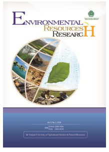

Environmental Resources Research
Vol. 6, No. 2, 2018

GUASNR

Extractability of heavy metals in saline and non-saline soils treated with municipal wastewater under two contrasting moisture regimes

M. Safari Sinegani[1*], A.A. Safari Sinegani[1], M. Hadipour[2]
[1]Soil Science Department, Bu-Ali Sina University, Hamadan, Iran,
[2] Environmental Science Department Faculty of Agriculture and Naturel Resources, ArakUniversity, Arak, Iran
Received: December 2017 ; Accepted: July 2018

Abstract

Solubility and bioavailability of heavy metals are important with respect to their toxicity. The discharge of municipal wastewater in soil and surface waters can affect bioavailability and mobility of heavy metals in soils and sediments. The effect of discharge of Arak municipal wastewater on the KNO_3 and DTPA extractable heavy metals in a saline soil sampled from Mighan playa (Iran) compared to a non-saline agricultural soil was studied in two moisture regimes (field capacity and flooding) in three incubation times (1, 150 and 365 day). In the saline soil, the addition of wastewater led to increase of organic carbon (OC) and decrease of Eh, pH and EC. However, in the non-saline soil, the addition of wastewater led to increase of EC and decrease of TOC and Eh simultaneously. With very few exceptions, the addition of wastewater increased the KNO_3 and DTPA extractable heavy metals significantly. These changes were higher in the saline submerged soil. So, the addition of municipal wastewater in soils for irrigation of saline and non-saline croplands was safer than when it was applied in waterlogged soils. The changes of the analyzed properties were higher in the saline soil compared to those in the non-saline soil. Hence, the resilience of the saline soil compared to the non-saline soil due to its lower buffering capacity was considerably lower. We can conclude that the release of wastewater to Mighan playa soil with high level of salinity may increase the bioavailability and mobility of heavy metals towards that lake.

***Keywords*: Flooding, Heavy metals, Mobility, Salinity, Wastewater**

---

*Corresponding author; safari_1365@yahoo.com

Introduction

The factors affecting metals availability and solubility in soils can control their toxicity levels and leaching quantities in soil environment. Metals are natural cationic elements in soil mineral particles. They are present in different forms in soils depending on soil biogeochemical properties and their reactivity. Many factors in soil can affect metal availability and solubility. Soil texture, mineralogy, equivalent calcium carbonate, pH, Eh, CEC, EC and OC are very important. Variation in these factors controls the release and availability of metals in soils (Jackson, 1958).

Oxidation-reduction potential (Eh) and pH are the main factors affecting the solubility and availability of metals in soils (Cressie, 1990; Kazemi Poshtmasari *et al.,* 2012). The difference between the sources of oxygen in the flooding and non-flooding moisture regimes are the cause of Eh and pH changes in soils (Sajwan and Lindsay, 1986). After soil waterlogging and oxygen depletion by aerobic respiration, redox potential (Eh) will reduce and alternate reductive reactions occurring in succession, leading to conversion of the oxide forms of elements (i.e. $NO3^{-1}$, $SO4^{-2}$, Mn^{+4} and Fe^{+3}) to their reduced forms. The reduced forms of Mn and Fe are more soluble. However continuous flooding of soil may lead to lower solubility of heavy metals in soil due to enhanced adsorption of metal (hydr) oxides and precipitation with sulfide (Krige, 1951).

Increase in organic carbon, pH and clay increases the adsorption and precipitation of heavy metals. In neutral and alkaline soils the high level of pH reduces the soluble and DTPA extractable forms of heavy metals. After addition of soluble Cd to soil, the contamination factor of Cd in temperate soils with lower pH remains considerably high in five months of soil incubation, but this factor decreases in semiarid calcareous soils markedly (Safari Sinegani and Jafari Monsef, 2016).

The addition of soluble organic matter enhances heavy metal mobility by formation of organo-mineral complexes but the addition of solid organic matter can increase soil surface charges and decrease metal mobility (Levy; Mamedov and Goldstein, 2003; Li *et al.,* 2014). However, metal availability and organic forms increases by addition of organic matter in semiarid calcareous soils (Ayoubi, Mohammad Zamani and Khormali, 2007).

Nowadays, tremendous volumes of wastewater are produced in large cities. The reuse of municipal wastewater may lower the severity of water deficiency in arid and semi-arid regions. However its use in agriculture and seasonal rivers requires special concern over environmental pollution and health hazards. The impacts of wastewater on soil properties have been studied by many researchers (Rezapour, Samadi and Khodaverdiloo, 2012; Atashpaz, Rezapour, and Ghaemian, 2018; Kapungwe 2013; Panahi Kordlaghari, Nikeghbali Sisakht, and Saleh, 2013). Atashpaz *et al.,* (2018) studied the effects of irrigation with treated wastewater on metal distribution and contamination of alkaline and calcareous soils. They found that irrigation with wastewater increased the available form of heavy metals in the rank of Ni (79-142%)> Cd (54-125%)> Zn (35-73%)> Cu (13-87%)>Pb (6-32%). The highest mobility potential and toxicity of heavy metals in soil was estimated for Cd and the lowest level was estimated for Pb.

The wastewater of Arak city in Markazi Province (Iran) discharges in Mighan Lake. It can change the properties of these saline soils by biogeochemical reactions. On the other hand, wastewater is an important water resource for agriculture in semiarid and arid regions. However, knowledge is insufficient about the effect of wastewater on saline soils. The objective of this study is to examine and compare the effects of irrigation with wastewater in two contrasting moisture regimes (field capacity and flooding) on soil pH, Eh, EC and OC which can change heavy metal bioavailability in two different soil types (saline and non-saline soils). The result of this study will be used to show the best method of wastewater reuse nowadays released in salty soil of Mighan Lake.

Materials and methods

Soil sampling and treatment

Soil sampling was implemented on the top layer (0-30 cm) of two areas with two different salinity levels, one in Mighan playa (the saline soil) and the other in Kerahrood agricultural land (the non-saline soil) located in Arak city in Markazi Province (Iran) with semi-arid climate. The soil samples were air-dried and passed through the 2 mm sieve. Twelve round plastic plant pots (4 L) were prepared. The dimensions of the used plant pots were 20.9 cm diameter at the top, 15.5cm diameter at the base and 16.5cm deep. Each of the sampled saline and non-saline soils were poured into six pots with 10 cm depth. Three of them were flooded with Arak municipal wastewater and the other three pots were moistened to field capacity moisture levels via addition of wastewater. The wastewater level stood at a height of 5±1 cm above the soil level in the flooding regime. The pots were kept in natural condition (open space) under the applied moisture regimes for one year. The soil subsamples were taken after 1, 150 and 365 days for analysis. Soil temperature was also measured during the experiment through inserting a thermometer in 10 cm depth of soils in pots in 1^{st}, 150^{th} and 365^{th} day of incubation. The mean temperature was 30, 7 and 22 ^{o}C, respectively.

Soil analysis

Soil characteristics were measured according to standard methods (Sparks, 1996). Size of soil particles were determined via the hydrometer method (Gee and Bauder, 1986). Cation exchange capacity (CEC) was determined by Na saturation of clays (Bower Reitmeir and Fireman, 1952). Equivalent calcium carbonate (ECC) was determined via back titration method (Loeppert and Suarez 1996). Total nitrogen (TN) was measured via the Kjeldahl method (Liu *et al.,* 2012). Nitrate (NO_3^-) was measured by method the introduced by MacCarthy *et al.,* (2013). Total phosphorus (TP) was extracted by acid digested with HNO_3 (4N) (Sposito, Lund, and Chang 1982). It was determined in soil extracts spectrophotometrically as blue molybdate-phosphate complexes under partial reduction with ascorbic acid (Mashayekhi *et al.,* 2007).

In pots with flooding moisture regime, soil pH, redox potential (Eh) and EC were determined by placing electrodes at 5 cm below soil-water interface. In pots with field capacity regime, Eh was determined by placing electrodes at 5 cm below soil surface but pH and EC were measured in 1:5 soil-water extract with 30 minutes of shaking (Mavi *et al.,* 2012). Eh, pH and EC were determined by millivolt meter with platinum electrode, pH meter and electrical conductivity meter, respectively. Organic carbon (OC) was determined by wet dichromate oxidation method (Walkley and Black, 1934). Soil basal respiration (BR) as an indicator of biological function and substrate induced respiration (SIR) as an indicator of biomass carbon in soil were calculated with the method introduced by McCauley, Jones, and Jacobsen (2009). The total Fe, Mn, Pb and Cd was extracted with HNO_3 (4N), and KNO_3 extractable forms of metals were extracted with KNO_3 (0.5 M) and distilled water. The DTPA extractable form of metals was extracted with DTPA (Sposito, Lund, and Chang, 1982). They were measured by flame atomic absorption spectrometry. Soil pH, Eh, EC, OC, and extractable KNO_3, extractable DTPA and total heavy metal were measured in wastewater irrigated soils in three sampling times.

Water analysis

Wastewater properties were studied based on standard method proposed by Andrew *et al.* (2005). EC and pH were measured with EC meter and pH meter, total nitrogen (TN) and phosphorus (P) by spectrophotometer, sulfate (SO_4^{2-}) by Turbidimetric Method, Sodium (Na^+) and Potassium (K^+) by flame photometer, Calcium (Ca^{2+}) and magnesium (Mg^{2+}) using complexometry, chlorine (Cl^-) by titration with $AgNO_3$, total Fe, Mn, Pb and Cd by flame atomic absorption spectrometry, and organic carbon by wet oxidation method (Walkley and Black, 1934) in wastewater.

Statistical analysis

This experiment was conducted using completely randomized factorial design with 3 replications. The studied factors were two soil types (saline and non-saline), two moisture regimes (field capacity and flooding) and three sampling time (1, 150 and 365 days). ANOVA (analysis of variance) and Duncan means test (at 0.05 level of significant) were performed.

Results and Discussion

Soils and wastewater properties

The characteristics of the saline soil sampled from Mighan Playa in Markazi Province, and non-saline soil sampled from Kerahrood agricultural lands and Arak municipal wastewater applied in this study are given in Table 1. The saline soil was mainly made of evaporative (Na-Ca-Mg) (SO4-Cl) minerals. The calculated sodium adsorption ratio (SAR) of 1:5 soil extract was 170 $(meq/L)^{1/2}$. The relative amounts of clastic and evaporative minerals depend on the duration and frequencies of flooding. Clastic minerals were mainly quartz, mica and chlorite, but evaporative minerals were glauberite, thenardite, gypsum, calcite, and halite (Dayani and Mohammadi, 2010). So it was impossible to determine the texture and CEC by standard method applied to the other soil. The soil was calcareous and its equivalent calcium carbonate (ECC) was 32%. The soil pH and EC in 1:5 extract were 8.66 and 14 dS/m respectively. This soil had low total organic carbon (TOC=0.8 %) and low total nitrogen (TN=0.08 %). Total phosphorus (TP) was 480 mg/kg. Nitrate (NO_3^-) concentration in 1:5 soil extract was 29 mg/kg soil. Soil basal respiration (BR) and substrate induced respiration (SIR) were 0.05 and 0.43 (mg CO2/g Soil day) respectively. The total amount of Fe, Mn, Pb and Cd were 12418, 193, 137 and 6.5 (mg/kg) respectively.

The texture of non-saline agricultural soil was loam with 51 % sand, 30 % silt and 19 % clay contents. The soil pH and EC in 1:5 extract were 7.8 and 0.9 dS/m respectively. The amount of SAR of soil 1:5 extract was 1.2 $(meq/L)^{1/2}$. This soil was also calcareous but its ECC content was comparatively lower (4.2%). The CEC value for this soil was fairly low (22 Cmolc/kg). Total nitrogen and phosphorus were 0.13 % and 716 (mg/kg) respectively. Nitrate concentration in 1:5 extract of this soil was 65 mg/kg soil. So TP, TN and NO_3^{-1} contents in the non-saline soil were considerably higher than those in the saline soil. Soil biological activity was also relatively higher compared to saline soil. The soil BR and SIR were 0.12 and 0.84 mg CO2/g soil day respectively. The total contents of heavy metals in this soil were also higher. They were 15106, 286, 155 and 6.1 (mg/kg) for Fe, Mn, Pb and Cd respectively.

Some properties of the applied wastewater in this study are shown in Table 1. The wastewater had a neutral pH (7.7) and high salinity (2.9 dS/m). The calculated sodium adsorption ratio (SAR) of waswater was 2.55 $(meq/L)^{1/2}$. Organic carbon and phosphorus contents were 60 and 5.4 mg/l respectively. Total nitrogen (TN) had high concentration (90 mg/l) in the wastewater. The concentration of Cl^-, $SO4^{2-}$, Na^+, k^+, Ca^{2+} and mg^{2+} was 82, 33, 194, 663, 160 and 72 (mg/l) respectively. The total concentration of Fe, Mn, Pb and Cd in the wastewater was 48, 1.4, 0.07 and 0.04 (mg/l) respectively.

Variations in geochemical properties of soils

Analysis of variance was used to examine the effects of soil type (ST), moisture regime (MR), incubation time (IT) and their interactions (ST*IT, MR*IT, ST*MR and ST*MR*IT) on soil pH, Eh, EC and TOC (table 2). The effects of soil type, moisture regime and incubation time on the examined soil properties were significant ($p<0.01$) except the pH that was not significantly changed by moisture regime. All interactions (ST*IT, MR*IT, ST*MR and ST*MR*IT) had significant effects on the pH and Eh. The interactions between soil type with incubation time (ST*IT) and moisture regime with incubation time (MR*IT) had significant effects on EC. Among the studied interactions only the interaction between soil type with incubation time (ST*IT) had significant effect on TOC in soils.

Table 1. Soils and wastewater properties used in this study

	Soil properties		Wastewater properties	
	Saline Soil	Non-saline Soil		
Texture	-	Loam	pH	7.7
Sand (%)	-	51	EC (dS/m)	2.9
Silt (%)	-	30	SAR $(meq/L)^{1/2}$	2.55
Clay (%)	-	19	TOC (mg/l)	60
CEC (Cmolc/kg)	-	22	TN (mg/l)	90
pH (1:5)	8.66	7.8	P (mg/l)	5.4
EC (1:5) (dS/m)	14	0.9	Cl^- (mg/l)	82
ECC (%)	32	4.2	$SO4^{2-}$ (mg/l)	33
TOC (%)	0.8	2.8	Na^+ (mg/l)	194
TN (%)	0.08	0.13	Ca^{2+} (mg/l)	160
TP (mg/kg)	480	716	Mg^{2+} (mg/l)	72
$NO3^-$ (mg/kg)	29	65	K^+ (mg/l)	663
SAR (1:5) $(meq/L)^{1/2}$	170	1.2	Total Fe (mg/l)	48
BR (mg CO_2/g Soil day)	0.05	0.12	Total Mn (mg/l)	1.4
SIR (mg CO_2/g Soil day)	0.43	0.84	Total Pb (mg/l)	0.07
Total Fe (mg/kg)	12418	15106	Total Cd (mg/l)	0.04
Total Mn (mg/kg)	193	286		
Total Pb (mg/kg)	137	155		
Total Cd (mg/kg)	6.5	6.1		

ECC–equivalent calcium carbonate, TOC–total organic carbon, BR–basal respiration, SIR–substrate induced respiration.

Table 2. Analysis of variance (mean square) of the effects of soil type (ST), moisture regime (MR), incubation time (IT) and their interactions (ST*IT, MR*IT, ST*MR and ST*MR*IT) on the studied soil parameters

Source	DF	pH	Eh	EC	TOC
Soil type (ST)	1	1.67**	4807**	261**	18**
moisture regime (MR)	1	0.003ns	839666**	136**	0.23**
Incubation time (IT)	2	0.921**	517685**	67**	0.14**
ST*IT	2	0.32**	5015**	80**	0.75**
MR*IT	2	0.018*	198123**	55*	0.06ns
ST*MR	1	0.393**	1521*	6.4E-5ns	0.014ns
ST*MR*IT	2	0.173**	1743**	0.14ns	0.005ns
Error	24	0.005	272	0.924	0.009

Mean square values marked with * and ** are significant at the 0.05 and 0.01 level respectively and values marked with ns are not significant

Duncan's test of the means of soil pH and Eh which were affected by the interaction between all of the sources of variations (ST*MR*IT interaction) are shown in Table 3. With increasing incubation time from day 1 to 150, pH of both soils decreased significantly in two soil types and two moisture regimes. However, after day 150 to day 365 pH increased significantly in both soil types and moisture regimes except in treatment of non-saline soil with field capacity regime that was not increased significantly. These pH changes are attributed to changes of temperature during incubation time and their impacts on the solubility of salts (especially calcium salts) and CO2. Soil temperature was 30, 7 and 22 ^oC in the 1st, 150th and 365th day of incubation. Changing season affects the formation, loss and accretion of evaporative salts (Thomas, 1996). In warm seasons the high temperature decreases the solubility of CO_2 and increases the precipitation of calcium salts that make the pH of soils more alkaline in the 1st and the 365th days of incubation. However, in non-saline flooded soil, the changes of pH are positive during soil incubation. It may be due to the accumulation of basic cations (Ca, Mg, K and Na) in soil solution from salty wastewater especially in flooding moisture regime in the 365th day with soil pH being clearly high. According to Mcgrath, Zhang and Carton (2004) increase in winter temperature led to rise in the amount of total salts and soil pH. The produced CO_2 in soil is more soluble in cold seasons and makes the soil more acidic. Conversely,

CO_2 is less soluble in warm seasons, but microbial respiration produces more CO_2, so the net effect on pH is variable (Mishra *et al.,* 2009; Morris *et al.,,* 2002).

Table 3. Duncan's new multiple range tests of means of pH and Eh (mv) as affected by soil type (ST), moisture regime (SR) and incubation time (IT)

ST*MR*IT	pH		Eh	
	Mean	SD	Mean	SD
saline*Fl*1	8.66a	0.057	364ab	7.37
saline*FC*1	8.66a	0.057	369a	3.21
non-saline*Fl*1	7.86d	0.028	338b	3.21
non-saline*FC*1	7.86d	0.028	351ab	9.84
saline*Fl*150	7.70e	0.17	-196g	15.1
saline*FC*150	7.90d	0.023	251d	1.52
non-saline*Fl*150	7.67ef	0.040	-160f	26.3
non-saline*FC*150	7.57fg	0.040	284c	7.93
saline*Fl*365	8.13c	0.057	-317h	26.5
saline*FC*365	8.33b	0.057	184e	22.4
non-saline*Fl*365	8.12c	0.075	-219g	27.9
non-saline*FC*365	7.54g	0.050	201e	10.8

Means followed by the same letter in each column are not significantly different ($P < 0.05$), saline soil and non-saline soil incubated in Fl- flooding moisture regime and FC-field capacity moisture regime, for 1, 150 and 365 days. SD=standard deviation

Saline soil had greater pH compared to non-saline soil in two moisture regimes and in all sampling times. This difference was significant except for soils sampled in 365 days when the saline and non-saline flooded soils had almost equal pH may be due to the increase of basic cations with wastewater in flooding regime. In this situation soils have received more amounts of wastewater without leaching. (Mueller *et al.,* 2003) stated that irrigation with wastewater leads to an increase in exchangeable cations, particularly sodium and subsequently lead to increase of soil pH. Studies by Nas (2009) and Nhapi (2004) also showed that the long-term irrigation with sewage and wastewater led to increase in soil pH.

The most important factors controlling pH of the studied calcareous soils may be the retention of the produced CO_2 by soil microorganisms in soil solution and the accumulation of evaporative wastewater basic salt in soil. In flooded soils the lowest pH values were measured in the 150th day of incubation. This finding may be related to more trapping of the produced CO_2 in soil pores in flooding regime. However, soils pH values increased in the 365th day. This result was in agreement with findings of Nyman and DeLaune (1991) that reported when an aerobic soil is flooded its pH is reduced to a minimum and then rises to reach almost constant value. Totally, the maximum amount of pH (8.66) was measured in the saline soil in the 1st day of incubation and the minimum amount of pH (7.54) was measured in the non-saline soil incubated in field capacity for 365 days.

The redox potential (Eh) of the soils decreased significantly in both moisture regimes with increasing incubation time. In fact, addition of the municipal wastewater and feeding of soil microorganisms led to a higher demand for oxygen. In addition, in the flooded soils gas diffusion was limited due to soil saturation and the layer (5cm depth) of wastewater on the soil surface (Panahi Kordlaghari, Nikeghbali Sisakht, and Saleh 2013). Addition of organic matter to the soil led to increase in demand for biological electron acceptor in soil, making favorable condition for anaerobic respiration (Peinemann, Guggenberger, and Zech 2005). Soil Eh decrease when using organic fertilizers was more obvious than when using mineral fertilizers (Peng *et al.,* 2013).

The effect of the addition of wastewater on Eh of the saline and non-saline soils was different. Adding wastewater during incubation time decreased Eh with greater intensity in the saline soil compared to non-saline soil in the two moisture regimes. This difference can be attributed to more nitrate content in the non-saline soil compared to the saline soil. This result is consistent with other findings (Pescode 1992; Pisinaras *et al.,* 2010). They suggested that the presence of more nitrates in the soil decreases Eh reduction.

Soils incubated in flooding moisture regime due to limited soil aeration had obviously lower Eh compared to those incubated in field capacity for 150 and 365 days. When dry soil is waterlogged in the first two weeks, Eh decreased sharply and after that fluctuated slightly, especially in shallow water (Peng *et al.,* 2013). The maximum value of Eh (369 mv) was determined in the saline soil in field capacity regime at 1st day of incubation and the minimum value of Eh (-317 mv) was measured in the saline soil in flooding regime at 365th day of incubation.

Table 4 shows Duncan's test of means of soil EC and TOC as affected by the interaction between soil type and incubation time. Expectedly, saline soil had significantly higher EC than non-saline soil in all treatments. In the saline soil with increasing incubation time from day 1 to day 150 or with decreasing soil temperature from 30 ^{o}C to 7 ^{o}C, EC decreased significantly, but in 365th day with increasing soil temperature (to 22 ^{o}C), once again EC increased significantly. These changes were related to the impact of soil and air temperature on the evaporation of the added wastewater and the higher solubility of salts in warm season. However, in the non-saline soil, EC increased with incubation time but this increase was significant only in the 365th day. This increase was related to addition of soluble salts in wastewater (2.9 ds/m) to non-saline soil and their accumulation by evaporation.

The study of soil EC in the interaction between moisture regime and incubation time (Table 5) showed that soils in the flooding moisture regime had higher EC than those incubated in field capacity. In both moisture regimes EC in the 150th day decreased but after that in the 365th day increased significantly due to changes of temperature. These variation as mentioned above may be explained by temperature changes and wastewater evaporation during soil incubation.

The study of TOC showed that in the saline soil with addition of wastewater, soil TOC increased from the 1st day to the 150th day, and after that it remained constant (Table 5). Irrigation with wastewater leads to increase in soil TOC, TN and TP (Pizarro *et al.,* 1995; Post and Kwon 2000). Increase of soil organic matter and primary productivity in submerged soils are related to the decrease in biodegradation and humification rate and the increase in biological N_2 fixation (Panahi Kordlaghari, Nikeghbali Sisakht, and Saleh, 2013). The applied wastewater had considerable OC which can accumulate in the saline soil. But TOC decreased significantly in the non-saline soil during incubation time. Decomposition rate of organic matter in non-saline soil with higher biological activity and soil substrate induced respiration (about 2 times) compared to the saline soil which was higher. Soil respiration is a good indicator to measure activities of soil microorganisms decomposing organic matter (Richardson *et al.,* 2007).

Table 4. Duncan's new multiple range tests of means of EC (dS/m) and total organic carbon (TOC, %) as affected by the interaction between soil type (ST) and incubation time (IT)

ST*IT	EC		TOC	
	Mean	SD	Mean	SD
Saline*1	12.77a	1.61	0.813e	0.02
Non-saline*1	1.38d	0.33	2.82a	0.01
Saline*150	3.88cd	1.88	1.26d	0.15
Non-saline*150	1.7cd	1.61	2.55b	0.12
Saline*365	7.98b	4.63	1.16d	0.22
Non-saline*365	5.37bc	4.85	2.21c	0.17

Means followed by the same letter in each column are not significantly different ($P < 0.05$), saline soil and non-saline soil incubated in Fl- flooding moisture regime and FC-field capacity moisture regime, for 1, 150 and 365 days. SD=standard deviation.

Table 5. Duncan's new multiple range test of means of EC (dS/m) as affected by the interaction between moisture regime (MR) and incubation time (IT)

MR*IT	EC	
	Mean	SD
Fl*1	7.078ab	6.34
FC*1	7.078ab	6.34
Fl*150	4.377bc	1.36
FC*150	1.210c	1.07
Fl*365	10.933a	1.64
FC*365	2.425bc	1.73

Means followed by the same letter in each column are not significantly different (P < 0.05), saline soil and non-saline soil incubated in Fl- flooding moisture regime and FC-field capacity moisture regime, for 1, 150 and 365 days. SD=standard deviation.

However, in each sampling time, soil TOC was significantly higher in the non-saline soil compared to the saline soil. The maximum amount of TOC (2.82%) was measured in the non-saline soil and the minimum amount of TOC (0.813%) was observed in the saline soil at 1st day of incubation.

Mean test of soil TOC in the studied moisture regime has been reported in Table 6. TOC in flooding moisture regime was significantly more than that in the field capacity regime, because of incomplete and lower decomposition rate of organic matter under anaerobic conditions (Panahi Kordlaghari, Nikeghbali Sisakht and Saleh, 2013). This result was consistent with the findings of other researchers (Pisinaras *et al.,* 2010).

Table 6. Duncan's new multiple range test of means of total organic carbon (TOC, %) as affected by moisture regime (MR)

MR	TOC	
	Mean	SD
Fl	1.88a	0.76
FC	1.72b	0.80

Means followed by the same letter in each column are not significantly different (P < 0.05), Fl- flooding moisture regime and FC- field capacity moisture regime, SD-standard deviation.

DTPA and KNO_3 extractable forms of heavy metals in soils

Analysis of variance was used in order to examine the effects of soil type (ST), moisture regime (MR), incubation time (IT) and their interaction (ST*IT, MR*IT, ST*MR and ST*MR*IT) on the KNO_3 and DTPA extractable forms of Fe, Mn, Pb and Cd in soils (Table 7). The effect of the interaction between soil type, moisture regime and incubation time (ST*MR*IT) was significant on the KNO_3 and DTPA extractable forms of heavy metals except on the KNO_3 extractable (S+Exch) forms of pb and Cd. Only the effect of incubation time was significant on S+Exch forms of pb and Cd in soils.

Table 7. Analysis of variance (mean square) of the effects of soil type (ST), moisture regime (MR), incubation time (IT) and their interactions (ST*IT, MR*IT, ST*MR and ST*MR*IT) on the KNO3 extractable (S+Exch) and DTPA extractable (avail.) forms of heavy metals

Source	DF	Fe (S+Exch)	Mn (S+Exch)	Pb (S+Exch)	Cd (S+Exch)	Fe (Avail.)	Mn (Avail.)	Pb (Avail.)	Cd (Avail.)
Soil type (ST)	1	122**	39**	0.185ns	0.001ns	2070**	3395**	15**	0.014**
moisture regime (MR)	1	0.019ns	55**	0.07ns	0.007ns	19795**	22419**	26**	40E-6ns
Incubation time (IT)	2	29**	23**	6.094**	16.7**	5152**	6240**	14**	0.029**
ST*IT	2	2.075**	11.54**	0.188ns	0.028ns	455**	194*	3.52**	0.002**
MR*IT	2	3.22**	14.83**	0.029ns	0.049ns	5521**	5690**	6.56**	7.6E-5ns
ST*MR	1	1.92**	22**	0.236ns	0.188ns	1660**	506**	9.5**	5.3E-5ns
ST*MR*IT	2	1.409**	9.63**	0.060ns	0.048ns	453**	154*	2.37**	1.3E-4*
Error	24	0.116	0.37	.078	0.015	7.97	36.73	0.128	3.8E-5

Mean square values marked with * and ** are significant at the 0.05 and 0.01 level respectively and values marked with ns is not significant.

Duncan's test of mean of the KNO_3 extractable form of soil heavy metals which was affected by the ST*MR*IT interaction is reported in Table 8. The KNO_3 extractable form of Fe increased significantly with increasing incubation time from day 1 to day 365 in both soil types and two moisture regimes. This increase was a result of Fe reduction due to the decrease of soil Eh during incubation time. Non-saline soil had significantly ($p<0.05$) higher KNO_3 extractable form of Fe compared to saline soil during incubation. It probably was due to higher organic acid and reducible iron contents in this soil because Eh of saline soil compared to non-saline soil decreased more in 365 days of soil incubation in the flooding regime.

Difference between the KNO_3 extractable forms of Fe in the two moisture regimes was only significant in 365th day of soil incubation. Soils in the flooding regime had significantly higher amounts of KNO_3 extractable form of Fe compared to that in field capacity regime. The maximum amounts of KNO_3 extractable form of Fe (9.7 mg/Kg) was calculated for non-saline soil in flooding regime at 365th day. The lowest KNO_3 extractable form of Fe (2.35 mg/Kg) was measured in the saline soil at the 1st day of soil incubation. The greatest amount of Fe^{2+} in the soil solution was found at a low Eh (Robinson and Metternicht 2006). Ruddiman (2007) stated that after 10 weeks of flooding, the soil Fe^{2+} concentration increased to 1700 (μmol L^{-1}) in pore water of soil. According to Sakan *et al.,* (2009) organic matter decomposition under anaerobic conditions resulted in reduction of Mn^{4+} (increasing soluble Mn^{2+} concentrations) and Fe^{3+} (increasing soluble Fe^{2+} concentrations), and $SO4^{2-}$ (formation of S^{2-}) in soil. Toxicity of Fe^{2+} occurs in low Eh and pH and deficiency of Fe can occur at a high Eh and pH (Sarangi *et al.,* 2005).

The KNO_3 extractable form of Mn increased significantly in both of the studied soils from the 1st day to the 150th day of soil incubation only in flooding regime. These results were consistent with the findings of other researchers (Sharpley *et al.,* 2015; Sakan *et al.,* 2009). The maximum amounts of the KNO_3 extractable form of Mn (10.2 mg/kg) were seen in the non-saline soil in flooding regime at 150th day. But it decreased significantly in 365th day. The decrease of soluble and exchangeable Mn from 150 to 365 days in the non-saline soil and flooding regime treatments and other treatments may be related to its precipitation with carbonates in soils. The presence of calcium carbonate in soils are conducive to the fixation and precipitation of metals (Shi *et al.,* 2007; Sposito, Lund, and Chang 1981). Non-saline soil had more significant amounts of the KNO_3 extractable form of Mn in flooding regime in the 150th and 365th days, that may be related to the higher clay mineral contents and more amounts of reducible Mn in this soil.

Although the KNO_3 extractable form of Cd and Pb was not affected by soil type and moisture regime, but this form of Cd and Pb was affected by incubation time (Table 7). Table 9 shows Duncan's test of means of the KNO_3 extractable form of Pb and Cd in soils. During incubation time, the KNO_3 extractable form of Pb and Cd increased significantly. The maximum amounts of KNO_3 extractable form of Pb (3.21 mg/kg) and Cd (3.52 mg/kg) were measured in the 365th day of soil incubation. Adding wastewater with high concentrations of soluble cadmium (1.5 mg/l) and lead (39 mg/l) may be the reason for increase of the KNO_3 extractable form of Pb and Cd in soils. On the other hand, adding wastewater with Cl^- (84 mg/l) may lead to increase in mobility of heavy metals especially Cd in the non-saline soil (Sherene, 2010).

The DTPA extractable form of heavy metals was affected by the interaction between soil type, moisture regime and incubation time (Table 7). The analysis of the means of the DTPA extractable form of heavy metals showed that the availability of Fe, Mn and Pb increased during incubation time in both of the studied soils only in the flooding regime (Table 8). This finding may be related to decrease of soil Eh. Flooding regime leads to increasing availability of metal (Stamm *et al.,* 2002). However, flooding regime only increased significantly availability of Cd in the 365th day in the non-saline soil.

Table 8. Duncan's new multiple range test of means of the KNO_3 extractable form of Fe and Mn (S+Exch) and DTPA (Avail.) extractable forms of heavy metals as affected by the interaction between soil type (saline and non-saline), moisture regime (F-flooding moisture regime and FC-field capacity moisture regime), and incubation time (day) (ST*MR*IT)

ST*MR*IT	Fe (S+Exch)		Mn (S+Exch)		Fe (Avail.)		Mn (Avail.)		Pb (Avail.)		Cd (Avail.)	
	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD
saline*Fl*1	2.35g	0.21	1.38ef	0.10	4.69e	0.26	9g	0.92	3.8e	0.16	0.07h	0.003
saline*FC*1	2.35g	0.21	1.38ef	0.10	4.69e	0.26	9g	0.92	3.8e	0.16	0.07h	0.003
non-saline*Fl*1	5.26d	0.33	1.6cdef	0.10	6.21e	0.85	21.3def	3.05	3.9e	0.74	0.09g	0.004
non-saline*FC*1	5.26d	0.33	1.6cdef	0.10	6.23e	0.85	21.3def	3.05	3.9e	0.74	0.09g	0.004
saline*Fl*150	3.35f	0.31	2.58cd	0.43	37d	2.18	65c	11.6	4.8d	0.06	0.11f	0.007
saline*FC*150	3.06f	0.05	1.81cdef	0.51	4.6e	0.18	10fg	1.22	4.0e	0.52	0.12f	0.004
non-saline*Fl*150	7.1c	0.32	10.2a	1.51	86b	4.21	108a	8.71	8.1b	0.11	0.16cd	0.003
non-saline*FC*150	7.71c	0.25	2.41cde	1.18	6e	0.26	24d	4.23	4.2e	0.04	0.17c	0.013
saline*Fl*365	5.26d	0.45	2.71c	0.24	70c	6.8	84b	0.88	5.6c	0.14	0.154e	0.003
saline*FC*365	4.02e	0.63	0.83f	0.15	2.9e	0.35	12efg	0.37	4.4de	0.15	0.158de	0.009
non-saline*Fl*365	9.70a	0.36	5.93b	0.37	105a	4.8	110a	13.7	9.2a	0.10	0.21a	0.005
non-saline*FC*365	8.73b	0.25	1.55def	0.15	4.62e	0.193	21.6de	0.04	5.0cd	0.18	0.20b	0.005

Means followed by the same letter in each column are not significantly different ($P < 0.05$), SD=standard deviation

Table 9. Duncan's new multiple range test of means of the KNO3 extractable form of Pb and Cd as affected by incubation time (day)

incubation time (day)	Pb		Cd	
	Mean	SD	Mean	SD
1	1.79c	0.13	1.16c	0.15
150	2.44b	0.33	2.41b	0.18
365	3.21a	0.36	3.52a	0.12

Means followed by the same letter in each column are not significantly different ($P < 0.05$), SD=standard deviation

The non-saline soil had more DTPA extractable form of Pb and Cd compared to that in the saline soil due to the more amounts of total Pb with higher organic acid and lower pH in this soil. The effect of incubation time compared to soil type and moisture regime on DTPA extractable Cd was more obvious. The DTPA extractable Cd was increased with duration time markedly. Totally, the maximum amounts of DTPA extractable Fe (105 mg/kg), Mn (110 mg/kg), Pb (9.2 mg/kg) and Cd (0.21 mg/kg) were measured in the flooded non-saline soil in the 365th day of soil incubation.

Conclusions

This study revealed that:

- Moisture regime strongly influenced Eh, EC and TOC contents in soils. The flooded saline soil compared to the soils incubated in FC had relatively lower Eh and higher EC and TOC. In each time of sampling, pH of the saline soil was lower in flooding regime compared to that in FC regime. Inversely, pH of non-saline soil in flooding regime was higher than that of FC regime.
- Discharge of wastewater changed significantly soil pH, Eh, EC and TOC with time duration. From 1st day to 150th day with adding wastewater, pH decreased but after that with increasing soil temperature, soil pH increased in 365th day. In the saline soil, EC was considerably higher in warm seasons (1st and 365th day) but in 150th day it was significantly lower. It may be depended on accumulation of evaporative salts. In contrast, in the non-saline soil, EC increased continuously during soil incubation as a result of adding wastewater. In the saline soil, TOC increased from the 1st day to the 150th day, and afterwards no significant changes occurred. However, in the non-saline soil, TOC decreased significantly during soil incubation.
- The changes of analyzed properties were lower in the non-saline soil compared to those in the saline soil, perhaps due to its higher buffer capacity. So, the resilience of saline soil was low and it was more sensitive to this anthropogenic impact compared to non-saline soil.

- Totally, this study showed that the discharge of wastewater in the waterlogged soils (like Mighan playa) had higher worse effects and environmental risks. But reuse of wastewater in the saline and non-saline soils in the field capacity regime improved the analyzed soil properties.

References

Atashpaz, B., Rezapour, S., and Ghaemian. N. 2018. Effects of treated wastewater irrigation on heavy metals concentration, distribution and contamination of soil. Journal of Water and Soil 32, 573-585.

Ayoubi, Sh., Mohammad Zamani, S., and Khormali, F. 2007. Spatial variability of some soil properties for site specific farming in northern Iran. International Journal of Plant Production 2, 225-236.

Bower, C.A., Reitmeir, R.F., and Fireman, M. 1952. Exchangeable cation analysis of saline and alkali soils. Soil Science, 73, 251-261.

Cressie, N. 1990. The origins of kriging. Mathematical Geology 22, 239-252.

Dayani, M., and Mohammadi, J. 2010. Geostatistical Assessment of Pb, Zn and Cd Contamination in Near-Surface Soils of the Urban-Mining Transitional Region of Isfahan, Iran. Pedosphere 205, 568–577.

Gee, G.W., and Bauder, J.W. 1986. Particle size analysis. In Method of soil analysis part 1: Physical and Mineralogical Methods, edited by K.A. Madison Wisconsin USA: Soil Science Society of America.

Jackson, M.L. 1958. Soil Chemical Analysis. Englewood Cliffs, N.J.: Prentice-Hall, Inc.

Kapungwe, E.M. 2013. Heavy metal contaminated water, soils and crops in peri urban wastewater irrigation farming in Mufulira and Kafue towns in Zambia. Journal Geography and Geology. 5 (2), 55.

Kazemi Poshtmasari, H., Tahmasebi Sarvestani, Z., Kamkar, B., Shataei, Sh., and Sadeghi, S. 2012. Comparison of interpolation methods for estimating pH and EC in agricultural fields of Golestan province north of Iran. International journal of agriculture and crop sciences. 44, 157-167.

Krige, D. 1951. A statistical approach to some basic mine valuation problems on the Witwatersrand. J. Chem. Metallurg. Min. Soc. South Afr. 52(6), 119–139.

Levy, G.J., Mamedov, A.I., and Goldstein, D. 2003. Sodicity and water quality effects on slaking of aggregates from semi arid soils. Soil Science. 168, 552-562.

Li, J., Pu, L., Zhu, M., Zhang, J., Li, P., Dai, X., and Liu, L. 2014. Evolution of soil properties following reclamation in coastal areas: a review. Geoderma 226–227, 130–139.

Liu, P., Bai, J., Ding, Q.., Shao, H., Gao, H., and Xiao, R. 2012. Effects of water level and salinity on TN and TP contents in marsh soils of the Yellow River Delta, China. Clean-Soil, Air, Water, 40, 1118–1124.

Loeppert, R.H., and Suarez, G.L. 1996. Carbonates and Gypsum. In Methods of Soil Analysis Part 3: Chemical Methods, edited by S. DL. Madison Wisconsin USA: Soil Science Society of America

MacCarthy, D.S., Agyare, W.A., Vlek, P.L.G., and Adiku. S.G.K. 2013. Spatial variability of some soil chemical and physical properties. West African Journal of Applied Ecology, 21(2), 47–61.

Mashayekhi, K., Asadi, Z., Movahedi Naeini, S.A., and Hajrasuliha, S. 2007. Salinity regionalization with geostatistic method in a wet soil in southern Lenjan-Isfahan Iran. Indian Journal of Agricultural Research, 41, 1-9.

Mavi, M.S., Marschner, P., Chittleborough, M.S., Cox, J.W., and Sanderman, J. 2012. Salinity and sodicity affect soil respiration and dissolved organic matter dynamics differentially in soils varying in texture. Soil Biology Biochemistry, 45, 8-13.

McCauley, A., Jones, C., and Jacobsen. J. 2009. Soil pH and Organic Matter. Nutrient Management Module, 8, 1-10.

Mcgrath, D., Zhang, C., and Carton, C.T. 2004. Geostatistical analyses and hazard assessment on soil lead in silvermines area. Environal pollution. 127, 239-248.

Mishra, U., Lai, R., Slater, F., Calhoun, F., Liu, D., and Van Meirvenne, M. 2009. Predicting soil organic carbon stock within different depth intervals using profile depth distribution functions and ordinary kriging. Soil Science Society American Journal. 73, 614-621.

Morris, J.T., Sundareshwar, P.V., Nietch, C.T., Kjerfve, B., and Cahoon, D.R. 2002. Responses of coastal wetlands to rising sea level. Ecology 83, 2869-2877.

Mueller, T.G., Hartsock, N.J., Stombaugh, T.S., Shearer, S.A., Cornelius, P.L., and Barnhise, R.I. 2003. Soil electrical conductivity map variability in limestone soil overlain by loess. Agronomy Journal. 95, 496–507.

Nas, B. 2009. Geostatistical approach to assessment of spatial distribution of groundwater quality. Polish Journal of Environmental Study. 18 (6), 1073-1082.

Nhapi, I. 2004. Options for Wastewater Management in Harare, Zimbabwe, Wageningen University,Wageningen, the Netherlands.

Nyman, J.A., and DeLaune, R.D. 1991. CO_2 emission and soil Eh response to different hydrological conditions in fresh, brackish, and saline marsh soils. Limnology and Oceanography 36, 1406–1414.

Panahi Kordlaghari, K., Nikeghbali Sisakht, S., and Saleh, A. 2013. Soil chemical properties affected by application of treated municipal wastewater. Annals of Biological Research 43, 105-108.

Peinemann, N., Guggenberger, G., and Zech, W. 2005. Soil organic matter and its lignin component in surface horizons of salt-affected soils of the Argentinian Pampa. Catena 60, 113–128.

Peng, G., Bing, W., Guangpo, G., and Guangcan, Z. 2013. Spatial Distribution of Soil Organic Carbon and Total Nitrogen Based on GIS and Geostatistics in a Small Watershed in a Hilly Area of Northern China. PLoS ONE 8 (12), e83592.

Pescode, M.B. 1992. Wastewater treatment and use in agriculture. In FAO Irrigation and Drainage. Rome, Italy: FAO.

Pisinaras, V., Tsihrintzis, V.A., Petalas, C., and Ouzounis. K. 2010. Soil salinization in the agricultural lands of Rhodope District, northeastern Greece. Environmental Monitoring Assessment, 166, 79-94.

Pizarro, N., Belzile, M., Filella, G.G., Leppard, J.C., Negre, D., and Perret. J. 1995. Buffle Coagulation/sedimentation of submicron iron particles in a eutrophic lake. Water Research, 29, 617–632.

Post, W.M., and Kwon, K.C. 2000. Soil carbon sequestration and land-use change: processes and potential. Global Change Biology. 6, 317–327.

Rezapour, S., Samadi, A., and Khodaverdiloo, H. 2012. An Investigation of the soil property changes and Heavy metal accumulation in relation to long-term wastewater irrigation in the semi-arid Region of Iran. Soil and Sediment contamination: An International Journal, 20, 841-856.

Richardson, C.J., King, R.S., Qian, S.S., Vaithiyanathan, P., Qualls, R.G., and Stow, C.A. 2007. Estimating ecological thresholds for phosphorus in the Everglades. Environmental Science and Technology 41 (23), 8084-8091.

Robinson, T.P., and Metternicht, G. 2006. Testing the performance of spatial interpolation techniques for mapping soil properties. Comput. Electron. Agri. 50, 97-108.

Ruddiman, W. 2007. Plows, Plagues, and Petroleum: How Humans Took Control of Climate. Princeton, NJ: Princeton University Press.

Safari Sinegani, A.A., and Jafari Monsef, M. 2016. Chemical speciation and bioavailability of cadmium in the temperate and semiarid soils treated with wheat residue. Environmental Science and Pollution Research, 23(10), 9750–9758.

Sajwan, K.S., and Lindsay, W.L. 1986. Effects of redox on zinc deficiency in paddy rice. Soil Science Society American Journal, 50, 1264–1269.

Sakan, S.M., D.S. Djordjevic, Manojlovic, D.D., and Polic, P.S. 2009. Assessment of heavy metal pollutants accumulation in the Tisza River sediments. Journal of Environmental Management 90(11), 3382–3390.

Sarangi, A., Madramootoo, C.A. Enright, P., and Chandrasekharan, H. 2005. Prediction of Spatial Variability of Phosphorous over the St-Esprit watershed. Water, air, and soil polluiton 168(1), 267-288.

Sharpley, A.N., Lars Bergström, L., Aronsson, H., Bechmann, M., Bolster, C.H., Börling, K., Djodjic, F., Jarvie, H.P., Schoumans, O.F., Stamm, C., Tonderski, K.S., Ulén, K.S., and Uusitalo, R. 2015. Withers Future agriculture with minimized phosphorus losses to waters: research needs and direction. Ambio. 44 (2), 163–179.

Shi, J., Wang, H., Xu, J., Wu, J., Liu, X., Zhu, H., and Yu, C. 2007. Spatial distribution of heavy metals in soils: A case study of Changxing China. Enviroment Geology. 52, 1–10.

Sparks, D.L. 1996. Methods of Soil Analysis. Edited by P.3. Vol. 5, Chemical Methods. SSSA Book Series, . Madison, WI, USA: American Society of Agronomy and Soil Science Society of America.

Sposito, G., Lund, L., and Chang, A. 1981. Trace metal chemistry in arid-zone field soils amended with sewage sludge: I. Fractionation of Ni, Cu, Zn, Cd and Pb in solid phases. Soil Science Society American Journal. 46, 260-264.

Sposito, G., Lund, L., and Chang, A. 1982. Trace metal chemistry in arid-zone field soils amended with sewage sludge: I. Fractionation of Ni, Cu, Zn, Cd, and Pb in solid phases. Soil Science Society of America Journal. 46 (2), 260–264.

Stamm, C., Sermet, R., Leuenberger, J., Wunderli, H., Wydler, H., Flühler, H., and Gehre, M. 2002. Multiple tracing of fast solute transport in a drained grassland soil. Geoderma, 109, 245–268.

Thomas, G.W. 1996. Soil pH and soil activity. In Methods of Soil Analysis Part 3: Chemical Methods, edited by klute. Madision Wislonsin USA: American Society of Agronomy and Soil Science Society of America.

Walkley, A., and Black, I.A. 1934. An examination of the Degtareff method for determining soil organic matter, and a proposed modification of the chromic acid titration method. Soil Science. 37, 29–38.