



Research article

Assessment of physicochemical properties and concentration of heavy metals in agricultural soils fertilized with chemical fertilizers

Mansour.A. Salem^{a,1}, Dattatray K. Bedade^{b,*}, Latif Al-Ethawi^c, Samira.M. Al-waleed^a^a Environmental Sciences Department, Faculty of Engineering and Technology Sciences, Sebha University, Libya^b Food Engineering and Technology Department, Institute of Chemical Technology, Nathalal Parekh Marg, Matunga (E), Mumbai, 400 019, India^c Environmental Sciences Department, College of Energy and Environment Science, University of Alkarkh, Iraq

ARTICLE INFO

Keywords:

Physicochemical properties
 Heavy metals
 Cultivation
 Fertilization
 Geochemical index
 Contamination
 Soil science
 Environmental analysis
 Environmental assessment
 Environmental hazard
 Environmental pollution
 Environmental risk assessment
 Environmental toxicology
 Environmental science
 Toxicology

ABSTRACT

The present study aim to assess the effect of phosphate and urea fertilizers on the physicochemical properties, pH and electrical conductivity (EC) of the soil. The effect of these fertilizers on cation exchange capacity (CEC), organic matter (OM), and the possibility of contamination with heavy metals (HM) (Cr, Cu, Cd, Mn, Zn, Ni, Fe, and Pb) were studied on the soils of Alshati agricultural project at different seasons after forty years of fertilization. Uncultivated soil samples were also analyzed for comparison and considered as reference. Mean values of soil pH, EC, CEC, and OM ranged between 6.88–7.32, 0.14–0.26 $\mu\text{S}/\text{cm}$, 2.95–4.19 Cmol/kg and 0.49–0.53%, respectively, in all seasons. Concentrations of HMs were 9.50–38.38, 0.0–2.05, 0.0–0.47, 0.0–29.81, 0.0–13.85, 2.83–25.95 and 104–512.20 mg/kg respectively, for Cr, Cu, Cd, Mn, Zn, Ni and Fe. The concentrations of the HMs in the soil were found to be vary significantly with the seasons (winter, spring, summer, and autumn). However, no traces of Pb was found in the soil samples. The result showed a significant correlation between, pH, EC, CEC, OM and HM content of the soil. The geochemical index of contamination shows that there was no contamination with Cu, Cd, Zn, Pb, Cr, Mn, Ni, and Fe.

1. Introduction

Heavy metals (HMs) are natural constituents of the earth crust and biologically important at trace levels (Juvanovic et al., 1995). The two major sources of HMs in the soil area are natural pedo-geochemical background and anthropogenic contamination occurred via composting, sewage sludge, aerosol deposition and waste animal manure (Abdolhossien et al., 2012). Soil is a substantive component of the biosphere and forms the major sink for metals released into the environment from a wide variety of anthropogenic activities such as transport, agricultural practices, municipal refuse, industrial activities and disposal of wastes (Wang et al., 2016; Enunekua et al., 2017; Jiang et al., 2018). Composition of soil reflects the distribution and the intensity of trace elements in the soil. It is also representing the integration of multiple physical, chemical and biological processes occurring concurrently within the soil. Applications of chemical fertilizers, manure, pesticides and untreated or partially treated wastewater to the agricultural soil for

long term leads to contamination of soil with HMs. Accumulation of pollutants in agricultural soils is of increasing concern due to food safety, surface run-off to nearby rivers, and leaching into underground water (Wilson and Pyatt, 2007).

HMs are most frequent contaminant of soil and has become increasingly a serious problem in many parts of the world (Zhou et al., 2015). HMs are non-degradable, biologically or thermally and keep on accumulating in the environment to levels exceeding permissible limits that can adversely affect the soil hydrology, biota and soil chemistry which leads to socio-economic implications (Rodrigo-Comino et al., 2018; Antonelli et al., 2018; Kirpichtchikova et al., 2006; Sharma et al., 2007). Due to their longer half-life and fairly immobile nature (some of them are mobile), HMs are persistent in soil, therefore, they are transferred to aquifer via soil and plant roots (McBride and Spiers, 2001; Inoti et al., 2012; Sherene, 2010). HMs are existing in the soil in a variety of chemical forms such as water-soluble, exchangeable and bound to specific sites of organic and inorganic components and in the structure of primary and

* Corresponding author.

E-mail address: bedadedattu03@gmail.com (D.K. Bedade).¹ Both authors have contributed equally.

secondary minerals (Violante et al., 2010). These forms of HMs affect their reactivity, mobility, and bioavailability (Cao et al., 2018).

The concentration of HMs tends to increase with soil development, its mobility can be changed by environmental conditions such as type of soil, agricultural input, climate change and saturation capacity of the soil (García-Carmona et al., 2019). The concentration of HMs in soil depends on the geochemical characteristics of soils. Quality of soil depends mainly on a high degree of spatiotemporal variability of their physical, chemical, and biological properties caused by natural and anthropogenic interferences (Maltas et al., 2013). Distribution of HMs in the soil is controlled by many reactions such as adsorption and desorption, mineral precipitation and dissolution, ion exchange, aqueous complexation, biological mobilization and immobilization and lastly by plant uptake (Kumperman and Carreiro, 1997). Various factors such as pH, temperature, nutrient concentration, and available water content can affect the accessibility of HMs to soils (Alloway, 1995).

Contamination of soil through HM mainly dependent on the location, organic matter content and source of fertilizer. Moreover, the application of agricultural fertilizers does not significantly increase total HM content in the soil above background levels for several years (Rutkowska et al., 2009).

Organic matter has a vital role in controlling the mobility of HMs in soil. It may decrease available concentrations of HMs in soils by precipitation, adsorption or complexation processes (Collin and Doelsch, 2010). Chemical fertilizers such as NPK which are added as a source of nitrogen, phosphorous and potassium may contain some HMs (Cd, As, Cr, Ni, and Pb) as impurities. The application of these fertilizers to agricultural soil, dramatically decreased the pH of the soil which causes desorption of HMs from the soil matrix (Nazir et al., 2015). Application of excessive amounts of chemical fertilizers and poultry manures can also increase levels of HMs such as Cd, Cu, Zn and Pb in soils and subsequently in plants. Increasing levels of HMs in the soil is a serious environmental concern, since HMs are causing serious health problems such as HM induced tumors and other diseases. Continuous increase of HM concentrations in terrestrial systems also affects the health of plants, animals, and humans. Hence, most countries brought a major shift of an international concern towards the prevention of HMs accumulation in soil, food and other ecosystems (Laidlaw and Taylor, 2011; Sidhu et al., 2017). Therefore, the reported results suggest that, a deeper effort must be made to understand the interaction of physicochemical properties with HM contents of the soil.

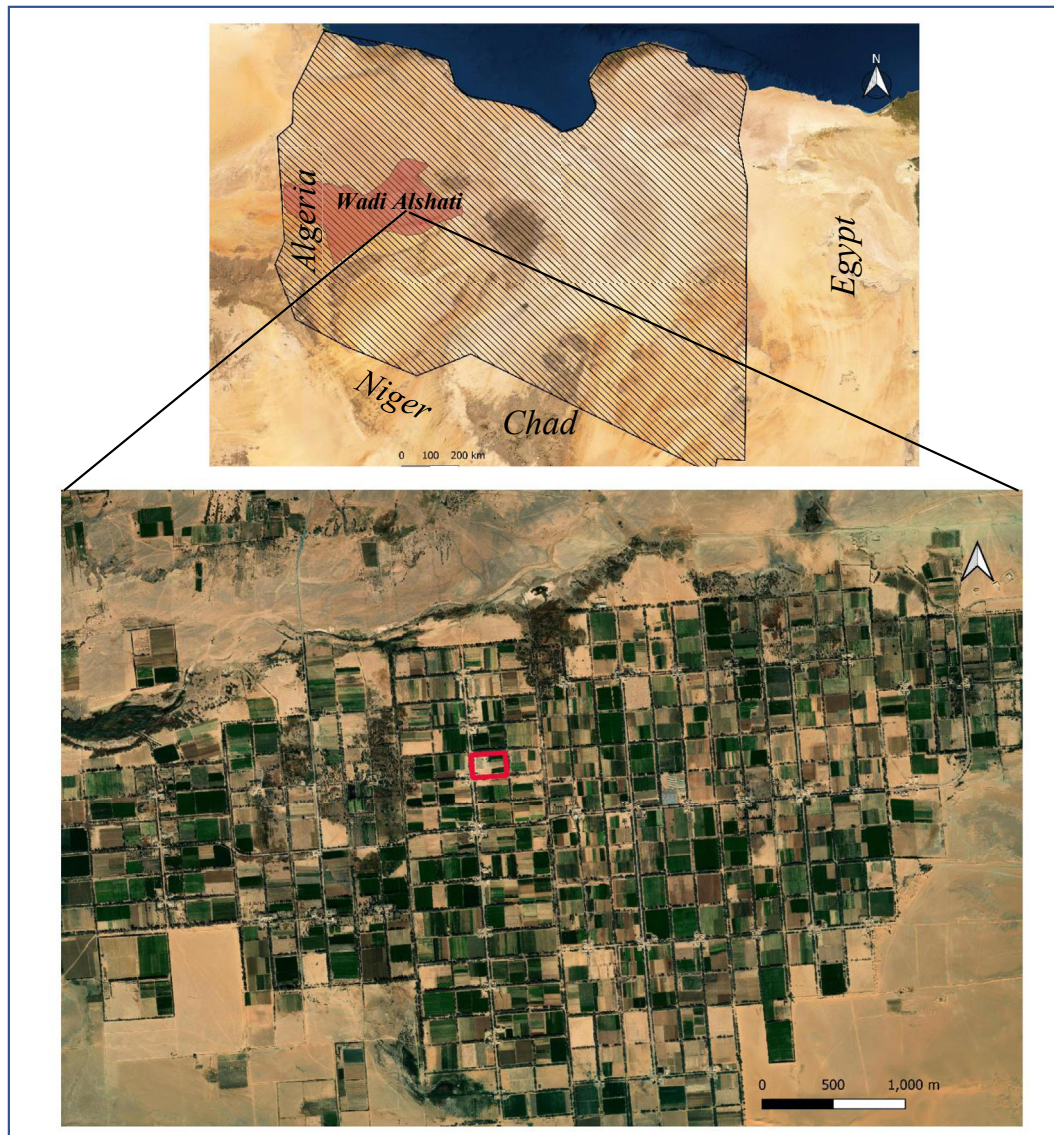


Figure 1. The location of the study area.

The present study was undertaken to investigate the physicochemical properties and HM contents (Pb, Cd, Cr, Cu, Fe, Mn, Cr, and Ni) in soil fertilized with chemical fertilizers such as urea and diammonium phosphate (DAP) in different seasons. The correlation between the physicochemical properties and HM contents of the soil were also investigated in different seasons.

2. Materials and methods

2.1. Study area

Al Shati province is located in the southern west part of Libya between North latitudes of 23° to 28.5° and East longitudes of 10° to 16° with an altitude of about 400 m above sea level (Figure 1). It is an arid zone with average temperature range between 10 °C in winter and up to 45 °C in summer. This region is one of the important agricultural regions in Libya as it's represented by a vast expanse of farmlands for the production of vegetables, cereals and forage for animals (Al-danasuri, 1967). Brack-Ashkada agriculture project built in 1975 and contains 300 farms with sprinkling irrigation, each 12 farms are irrigated with one artesian well, the area of each farm is about 10 ha. This agricultural project was aimed to provide vegetables, fruits and grasses for human being and animals, respectively. We chose one farm that had been intensively cultivated along the year and fertilize systematically with chemical fertilizers.

2.2. Geological and geographical features of the study area

Libyan soil is affected to the great extent by nature and conditions in which soil was formed. Aridity is the main characteristics of such soil however, most of the soil is undeveloped or partly developed. Desert region is spread across the southern parts, where the climate is hot in summers and cool in winters. Aeolian deposits are one of the important process in the formation of the Libyan soils with a sandy texture (Ben-Mahmoud; 1995; Zurqani et al., 2018). Libyan soil is typically shallow, sandy in texture, low in organic matter content and low water holding capacity. According to the modern soil classification of Russia and USDA soil classifications, Aridisols and Entisols are the main soil orders in the study area, and can be classified as sandy texture and low organic matter content (Zurqani et al., 2012).

2.3. Collections of soil samples

As mentioned in study area we choose one of the farms that was most exposed to the chemical fertilizers, and intensively cultivated by vegetables. The farm was divided into six sectors and 1kg of soil sample was collected from each section with auger sampler at depth of 0–30 cm. The samples were collected from the six different spots of each sector, therefore the total of 36 samples were collected from the six sectors for analysis.

Soil samples were collected in Summer (July) and Autumn (November) of 2017 and Winter (January) and Spring (March) of 2018. The soil samples were collected randomly (randomized design) in each season. Soil samples were collected in clean polyethylene bags, labeled properly and transferred to the laboratory for analysis. Uncultivated and undisturbed soil samples were also collected from area nearby to the study area in triplicate (collected with auger sampler from depth of 0–30 cm). Uncultivated and undisturbed soil sample was considered as a reference soil. All soil samples were air-dried to constant weight at room temperature, grounded to passed through 2 mm sieve. All soil samples were stored in a dry place for physicochemical and HM analysis (Bhatti et al., 2016).

2.4. Collection of water and fertilizer samples

A total of six samples were collected each from urea and diammonium phosphate fertilizers and four samples from irrigation water. Approximately 1L of water sample was collected from the irrigation well for analysis of physicochemical properties. Chemical fertilizers used for fertilization are mainly urea (46%) and diammonium phosphate (DAP). Samples of these fertilizers were subjected to chemical analysis to check its purity of HMs impurities.

2.5. Physicochemical analysis of soil

Physicochemical characterization was carried out on air-dried soil samples in the laboratory. The soil samples were suspended in water (1:2.5 ratio w/v) for analysis of pH and electrical conductivity (EC). The pH and electrical conductivity of soil was measured using laboratory pH meter (JENWAY3310) and conductivity meter (JENWAY4310), respectively. The cation exchange capacity (CEC) of the soil was determined by the protocol reported by Peris et al. (2008). In brief, soil samples were saturated with sodium acetate solution (pH-8.2) and the adsorbed sodium ions were displaced with ammonium acetate solution (pH-7.0). The amount of displaced sodium ion was analyzed by flame atomic absorption spectrometry (Analytik Jena, NOVA-A400, Germany).

Organic matter (OC) content of the soil sample was determined by the procedure reported by Walkley and Black (1974). The amount of organic carbon (%) and total organic matter (%) were determined by Eqs. (1) and (2),

$$OC (\%) = N ((B-S))/W \times 0.003 \times 100 \quad (1)$$

$$OM (\%) = OC (\%) \times 1.724 \quad (2)$$

Where, N = normality of ferrous ammonium sulfate, B = volume of ferrous ammonium sulfate required for blank (mL), S = volume of ferrous ammonium sulfate required for soil sample (mL) and W = mass of soil sample (g).

2.6. Determination of HMs in soil, irrigation water, and chemical fertilizer samples

The dried soil samples (~1g) were digested in aqua-regia (HCl: HNO₃, 3:1 ratio) (15 mL) at 110 °C (hotplate) for 4-5 h. The digest was cool down, filtered through filter paper (Whatman no. 42) and diluted with deionized water up to 50 mL in the volumetric flask (Rahman et al., 2012). These diluted samples were analyzed for HM content using the atomic absorption spectrophotometer (air-acetylene flame) (Analytik Jena, NOVA-A400, Germany).

The HMs content of the irrigation water was analyzed as per the protocol reported by Inoti et al. [13]. In brief, approximately 1 L of irrigation water was taken in a clean plastic container and 2.5 mL of concentrated nitric acid was added to it. These diluted samples were analyzed for HM content by atomic absorption spectrophotometer (Analytik Jena, NOVA-A400, Germany). The blanks samples containing only distilled water were analyzed using the same procedure. The HM contents of the chemical fertilizers (diammonium phosphate and urea) were determined by placing fertilizer samples (5 g) in 5 % (v/v) HNO₃ (40 mL) in 150 mL beaker and heated at 80 °C. The samples were then filtered through filter paper (Whatman no. 42) and transferred to the volumetric flask and diluted up to 50 mL with 5 % v/v HNO₃ and analyzed using atomic absorption spectrophotometer (Alloway, 1995).

Validation of analytical results was assessed by analyzing all samples in triplicates. The working standard solutions for each metal ion were prepared freshly before every analysis. The concentration of all HMs was

measured at 358 nm for Cr, 325 nm for Cu, 229 nm for Cd, 279 nm for Mn, 214 nm for Zn, 232 nm for Ni, 248 nm for Fe and 283 nm for Pb. The detection limit of atomic absorption spectrophotometer is 0.081, 0.133, 0.151, 0.068, 0.137, 0.084, 0.032 and 0.049 ppm for Cd, Cr, Pb, Zn, Cu, Mn, Ni and Fe, respectively.

2.7. Geochemical index (Igeo)

The geochemical index (Igeo) was calculated as per the method described by Muller (1969). This method is widely used for the assessment of the degree of contamination by comparing the levels of HMs obtained to background levels (uncultivated soil) originally used with bottom sediments. The contamination in soil is assessed by using Eq. (3),

$$I_{geo} = \log_2 C_n / (1.5B_n) \quad (3)$$

Where, C_n = concentration of the element in the enriched samples. B_n = background or pristine value of the element, and constant 1.5 is introduced to minimize the effect of possible variations in the background values which could be attributed to lithological variations. The method assesses the degree of metal pollution in terms of seven enrichment classes (Table 1) based on the increasing values of the geochemical index.

2.8. Statistical analysis

All the experiments were carried out in triplicates. Statistical analysis of the data was performed using the SPSS 16 software package. Pearson correlation significance was computed among various physicochemical parameters and concentrations of HMs in the soil at 0.95 and 0.01 confidence levels ($P < 0.05$ and $P < 0.01$) using a one-way analysis of variance (ANOVA).

3. Results and discussion

Alshati agricultural project serve the region as a source of vegetables, cereals, fruits for human consumption and grasses for animals. The texture of the studied soil was sandy which was characterized by its low organic matter, high porosity and low water retention capacity (Mahmoud and Ramadan, 1995). To evaluate the effect of chemical fertilizers on soil, uncultivated soil samples were used as reference for comparison of physicochemical properties and accumulation of HMs with cultivated soil samples.

3.1. Physicochemical properties of selected soils in different seasons

The physicochemical properties of the soil samples in different seasons are presented in Table 2 pH of soil plays an important role in regulating solubility and mobility of HMs. Most of the HMs are found be available for the plants in acidic pH (Wang et al., 2018). However, the alkaline pH of the uncultivated soil does not affect the fertility of soil since these pH values are still close to neutrality. The mean pH of the soil samples was found to be 6.68 and 7.32 in the autumn and winter season, respectively. Lower pH value of the soil sample in autumn season might

be probably due to the applications of urea fertilizer, while the pH of uncultivated soil was tending to slightly alkaline (8.14). Another reason for decrease in pH of soil is due to the long-term applications of nitrogen-containing fertilizers such as diammonium phosphate and urea. Another reason for decrease in pH of soil is due to release of H^+ ions by the plant roots leads to acidification of soil (Constantin et al., 2010). The present finding is in agreement with an earlier report (Geetha et al., 2017).

Electrical conductivity is used to estimate the concentration of soluble salts in the soil. The electrical conductivity of soil samples was found to be 0.14 $\mu S/cm$ and 0.26 $\mu S/cm$ in winter and summer seasons respectively, whereas the mean electrical conductivity of uncultivated soil sample was found to be 4.05 $\mu S/cm$ (Table 2). The low electrical conductivity of the of the cultivated soil is due to low salt content which had washed down during the irrigation processes. The washing out of the salts during irrigation process might be attributed due to sandy texture of the soil. Another reason for decrease in electrical conductivity might be due to complex precipitation of salts and transport to plants. The decrease in electrical conductivity of the cultivated soil is in agreement with the previous study (Geetha et al., 2017).

Cation exchange capacity (CEC) is a measure of the soil ability to bind or hold exchangeable cations. The results showed that mean CEC was found to be 2.95 Cmol/kg and 4.19 Cmol/kg in summer and spring season, respectively. The mean value of CEC for uncultivated soil was found to be 5.17 Cmol/kg. The increase in CEC of cultivated soil in the summer season might be attributed to an increase in temperature or some stimulation of biological activity by temperature in summer. However, CEC was found to be decreased in autumn and winter season. The present results corroborate with the earlier finding (Abah et al., 2014).

The organic matter of the cultivated soil samples was found to be 0.44% and 0.53% in autumn and spring season, respectively, while it was 0.93% for uncultivated soil samples. The decrease in the organic matter content of cultivated soil over uncultivated soil might be attributed to the sandy texture of the soil. Also, the higher temperature of soil enhances the degradation of OM. The low organic matter in the soil is not favorable for HM absorption. The present finding corroborates with the previous reports (Bhatti et al., 2016).

3.2. Chemical analysis of irrigation water and fertilizer samples

The chemical fertilizers such as diammonium phosphate (DAP) and urea are usually added in the beginning of November and middle of January with random quantities regardless of actual need. The HM contents of the fertilizers are represented in Table 3. The results showed concentrations of Cd (1.15 mg/kg), Cr (3.3 mg/kg) and Ni (2.6 mg/kg) were found to be significantly higher in DAP than permissible limits (WHO/FAO, 2001). However, urea contains only traces of Zn, Ni, and Cr (Table 3). Phosphate fertilizers have been reported to contain high amounts of HMs including Cd and Ni whereas HMs contents in urea fertilizers were reported to be within the permissible limits (WHO/FAO, 2001). It has been reported that phosphate fertilizers from different countries contain high concentrations of Cr and low concentrations of Hg

Table 1. Geochemical index (Igeo) for contamination levels in soil.

I_{geo} value	I_{geo} class	Contamination level
>5	6	Extremely contaminated
4–5	5	Strongly to extremely contaminated
3–4	4	Strongly contaminated
2–3	3	Moderately to strongly contaminated
1–2	2	Moderately contaminated
0–1	1	Uncontaminated to moderately contaminated
0	0	Uncontaminated

Table 2. Physiochemical properties of the selected soil samples in different seasons.

Parameter	Values	Seasons				Uncultivated soil
		Winter	Spring	Summer	Autumn	
pH	Mean	7.32	7.01	6.95	6.88	8.14
	Std. Error of Mean	0.10	0.14	0.07	0.10	0.04
	Minimum	7.12	6.69	6.68	6.62	8.00
	Maximum	7.68	7.45	7.14	7.28	8.22
EC ($\mu\text{S}/\text{cm}$)	Mean	0.14	0.15	0.26	0.18	4.05
	Std. Error of Mean	0.01	0.01	0.01	0.01	2.79
	Minimum	0.12	0.13	0.23	0.14	0.83
	Maximum	0.16	0.17	0.31	0.22	17.97
CEC (Cmol/kg)	Mean	3.39	4.19	2.95	3.16	5.17
	Std. Error of Mean	0.18	0.39	0.37	0.28	0.67
	Minimum	2.97	3.13	1.83	2.25	2.70
	Maximum	4.00	5.40	4.25	3.90	6.80
OM (%)	Mean	0.49	0.53	0.48	0.44	0.93
	Std. Error of Mean	0.10	0.07	0.08	0.09	0.18
	Minimum	0.20	0.33	0.27	0.23	0.60
	Maximum	0.85	0.75	0.70	0.77	1.80

Table 3. Concentration of heavy metals (ppm) in chemical fertilizers and irrigation water.

Samples	Heavy metals (mg/kg)							
	Cr	Cu	Mn	Zn	Cd	Ni	Fe	Pb
Diammonium Phosphate	3.40 \pm 0.25	0.87 \pm 0.01	ND	33.86 \pm 2.06	1.18 \pm 0.02	2.64 \pm 0.05	6.49 \pm 0.80	ND
Urea	0.15 \pm 0.10	ND	ND	0.34 \pm 0.05	ND	0.26 \pm 0.03	1.98 \pm 0.01	ND
Irrigation water	ND	ND	1.64 \pm 0.04	0.31 \pm 0.03	0.04 \pm 0.01	0.46 \pm 0.07	2.64 \pm 0.01	ND
Cultivated soil	25.683 \pm 0.32	0.678 \pm 0.09	12.229 \pm 2.90	2.912 \pm 0.65	0.067 \pm 0.027	10.444 \pm 0.29	263.64 \pm 34.22	ND
Uncultivated soil	27.43 \pm 0.54	ND	13.51 \pm 1.117	ND	ND	6.923 \pm 0.25	649.5 \pm 59.73	ND
*Canadian Standard	ND	ND	ND	1850	20	180	ND	500

(ND) Not Detected

* Canadian Standard for fertilizers.

(Mortvedt, 1995). The results of HM contents in chemical fertilizers used for cultivation were found to be low (Table 3). However, an earlier study on superphosphate fertilizer reported to contain a considerable amount of Cu (7.8 mg/kg) and Zn (15.80 mg/kg) as impurities (Banson et al., 2014). It is also reported in the literature that, phosphate fertilizers manufactured in Turkey contains high impurities than ammonium and urea fertilizers (Saltali et al., 2005). However, considerable amount of Fe (6.4 mg/kg), Mn (1.7 mg/kg), Zn (0.3 mg/kg) and Cd (0.25 mg/kg) were also detected in irrigation water. These values of metal ions exceeded the permissible limits for irrigation water set by Canadian standards (Table 3) (Heekmah, 2006).

3.3. The concentration of HMs in soil samples

HM contents of soil samples were analyzed in winter, spring, summer and autumn seasons, and were compared with HM content of uncultivated soils as a reference (Table 4). The mean concentration of Cr was found to be 37.56, 31.89, 20.13 and 13.15 mg/kg in autumn, spring, winter, and summer season, respectively, while it was found to be 27.43 mg/kg in an uncultivated soil sample. However, the mean concentration of Cr in cultivated and uncultivated soil was found to be below the permissible limits of WHO/FAO (2001). The high concentration of Cr (58.3–62.3 mg/kg) in agricultural soil was reported as a result of irrigation with wastewater (Belay et al., 2002). Moreover, 47.76–89.23 mg/kg of Cr was reported in cultivated soils that were exposed to chemical fertilizers for a long time (Li et al., 2011). The mean concentrations of Cr in cultivated soil were found to be in the range of

8.86–35.58 mg/kg in Punjab, India (Bhatti et al., 2016). The significant changes of Cr concentrations in different seasons, refer to the fact that farmers usually adding chemical fertilizers to the soil at the first month of autumn (August), and they didn't add any fertilizers at the beginning of March. Therefore, crops consumed most of the HM present in fertilizers before summer time. The present results corroborate with the earlier finding where the 28.3 mg/kg of Cr was reported in Spanish agricultural soil due to climatic variations (Rodriguez et al., 2008).

The mean concentration of Cu was found to be 0.028, 0.122, 0.155 and 0.051 mg/kg in winter, spring, summer, and autumn, respectively. However, Cu was not detected in uncultivated soil samples. The low content of Cu in the soil attributed to i) non-industrial area of studies ii) low contents of Cu in applied chemical fertilizers and irrigation water. Therefore, there is no apparent source of contamination with this element. Contamination with Cu was attributed to anthropogenic activities such as the application of excessive and low quality of chemical fertilizers and irrigation water (Bhatti et al., 2016).

Cd is considered as one of most ecotoxic HM and reported to exhibit an adverse effect on soil health, plant metabolism, biological activity and health of animals and human beings (Sun et al., 2016). The concentration of Cd in soil samples was found to 0.068, 0.013 and 0.185 mg/kg in winter, spring and summer season, respectively, which were below the permissible limits (WHO/FAO, 2001). The detection of Cd (cultivated soil samples) in winter, spring and summer season attributed to cultivation and fertilization with chemical fertilizers which contains traces of Cd during 40 years of cultivation. However, Cd was not detected in the autumn season and uncultivated soil

Table 4. Mean values of total heavy metal concentration in soil samples (cultivated and uncultivated) in different seasons.

HM (mg/kg)	Values	Cultivated soil				Uncultivated soil	Permissible limit (mg/kg)
		Winter	Spring	Summer	Autumn		
Cr	Min.	19.49	31.45	9.50	37.24	25.56	100
	Max.	20.63	32.40	14.89	38.35	29.43	
	Mean	20.130	31.89	13.15	37.560	27.43	
	SD. Mean	0.165	0.165	0.791	0.175	0.546	
Cu	Min.	-	0.08	0.99	0.49	-	100
	Max.	0.15	1.00	2.05	0.85	-	
	Mean	0.043	0.475	1.487	0.705	-	
	SD. Mean	0.028	0.122	0.155	0.051	-	
Cd	Min.	-	-	0.010	-	-	3.0
	Max.	0.240	0.040	0.470	-	-	
	Mean	0.068	0.013	0.185	-	-	
	SD. Mean	0.037	0.006	0.067	-	-	
Mn	Min.	18.58	6.92	-	-	10.66	2000
	Max.	28.87	18.52	29.81	18.40	17.90	
	Mean	22.75	12.77	7.088	6.308	13.51	
	SD. Mean	1.872	1.931	4.662	3.120	1.117	
Zn	Min.	0.1	-	2.62	2.00	-	300
	Max.	0.52	-	13.85	7.29	-	
	Mean	0.256	-	6.802	4.588	-	
	SD. Mean	0.093	-	1.596	0.935	-	
Ni	Min.	2.83	5.40	6.18	23.61	6.35	50
	Max.	4.31	6.06	9.95	25.95	8.05	
	Mean	3.697	5.715	7.663	24.70	6.923	
	SD. Mean	0.230	0.100	0.521	0.330	0.254	
Fe	Min.	104	257.65	187.70	266.81	516.0	50,000
	Max.	296.60	382.83	427.15	512.20	886.00	
	Mean	140.92	308.09	258.34	347.21	649.50	
	SD. Mean	40.333	18.080	36.687	41.804	59.739	
Pb	Min.	-	-	-	-	-	50
	Max.	-	-	-	-	-	
	Mean	-	-	-	-	-	
	SD. Mean	-	-	-	-	-	

Data shown are Mean \pm S.D; ND = Not Detected; Permissible Limit, WHO/FAO 2001.

samples. The Cd unable to adhere to the soil due to its solubility under set environmental conditions and potentially bioavailable for uptake by plants. The present finding is in agreement with the earlier study (Yahaya et al., 2009). The present finding suggests that the application of phosphate fertilizers for more than 40 years has not influenced the available Cd content of soils significantly. The present results are in agreement with the earlier finding reported by Lehoczyk et al. (2004). However, high levels of Cd were reported in soils irrigated with wastewater and excessive use of agrochemicals or located in heavy traffic and industrial area (Bhatti et al., 2016; Ebong and Ekong, 2015).

The mean concentration of Mn in cultivated (winter, spring, summer and autumn seasons) and uncultivated soil were found to be below the permissible limits (Table 4) (WHO/FAO, 2001). However, the concentration of Mn higher in winter than in summer, this might be attributed to the precipitation observed in rainy and, summer season which partially removes the soluble metal contents from the soil. Low concentrations of Mn, Cr, Cu, Ni, C, and Zn, reported in soil samples irrigated with river water in the Swat district in Pakistan (Khan et al., 2013).

The mean concentration of Zn in cultivated and uncultivated soil samples was found to be very low in comparison with the permissible limits (WHO/FAO, 2001). However, Zn was not detected in the spring season and uncultivated soil samples. The low concentrations of Zn attributed to the sandy nature of the soil and the low accumulation of Zn ions from the added chemical fertilizers. Earlier reports also indicated the

lower concentrations of Zn in soil samples from Accra and Ghana (Fosu-Mensah et al., 2017). However, higher concentrations of Zn were reported in soil samples collected from e-waste and dump sites (Li et al., 2011).

The mean concentrations of Ni in the cultivated and uncultivated soil were found to be below the permissible limits for agricultural soil (WHO/FAO, 2001). The existence of Ni in the soil samples could be attributed to impurities in the chemical fertilizers and sandy nature of soil (Shahbaz et al., 2018). Ni occurs in a very low amount in nature and essential in small doses, but it can be toxic when maximum tolerable concentration is exceeded (Srekanth et al., 2013). The Ni concentrations of 15.1 mg/kg were reported in cultivated and uncultivated soil in Turkey (Saltali et al., 2005). Also, the Ni concentrations of 21.16–41.18 mg/kg were also reported for agricultural soil as a result of long-term agricultural activities (Jia et al., 2010). The concentration of Ni from four different locations of soil samples collected from Punjab (India) was found to be in the range of 9.67–24.32 mg/kg (Chahal et al., 2014).

Iron was found to be the most predominant metal ion among essential elements in agriculture soil samples. The iron content of uncultivated soil samples was found to be higher than the cultivated soil samples and was much lower than the permissible limits for agricultural soil (WHO/FAO, 2001). High concentrations of Fe, range between 10979–19807 mg/kg, have been reported in agriculture soil samples in the Segura river valley in Spain (MicoLlopis et al., 2006). While low concentrations of Fe 2809–5304 mg/kg were found in agriculture soil samples of Punjab, India, as a

Table 5. Average I_{geo} and contamination levels in soil samples.

Heavy metal	I_{geo} value	Contamination level
Cr	0.188	Uncontaminated to moderately contaminated
Cu	0.0	Uncontaminated
Cd	0.0	Uncontaminated
Mn	0.230	Uncontaminated to moderately contaminated
Zn	0.0	Uncontaminated
Ni	0.326	Uncontaminated to moderately contaminated
Fe	0.081	Uncontaminated to moderately contaminated
Pb	0.0	Uncontaminated

Table 6. Correlation between physical properties and heavy metal contents of the soil.

	pH	EC	CEC	OM	Cr	Cu	Cd	Mn	Zn	Ni	Fe	Pb
pH	1											
EC	-0.53	1										
CEC	-0.95**	0.69	1									
OM	-0.82*	0.75	0.96**	1								
Cr	0.76	-0.92**	-0.82**	-0.78	1							
Cu	0.43	0.45	-0.17	0.06	-0.14	1						
Cd	0.55	-0.17	-0.38	-0.15	0.50	0.42	1					
Mn	-0.78	0.90*	0.91*	0.93**	-0.94**	0.17	-0.34	1				
Zn	-0.28	0.81*	0.51	0.64	-0.71	0.69	-0.15	0.78	1			
Ni	-0.02	-0.63	-0.02	-0.07	0.47	-0.53	-0.07	-0.26	-0.34	1		
Fe	-0.77	0.85*	0.92**	0.96**	-0.88*	0.16	-0.24	0.99**	0.76	-0.15	1	
Pb	a	a	a	a	a	a	a	a	a	a	a	a

a Cannot be computed because at least one of the variables is constant.

** Correlation is significant at the 0.01 level (2-tailed).

* Correlation is significant at the 0.05 level (2-tailed).

result of long-term irrigation with wastewater and continuous use of inorganic fertilizers (Chahal et al., 2014).

The results of HM concentrations showed that the concentration of Cu, Zn, Ni, and Fe were found to be lower in the winter season than other seasons. It has been reported that the concentration of HMs was lower in the wet season than the dry season. In a heavy rainy season. Most of the suspended materials which are not complexed and precipitated with soil or organic matter and other compounds may be flashed out through the canal into adjoining vast flood zone (Rahman et al., 2012).

Among the HMs studied Pb was not detected in cultivated and uncultivated soil samples. The possible reason could be the use of irrigation water and chemical fertilizers free of Pb metal ion. The study area is also far away from the heavy traffic/industrial area and farms do not have irrigation history with wastewater. However, contamination with Pb exceeded the maximum permissible limit of 100 mg/kg had been reported in agricultural soils in some sites, for instance in Italy up to 582 mg/kg (Abollino et al., 2002). The high total content of Pb up to 4705 mg/kg reported in alluvial soils in the Pribram region in the Czech Republic as a result of the smelting industry (Vanek et al., 2005). The concentration of Pb up to 350 mg/kg also reported in agriculture soils as a result of the application of Pb containing compounds on to the field of Amritsar, Punjab India by Bhatti et al. (2016). In the Olkusz district of Poland, concentration Pb up to 404 mg/kg reported in some arable soils close to industrial areas (Miskowicz et al., 2015). The high concentration of Pb was also found in soil samples from the recycling site of e-waste in Accra Ghana by Fosu-Mensah et al. (2017).

The decrease in HM content (cultivated soils) in different seasons might be attributed to transport of HMs to plants.

3.4. Geoaccumulation index

The average of I_{geo} and contamination levels of different metals in soil samples are presented in Table 5. The results show that the study area was particularly uncontaminated with Cu, Cd, Zn, and Pb. Due to the absence of pollutant sources such as anthropogenic activities, heavy traffic or irrigation with polluted waters. The low values of I_{geo} might have also raised from the metals geochemical and biological interactions and variations. However, the soil samples were uncontaminated to moderately contaminated with Cr, Mn, Ni, and Fe. This contamination could be attributed to the application of chemical fertilizers for the long-term. The present results corroborate with the earlier results reported by Fosu-Mensah et al. (2017).

3.5. Statistical analysis

The correlation between HMs and physicochemical properties of soil are presented in Table 6. The correlation among various physicochemical parameters and concentrations of HMs in the soil at 0.95 and 0.01 confidence levels ($P < 0.05$ and $P < 0.01$) using ANOVA are presented in Table 7. The results show that there is significant difference at 95% confidence level for metals and physicochemical properties and non-significant for OM at F3,20. The significant differences between the concentration of metals and the physicochemical properties may be due to the variation of temperature in different seasons which affect the absorption of heavy metals in the soils. Pearson correlation with 2-tailed test showed that, at 0.01 level ($p < 0.01$) positive significant relationships existed between CEC-OM ($r = 0.960$), CEC-Fe ($r = 0.924$), OM-Mn

Table 7. Analysis of variance (ANOVA) between and with heavy metals and physicochemical properties at different seasons at 95% confidence level.

Parameters		DF	F	Sig.
pH	Between groups	3	5.0	0.008
	Within groups	20		
	Total	23		
CEC	Between groups	3	3.0	0.039
	Within groups	20		
	Total	23		
EC	Between groups	3	33.0	0.000
	Within groups	20		
	Total	23		
OM	Between groups	3	0.165	0.919
	Within groups	20		
	Total	23		
Cr	Between groups	3	143.0	0.000
	Within groups	20		
	Total	23		
Cu	Between groups	3	43.8	0.000
	Within groups	20		
	Total	23		
Cd	Between groups	3	7.1	0.002
	Within groups	20		
	Total	23		
Mn	Between groups	3	6.0	0.004
	Within groups	20		
	Total	23		
Zn	Between groups	3	11.0	0.000
	Within groups	20		
	Total	23		
Ni	Between groups	3	595.0	0.000
	Within groups	20		
	Total	23		
Fe	Between groups	3	5.0	0.007
	Within groups	20		
	Total	23		
Pb	Between groups	3	0.0	-
	Within groups	20		
	Total	23		

DF: Degree of freedom used to estimate the variance, F: ratio of two variances or technically two mean squares.

($r = 0.931$), OM-Fe ($r = 0.966$) and Mn-Fe ($r = 0.987$) due to the high affinity of metals to soil organic matter. Similarly, significant positive correlation between the HMs themselves suggesting the similar and identical origin of the HMs, and indicating that the anthropogenic activities could enhancing the mobility of these elements. The present finding corroborates with the earlier results (Qfishlaqi and Moore, 2007). Adverse correlation was found between pH-CEC ($r = -0.949$), EC-Cr ($r = -0.926$), Cr-Mn ($r = -0.943$). The negative correlation might be attributed to the low content of organic matter which plays a significant role in determining the availability and mobility of HMs in soil, and/or to the nature of soil texture. The present finding corroborates with the earlier results reported by Wokhe et al. (2013). At level 0.05 level ($p < 0.05$) there is also positive significant correlation between EC-Mn ($r = 0.90$), EC-Zn ($r = 0.81$), EC-Fe ($r = 0.85$), CEC-Mn ($r = 0.91$), while there is an adverse correlation between pH-OM ($r = -0.82$), CEC-Cr ($r = -0.82$) and Cr-Fe ($r = -0.88$). The present results corroborate with the earlier results reported by Zeng et al. (2011). Soil parameters had common sources or mutual dependences subject to certain factor controls. The high correlation between HMs in soil may reveal that the accumulated concentrations of these HMs result from similar pollution sources (Nagarajan et al., 2010).

4. Conclusions

The results indicate the fluctuation of physicochemical parameters was observed from season to season. The concentration of all studied HMs was below the maximum permissible limits for agriculture soils set by WHO/FAO 2001. The fluctuation of HMs concentration observed in different seasons. This fluctuation is attributed to the intensive agriculture practices and to the nature of soil texture which considered to be sandy. Both factors can cause leaching of metals to lower ground layers.

The geochemical index showed that soil samples were uncontaminated with Cu, Cd, Zn and Pb whereas uncontaminated to moderately contaminated with Cr, Mn, Ni and Fe. Significant correlation relationships were found between HM contents (Cr, Mn, and Zn) and studied soil physical parameters (pH, EC, CEC, OM). The results also show that, despite the application of phosphate and urea fertilizers for more than forty years, the concentration of studied HMs was still below the permissible limits set by WHO/FAO 2001. The use of these fertilizers is not expected to cause a detrimental effect with regards to HM pollution, however, a slight annual increase could be expected. Possible increasing of HMs content, in agriculture soils, might occur from other sources.

Therefore, it is necessary to monitoring the changes of HMs concentrations in soils and developing pollution control strategies.

Declarations

Author contribution statement

Mansour.

A. Salem: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

Latif Al-Ethawi: Conceived and designed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data.

Samira. M. Al-waleed: Conceived and designed the experiments; Performed the experiments.

Dattatray K. Bedade: Analyzed and interpreted the data; Wrote the paper.

Funding statement

This research did not receive any specific grant from funding agencies in the public, commercial, or not-for-profit sectors.

Competing interest statement

The authors declare no conflict of interest.

Additional information

No additional information is available for this paper.

References

- Abah, J., Mashebe, P., Ubwa, S.T., Denuga, D.D., 2014. Some heavy metals content of Cabbage and soil cultivated in the Bezi Bar farm area of Katima Mulilo, Namibia. *Am. J. Chem.* 4 (3), 101–108.
- Abdolhossien, H.P., Vahid, B., Abasali, A.Z., Ali, H., 2012. Concentration, distribution and comparison of total and bioavailable heavy metals in top soils of Bonab District in Zanjan Province. *Open J. Soil Sci.* 2, 123–132.
- Abollino, O., Aceto, M., Malandrino, M., Mentasti, E., Sarzanini, C., Petrella, F., 2002. Heavy metals in agricultural soils from Piedmont, Italy. Distribution, speciation and chemometric data treatment. *Chemosphere* 49, 545–557.
- Al-danasuri, J., 1967. Geography of Fezzan, a Regional Study. Dar-Libya for publication and distribution, Tripoli Libya.
- Alloway, B.J., 1995. Soil Processes and the Behavior of Metals. Wiley, New York.
- Antonelli, A., Zizka, A., Carvalho, F.A., Scham, R., Bacon, C.D., Silvestro, D., Condamine, F.L., 2018. Amazonia is the primary source of neotropical biodiversity. *Proc. Natl. Acad. Sci. Unit. States Am.* 115 (23), 6034–6039.
- Banson, N.U., Anake, W.U., Etesin, U.M., 2014. Trace metals levels in inorganic fertilizers commercially available in Nigeria. *J. Sci. Res. Rep.* 3 (4), 610–620.
- Belay, A., Claassens, A.S., Wehner, F.C., 2002. Effects of direct nitrogen and potassium and residual phosphorus fertilizers on soil chemical properties, microbiological components and maize yield under long-term crop rotation. *Biol. Fertil. Soils* 35, 420–427.
- Ben-Mahmoud, K.B., 1995. Libyan Soils, first ed. National Research Scientific Organization, Tripoli, Italy.
- Bhatti, S.S., Kumar, V., Singh, N., Sambyal, V., Singh, J., Katnoria, J.K., Nagpal, A.K., 2016. Physico-chemical properties and heavy metals contents of soils and Kharif crops of Punjab, India. *Procedia Environ. Sci.* 35, 801–808.
- Cao, C., Zhang, Q., Ma, Z.-B., Wang, X.-M., Chen, H., Wang, J.-J., 2018. Fractionation and mobility risks of heavy metals and metalloids in wastewater-irrigated agricultural soils from greenhouses and fields in Gansu, China. *Geoderma* 328, 1–9.
- Chahal, V., Chand, P., Avinash, N., Kaur, K., Yogesh, P., 2014. Evaluation of heavy metals contamination and its genotoxicity in agricultural soil of Amirstar, Punjab, India. *Int. J. Res. Chem. Environ.* 4 (4), 20–28.
- Collin, B., Doelsch, E., 2010. Impact of high natural soilborne heavy metal concentrations on the mobility and phytoavailability of these elements for sugarcane. *Geoderma* 159, 452–458.
- Constantin, J., Mary, B., Laurent, F., Aubrion, G., Fontaine, A., Kerveillant, P., Beaudoin, N., 2010. Effects of catch crops, no till and reduced nitrogen fertilization on nitrogen leaching and balance in three long-term experiments. *Agric. Ecosyst. Environ.* 135, 268–278.
- Ebong, G.A., Ekong, C.I., 2015. Pollution status of trace metals in waste impacted soils within Borokiri town, port Harcourt metropolis, Rivers State, Nigeria. *Int. J. Sci. Res. Environ. Sci.* 3 (2), 436–444.
- Enunekua, A., Biose, E., Ezemonye, L., 2017. Levels, distribution, characterization and ecological risk assessment of heavy metals in road side soils and earthworms from urban high traffic areas in Benin metropolis, Southern Nigeria. *J. Environ. Chem. Engg.* 5, 2773–2781.
- Fosu-Mensah, B.Y., Adda, E., Yiernyo-Towiah, D., Nyam, F., 2017. Heavy metals concentration and distribution in soils and vegetation at Korle Lagoon in Accra, Ghana. *Cogent Environ. Sci.* 3, 1–14.
- García-Carmona, M., Romero-Freire, A., Sierra Aragón, M., Martín Peinado, F.J., 2019. Effectiveness of ecotoxicological tests in relation to physicochemical properties of Zn and Cu polluted Mediterranean soils. *Geoderma* 338, 259–268.
- Geetha, S., Reddy, B., Hemalatha, K.P.J., 2017. Physico-chemical analysis of selected agricultural soil samples in Kommangi panchyathi, Chintapalli mandal, Visakhapatnam. *Int. J. Inf. Retr. Res. (IJRR)* 4 (1), 3530–3532.
- Heekmah, J.K., 2006. Public concerns with hazardous materials in fertilizers. The soil Profile, A newsletter providing information on issues relating to soils and plant nutrition. In: New Jersey, USA, 16, pp. 1–10.
- Inoti, J.K., Fanuel, K., George, O., Paul, O., 2012. Assessment of heavy metals concentrations in urban grown vegetables in Thika Town, Kenya. *Afr. J. Food Sci.* 6 (3), 41–46.
- Jia, L., Wang, W., Li, Y., Yang, L., 2010. Heavy metals in soil and crops of an intensively farmed area: a case study in Yucheng city, Shandong province, China. *Int. J. Environ. Res. Publ. Health* 7, 395–412.
- Jiang, R., Wang, M., Chen, W., 2018. Characterization of adsorption and desorption of lawn herbicide siduron in heavy metal contaminated soils. *Chemosphere* 204, 483–549.
- Juvanovic, S., Carrot, F., Deschamps, N., Vukotic, P., 1995. A study of the air pollution in the surroundings of an aluminum smelter using epiphytic and litophytic Li-chem. *J. Trace Microprobe Tech.* 13, 463–471.
- Khan, K., Lu, Y., Khan, H., Ishtiaq, M., Khan, S., Waqas, M., Wei, L., Wang, T., 2013. Heavy metals in agricultural soils and crops and their health risks in Swat District, northern Pakistan. *Food Chem. Toxicol.* 58, 449–458.
- Kirpichtchikova, T.A., Manceau, A., Spadini, L., Panfilii, F., Marcus, M.A., Jacquet, T., 2006. Speciation and solubility of heavy metals in contaminated soil using X-ray microfluorescence, EXAFS spectroscopy, chemical extraction, and thermodynamic modeling. *Geochem. Cosmochim. Acta* 70, 2163–2190.
- Kumperman, R.G., Crreiro, M., 1997. Soil heavy metal concentrations, microbial biomass and enzyme activities in a contaminated grassland ecosystem. *Soil Biol. Biochem.* 29, 179–190.
- Laidlaw, M.A., Taylor, M.P., 2011. Potential for childhood lead poisoning in the inner cities of Australia due to exposure to lead in soil dust. *Environ. Pollut.* 159 (1), 1–9.
- Lehoczy, E., Debreczeni, K., Kiss, Z., Szala, T., 2004. Effect of long-term fertilization on the available toxic element content of different soils. *J. Cent. Eur. Agric.* 5 (4), 309–314.
- Li, H.Z., Bai, J.M., Li, Y.T., Cheng, H.F., Zeng, E.Y., You, J., 2011. Short-range transport of contaminants released from e-waste recycling site in South China. *J. Environ. Monit.* 13 (4), 836–843.
- Mahmoud, B., Ramadan, K., 1995. Libyan Soil (Composition, Classification, Characteristics, Agricultural Potential, the First Edition, the Definition of the Scientific branch Zawia Dahmani Tripoli-Libya.
- Maltas, A., Charles, R., Jeangros, B., Sokart, S., 2013. Effect of organic fertilizers and reduced-tillage on soil properties, crop nitrogen response and crop yield: results of a 12-year experiment in Changins, Switzerland. *Soil Till. Res.* 126, 11–18.
- McBride, M.B., Spiers, G., 2001. Trace element content selected fertilizers and dairy manures as determined by ICP-MS. *Commun. Soil Sci. Plant Anal.* 32 (1/2), 139–156.
- Micollopi, C., Peris, M., Sánchez, J., Recatalá, L., 2006. Heavy metal content of agricultural soils in a Mediterranean semiarid area: the Segura River Valley (Alicante, Spain). *Spanish J. Agric. Res.* 4 (4), 363–372.
- Miskowicz, P., Laptas, A., Zieba, K., 2015. Soil pollution with heavy metals in industrial and agricultural areas: a case study of Olkusz District. *J. Elementol.* 20 (2), 353–362.
- Mortvedt, J.J., 1995. Heavy metals contaminants in inorganic and organic fertilizers. *Fert. Res.* 43, 55–61.
- Muller, G., 1969. Index of geoaccumulation in sediments of the rhine river. *Geol. J.* 2, 108–118.
- Nagarajan, R., Rajmohan, N., Mahendran, U., Senthamilkumar, S., 2010. Evaluation of groundwater quality and its suitability for drinking and agricultural use in Thanjavur city, Tamilnadu, India. *Environ. Monit. Assess.* 171, 289–308.
- Nazir, R., Khan, M., Masab, M., Ur Rehman, H., Ur Rauf, N., Shahab, S., Ameer, N., Sajed, M., MohibUllah, Rafeeq, M., Shaheen, Z., 2015. Accumulation of heavy metals (Ni, Cu, Cd, Cr, Pb, Zn, Fe) in the soil, water and plants and analysis of physicochemical parameters of soil and water collected from Tanda Dam Kohat. *J. Pharmacol. Sci.* 7 (3), 89–97.
- Peris, M., Recatalá, L., Mico, C., Sanchez, R., Sanchez, J., 2008. Increasing the knowledge of heavy metal contents and sources in agricultural soils of the European Mediterranean region. *Water, Air, Soil Pollut.* 192, 25–37.
- Qfishlaqi, A., Moore, F., 2007. Statistical analysis of accumulation and sources of heavy metals occurrence in agricultural soils of Khoshk river banks, Shiraz, Iran. *Am-Euras. J. Agri. Environ. Sci.* 2 (5), 565–573.
- Rahman, S.A., Khanam, D., Adyel, T.M., Islam, M.S., Ahsan, M.A., Akbor, M.A., 2012. Assessment of heavy metals contamination of agricultural soil around Dhaka export processing zone (DEPZ), Bangladesh: implication of seasonal variation and indices. *Appl. Sci.* 2, 584–601.
- Rodrigo-Comino, J., Taguas, E., Seeger, M., Ries, J.B., 2018. Quantification of soil and water losses in an extensive olive orchard catchment in Southern Spain. *J. Hydrol* 556, 749–758.

- Rodriguez, J.A., Nanos, N., Grau, J.M., Gil, L., Lopez-Arias, M., 2008. Multi scale analysis of heavy metal contents in Spanish agricultural top soils. *Chemosphere* 70, 1085–1096.
- Rutkowska, B., Szulc, W., Labetowicz, J., 2009. Influence of soil fertilization on concentration of micronutrients in soil solution of sandy soil. *J. Elemenetol.* 14 (2), 349–355.
- Saltali, K., Mendil, D.A., Sari, H., 2005. Assessment of trace metal contents of fertilizers and accumulation risk in soils, Turkey. *Agrochimica* 49 (3/4), 104–111.
- Sharma, R.K., Agrawal, M., Marshall, F., 2007. Heavy metal contamination of soil and vegetables in suburban areas of Varanasi, India. *Ecotox. Environ. Saf.* 66 (2), 258–266.
- Shahbaz, A.K., Lewinska, K., Iqbal, J., Ali, Q., Rahman, M.U., Iqbal, M., Abbas, F., Tauqeer, H.M., Ramzani, P.M.A., 2018. Improvement in productivity, nutritional quality, and antioxidative defense mechanisms of sunflower (*Helianthus annuus* L.) and maize (*Zea mays* L.) in nickel contaminated soil amended with different biochar and zeolite ratios. *J. Environ. Manag.* 218, 256–270.
- Sherene, T., 2010. Mobility and transport of heavy metals in polluted soil environment. *Biol. Forum-An Int. J.* 2 (2), 112–121.
- Sidhu, G.P.S., Singh, H.P., Batish, D.R., Kohli, R.K., 2017. Appraising the role of environment friendly chelants in alleviating lead by *Coronopusdidymus* from Pb-contaminated soils. *Chemosphere* 182, 129–136.
- Sreekanth, T.V.M., Nagajyothi, P.C., Lee, T.N.V., Prasad, K.V., 2013. Occurrence, physiological responses and toxicity of nickel in plants. *Int. J. Environ. Sci. Tech.* 10 (5), 1129–1140.
- Sun, Y., Sun, G., Xu, Y., Liu, W., Liang, X., Wang, L., 2016. Evaluation of the effectiveness of sepiolite, bentonite, and phosphate amendments on the stabilization remediation of cadmium contaminated soils. *J. Environ. Manag.* 166, 204–210.
- Vanek, A., Boruvka, L., Drabek, O., Mihaljevic, M., Komarek, M., 2005. Mobility of Lead, Zinc and Cadmium in alluvial soils heavily polluted by smelting industry. *Plant Soil Environ.* 51 (7), 316–412.
- Violante, A., Cozzolino, V., Perelomov, L., Caporale, A.G., Pigna1, M., 2010. Mobility and bioavailability of heavy metals and metalloids in soil environments. *J. Soil Sci. Plant Nutr.* 10 (3), 268–292.
- Walkley, A., Black, C.A., 1974. Critical examination of rapid method of determining organic carbon in soil. *Soil Sci.* 63, 251–264.
- Wang, X.L., Wanga, M.H., Quana, X.S., Yan, B., Xiao, X.M., 2016. Influence of thermal treatment on fixation rate and leaching behavior of heavy metals in soils from a typical e-waste processing site. *J. Environ. Chem. Engg.* 4, 82–88.
- Wang, Y., Zhong, B., Shafi, M., Ma, J., Guo, J., Wu, J., Ye, Z., Liu, D., Jin, H., 2018. Effects of biochar on growth, and heavy metals accumulation of Moso bamboo (*Phyllostachypubescens*) soil physical properties, and heavy metals solubility in soil. *Chemosphere* 219, 510–516.
- WHO/FAO, 2001. Food and Additives and Contaminants, Joint Codex. Alimentarius, FAO/WHO. Food Standard Programme, Alinorm, 01/12A.
- Wokhe, T.B., Mohammed, Y., Chima, M.P., 2013. Evaluation of physicochemical properties of irrigated soil. *J. Nat. Sci.* 3 (9), 135–140.
- Wilson, B., Pyatt, F.B., 2007. Heavy metal dispersion, persistence and bioaccumulation around an ancient copper mine situated in Anglesey, UK. *Ecotoxicol. Environ. Saf.* 66, 224–231.
- Yahaya, M.I., Muhammad, S., Abdullah, B.K., 2009. Seasonal variations of heavy metals concentration in abattoir dumping site soil in Nigeria. *J. Appl. Sci. Environ. Manag.* 13 (4), 9–13.
- Zeng, F., Ali, S., Zhang, H., Ouyang, Y., Qiu, B., Wu, F., Zhang, G., 2011. The influence of pH and organic matter content in paddy soil on heavy metal availability and their uptake by rice plants. *Environ. Pollut.* 159, 84–91.
- Zhou, P., Zhaob, Y., Zhaoc, Z., Chaia, T., 2015. Source mapping and determining of soil contamination by heavy metals using statistical analysis, artificial neural network, and adaptive genetic algorithm. *J. Environ. Chem. Engg.* 3, 2569–2579.
- Zurqani, H.A., Mikhailova, E.A., Post, C.J., Schlautman, M.A., Sharp, J.L., 2018. Predicting the classes and distribution of salt-affected soils in northwest Libya. *Commun. Soil plant anal.* 49, 689–700.
- Zurqani, H.A., Nwer, B.A., Rhoma, A.R., 2012. Assessment of spatial and temporal variations of soil salinity using remote sensing and geographic information system in Libya. In: *Proceeding of the 1st Annual International Conference on Geological and Earth Sciences*. Singapore.