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Evaluation of the environmental and human health risk related to metallic contamination in agricultural soils in the Mediterranean semi-arid area (Saiss plain, Morocco)

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Abstract

In the plain of Saiss, the most agricultural region of Morocco, the studies concerning the assessment of environmental and human risks related to metal contamination of agricultural soils are severely missing. To overcome the lack of such studies, trace-element analyses were carried out on six sampling sites of agricultural surface soils (66 sampling points), irrigated by superficial watercourses with high heavy metal contents. The average trace-element contents were 78, 55, 33, and 119 (mg kg^{-1}), respectively, for Cr, Cu, Ni, and Zn. These values are above average worldwide soil and geochemical background levels. Multivariate statistical analyses, principal component, and cluster analyses suggest that soil contamination by Cr, Cu, and Zn is mainly due to wastewater irrigation, with the exception of Ni, which is probably of pedo-lithogenic origin. To provide further information on contamination transmission, the bioavailability and distribution of the four heavy metals in the soils were studied by sequential and single extractions. The results indicate that Cu and Zn are potentially available and can constitute a potential risk to the environment. The risk assessment of soil contamination was also carried out using risk assessment code, enrichment factor, contamination factor, degree of contamination, pollution lead index, geoaccumulation index, and potential ecological risk factors. The health risk evaluation by the Hazard Index was used to derive a combined risk of soil ingestion, dermal contact, and inhalation for adults and children. According to these indices, the soils present a moderate-to-high contamination for Cu and Zn elements, respectively. Hazard Index values indicate the relative absence of health risks associated to heavy metals for both adults and children.

Introduction

Like many regions in the world, the Saiss plain has been under great environmental threat in recent years, following the development of urban, industrial, and agricultural activities. This is particularly the case for the agricultural soils irrigated by Oued Fez, which is an intermittent river that receives raw wastewater of a population of 1.2 million inhabitants, plus handcraft activities, such as tanneries and brass making. It is one of the main tributaries of Oued Sebou which waters are used for the irrigation of agricultural zones and other purposes such as drinking water and industry (Perrin et al. 2014). Contaminants emitted by anthropogenic activities accumulate in the soil and undergo various physical, chemical, and biological processes that can lead some of the toxicants to migrate to the

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groundwater, or to integrate the food chain (Wong et al. 2006; Vegter 2007; Morel and Heinrich 2008; Foti et al. 2017). Indeed, heavy metals remaining in the environment have the ability to bioaccumulate in the food chain, and, at high concentrations, may be toxic to humans and other organisms (Dudka and Miller 1999; Raghunath et al. 1999; Adriano 2001).

Several experimental and mathematical methods have been proposed to estimate the risks induced by high levels of heavy metals in soil which constitutes the first receptor of these elements in the agricultural system.

The experimental methods which have been developed are mainly based first on the pseudo-total chemical extraction of heavy metals from contaminated soils, and thereafter on the selective ones for instance "the single extraction" using a chelating agent like ethylenediaminetetraacetic acid (EDTA) or the "sequential extraction" using specific solvent for each step of extraction (Bruder-Hubscher et al. 2002). This multi-step extraction makes it possible to differentiate the mobile and residual fractions and to characterize the different labile fractions (Leleyter and Probst 1999; Leleyter and Baraud 2006; Leleyter et al. 2012). EDTA is used as a complexing agent because of its high extraction capacity of metals on exchange sites of both organic and inorganic complexes (Sahuquillo et al. 2003; Zhang et al. 2010; Leleyter et al. 2012).

Numerous calculation methods and approaches have been used to assess contamination and environmental quality of soil (Cheng et al. 2007; Qingjie et al. 2008; Marrugo-Negrete et al. 2017) namely the risk assessment code (RAC), enrichment factor (EF), contamination factor (CF), degree of contamination (DC), the pollution load index (PLI), and the geoaccumulation index (Igeo). Furthermore, in the case of agricultural soils, it is wiser to evaluate the ecological and health risks of a pollution source (Ma et al. 2007) by calculating different indexes such the index of ecological risk (ER), potential ecological risk (RI), hazard quotient (HQ), and the overall potential risk (HI hazard index).

Despite the importance of agriculture in the semi-arid Mediterranean region, there is little information on the present state of contamination level of agricultural soils. In fact, such studies have mainly been conducted in the European countries (Reimann et al. 2001; Micó et al. 2006). In Saiss plain that is the most important agricultural zone in Morocco where olive groves, orange trees, cereals, vines, and various vegetables are cultivated, some studies, based on the total concentrations of heavy metals and their mobility via sequential extraction, were conducted on soils irrigated by the raw wastewater of Oued Fez and Oued Sebou (El Ass et al. 2004; Bellarbi et al. 2015). However, to our knowledge, as regards the study of ecological and human health risk, this study will be the first to evaluate these indexes, and it will be used to provide baseline information of this area.

Thus, the aims of the present study were to evaluate the quality of agricultural soils irrigated by wastewater in the urban and suburban area at Saiss plain by (i) examining the concentration of four selected heavy metals (Cr, Cu, Ni, and Zn) in soils from six sites with 66 samples using different experimental methods such as pseudo-total extraction, and sequential and single extraction; (ii) using a multivariate analysis to identify the metal contamination sources and to evaluate their extents in study area; (iii) considering several indexes such as risk assessment code, indexes of soil contamination and pollution, ecological risk assessment, and human health risk with different concentration of Cr, Cu, Zn, and Ni.

Materials and methods

Description of study area

This study was conducted at Saiss plain in the region of Fez-Meknes, located in the northern part of Morocco. The Saiss plain, at an elevation of 400 m, is boarded by mountains to the North and the South, cut by the Oued Sebou valley, and opening to the Atlantic Ocean to the West. The Saiss plain is an intracontinental basin located between the two major structural domains of the northern part of Morocco namely The Rif and The Middle Atlas mountains. Overlying a Paleozoic basement, this basin is filled with Post-Miocene terrigenous sediment predominantly by Liassic carbonates, Miocene shale, and Plio-quaternary lacustrine deposits (Charrière 1990; Dauteuil et al. 2016).

The climate is continental semi-arid with cold winters and hot summers. However, over the period 1980–2010, January has the coldest days of the year, with a monthly average of 8.45 °C, while the hottest days are concentrated in August, with a monthly average 24.94 °C (Lasri 2015). The precipitation data recorded at the Sebou Hydraulic Basin Agency station over the period 1978–2017 revealed that the study area has a contrasting seasons and a relatively dry summer compared to other seasons. Thus, a strong inter and intra-annual rainfall variation was observed in the rainfall of this period, a characteristic of semi-arid climates.

Soil sampling analyses

We considered five soil sites situated before and after the confluence of the two rivers (FES1 and FES2: soils along Fez river (urban soils), CFS: soil at confluence, and SAV1 and SAV2: respectively at 4 km and 14 km to the confluence downstream of Sebou river (suburban soils). The SAM which is a suburban soil irrigated with uncontaminated Oued Sebou courses is considered as a control soil. It is located upstream of Sebou river before the confluence

which does not receive wastewaters, neither domestic, nor from artisanal activities. These sites were selected following a contamination gradient, according to reference studies (Koukal et al. 2004; Perrin et al. 2014; Bellarbi et al. 2015) which showed the lowest values of heavy metals and dissolved organic matter in the irrigation water and soil at SAM site, and pointed the low water quality of Sebou and Fez downstream and contamination of soils (Fig. 1). All the sampling site areas do not exhibit significant differences regarding to the plant community, the crop management, and the farm practices.

To carry out this work, 66 topsoil samples were collected from surface horizons (0–10 cm) of the studied sites using a plastic scoop. Then, the samples were stored in clean polyethylene bags before transportation to the laboratory where they were disaggregated and thoroughly mixed by hand, air-dried at room temperature (20–22 °C), and sieved to 2 mm which is the most reactive size fraction of soils. All the analyses were carried out on triplicate subsamples.

Fig. 1 Map of sampling site locations along Fez and Sebou Rivers

Soil physical and chemical characterization

Physical and chemical characteristics of soil samples were determined, using the following standard analytical procedures: for pH and EC by electrometry in, respectively, (1:2.5) and (1:5) soil–water suspension (NF-ISO 10390, NF-ISO 11265); carbonate content ($CaCO_3$) by volumetric calcimetry (NF-ISO 10693); organic matter (OM) content by pyrolyse at 375 °C during 16 h after predrying at 150 °C (NF EN 12879); clay, silt, and sand were measured by laser particle size (NF X 31-107).

The measurement of the dissolved organic carbon (DOC) was carried out using a Shimadsu TOC-5000 Total Organic Carbon Analyzer. The soil samples were first rewetted with water in 1:5 ratio. They were then shaken for 30 min at 300 rpm and centrifuged at 75,000g for 10 min. They were then filtered and the filtrate was further acidified to pH 2 (ultrapure HCl) (Bolan et al. 1996). Acidification allowed the preservation of the sample and the degassing of inorganic carbon.

Soil heavy metal analyses

Total of heavy metal concentrations

For total trace metal analysis, the solid was digested with a mixture of fluoro-nitro-perchloric acid following the standard procedure of NF-ISO 14869-1. For a 1 g (dry weight) of soil, the sample was first digested in a teflon crucible with a solution of concentrated (5 mL) nitric acid, (5 mL) perchloric acid, and (10 mL) hydrofluoric acid were added; and then placed on a hot plate (100 °C without boiling), to evaporate the acids and until the appearance of white fumes. After evaporation, the samples were cooled and 2 mL of 35% H_2O_2 were added to attack the persistent organic matter. The temperature was increased until all the liquid is dry and a viscous mixture is obtained. It is allowed to cool, and then, 2.5 mL of nitric acid was added and the total evaporation was resumed (a pearl is obtained). The residue was dissolved with 5 mL of 50% nitric acid and 10 mL of distilled water, and boiled for 5 min. The resulting solution was transferred to a volumetric flask and diluted to 100 mL by bidistilled water.

The accuracy of the analysis was regularly verified; an intercomparison of concentrations of trace elements was determined in reference materials and measured by ICP-AES radiale Thermo Scientific ICAP 6500. The results agreed within ± 5% of the certified values. Several samples of soil were taken for inter-laboratory analysis to further ensure the validity of the results. The instrument was calibrated before analyzing the samples with a blank and appropriate calibration standard with only R^2 above 0.999 was accepted. The calibration was verified with appropriate internal standard.
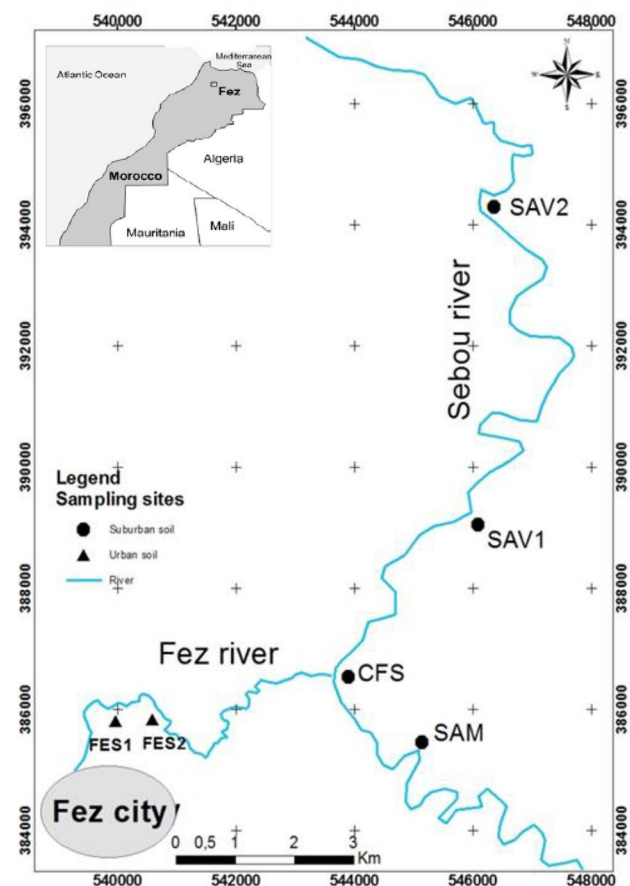
A quality assurance program was established to ensure and to examine the production of validate results for all samples, and this process entailed instrument calibration and parallel sample experiments. The parallel sample experiments were performed in triplicate and data were reported as an averaged value with standard deviations (SD). Data was considered acceptable when percentage difference within triplicate samples and percent error were below 10%.

All reagents used in the preparation of the samples for chemical analyses were of analytical grade. All the relevant material was cleaned prior to digestion with heated aqua regia and distilled water.

Sequential extraction

An amount of 1 g dry wt of soil sample was transferred to a centrifuge tube to perform successive extractions and to minimize the risk of contamination and losses through handling. It should be mentioned that the method of extraction used in this study is that developed by Tessier et al. (1979).

Fractions were identified and measured according to the elements leached from the solid phase into solution. For all fractions (F1, F2, F3, F4, and F5), different extraction reagents were used as follows:

Fraction 1 (exchangeable) The sample was extracted at room temperature for 1 h with 8 mL of either magnesium chloride solution (1 M: $MgCl_2$, pH 7.0) with continuous agitation.

Fraction 2 (bound to carbonates) The residue from (F1) was leached at room temperature with 8 mL of 1 M: NaOAc adjusted to pH 5.0 with acetic acid (HOAc). Continuous agitation was maintained and the time necessary for complete extraction was evaluated.

Fraction 3 (bound to iron and manganese oxides) The residue from (F2) was extracted with 20 mL, 0.04 M $NH_2OH.HCl$ in 25% acetic acid. The latter experiments were performed at 96 ± 3 °C with occasional agitation and the time needed for complete dissolution of the free iron oxides was evaluated.

Fraction 4 (bound to organic matter) To the residue from (F3), were added 3 mL of 0.02 M HNO_3 and 8 mL of 30% H_2O_2, adjusted to pH 2.0 with HNO_3, and the mixture was heated to 85 ± 2 °C for 5 h with occasional agitation. A second 3 mL aliquot of 30% H_2O_2 (pH 2 with HNO_3) was then added and the sample was heated again to 85 ± 2 °C for 3 h with intermittent agitation. After cooling, 5 mL of 3.2 M CH_3COONH_4 in 20% HNO_3 was added and the sample was diluted to 20 mL and agitated continuously for 30 min.

Fraction 5 (residual) The residue from (F4) was digested with a fluoro-nitro-perchlorique mixture. Minerals such as aluminosilicates (feldspars and clay minerals) are destroyed.

Between each successive extraction, separation was effected by centrifuging at 4500 rpm for 30 min. The supernatant was removed with a pipette and stored in polyethylene bottles to which 0.1 mL of 70% HNO_3 were added for sample preservation. The residue was washed with 8 mL of bidistilled water; after centrifugation for 30 min, this second supernatant was discarded.

The metal concentrations were determined by ICP-AES (ICAP 6500).

Single extractions

An amount of 2 g of soil sample was transferred to an extraction bottle in which 20 mL of 0.05 mol L^{-1} ethylenediaminetetraacetic acid (EDTA) was added. The mixture was shaken using an end-over-end shaker operating at 30 revolutions per minute for 1 h at 20 ± 2 °C (Wear and Evans 1968). The resulting mixture was filtered at 0.45 μm, and the filtrate was analyzed using ICP-AES (ICAP 6500).

Data processing

Contamination source identification and spatial patterns of the heavy metals

Principal component analysis (PCA) was employed using XLSTAT software with the aim of identifying associations and common origins among metals. Varimax rotation was employed to facilitate the interpretation of PCA results, because orthogonal rotation minimizes the number of variables with a high loading on each component. Cluster analysis (CA) was applied to identify different geochemical groups, clustering the samples with similar heavy metal contents. CA was formulated according to the Ward-algorithmic method, and the squared Euclidean distance was employed for measuring the distance between clusters of similar metal contents. Pearson's product moment correlation matrix was used to identify the relationships among metals and to support the results obtained by multivariate analysis.

Assessment of soil contamination

The impact studies of soil contamination by heavy metals can be addressed by several approaches. In this study, four methods were used such as the following:

Risk assessment code (RAC) It is known that the percentage of bioavailable concentrations of heavy metals is important for assessing the environmental risk (Oomen et al. 2003; Naji and Ismail 2012; Luo et al. 2012; Sany

et al. 2013; Yuswir et al. 2015; Marrugo-Negrete et al. 2017). The RAC assesses the availability of metals in solution by applying a scale to the percentage of metals in the adsorptive and exchangeable, and bound to carbonate fractions (Sundaray et al. 2011). These fractions are considered to be weakly bonded metals which may equilibrate with the aqueous phase, and thus become more rapidly bioavailabile (Pardo et al. 1990). When the percentage F1 + F2 (water-soluble and exchangeable fraction + carbonate-bound) is less than 1%, there is no risk. For a range of 1–10%, there is low risk, medium risk for a range of 11–30%, high risk for 31–50%, and very high risk for 51–100% (Marrugo-Negrete et al. 2017).

Indexes of soil contamination and pollution Several approaches reported in the literature were used in this study to assess the contamination level. The formulae are given in Table 1.

The enrichment factor (EF) for each metal is calculated referring to a chosen baseline and to a specific immobile element. The determination of the EF requires the measured heavy metal to be standardized against a reference element. In this study, iron (Fe) was taken as the reference element, because its origin is believed to be strongly related to the bedrock (Reimann and de Caritat 2005).

The contamination factor (CF) accounts for the contamination of a single heavy metal relative to its background reference value (Wedepohl 1995).

The Pollution Load Index (PLI) developed by Tomlinson et al. (1980) provides a simple, comparative means for assessing the level of heavy metal pollution.

Another indicator that can assess the degree of soil pollution is called index of geoaccumulation (Igeo) which was introduced by Müller (1979). Where $\log_2$ is logarithm base two, Cn is the concentration of element in soil and Bn represents the background concentration or the average shale concentration. The coefficient of 1.5 has been used in this relation to correct the effects of soil parent material and content of natural fluctuations and very little changes in the environment caused by human activities.

Ecological risk assessment Individual heavy ecological risk indexes (ER) were used to determine the degree of individual heavy pollution's effect. The ER formulae (Table 1) used a specific biological toxic-response factor (TR) for each individual heavy metal (2, 5, 6, and 1 for Cr, Cu, Ni, and Zn, respectively). This study used the toxic-response factors proposed by Hakanson (1980), who determined them in accordance with the toxicity level of each heavy metal and the response of the biological communities to this toxicity level. It is used as a diagnostic tool to determine the overall degree of heavy metal pollution in soil (Qingjie et al. 2008). All heavy metal index equations and grades are shown in Table 1.

Human health risk assessment The human health risk posed by exposure to heavy metal is usually characterized by the target hazard quotient (HQ) (US EPA 1997), and the ratio of the chronic daily intake (CDI) resulting from exposure to site media compared to the reference dose (RfD) for an individual pathway and chemical (Zhuang et al. 2014). The HQ is determined using the equation in Table 1. The chronic estimated daily intake (CDI ingestion, CDI dermal, and CDI inhalation) of heavy metals by the human beings was calculated using the following equation, which is recommended by US EPA (US EPA 2004):

$$CDI\ ingest-soil = \frac{Cs \times IRS \times Ef \times Ed}{Bw \times At} \times Cf$$

$$CDI\ dermal-soil = \frac{Cs \times Sa \times Af \times ABS \times Ef \times Ed}{Bw \times At} \times Cf$$

$$CDI\ inhale-soil = \frac{Cs \times Et \times Ef \times Ed}{PEF \times 24 \times At}.$$

CDI is the chronic daily intake, Cs is the exposure-point concentration: mg kg^{-1}, Ef is the exposure frequency (350 day a^{-1}) (US EPA 2011), Ed is the exposure duration (30 a) (US EPA 2011), Et is the exposure time (24 h day^{-1}) (UDOE 2011), At is the average time for non-carcinogens, which was set to 365*Ed day (US EPA 2002), Bw is the body weight (70 kg for adult and 16 kg for children) (US EPA 1991), Sa is the exposed skin area (5700 cm^2 for adult and 3317 cm^2 for children) (US EPA 2011), AF is the adherence factor (0.07 mg cm^{-2} for adult and 0.2 mg cm^{-2} for children) (US EPA 2011), ABS is the dermal absorption fraction (0.001) (US EPA 2011), Cf is the units conversion factor (10^{-6} kg mg^{-1}) (US EPA 2002), IRS is the ingestion rate (100 mg day^{-1}for adult and 200 mg day^{-1} for children) (US EPA 2011), and PEF is the particle emission factor (1.36×10^9 m^3 kg^{-1}) (US EPA 2002).

The reference dose obtained from the Integrated Risk Information System (US EPA 2007) is an estimation of maximum permissible risk to a human population through daily exposure when taking into consideration a sensitive group during a lifetime (Zhuang 2014). The applied RfD for Cr, Cu, Ni, and Zn was 1.5, 0.04, 0.02, and 0.3 mg kg^{-1}day^{-1}, respectively. In general, the RfD is an estimate of a daily exposure to the human population that is likely to be without an appreciable risk of deleterious effects during a lifetime (US EPA IRIS).

To assess the overall potential risk of adverse health effects posed by more than one metal, the HQ can be summed across contaminants to generate a hazard index (HI)

Table 1 Equations for indices and grades of heavy metal enrichment, contamination, and pollution factors

Indexes	Codes	Formula	Grades	
(a) Enrichment factor	EF	$EF_n = (C_n/Fe) \text{ sample}/(C_n/Fe)\text{background}$	$EF < 2$	Natural variability
			$2 < EF < 5$	Moderate enrichment
			$5 < EF < 20$	Significant enrichment
			$20 < EF < 40$	Very high enrichment
			$EF > 40$	Extremely highly enriched
(a) Contamination factor	CF	$CF_n = C_n \text{ sample}/C_n \text{ background}$	$CF < 1$	Low contamination
			$1 \leq CF < 3$	Moderate contamination
			$3 \leq CF < 6$	Considerable contamination
			$CF > 6$	Very high contamination
(a) Degree of contamination	DC	$DC_n = \Sigma CF_n$	$DC < 5$	Low contamination
			$5 \leq DC < 10$	Moderate contamination
			$10 \leq DC < 20$	Considerable contamination
			$DC \leq 20$	Very high contamination
(b) Index of geoaccumulation	Igeo	$Igeo = \log_2(C_n/1.5\ B_n)$	$Igeo < 0.42$	Unpolluted
			$0.42 < Igeo < 1.42$	Low polluted
			$1.42 < Igeo < 3.42$	Moderately polluted
			$3.42 < Igeo < 4.42$	Strongly polluted
			$Igeo > 4.42$	Extremely polluted
(b) Pollution load index	PLI	$PLI = (CF1 \times CF2 \times CF3 \times \cdots \times CFn)^{1/n}$	$PLI < 1$	Unpolluted
			$PLI = 1$	Indicate heavy metal loads close to the background level
			$PLI > 1$	Polluted
(a) Potential ecological risk index	ER	$ER_n = TR_n \times CF$	$ER < 40$	Low risk
			$40 \leq ER < 80$	Moderate risk
			$80 \leq ER < 160$	Considerable risk
			$160 \leq ER < 320$	High risk
			$ER \leq 320$	Very high risk
(a) Potential ecological risk	RI	$RI_n = \Sigma ER_n$	$RI < 65$	Low risk
			$65 \leq RI < 130$	Moderate risk
			$130 \leq RI < 260$	Considerable risk
			$RI \leq 260$	Very high risk
(c) Hazard quotient	HQ	$HQ = CDI/RfD$	$HQ < 1$	Absence of health risks
			$HQ > 1$	There is a chance that a health risk may occur
(c) Hazard index	HI	$HI = \Sigma HQ_i$	$HI < 1$	Absence of health risks
			$HI > 1$	There is a chance that a health risk may occur

TR biological toxic factor of an individual heavy metal

a—The different grades were given according to Hakanson (1980) and Qingjie et al. (2008) in Foti et al. (2017)

b—The different grades were given according to Hakanson (1980) and Qingjie et al. (2008)

c—The different grades were given according to (US EPA 2002)

to estimate the risk of a mixture of contaminants (Table 1). The HI refers to the sum of HQ through oral, dermal, and inhalation routes (HQ ingestion, HQ dermal contact, and HQ inhalation) (US EPA 1989) for multiple substances and/or multiple exposure pathways. In the present study, the HI was used as a screening value to identify whether there is significant risk caused by heavy metals through average dietary consumption for the residents living near the study area.

Results and discussion

Soil physical and chemical characterization

The main soil properties of the soils analyzed are shown in Table 2. The pH can be considered the most influential factor; it controls precipitation/solubilization and adsorption/ desorption reactions (Basta et al. 2005), causing an

Table 2 Physical and chemical parameters of soil samples

	Mean	Median	Minimum	Maximum	SD
pH	8.3	8.3	8	8.6	0.2
EC µS cm^{-1}	184.1	92.4	13.8	1107	243.2
CaCO$_3$ (%)	42.4	36.3	24.7	65.9	14.1
OM (%)	5.8	4.9	0.4	12.8	3.2
DOC mg kg^{-1}	95.1	98.9	33.6	170.4	40
Clay (%)	17.2	15	12	26	5.2
Silt (%)	48.2	51	33	60	9.8
Sand (%)	34	35	13	56	15.2

increase in solubility and, therefore, the bioavailability of the elements inversely proportional to soil pH (Silveira et al. 2003; Antoniadis et al. 2008). The data proved that soils are basic with variations from 8 to 8.6 (8.3 on average), as a result of calcareous parent material presence. These conditions favor the adsorption of metals and decreasing bioavailability (Lasat 2002). The EC was lower than 4 dS m^{-1} in all samples, reflecting that soils do not present a problem of excess salinity according to USDA's criteria. The ability of soils for retaining heavy metals in an exchangeable form is generally attributed to the organic matter. It was shown that the adsorption of heavy metals onto soil constituents was reduced with decreased organic matter content in soils (Hettiarachchi et al. 2003; Antoniadis et al. 2008), which may serve as chelates and increase metal availability to plants (Vega et al. 2004; McCauley et al. 2009). The percentage of organic matter (OM) in the analyzed soils is relatively high (5.8% on average), with variations from 0.4 to 12.8% suggesting bioavailability of heavy metals and higher formation of organometallic complexes based on the OM content, as a result of intensive use of irrigated wastewater. Moreover, the dissolved organic matter in soils would increase the mobility and uptake of heavy metals to plant roots (Impellitteri et al. 2002; Du Laing et al. 2009). The DOC content was 95.1 mg kg^{-1}, ranging from 33.6 to 170.4 mg kg^{-1}. Kouchou et al. (2017) reported that the possible formation of metal–organic complexes could increase metal retention and mitigate enzyme inhibition by metals and/or the organisms that produce them. The carbonate content (CaCO$_3$) was also high (42% on average) ranging from 24.7 to 65.9%. It is known that the carbonated nature of the soil may also promote the binding of cations in alkaline environment (Adriano 2001). Park et al. (2011) showed that when pH increases, the surface functional groups of organic matter or clay are negatively charged, the metal cations are bound, and toxic metal fractions are transformed to biologically inactive forms.

Sand content is 34%, and ranged from 13 to 56%, whereas the soil clay content is 17.2%, ranging from 12 to 26%, the silt content is 42.2%, and ranged from 33 to 60%. A predominance of silt and sand fractions was observed. Previous studies reported that soil type is an important factor influencing the concentration of heavy metals (Temminghoff et al. 1997; Yan et al. 2013). While the enrichment by soil clay can play a limiting factor for Cr, Cu, and Ni availabilities, because the heavy metal ions may undergo fixation in the interlayer spaces, or with time those possessing appropriate ionic radius, may become incorporated into the octahedral layer of clay minerals (Helios-Rybicka and Förstner 1986). The sandy soils thus allow a transfer of heavy metals.

Heavy metal contents

Pseudo-total chemical extraction of heavy metal in the agricultural soils

Descriptive statistics for the heavy metal contents in the agricultural soils of the study area are shown in Table 3. Because of a lack in the Moroccan regulations on soils, results were compared with the heavy metal concentration values compiled from Kabata-Pendias (2010) and the UCC (Upper Continental Crust) (Wedepohl 1995) (Table 3). The mean concentrations of all the analyzed heavy metals in the agricultural soils were higher than UCC and average worldwide soils (Table 3). However, their contents vary depending on the location of the soils. The concentration of the investigated element not exceeds the lower guideline value standards of the Ministry of Environment of Finland (2007) for all samples.

The median values of the elements if all sampling points are considered altogether followed the decreasing order: Zn > Cr > Cu > Ni. Average concentration of Cr, Cu, Ni, and Zn in the study area was 78, 55, 31, and 119 mg kg^{-1}, respectively.

For each site, the median values followed a decreasing sequence: Zn > Cr > Cu > Ni for SAM and SAV1 and the following sequence: Zn > Ni > Cr > Cu; Zn > Cu > Cr > Ni; Cr > Zn > Cu > Ni; Cr > Zn > Cu > Ni for FES1, FES2, CFS, and SAV2, respectively.

Among the six sites in the study area of Saiss plain [two urban areas (FES1 and FES2) and three suburban areas (SAM, CFS, SAV1 and SAV2)], the soil samples collected from FES2 showed the highest concentrations of Cr (103 mg kg^{-1}), Cu (157 mg kg^{-1}), and Zn (294 mg kg^{-1}) (Table 3). The level of Ni was higher at FES1 (71 mg kg^{-1}). The highest concentration of all heavy metals was found in urban soils.

The heavy metal contents can be related to natural concentrations of the soil and to anthropogenic activities. High values of heavy metals and their accumulations are mainly the result of anthropogenic activities such as industrial and artisanal activities, irrigation, fertilization, and intensive use of pesticides and herbicides (Smith 2009; Chen et al. 2015).

Table 3 Total concentrations of heavy metals (mg kg^{-1}) in soil samples

	Cr	Cu	Ni	Zn
All sites ($n=66$)				
Mean	78	55	31	119
Median	75	34	24	80
SD	32	60	22	95
Minimum	34	13	14	36
Maximum	253	322	135	434
FES1 ($n=6$)				
Mean	59	36	71	101
Median	62	40	69	105
SD	13	8	45	24
Minimum	34	20	22	61
Maximum	72	43	135	122
FES2 ($n=13$)				
Mean	103	157	28	294
Median	99	148	24	293
SD	54	73	10	74
Minimum	39	65	18	168
Maximum	253	322	53	434
SAM ($n=13$)				
Moy	69	27	26	69
Median	56	32	21	66
SD	25	9	14	29
Minimum	48	13	14	43
Maximum	106	40	58	159
CFS ($n=13$)				
Mean	71	28	29	64
Median	71	34	19	69
SD	26	10	21	16
Minimum	36	14	14	36
Maximum	108	40	70	85
SAV1 ($n=13$)				
Mean	75	31	24	84
Median	78	34	22	84
SD	17	8	6	17
Minimum	49	18	16	60
Maximum	97	44	33	115
SAV2 ($n=8$)				
Mean	83	33	27	76
Median	85	28	27	71
SD	5	9	7	13
Minimum	75	23	20	63
Maximum	88	44	40	101
(a) World-soil				
Mean	60	39	29	70
(b) UCC				
Mean	35	14	19	52
(d) MEF				
LGV	200	150	100	250
HGV	300	200	150	400

SD standard deviation

a—Mean values compiled from Kabata-Pendias (2010)

b—UCC (Upper Continental Crust) (Wedepohl 1995)

Table 3 (continued)

d—MEF Ministry of Environment of Finland 2007. Lower guideline value (LGV) and Higher guideline value (HGV). The guideline values have been defined on the basis of either ecological risk

The long-term use of wastewater irrigation for agricultural production is a significant source of soil heavy metal pollution worldwide (Gupta et al. 2012; Lu et al. 2015). This may have been the case in agricultural urban soil of Saiss plain where urban districts discharged their wastewater into the Fez River. This is corroborated by the previous studies that identified the presence of high concentrations of Cr, Cu, Ni, and Zn in wastewater used in soil irrigation of Saiss plain (Koukal et al. 2004; Perrin et al. 2014; Hayzoun et al. 2015). In addition, other parameters as, for example, crop type, irrigation frequency, and rate of fertilizer applications may all have a role in determining the concentrations that accumulate (Marrugo-Negrete et al. 2017). In our case, the use of the phosphate fertilizers may have had some impact on introducing some of these metals to soils.
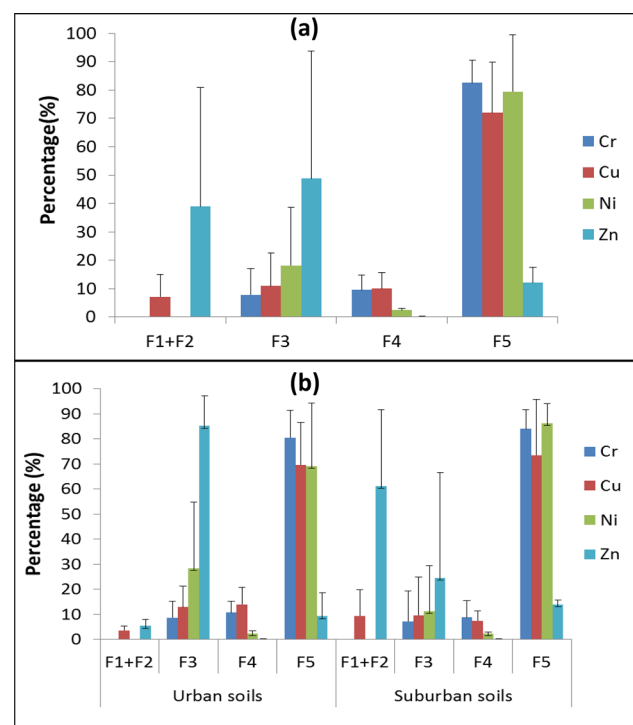

Fig. 2 Percentage of heavy metal in different fractions in **a** all of agricultural soils and for **b** each category of agricultural soil: urban soil (FES1, FES2) and suburban soils (SAM, CFS, SAV1 and SAV2). Mean ± SD. F1 + F2: water-soluble and exchangeable + carbonate-bound; F3: reducible metals; F4: OM-sulfides; F5: residual metals

Sequential extraction

Figure 2a shows the percentage of the chemical fractions of Cr, Cu, Ni, and Zn analyzed in soils. Cr, Cu, and Zn content in soils associated with the residual fraction (F5) represents 82% (Cr), 79% (Ni), and 72% (Cu). While Zn represents a low proportion in this fraction (12%) of the total content. In this fraction, Cr, Ni, and Cu are bound to minerals as part of their crystal structures and are, therefore, difficult to mobilize. The oxidizable fraction bound to organic matter and sulfides (F4) represents 10% (Cr), 10% (Cu), 2% (Ni), and 0% (Zn). In this phase, the heavy metals exhibit a moderate mobility and may be associated with organic ligands (humic and fulvic acids). The reducible fraction (F3) represents 8% (Cr), 11% (Cu), 18% (Ni), and 49% (Zn), showing that a great part of Zn at the different sampling sites is associated with amorphous aluminosilicate materials, such as oxides of Fe and Mn. The most available fraction (F1 + F2) represents 0% (Cr), 7% (Cu), 0% (Ni), and 39% (Zn). This fraction corresponds to the fraction of the total contaminant in the interstitial water and soil particles that are available to organisms, while Cu and Zn are easily mobilized compared to the Cr and Ni elements. The mobility sequence of heavy metals for all agricultural soils may be resumed as the following: Zn > Cu > Ni > Cr.

Figure 2b shows that the Cr, Cu, and Ni are always bound to the residual fraction (F5) with a percentage of 80% (Cr), 69% (Cu), and 69% (Ni) for urban soils, and 84% (Cr), 74% (Cu), and 86% (Ni) for suburban soils. In contrast, the large part of Zn (61%) is bound to the bioavailable fraction (F1 + F2) for suburban soils, and to the reducible fraction (F3) (85%) for urban soils. Only Cu and Zn are present in the bioavailable fraction (F1 + F2) with 4% and 5%, respectively, for Cu and Zn in urban soils, and 9% and 61%, respectively, for suburban soils, implying that these two elements presenting a higher risk to be free are, therefore, absorbed by living beings, which presents a higher environmental risk compared to Cr and Ni regardless of the type of our agricultural soils (urban or suburban soils).

Single EDTA extraction

The results of the extraction of Cr, Cu, Ni, and Zn by EDTA (Fig. 3) show that the percentages of Cr, Cu, Ni, and Zn released are 0.1%, 16%, 1%, and 11%, respectively for all agricultural soils (urban and suburban soils). These results mean that Cu and Zn are potentially more available than Cr and Ni, and can constitute an environmental threat. The mobility sequence for all agricultural soils may be resumed as the following: Cu > Zn > Ni > Cr.

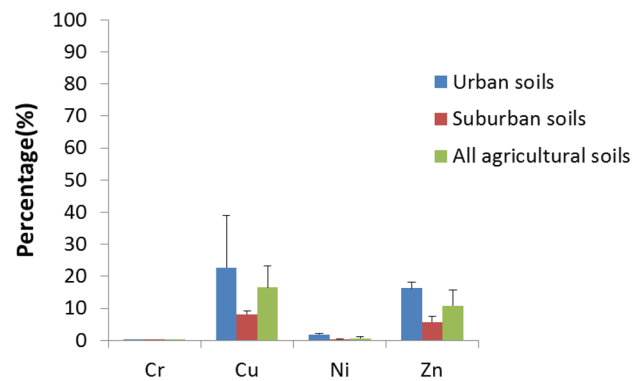The results of EDTA confirm the results of the sequential extraction, which is that Zn and Cu are the most

Fig. 3 Percentage of heavy metals leached by EDTA in urban soils (FES1 and FES2) and suburban soils (SAM, CFS, SAV1, and SAV2), and in all agricultural soils (urban and suburban soils)

available elements regardless the extraction method. There is also a difference in the extraction sequence as EDTA has more affinity for Cu than Zn, which is the result of the affinity between EDTA and Cu and the dissolution of organic compounds by the chelating agent to which Cu is strongly bound (Andersson 1975).

The EDTA single leachate in this case may be considered as an underestimate, because the sequential extraction (F1 + F2 + F3 + F4) (Fig. 2a) is more aggressive to removing Cr, Cu, Ni, and Zn from all the studied samples. Several authors have reported a decrease in metal removal efficiency of EDTA in calcareous soils due to the alkaline pH. It is due to the hydrolysis of aquo-complexed metals at higher pH, and their low solubility compared to that of Ca (Nowack et al. 2006). Moreover, in calcareous soils, the higher affinity of a Ca-EDTA complexation reduces EDTA efficiency to solubilize heavy metals (Manouchehri et al. 2011; Chatterjee and SenGupta 2011).

Figure 3 shows that Cu and Zn extracted by EDTA were very high in urban soils compared to suburban soils, this result confirms the finding study conducted by Kouchou et al. (2017) who suggests that these heavy metals are linked to the bioavailable fraction of organic matter and explained that to an external source of labile natural organic matter, coming from the contaminated water courses used for irrigation. When EDTA extraction is compared with all the fractions considered as the mobile fractions (F1 + F2 + F3 + F4) (Rauret 1998), the sequential extraction procedure (SE) seemed more aggressive than the EDTA single leachate at removing Cr, Cu, Ni, and Zn from all the studied samples. However, these results show that the EDTA single leachate provided a poor prediction to estimate Cr, Cu, Ni, and Zn mobility. This conclusion agrees with the results obtained by Kubová et al. (2008), Menzies et al. (2007) and Leleyter et al. (2012). Other

studies carried out by Madrid et al. (2007) and Leleyter et al. (2012) showed that only a small proportion of the metals accessible to the mobile fractions of sequential extraction are likely to be soluble in EDTA.

Contamination source identification and spatial patterns of the heavy metals

To identify the metal contamination sources and to evaluate their extents in study area, the PCA was performed. This is a technique that clusters variables into highly correlated groups (Dragovic et al. 2008).

The results of the PCA of heavy metal contents and sampling points are presented in Fig. 4. Two principal components with eigenvalues greater than 1 were extracted. The PCA method permitted to reduce the initial data set to two components explaining 77.7% of the data variation. Therefore, these two factors afforded the suitable explanation related to metal contamination in the study area. As shown in Fig. 4a the rotated component matrix demonstrated that Cr, Cu, and Zn were involved and correlated to the first component (PC1), whereas the second component (PC2) included Ni (0.9429). The PC1, which has the highest loadings of Cr, Cu, and Zn accounts for 51.5% of variance and is the most important component. In more detail, PC1 could be better explained as an anthropogenic source, specifically related to the agricultural activities taking place in the area for a long period of time. Cr, Cu, and Zn are well-known

marker elements of agricultural activities, specifically related to the irrigation which probably amplified the pollutant loads (Acosta et al. 2011; Kelepertzis 2014), which shows an increased accumulation in soils after long-term wastewater irrigation. Several authors confirm the elevated concentration of organic matter, nutrients (P, N, and C), and four heavy metals Cr, Cu, Ni, and Zn of the water used for irrigation, particularly in the wastewater irrigation of oued Fez (Koukal et al. 2004; Perrin et al. 2014; Hayzoun et al., 2015). PC2 accounts for 26.2% of the total variability and can be presumed to represent a different source, probably from a different origin than those related to wastewater irrigation, like pedo-lithogenic origin.

Based on information obtained from principal component analysis, hierarchical cluster analysis (CA) was performed (Gotelle et al. 2004). Two main clusters can be distinguished in the dendrogram obtained from the CA performed on the analyzed parameters with Ward's method and the squared Euclidean distance as a similarity measure (Fig. 5a). Cluster 1 includes elements Zn, Cu, and Cr, which, in the previous section, were identified as contaminants derived from agricultural activities, which is mostly controlled by anthropogenic sources as irrigation activities. Cluster 2, which contains Ni, is probably derived from a different origin which can be due to pedo-lithogenic source.

Similarly, sampling points were also analyzed by clustering methods and organized in a dendrogram to identify similar groups (Fig. 5b). The sampling sites could
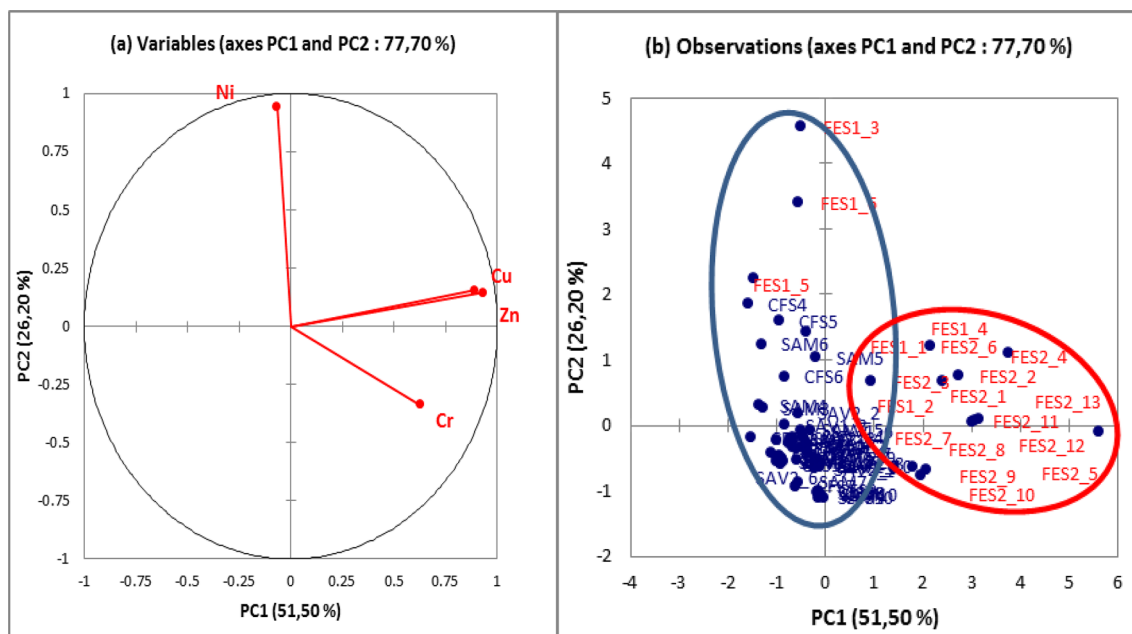

Fig. 4 Principal component analysis (PCA) results. **a** Loading plot of the two components influencing geochemical variation of agricultural soils from Saiss plain, **b** Score plot PC1 vs. PC2 of sampling sites.

Red labels: FES1_1–FES1_6 and FES2_1–FES2_13: Urban soils, blue labels: SAM1–SAM13, CFS1–CFS 13, SAV1_1–SAV1_13, and SAV2_1–SAV2_8: suburban soils
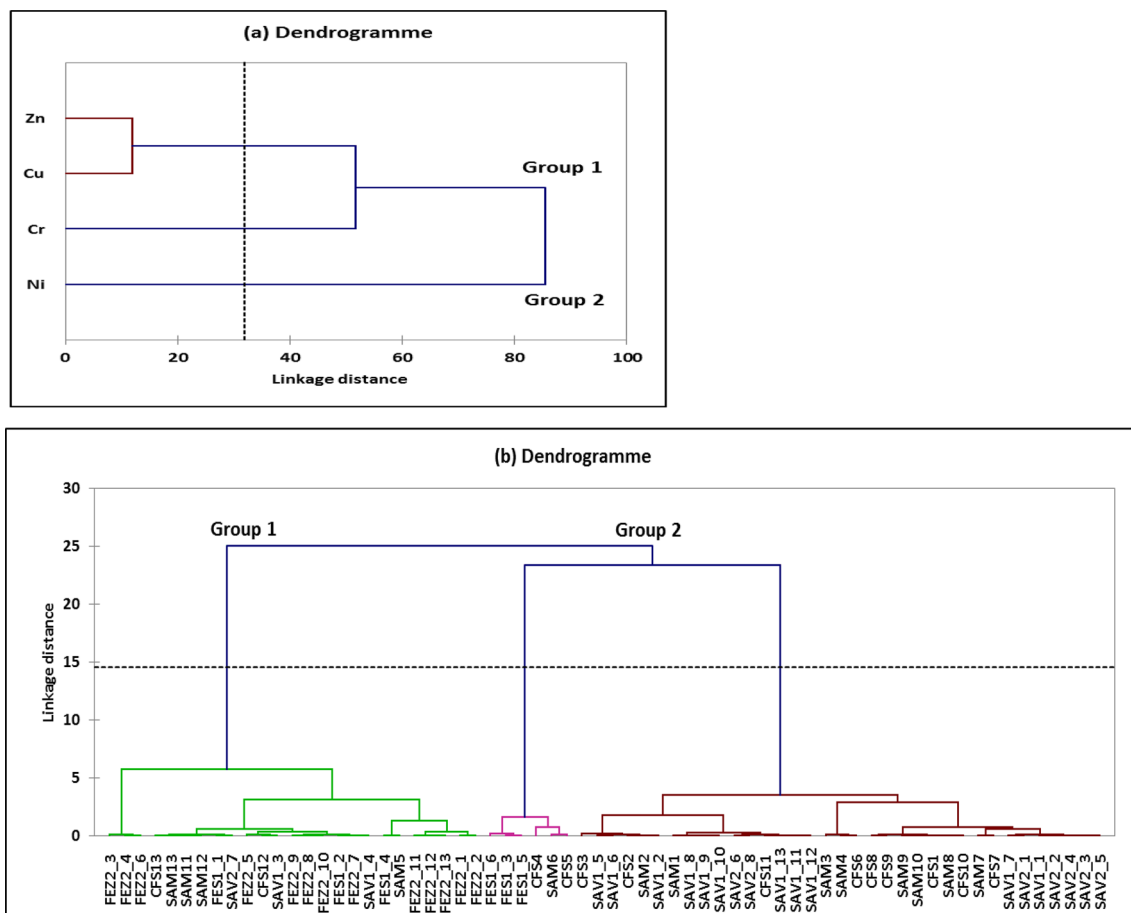
Fig. 5 Dendrogram obtained by hierarchical clustering analysis for **a** the heavy metals and **b** the sampling sites

be grouped in two clusters, with the majority in cluster 2 with 41 samples, and cluster 1 with 25 samples. In addition, among all the sampling sites, 62% represent cluster 2. Interestingly, in cluster 2, 92.68% of the sampling sites are located in the suburban agricultural soils irrigated by Sebou River SAM (69.23% of sampling site), CFS (84.61% of sampling site), SAV1 (84.61% of sampling site), and SAV2 (92.30% of sampling site). This distribution is also observed in Fig. 4b, where sites SAM, CFS, SAV1, and SAV2 (blue circle) exhibit high PC2 scores. There are 25 sampling sites with high scores in PC1 (> 1) (red circle) corresponding that 64% represents the urban soil FES2 (100% of sampling site) and FES1 (50% of sampling site) which are enriched in Cr, Cu, and Zn.

The correlative data between Cr, Cu, and Zn concentrations in the soil (Table 4) imply that Cr, Cu, and Zn are co-contaminants with an external source, and thus, a common pollution source could be invoqued. This external source would be the contaminated water courses

Table 4 Correlations between heavy metals in the studied soils

	Cr	Cu	Ni	Zn
Cr	1	0.2909 (0.0178)*	− 0.1303	0.4231 (0.0004)*
Cu		1	− 0.0133	0.8156 (< 0.0001)*
Ni			1	0.0238
Zn				1

Each value represents the Pearson correlation coefficient with the p value in parenthesis. Correlations were carried out based on 66 samples. Significance was corrected for multiple comparisons with Pearson's correlation coefficients $\alpha = 0.05$

*Significant correlations

used for irrigation. In general, correlations between metals (Table 4) agreed with the results obtained by PCA, and CA was useful to confirm some new associations

Table 5 Level of bioavailable and non-bioavailable fractions (%) in all agricultural soils, urban soils, and suburban soils of studied sampling

	All agricultural soils		Urban soils		Suburban soils	
	Bioavailable metal (%)	Non-bioavailable metal (%)	Bioavailable metal (%)	Non-bioavailable metal (%)	Bioavailable metal (%)	Non-bioavailable metal (%)
Cr	0.0	100.0	0.0	100.0	0.0	100.0
Cu	7.1	92.9	3.6	96.4	9.4	90.6
Ni	0.0	100.0	0.0	100.0	0.0	100.0
Zn	38.9	61.1	5.4	94.6	61.2	38.8

between metals that were not clearly stated in the previous analysis.

Assessment of soil contamination

Risk assessment code (RAC)

According to the RAC which distinguishes the bioavailable fraction (F1 + F2) from the non-bioavailable fraction (F3 + F4 + F5) (Table 5), it is possible to identify according to the risk categories, that Cu presents a low risk regardless the soil type (urban or suburban). While Zn represents a very high risk in suburban soils, and a low environmental risk in urban soils. The presence of the high percentage of bioavailable fraction of Zn in suburban soils could be probably explained by the extensive use of fertilizers by farmers in this area (Bouih et al. 2005). Zn is bound either in exchangeable or in carbonate fraction (about 61.2%) in the suburban soils, which reflects that Zn comes more than 50% of the total metal, which can easily enter the food chain, and can pose serious threat to the ecosystem. However, Cr and Ni are present mostly in residual form, from which it cannot be easily leached out and comes under the no-risk category (<1%).

Indexes of soil contamination and pollution

The EF, CF, and Igeo values in soils are summarized in Fig. 6. The EF values calculated for each metal studied are shown in Fig. 6a. The range of EF for the different elements was 0.9–14.8 (Cr), 0.9–46 (Cu), 0.6–30.3 (Ni), and 0.6–32.9 (Zn). Overall, the average order of EF values is: Cu (7.7) > Zn (4.6) > Cr (4.2) > Ni (3.7). According to the EF grades (2 < EF < 5), Zn, Cr, and Ni are moderately enriched, unlike Cu which is significantly enriched (5 < EF < 20). The EF values of heavy metals in this study are higher than those conducted by Loska et al. (2004) in the farming soils of southern Poland and Marrugo-Negrete et al. (2017) in agricultural soil in Colombia. For each site (Table 4) according to the EF grade, FES1 records a significant enrichment for all the heavy metals studied [Cr (6.7), Cu (10.5), Ni (18.1), and Zn (8.3)]. While FES2 records a moderate enrichment for Ni (3.1), significant enrichment for Cr (6.0) and Zn (11.9), and a very high enrichment for Cu (22.9). The
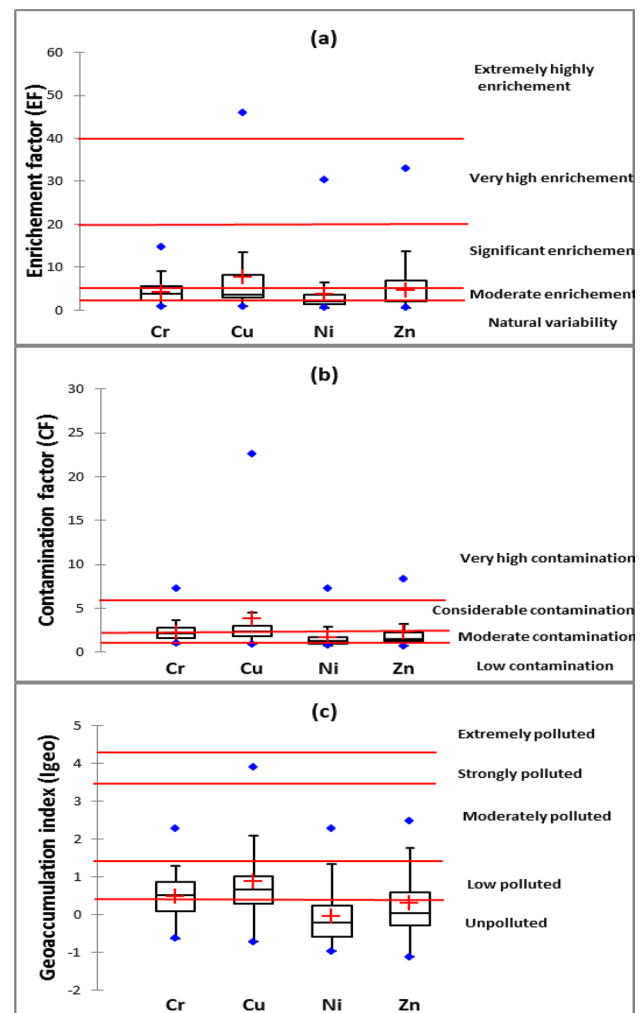

Fig. 6 Box and whisker plots display of the distributions of the different contamination indexes: enrichment factor (**a**), contamination factor (**b**), and geoaccumulation index (**c**). Boxes depict 25th, 50th (median), and 95th percentiles and whiskers depict minimum and maximum values. Mean values (+); outliers (.)

suburban areas SAM, CFS, SAV1, and SAV2 exhibit a moderate enrichment for all the heavy metals studied.

The range of CF for the different metals was 1–7.2 (Cr), 0.9–22.5 (Cu), 0.8–7.2 (Ni), and 0.7–8.3 (Zn). According to our results (Fig. 6b), the CF average value for all metals follows the decreasing order: Cu (3.9) > Zn (2.3) > Cr

(2.2) > Ni (1.7). The CF average value based on background values for all metals indicates contamination by human sources (CF > 1), with metals such as Zn, Cr, and Ni presenting a moderate degree of contamination (CF of 1–3), whereas Cu showed considerable contamination (CF of 3–6). In comparison with other countries, values of CF in different soils collected in Saiss plain are lower than those reported by Marrugo-Negrete et al. (2017) in Colombia and Liu et al. (2013) in China for Cu, Ni, and Zn. Nevertheless, the research conducted by Khan et al. (2008) in agricultural soils irrigated with wastewater in China showed that the CF of Cr, Cu, Ni, and Zn were 3.0, 3.9, 10.9, and 2.1, respectively. The contamination by heavy metals, especially Ni, was more severe than that in our study area. For each site (Table 6) and according to the CF grade, FES1 was classified as considerably contaminated for Ni (4.3) but moderately contaminated for Cr (1.6), Cu (2.5), and Zn (2); FES 2 was moderately contaminated for Cr (2.9) and Ni (1.5), considerably contaminated for Zn (5.7), and severely contaminated for Cu (11). While all the suburban soils SAM, CFS, SAV1, and SAV2 were classified as moderately contaminated for all heavy metals.

The degree of contamination (DC) calculated from the sum of CF shows that all agricultural soils are considerably contaminated by heavy metals (Table 7). The overall degree of contamination (DC) was in the following order: FES2 [very high contamination (21.1)] > FES1 [considerable contamination (10)] > SAV2 (7.6) > SAV1 (7.2) > CFS (6.7) (moderate contamination) > SAM [low contamination (4)] (Table 7).

The Igeo was also used as a reference for estimating the extent of metal pollution (Fig. 6c). Mean Igeo values are in the order Cu (0.87) > Cr (0.47) > Zn (0.29) > Ni (−0.06). Therefore, the Igeo indicates that the soils are unpolluted for Ni and Zn (Igeo < 0.42), and that pollution is low to heavy for Cr and Cu in the study area, depending on each metal and sampling station location. In comparison with other countries, our values of Igeo are higher than those reported by Loska et al. (2004) in the farming soils of southern Poland and lower than those reported by Marrugo-Negrete et al. (2017) in agricultural soil in Colombia. For each site (Table 6) according to Igeo grade, FES1 exhibits a low degree of pollution for Cu (0.7) and Ni (1.1). FES2 is moderately polluted for Cu (2.7) and Zn (1.9). While SAV1 and SAV2 present a low degree of pollution for Cr (0.5 and 0.7, respectively), Cu (0.5 and 0.6, respectively), and Zn (0.7 and 0.6, respectively).

The pollution load index (PLI) calculated from CF shows that the soils are heavily contaminated by all investigated heavy metals with a value ranging from 1.0 to 6.7 for all agricultural soils (Table 7). The FES2 soil shows the highest average value of PLI (3.9) within the study area, and the rest of the area (FES1, SAM, CFS, SAV1, and SAV2) is low-to-moderately polluted (mean of PLI around 2).

In conclusion, we can deduce that the sequence of the contamination Cu > Zn > Cr > Ni is kept for EF and CF index. In the case of the Igeo, the Zn and Cr exchanged their places (Cu > Cr > Zn > Ni), it can be considered as the least reliable index compared to the two others indexes EF and CF, and may mislead us in our case study. Considering the indexes for each site for all the heavy metals studied (PLI and DC), we see that FES2 is always the most contaminated and polluted compared to other sites. These results affirm the reliability of the use of these indexes.

Ecological risk assessment

The range of ER for the different metals was 1.9–14.5 (Cr), 4.5–112.6 (Cu), 4.6–43.5 (Ni), and 0.7–8.3 (Zn). According to our results (Table 7), the ER average values for all metals follow the decreasing order: Cu (19.3) > Ni (10.0) > Cr (4.5) > Zn (2.3). All the sampling sites, for all heavy metals, present a low risk except for FES2 which presents a moderate risk for Cu (55.6), while the ecological risk (RI) calculated from ER shows a low risk for all heavy metals. The overall degree of risk (RI) was in the following order: FES2 [moderate risk (75.5)] > FES1 [low risk (41.7)] > SAV2 [low risk (26.5)] > SAV1 [low risk (24.6)] > CFS [low risk (24.3)] > SAM [low risk (23.2)] (Table 7). FES2 followed by FES1 exhibits higher anthropogenic heavy metal concentrations and risk assessment values than all suburban soils (SAM, CFS, SAV1, and SAV2). As previously explained, urban soils, at the origin agricultural soils already rich in organic matter, were fertilized for more than a century using wastewater in large quantities as irrigation source. This wastewater not only contained organic matter but was also very rich in heavy metals (Koukal et al. 2004; Perrin et al. 2014; Hayzoun et al. 2015). Moreover, these soils may have also accumulated more heavy metals than the soils from the other sites, especially for heavy metals produced by human activities (air borne inputs from traffic road, effluent from industrial areas and artisanal activities, etc.). Indeed, the agricultural urban soils, especially FES2, have higher organic matter contents than suburban soils (Kouchou et al. 2017) that probably contribute to accumulation of heavy metals in urban soils, since the soil organic matter tends readily to adsorb heavy metals (Kabała and Szerszeń 2002). These results are consistent with the findings of other studies on heavy metals in urban and agricultural areas (Li et al. 2001; Chen et al. 2005; Cheng et al. 2007; Bhuiyan et al. 2010; Liu et al. 2013). The levels of individual and overall contamination and risk are the highest in the agricultural urban area, especially at FES2, according to the pattern of heavy metals concentrations and enrichments along

Table 6 Values of contamination factor (CF), enrichment factor (EF), and geoaccumulation index (Igeo) for each site

Indexes codes	Heavy metals	FES1 ($n=6$)	FES2 ($n=13$)	SAM ($n=13$)	CFS ($n=13$)	SAV1 ($n=13$)	SAV2 ($n=8$)
EF	Cr						
	Mean	6.7	6	3.1	4.1	2.9	3.9
	Median	7.4	5.9	2.4	3.8	2.7	4
	SD	1.5	3.4	1.3	2.2	1.9	0.2
	Minimum	4	1.2	0.9	1.2	1.1	3.5
	Maximum	7.9	14.8	4.8	9.1	8.7	4.2
	Cu						
	Mean	10.5	22.9	2.9	3.9	2.9	3.8
	Median	11.8	25.6	3.6	4.7	2.9	3.2
	SD	2.7	12	1.2	2	1.4	1
	Minimum	6	4	0.9	1.4	0.9	2.7
	Maximum	12.4	46	4.5	8.7	6.6	5.1
	Ni						
	Mean	18.1	3.1	2.2	3.1	1.8	2.4
	Median	17.2	2.5	1.4	1.6	1.4	2.4
	SD	9.7	1.5	1.3	2.4	1.2	0.6
	Minimum	4.9	1	0.6	0.8	0.7	1.7
	Maximum	30.3	6.4	4.9	7.5	5.5	3.5
	Zn						
	Mean	8.3	11.9	2.1	2.6	2.2	2.4
	Median	9.4	10.3	1.9	2.3	2	2.3
	SD	2.1	6.9	1	1.5	1.6	0.4
	Minimum	4.9	3.8	0.6	0.6	0.6	2
	Maximum	9.8	32.9	4.9	7	7.2	3.2
CF	Cr						
	Mean	1.6	2.9	2	2	2.1	2.4
	Median	1.8	2.8	1.6	2	2.2	2.4
	SD	0.4	1.5	0.7	0.7	0.5	0.2
	Minimum	1	1.1	1.4	1	1.4	2.1
	Maximum	1.9	7.2	3	3.1	2.8	2.5
	Cu						
	Mean	2.5	11	1.9	1.9	2.2	2.3
	Median	2.8	10.4	2.2	2.4	2.4	2
	SD	0.6	5.1	0.6	0.7	0.6	0.6
	Minimum	1.4	4.5	0.9	1	1.3	1.6
	Maximum	3	22.5	2.8	2.8	3.1	3.1
	Ni						
	Mean	4.3	1.5	1.4	1.6	1.3	1.5
	Median	4.1	1.3	1.1	1	1.2	1.4
	SD	2.3	0.5	0.8	1.1	0.3	0.4
	Minimum	1.2	1	0.8	0.8	0.9	1.1
	Maximum	7.2	2.9	3.1	3.8	1.8	2.1
	Zn						
	Mean	2	5.7	1.3	1.2	1.6	1.5
	Median	2.3	5.6	1.3	1.3	1.6	1.4
	SD	0.5	1.4	0.6	0.3	0.3	0.2
	Minimum	1.2	3.2	0.8	0.7	1.2	1.2
	Maximum	2.4	8.3	3.1	1.6	2.2	1.9

Table 6 (continued)

Indexes codes	Heavy metals	FES1 ($n=6$)	FES2 ($n=13$)	SAM ($n=13$)	CFS ($n=13$)	SAV1 ($n=13$)	SAV2 ($n=8$)
Igeo	Cr						
	Mean	0.1	0.8	0.3	0.3	0.5	0.7
	Median	0.2	0.9	0.1	0.4	0.6	0.7
	SD	0.4	0.7	0.5	0.6	0.4	0.1
	Minimum	−0.6	−0.4	−0.1	−0.6	−0.1	0.5
	Maximum	0.5	2.3	1	1	0.9	0.7
	Cu						
	Mean	0.7	2.7	0.2	0.3	0.5	0.6
	Median	0.9	2.8	0.6	0.7	0.6	0.4
	SD	0.4	0.7	0.5	0.6	0.4	0.4
	Minimum	−0.1	1.6	−0.7	−0.6	−0.3	0.1
	Maximum	1	3.9	0.9	0.9	1	1
	Ni						
	Mean	1.1	−0.1	−0.2	−0.2	−0.3	−0.1
	Median	1.3	−0.2	−0.4	−0.6	−0.4	−0.1
	SD	1.1	0.5	0.7	0.9	0.3	0.3
	Minimum	−0.3	−0.6	−1	−1	−0.8	−0.5
	Maximum	2.3	0.9	1	1.3	0.2	0.5
	Zn						
	Mean	0.3	1.9	−0.3	−0.3	0.1	−0.1
	Median	0.4	1.9	−0.2	−0.2	0.1	−0.1
	SD	0.4	0.4	0.5	0.4	0.3	0.2
	Minimum	−0.4	1.1	−0.9	−1.1	−0.4	−0.3
	Maximum	0.6	2.5	1	0.1	0.6	0.4

the urban pressure gradient. Despite these high levels of contamination and risk compared to the other sites, the associated grades of individual risk (ER) show that only urban soils present a moderate level of pollution. The Cu concentration may be classified at moderate-risk level, and the associated overall risk (RI) at low-risk level for biological communities (Table 7). In addition, besides the inhalation of dust, through hand-to-mouth ingestion or dermal contact agricultural urban soils could be transferred to humans, especially the most vulnerable, namely children (Bright et al. 2006).

Human health risk assessment

The study of the chemical contaminant risks on a target organism requires an estimate of the level of exposure to hazard. Thereby, in this study, to estimate the risk on human through inhalation, ingestion, and dermal contact of soils,

we used the total heavy metal concentrations to calculate hazard quotient (HQ). The HQ of metals on soil for both adults and children is given in Table 8. The HQ of ingestion, dermal contact, and inhalation of soils for Cr, Cu, Ni, and Zn ranged from 5.38 E−05 to 9.47 E−05, 9.41 E−04 to 5.42 E−03, 1.65 E−03 to 4.91 E−03, and 2.93 E−04 to 1.35 E−03, respectively for adults, while it ranged from 4.70 E−04 to 8.27 E−04, 8.09 E−03 to 4.73 E−02, 1.44 E−02 to 4.29 E−02, and 2.56 E−03 to 1.18 E−02, respectively for children. The data indicated that the HQ values were < 1; therefore, the health risk of heavy metal exposure through the inhalation, dermal contact, and ingestion of soils had not harmful consequences. In comparison with other countries, our values of HQ are lower than those reported by BBodshV (1999) and Carlon (2007) in the farming soils of Europe, CCME (2018) in Canada, MoE (2018) in Korea, and Perez-Vazquez et al. (2016) in Australia.

Table 7 Values of pollution lead index (PLI), degree of contamination (DC), potential ecological risk index of an individual metal (ER), and potential ecological risk index (RI) for each site and for all agricultural soils

	FES1 (n=6)	FES2 (n=13)	SAM (n=13)	CFS (n=13)	SAV1 (n=13)	SAV2 (n=8)	All agricultural soils (n=66)
PLI							
Mean	2.3	3.9	1.5	1.5	1.7	1.8	2.1
Median	2.2	3.9	1.4	1.7	1.8	1.9	1.8
SD	0.6	1	0.3	0.3	0.2	0.2	1
Min	1.6	3	1.2	1	1.4	1.6	1
Max	3.1	6.8	2.5	2	2	2	6.8
CD							
Mean	10	21.1	4	6.7	7.2	7.6	10
Median	9.2	20.7	3.2	6.9	7.2	7.7	7.6
SD	3	5.9	1.4	1.3	0.8	0.8	6.3
Min	6.9	13.4	2.7	3.9	6	6.6	3.9
Max	14.5	32	6.1	8.3	8.3	8.6	32
ER							
Cr							
Mean	3.3	5.9	4	4	4.3	4.7	4.5
Median	3.6	5.7	3.2	4	4.5	4.9	4.3
SD	0.8	3.1	1.4	1.5	1	0.3	1.8
Min	1.9	2.3	2.7	2	2.8	4.3	1.9
Max	4.1	14.5	6.1	6.2	5.5	5	14.5
Cu							
Mean	12.8	55.1	9.4	9.7	10.9	11.5	19.3
Median	14	51.8	11.1	11.9	11.8	9.8	11.9
SD	2.9	25.4	3.1	3.4	3	3.2	21.1
Min	7.1	22.7	4.5	4.9	6.3	8	4.5
Max	14.9	112.6	14.1	14	15.3	15.3	112.6
Ni							
Mean	23	9.1	8.5	9.3	7.7	8.8	10
Median	22.3	7.6	6.8	6.1	7	8.6	7.7
SD	14.4	3.1	4.6	6.7	1.8	2.2	7
Min	7.1	6	4.6	4.6	5.3	6.3	4.6
Max	43.5	17.1	18.6	22.7	10.5	12.8	43.5
Zn							
Mean	1.9	5.7	1.3	1.2	1.6	1.5	2.3
Median	2	5.6	1.3	1.3	1.6	1.4	1.5
SD	0.5	1.4	0.6	0.3	0.3	0.2	1.8
Min	1.2	3.2	0.8	0.7	1.2	1.2	0.7
Max	2.4	8.3	3.1	1.6	2.2	1.9	8.3
RI							
Mean	41.1	75.7	23.2	24.3	24.6	26.5	36
Median	37.6	68.8	21.1	24.1	24.3	27.5	26.7
SD	15.6	27.2	4.9	5.5	2.4	2.7	24.1
Min	24	41.4	18.1	14.8	21.5	21.9	14.8
Max	64.5	131.9	36.5	34.3	28.1	29.2	131.9

The chronic daily intake (CDI) of Cr, Cu, Ni, and Zn was below the tolerable limits. The CDI of heavy metals for children are higher than those for adults. Oral reference dose (RfD) for Cr, Cu, Ni, and Zn is 1.5 E−0, 4 E−2, 2 E−2, and 0.3 E−0 mg kg^{-1} day^{-1}, respectively (US EPA IRIS).

Type of sampling soil	Sites	Individuals	Cr	Cu	Ni	Zn
Urban soils	FES1 ($n=6$)	Adults				
		CDI	8.07E−05	5.02E−05	9.81E−05	1.39E−04
		HQ	5.38E−05	1.25E−03	4.91E−03	4.62E−04
		Children				
		CDI	7.05E−04	4.38E−04	8.58E−04	1.21E−03
		HQ	4.70E−04	1.10E−02	4.29E−02	4.04E−03
	FES2 ($n=13$)	Adults				
		CDI	4.72E−05	7.23E−05	1.29E−05	1.35E−04
		HQ	9.47E−05	5.42E−03	1.94E−03	1.35E−03
		Children				
		CDI	1.24E−03	1.90E−03	3.38E−04	3.53E−03
		HQ	8.27E−04	4.73E−02	1.69E−02	1.18E−02
Suburban soils	SAM ($n=13$)	Adults				
		CDI	9.63E−05	3.77E−05	3.81E−05	9.11E−05
		HQ	6.42E−05	9.41E−04	1.90E−03	3.04E−04
		Children				
		CDI	8.33E−04	3.24E−04	3.18E−04	8.25E−04
		HQ	5.55E−04	8.09E−03	1.59E−02	2.75E−03
	CFS ($n=13$)	Adults				
		CDI	9.73E−05	3.83E−05	3.97E−05	8.79E−05
		HQ	6.49E−05	9.56E−04	1.99E−03	2.93E−04
		Children				
		CDI	8.51E−04	3.34E−04	3.47E−04	7.68E−04
		HQ	5.67E−04	8.35E−03	1.73E−02	2.56E−03
	SAV1 ($n=13$)	Adults				
		CDI	1.02E−04	4.31E−05	3.30E−05	1.16E−04
		HQ	6.85E−05	1.08E−03	1.65E−03	3.83E−04
		Children				
		CDI	8.98E−04	3.76E−04	2.88E−04	1.00E−03
		HQ	5.99E−04	9.41E−03	1.44E−02	3.35E−03
	SAV2 ($n=8$)	Adults				
		CDI	1.15E−04	4.52E−05	3.77E−05	1.04E−04
		HQ	7.62E−05	1.13E−03	1.88E−03	3.47E−04
		Children				
		CDI	9.98E−04	3.95E−04	3.29E−04	9.09E−04
		HQ	6.66E−04	9.87E−03	1.65E−02	3.03E−03

Table 8 CDI and HQ of ingestion, dermal contact, and inhalation of soils on adult and children in six agricultural soils based on total heavy metal concentrations

However, it seems that this parameter does not have a significant risk on the scale of lifetime (US EPA IRIS).

According to Fig. 7, the total exposure HI of ingestion, dermal contact, and inhalation soils for both adults and children did not exceed 1 in all sampling sites. The HI for adults and children is higher on agricultural urban soils (FES1 and FES2) compared to agricultural suburban soils. The elevated non-cancer risk noted in agricultural urban soils was mainly attributed to the level of Cu, Ni, and Zn from both natural and anthropogenic sources such as wastewater irrigation and a probably use of fertilizers. Figure 7 clearly shows that the HI ingestion of soil is higher for children than those for adults, what could be explained because children tend to be exposed to greater amounts of soil than adults through ingestion due to pica and play behavior (Murgueytio et al. 1998; CDC 2005). From Fig. 8, we observed a similar profile for inhalation and dermal contact of soils on both adults and children. Although there are many of human exposures to heavy metals, it must be noted that our assessment only considered the intake of those elements through direct soil exposure. Indeed, humans are mostly exposed to chemical contaminants through other routes of exposure such as food (vegetables, meats, water, and other liquids) (Wang et al. 2005; Zheng et al. 2007; Chary et al. 2008; Sipter et al. 2008). Therefore, to successfully identify the prevailing exposure routes of potential concern, it is recommended
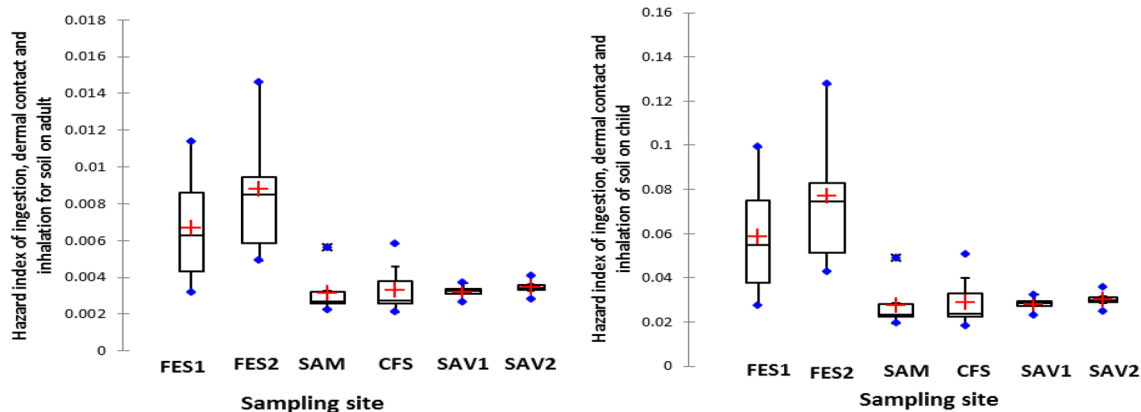
Fig. 7 Box plot of total exposure hazard index (HI) of ingestion, dermal contact, and inhalation of soils based on total heavy metal concentrations on adult and children in six agricultural soils. Boxes depict 25th, 50th (median), and 95th percentiles and whiskers depict minimum and maximum values. Mean values (+); outliers (.)
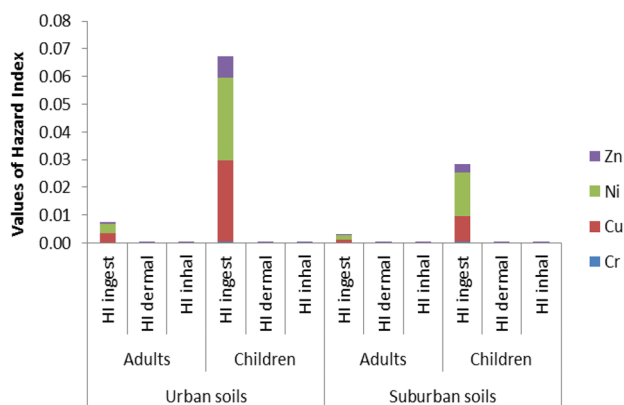

Fig. 8 Values of each hazard index (HI ingestion, HI dermal and HI inhalation) for adults and children in urban (FES1 and FES2) and suburban soils (SAM, CFS, SAV1 and SAV2)

to apply multi-pathway risk analyses related to suitable environmental media (Dong and Hu 2012; Qu et al. 2012; Zhuang et al. 2014).

Conclusion

The present study showed that the heavy metal total concentrations in all urban and suburban agricultural soils of Saiss plain in Morocco were higher compared to crustal and average worldwide soils, which implies that the soil quality status related to heavy metals content, particulary to Cu and Zn and to a lesser extent to Cr, is pretty threatened. Moreover, the two chemical extraction methods (single and sequential) showed that Cu and Zn are more potentially available than Cr and Ni, with a special affinity for Cu by EDTA. Besides the aforementioned results, we confirm that the sequential extraction is more aggressive than the EDTA for extraction in our alkaline agricultural soils. Multivariate analyses (PCA, CA) and correlation matrix used in this study provide important tools for better understanding of the source identification and spatial variations of selected heavy metals in the agricultural soils of the studied area. The results showed that Cr, Cu, and Zn contamination in soils mainly originates from anthropogenic origin, while Ni exhibits a different origin like a pedo-lithogenic origin. The application of the enrichment factor (EF), contamination factor (CF), degree of contamination (DC), pollution lead index (PLI), and index of geoaccumulation (Igeo) enables us to find considerable to high levels of Cu and Zn, respectively, in the urban agricultural soils irrigated by wastewater of the studied area. The present study suggests that Igeo index was the less reliable index in our case study, compared to the EF, CF, DC, and PLI indexes. However, the results show that the potential ecological risks were low-to-moderate in urban agricultural soils irrigated by wastewater. The hazard indexes (HI) of the studied metals were < 1 for both adults and children, indicating that there is not a health risks associated with the ingestion, dermal contact, and inhalation of contaminated soils. Future studies should pay attention to understanding the dynamics of heavy metals, in agricultural soils of the Saiss plain area, and to monitoring where and which heavy metal accumulate. This should involve studying the deeper soil layers and not only the surface soil layer, and apply a multi-pathway risk analysis considering all relevant environmental media to identify the dominant pathway of potential concern. Ultimately, this study will fill a gap in the literature by reporting the human health impacts of heavy metals in agricultural soil from urban and suburban areas in the Saiss plain. This study may also guide policy decisions aimed at protecting human health and the environment.

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