	Min	101	26.83	25.08	10.2	2.01	1.1	0.3	0.15
	Max	642.03	61.76	54.56	22.5	18.5	25.51	6.2	1.5
	Ave	334.83	39.59	36.47	17.8	9.77	11.51	5.5	0.66
S	St. dev	107.47	17.04	15.47	5.3	3.57	4.5	2.1	0.25
	Min	82.04	16.2	15.2	7.5	0.8	0.9	0.45	0.02
	Max	169	55.4	44.56	20.27	4	5.51	3.2	1.5
	Ave	129.11	42.0	30.52	18.39	3.2	2.06	2.28	1.2
L	St. dev	44.67	10.2	12.55	7.02	0.8	1.1	0.8	0.4
	Min	11.26	11.6	7.8	5.2	0.7	0.4	0.2	0.07
	Max	70	31	21.02	17.4	0.9	0.8	1.8	1.4
	Ave	51.1	21.3	16.4	8.7	0.6	0.5	1.3	1.1
C	St. dev	15	7.8	6.3	3.2	0.25	0.22	0.95	0.4
	Min	9.3	7.2	5.1	3.2	0.3	0.35	0.07	0.06
	Max	42.3	25.3	9.3	7.5	0.6	0.7	0.5	0.5
	Ave	26.34	14.3	7.5	5.4	0.3	0.4	0.32	0.35
J	St. dev	7.2	4.2	3.1	2	0.12	0.07	0.06	0.1

S = Stem of the tree, L=leaves of the tree1, C = Outer peel of the Citrus fruit, J= Juice of the Citrus fruit

Citrus senensis (Lime citrus fruit) Species (C)

The results are given in Table (8). The level of metals in this Lime citrus fruit can be arranged according to the following descending order:

Fe > Mn > Zn > Cu > Ni > Cr >Pb > Cd

Meanwhile, the distribution order of heavy metals the different parts of the Lime citrus fruit can be arranged as follow:

S > L > C > J

Table 8: Level of macro-micro-nutrient elements and heavy metals in citrus trees irrigated by treated sewage water at Abu-Rawash Sewage Experimental Farm (during 2019, *Citrus senensis* (Lime) (species C) (mg/kg as dry weight).

Table 8

Level of macro-micro-nutrient elements and heavy metals in Citrus trees irrigated by treated sewage water at Abu-Rawash Sewage Farm (during 2019, *Citrus senensis (Lime)* (species C) (mg/kg as dry weight)

Part of plant		Fe	Mn	Zn	Cu	Cr	Ni	Pb	Cd
	Min	95.3	25.4	29.5	9.6	2.5	1.2	0.3	0.2
	Max	548.2	60.1	62.3	24.3	19.2	22.3	7.1	2.1
	Ave	322.3	41.7	38.3	16.9	10.2	12.3	5.8	0.9
S	St. dev	120	19.36	16.2	4.5	4.1	5	3.1	0.3
	Min	75.3	16.9	16.2	8.1	1.02	1.1	0.5	0.04
	Max	155.6	61.2	45.2	21.2	4.5	6.1	4.1	1.2
	Ave	122.7	36.2	33.5	15.0	3.8	4.8	3.1	0.7
L	St. dev	41.3	11	17.2	8	0.9	1.5	1	0.5
	Min	10.55	10.2	8.9	6.0	0.40	0.44	0.31	0.09
	Max	65.05	35	22.3	16.2	1.2	1.7	1.0	0.5
	Ave	48.3	22.3	18.3	9.1	0.50	0.64	0.42	0.35
C	St.dev	15	8.1	7.5	3.3	0.3	0.3	1.2	0.5
	Min	8.7	8.1	6.1	3.8	0.3	0.4	0.1	0.07
	Max	40.2	31.2	8.7	8.2	0.7	0.9	0.7	0.6
	Ave	25.3	15.7	8.1	6.1	0.40	0.45	0.35	0.30
J	St. dev	8.2	5.5	3.2	2.5	0.1	0.1	0.1	0.2

S = Stem of the tree, L=leaves of the tree1, C = Outer peel of the citrus fruit, J= Juice of the citrus fruit

Heavy Metals in Citrus Trees Irrigated by Fresh Canal Water

Level of heavy metals in the different parts of the three different citrus plant samples namely *Citrus sinensis*-variety Washington Navel (Species A), *Citrus sinensis*-variety Laring (Species B), and *Citrus sinensis*-Lime citrus fruit (Species C) are given in Table (9). These results indicated that the level of metals in the stem and leaves can be arranged according to the following decreasing order:

Fe > Mn > Zn > Cu > Cr > Ni > Pb > Cd

For the outer crust and the juice of the citrus fruits, the Cr, Ni, Pb, and Cd are below 0.01 or zero, therefore, the metals can be arranged as follow:

Fe > Mn > Zn > Cu

In all cases, the level of metals in the studied parts of the citrus trees irrigated by fresh canal water can be arranged as follow:

S > L > C > J

By correlating the present results with the previous ones, it is obvious that the levels of metals in these citrus trees are much less than the form ones. Figure (1) presents the level of Fe, Mn, Zn, and Cu in the juice of citrus fruits irrigated by the three different types of water, namely: treated sewage water, Canal water, and groundwater. One important notice is that the toxic metals including Cd, Pb, Ni, Cr are almost below detection limits in the citrus juice.

Table 9
Toxicity limits in water, soil, and plant

Element	Maximum conc. in irrigation water (ppm) (24)	Toxic conc. in soil (ppm) (25)	Toxic conc. in plant (ppm) (26)	Egyptian Law (ppm) (27)
Fe	5	10 - 200	--	1
Cu	0.2	160	>20	1
Mn	0.2	100	>500	0.2
Zn	2	400	>400	1
Pb	0.05	20 - 41	>60	0.05
Cd	0.01	2-9	>100	0.01
Ni	0.2	100	>80	0.1

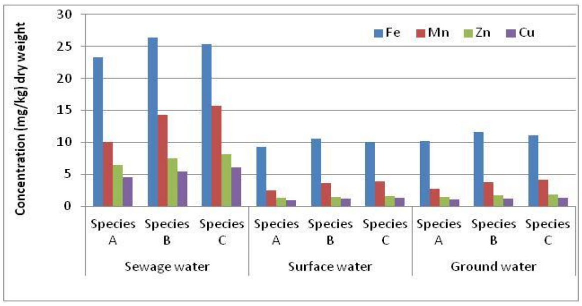

Fig. 1. Accumulation of Fe, Mn, Zn, and Cu in the juice of different citrus tree species as affected by the source of irrigated water.

4. Discussions

In correlation with the level of metals in treated wastewater (Table 5) with the permissible limits Table (9), it can be indicated that it is within or less the acceptable limits [35; 37; 40]. Meanwhile, this treated wastewater is within the acceptable level in terms of the physical and chemical characteristics for irrigating Lumber trees only. Correlation between the physical and chemical characteristics of the primary treated sewage, Nile freshwater, and groundwater showed that the former should be reused only for irrigating lumber trees as previously recommended [8; 14; 35].

The general notice is that the concentrations of all elements in fruit crust and juice were much less than the level in the irrigation water in all cases. This could be explained by the fact that heavy metals are taken up by the roots and only smaller fractions were trans-located to the other parts of the plant [32; 43; 41; 42]. It is worth mentioning that the essential nutrient metals including Fe, Mn, and Zn were accumulated mostly by leaves and stems. While, the most toxic metals including Cr, Ni, Pb, and Cd were at the lowest level in all parts of the plants and were at the lowest in the fruit crust and juice (Figure 2).

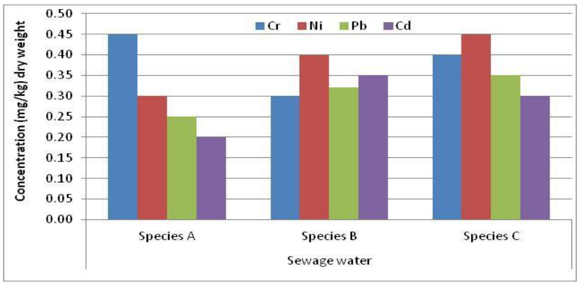

Figure 2: Level of Cr, Ni, Pb, and Cd in the juice three different species of citrus trees irrigated by primary treated sewage water.

Level of metals in the stems, leaves, crust, and the juice in the all studied sample species followed the same decreasing order. The order of heavy metals in the studied citrus trees was uniform. Iron showed the highest level while lead and cadmium exhibited the lowest level in all cases. It is worth to notice that the level of metals in all the studied parts of these fruits followed the same decreasing order. The stem of the trees accumulated the highest level of all the studied metals followed by the leaves. From the obtained results the level of metals in juice in all cases was the lowest compared to the other parts of the studied fruits. The outer crust of the citrus fruits contained also the second-lowest level of all metal and was slightly higher than the juice. The results indicated that heavy metal accumulated differently according to the part of the tree and the fruit. These findings are in harmony with Arora et al., [43] who recorded different levels of heavy metals accumulation in the edible parts of different kinds of plants, irrigated with the same wastewater. Such fluctuations may be attributed to the variations in source of irrigation water [41; 44] as well as other factors including temperature, pH, moisture, organic matter, soil pH, organic matter, phosphorous content as well as the availability of the other nutrient elements [8; 45; 46].

Additionally, heavy metal accumulation depends on the plant type. Consequently, the efficiency of plants to absorb a given metal is governed by the irrigating water, availability of metals in the soil, plant uptake and/or water-soil-to-plant transfer factors [44; 45]. In this respect, elevated levels of cadmium in soils may inhibit soil productivity, while a very low cadmium concentration may decrease the vital plant processes including photosynthesis process, water absorption, and mitosis. The same phenomenon is true for lead [46; 47]. Thus, developing toxicity symptoms, wilting of older leaves, dark green leaves, brown short roots, and stunted foliage may take place [47-49]. It is documented that heavy metals are toxic, resulting in weak plant growth, chlorosis, and low yield [48]. Such a problem may be accompanied by a reduction in the nutrient uptake plant, disorders in their metabolism, and a reduction in the ability to fix phosphorous and / or nitrogen in the plant leguminous [50].

According to Feitknecht and Schindler [51], the relationship between the metal solubility product (K_{sp}) follows the following equation:

$$(M^{+2})\ (OH)_2 ===== K_{sp} \text{ (solubility constant)}$$

Such solubility products provide an important general guide to the available soluble metals that can be expected as a result of incomplete solid separation, precipitates aging, and/or co-precipitation/adsorption effects in water [29; 51; 52].

In the present study, the average pH of the irrigated water is slightly alkaline at 7.5, thus heavy metals are in the range between slightly insoluble and/or precipitated form [52]. Consequently, it can be concluded that the availability of heavy metals from the irrigated water was greatly controlled and restricted by such slightly alkaline pH. This fact explains clearly the limited uptake of heavy metals by the studied citrus plants.

In Egypt, local restricted regulations are followed precisely that defines all type of irrigated plants according to the type and quality of irrigated water [35]. Consequently, this Code assigns the type of agricultural groups that can be irrigated by water reuse. Effluent limit values for heavy metals and microbial parameters are listed to define the suitability of water reuse in irrigation.

5. Conclusions

The successful implementation of wastewater reuse options as irrigation water requires careful planning, efficient wastewater reclamation, effective design, and safe operation, storage, and controlled distribution mechanisms.

The orange fruit displays no heavy metals accumulations.

Agriculture is a major consumer of water. Consequently, the reuse of thoroughly treated wastewater will contribute to the water resources.

Current wastewater reclamation approaches include several steps to mitigate the safety and environmental threats associated with different reuse applications.

The treated effluents contain considerable amounts of macro and micro-nutrient. This may compensate for the required amount of fertilizers, thus reducing the fertilization cost in agriculture activities.

Reuse of treated sewage water and wastewater as unconventional water resources should be also classified according to the level of heavy metals besides their physico-chemical characteristics.

The present experimental study showed that the primary treated wastewater should not be used for irrigating any edible plant.

6. Conflicts of interest

The authors declare that there are no conflicts of interest of any kind.

7. Acknowledgement

The author wishes to express their deep appreciation and gratitude to the fund provided by the project titled “Towards Innovative and Green Water Reuse with Integrated Constructed Wetlands and Ferrate(VI) Treatment”. This work is derived from the Subject Data supported in whole or part by NAS and USAID, USA-Egypt Science Technology Joint Fund-(Cycle.19), and the Science and Technology Development Fund (STDF-Egypt) and the Egyptian Ministry of Higher Education and Scientific Research (MHESR).

This work is also supported by the Academy of Scientific Research and Technology (ASRT) under the project entitled "Production of low cost innovative unit for wastewater treatment for reuse in rural and un-served areas".

8. References

[1] Abdel-Shafy H.I., Aly R.O. (2002). Water issue in Egypt: resources, pollution and protection endeavors. Central European J. of Occupational & Environ. Medicine, 8(1), 1-21.

[2] El-Khateeb M.A., Emam W.M., Darweesh W.A., El-Sayed E.S.A. (2019). Integration of UASB and down flow hanging non-woven fabric (DHNW) reactors for the treatment of sewage water. Desalination and Water Treatment, 164, 48-55.

[3] Elagouz M., Abou-Shleel S., Belal A., El-Mohandes M. (2019). Detection of land use/cover change in Egyptian Nile Delta using remote sensing. The Egyptian Journal of Remote Sensing and Space Science.

[4] Nayl A.E.A., Elkhashab R.A., El Malah T., Yakout S.M., El-Khateeb M.A., Ali M.M., Hazim M. Ali. (2017). Adsorption studies on the removal of COD and BOD from treated sewage using activated carbon prepared from date palm waste. Environmental Science and Pollution Research, 24(28), 22284-22293.

[5] Abdel-Shafy H.I., Salem M.A., Mansour M.S., El-Khateeb M. A., Abdel-Shafy S.H. (2018). Physico-Chemical Evaluation of Drinking Water Treatment Plant and Sand Filter Backwashing Water for Possible Recycling: A Case Study. Egyptian Journal of Chemistry, 61(6), 1039-1047.

[6] Bakr N., Afifi A.A. (2019). Quantifying land use/land cover change and its potential impact on rice production in the Northern Nile Delta, Egypt. Remote Sensing Applications: Society and Environment, 13, 348-360.

[7] Moretti M., Van Passel S., Camposeo S., Pedrero F., Dogot T., Lebailly P., Vivaldi G. (2019). Modelling environmental impacts of treated municipal wastewater reuse for tree crops irrigation in the Mediterranean coastal region. Science of the Total Environment, 660, 1513-1521.

[8] Abdel-Shafy H.I., El-Khateeb M.A. (2019). Fate of Heavy Metals in Selective Vegetable Plants Irrigated with Primary Treated Sewage Water at Slightly Alkaline Medium. Egyptian Journal of Chemistry, 62(12), 2303-2312.

[9] El-Khateeb M.A., Saad M., Abdel-Shafy H.I., Samhan F., Shaaban M. (2018). The feasibility of using non-woven fabric as packing material for wastewater treatment. Desalination and Water Treatment, 111, 94-100.

[10] Hegazy B., El-Khateeb M.A., El-adly Amira A., Kamel M. (2007). Low-cost wastewater treatment technology. Journal of Applied Sciences, 7(6), 815-9.

[11] Tran Q.K., Jassby D., Schwabe K.A. (2017). The implications of drought and water conservation on the reuse of municipal wastewater: Recognizing impacts and identifying

mitigation possibilities. Water research, 124, 472-481.

[12] Carr G., Potter R.B., Nortcliff S. (2011). Water reuse for irrigation in Jordan: Perceptions of water quality among farmers. Agricultural Water Management, 98(5), 847-854.

[13] Al-Enazi M., El-Khateeb M.A., El-Bahrawy A. (2012). Feasibility of sewage water treatment in Skaka City using up-flow anaerobic sludge blanket (UASB) reactor. Bioscience Research, 9(1), 23-9.

[14] Saber M., Hoballah E., Abouziena H., Haggag W.M., El-Ashry S., Zaghloul A. (2016). Management of sewage farming in arid region: Egyptian experience. Int. Sci. Res. J, 72(3), 28-56.

[15] El-Khateeb M.A., Al-Herrawy A, Kamel M, El-Gohary F. (2009). Use of wetlands as post-treatment of anaerobically treated effluent. Desalination, 245(1-3), 50-9.

[16] Moawad A., Mahmoud U.F., El-Khateeb M.A., El-Mola E. (2009). Coupling of sequencing batch reactor and UASB reactor for domestic wastewater treatment. Desalination, 242, 325-335.

[17] El-Shahat Nashy H.A., El-Khateeb M.A. (2015). Agro-substances and non-agro-substances as efficient and cost-effective materials for wastewater treatment. Desalination and Water Treatment, 54(9):2357-63

[18] Abdel-Shafy H.I., El-Khateeb M.A. (2013). Integration of septic tank and constructed wetland for the treatment of wastewater in Egypt. Desalination and Water Treatment, 51(16-18):3539-3546

[19] Housing & Building National Research Center (HBNRC) (2004). The Egyptian Manual as Guidelines for Treated Waste Water Reuse in Agriculture. Ministry of Housing & Utilities and New Communities, Cairo.

[20] Abdel-Shafy, H.I., Aly, R.O. (2007). Wastewater management in Egypt Wastewater reuse–Risk assessment, decision-making and environmental security (pp. 375-382): Springer.

[21] Abdel-Shafy H.I., Mansour M.S. (2013). Overview on water reuse in Egypt: present and future. J. Sustainable Sanitation Practice, 14, 17-25.

[22] Abdel-Shafy H.I., Kamel A.H. (2016). Groundwater in Egypt issue: resources, location, amount, contamination, protection, renewal, future overview. Egyptian. J. Chemistry, 59(3), 321-362.

[23] Abou-Elela S., El-Khateeb M.A; Fawzy M., Abdel-Halim W. (2013). Innovative sustainable anaerobic treatment for wastewater, Desalination and Water Treatment, 51(40-42),7490-8.

[24] Nasr F., Ashmawy A., Ibrahim H., El-Khateeb M.A. (2010). Management of wastewater from ink production and metal plating industries in an Egyptian industrial city. Desalination and Water Treatment, 21(1-3), 8-16.

[25] Abou-Elela S., El-Khateeb M.A. (2009). Treatment of ink wastewater via heterogeneous photocatalytic oxidation. Desalination and Water Treatment, 7(1-3), 1-5

[26] Abdel-Shafy H.I. (2015). Chemical treatment for removal of heavy metals from industrial wastewater. Egypt. J. Chemistry, 58(1), 1-12.

[27] Abdel-Shafy H.I., Hewehy M.A., Razek T., Hamid M., Morsy R.M. (2019). Treatment of Industrial Electroplating Wastewater by Electrochemical Coagulation Using Carbon and Aluminum Electrodes. Egyptian Journal of Chemistry, 62(Special Issue (Part 1) Innovation in Chemistry), 383-392.

[28] Abd El-Aziz M.E., Essam Saber, El-Khateeb M.A. (2019). Preparation and characterization of CMC/HA-nps/pulp nanocomposites for the removal of heavy metal ions. KGK Kautschuk Gummi Kunststoffe, 4(19): 36-41.

[29] Rattan R., Datta S., Chhonkar P., Suribabu K., Singh A. (2005). Long-term impact of irrigation with sewage effluents on heavy metal content in soils, crops and groundwater—a case study. Agriculture, ecosystems & environment, 109(3-4), 310-322.

[30] Abdel-Shafy H.I., El-Khateeb M.A., Shehata M. (2014). Greywater treatment using different designs of sand filters. Desalination and Water Treatment, 52(28-30), 5237-5242.

[31] Abdel-Sabour M. F., Abdel-Shafy H.I., Mosalem T. (2001). Heavy metals and plant-growth-yield as affected by water hyacinth compost applied to sandy soil. Environment Protection Engineering, 27(2), 43-53.

[32] Abobatta W.F. (2019). Citrus Varieties in Egypt: An Impression. International Research Journal of Applied Sciences, 1-4.

[33] Rice E.W., Baird R.B., Eaton A.D., Clesceri, L. S. (2012). Standard methods for the examination of water and wastewater. American Public Health Association, Washington, DC, 541.

[34] Abdel-Shafy H.I., Farid M. R., El-Din A. (2016). Water-hyacinth from Nile River: chemical contents, nutrient elements and heavy metals. Egyptian Journal of Chemistry, 59(2), 131-143

[35] Egyptian code. (2005). The Reuse of Treated Wastewater in Agriculture: Ministry of Housing, Utilities and New Communities. 501.

[36] EEAA. (2013). (Egyptian Environmental Affairs Agency) Law 48, No. 61–63 updating No. (44), 2009. Cairo, Egypt. Permissible values for wastes in River Nile, Law of the Environmental Protection.

[37] Griffiths C., Klemick H., Massey M., Moore C., Newbold S., Simpson, D., Wheeler W. (2012). US Environmental Protection Agency valuation of surface water quality improvements. Review of Environmental Economics and Policy, 6(1), 130-146.

[38] Newman W.A. (1972). The National Academy of Science Committee on the ecology of the interoceanic canal. Bull. biol. Soc. Wash, 1972, 247-259.

[39] Tietjen C. (1975). Principal problems of the use of city wastes for crop production and soil conservation. Soils Bulletin (FAO). no. 27.

[40] FAO, WHO, & Additives, E. C. o. F. (2002). Safety evaluation of certain food additives and contaminants.

[41] Abdel-Shafy H.I., Abdel-Sabour M.F. (2006). Wastewater reuse for irrigation on the desert

sandy soil of Egypt: long-term effect Integrated urban water resources management (pp. 301-312): Springer.

[42] Ali M.H., Al-Qahtani K.M. (2012). Assessment of some heavy metals in vegetables, cereals and fruits in Saudi Arabian markets. The Egyptian Journal of Aquatic Research, 38(1), 31-37.

[43] Arora M., Kiran B., Rani S., Rani A., Kaur B., Mittal N. (2008). Heavy metal accumulation in vegetables irrigated with water from different sources. Food chemistry, 111(4), 811-815.

[44] Abdel-Sabour M., Abdel-Shafy H.I.; Mohamed A. (2005). Plant yield production and heavy metals accumulation as affected by sewage sludge application on desert soil. Sustainable Water Management, 1, 27-31.

[45] Abdel-Shafy H.I., Mansour M.S. (2018). Phytoremediation for the elimination of metals, pesticides, PAHs, and other Pollutants from wastewater and soil Phytobiont and Ecosystem Restitution (pp. 101-136): Springer.

[46] Tangahu B.V., Abdullah S., Rozaimah S., Basri H., Idris M., Anuar N., Mukhlisin M. (2011). A review on heavy metals (As, Pb, and Hg) uptake by plants through phytoremediation. International Journal of Chemical Engineering, 2011.

[47] Jiwan S., Ajah K. (2011). Effects of heavy metals on soil, plants, human health and aquatic life. International Journal of Research in Chemistry and Environment, 1(2), 15-21.

[48] Abdel-Sabour M., Abdel-Shafy H. I. (1990). Uptake of Some Metals by Sorgham Plants as Affected by Cadmium Level in the Environment. Environment Protection Engineering, 16(1), 13-23.

[49] Guala S.D., Vega F.A., Covelo E.F. (2010). The dynamics of heavy metals in plant–soil interactions. Ecological Modelling, 221(8), 1148-1152.

[50] Abdel-Shafy H.I., Hegemann W., Teiner, A. (1994). Accumulation of metals by vascular plants. Environmental Management and Health.

[51] Feitknecht W., Schindler P. (1963). Solubility constants of metal oxides, metal hydroxides and metal hydroxide salts in aqueous solution. Pure and Applied Chemistry, 6(2), 125-206.

[52] Abdel-Shafy H.I., Guindi K. A., Tawfik N.S. (2008). Groundwater contamination as affected by long-term sewage irrigation in Egypt Efficient Management of Wastewater (pp. 53-63): Springer.