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ORIGINAL ARTICLE

Assessment of heavy metal availability (Pb, Cu, Cr, Cd, Zn) and speciation in contaminated soils and sediment of discharge by sequential extraction

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Abstract The accumulation of the heavy metals in the soil received a particular interest because of their toxicity and retention time in the soil which is slower than in other compartments of the biosphere. Knowledge of the total concentration of metals in soils and sediments is frequently insufficient to ascertain environmental risk. Simple and sequential extractions are useful tools for estimating the mobility of metals. In this study we were interested in highly toxic metals such as cadmium, lead, chromium, copper, and zinc in the soil of a controlled dump and the witness soil as well as the sediment of this dump in order to assess the mobility of these metals and their toxicity. The physico-chemical parameters pH, organic matter, total calcium, cation exchange capacity, and total nitrogen were determined on the samples. Results show that average contents of heavy metals exceed the threshold recommended by the AFNOR NF U 44-041 standard. The results of the sequential extraction of heavy metals in the composite samples of soil and sediment according to the Community Bureau of Reference method show that cadmium is mainly associated with the exchangeable fraction (for sediment 77.7 % and for soil 40 %). Cadmium is therefore mainly associated with the mobile fraction and the risk of its transfer is high. Zinc is mainly bound to the metallic oxyhydroxides and carbonates, while Cu and Pb are mostly bound to organic matter and metallic oxyhydroxides in the proportions of 96.12 % (Cu) and 84.38 % (Pb), respectively.

Introduction

The soil is a natural resource that fulfills several vital functions for humans. It is an important pole of the water–soil–plant–atmosphere compartment. The role of soil and its functions depend closely on the nature and amount of these minerals and organic constituents that determine its properties and its physicochemical, mineralogical, and biological behavior (Mojahid 2007). Like the largest cities in Africa, Marrakech knew this last year's an important industrial and population growth, resulting in an increase of waste production.

Some authors such as Mehdi et al. (2007), showed that discharges have a negative impact on the environment. The huge quantity and heterogeneity of urban waste (electronic waste, batteries, paper cartons, etc.) makes urban discharges a place of accumulation of heavy metals. During the last decades, heavy metals stemming from garbage dumps are very dangerous for the health of both humans and animals (Wang et al. 2003). For this reason, it is essential to measure the contents of heavy metals in the soil (Sirvens 2006). The determination of the total concentration of metals gives no information on their various forms. One of the most crucial properties of these metals which differentiates them from other toxic pollutants is that they are not biodegradable in the environment. Therefore, the determination and monitoring of specific chemical forms of heavy metals in the environmental samples such as airborne particulates, waters,

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biological materials, soils, or sediments are extremely important (Tokaliŏglu et al. 2000). The occurrence of metals in soils or sediments results from natural weathering processes affecting soils and rocks potentially with additional anthropogenic inputs. The fate of these metals in the environment depends on several factors, such as soils or sediment properties, (e.g., metal source, loading rate, soil pH, redox potential, texture, organic matter, and mineral composition), as well as external factors, such as chemical and biological processes. Metals can be bound in various ways. For example, they may be adsorbed on clay surfaces, or iron and manganese oxyhydroxides, and or, also present in the lattice of residual primary mineral phases (e.g., silicates) and or, secondary mineral phases, such as carbonates, sulfates, and oxides. Metals may also be bound in amorphous materials, such as iron and manganese oxyhydroxides, or complexed with organic matter (Gismera et al. 2004).

Heavy metals in the soil are distributed in the solid and liquid phases, and their speciation in every phase depends on several factors. Complexation by organic and inorganic ligands, the oxidation–reduction reactions, adsorption, ion exchange, and dissolution–precipitation phenomena are the main processes that determine the metal content in each phase. Therefore, these processes control the mobility and the bioavailability of heavy metals in grounds (Elass et al. 2003).

Speciation techniques have been widely used for the determination of heavy metals in sediments in the past two decades. These sequential extraction procedures are a useful tool for solid speciation of particulate elements, to study the origin, the fate, the biological and physicochemical availability, and the transport of sorbed elements. As many chemical extraction procedure have been proposed in the literature (Alvarez et al. 2006).

In our study, a sequential extraction method has been applied for heavy metals, in accordance with many chemical extraction procedures that are proposed in literature and by Community Bureau of Reference (BCR) (Tokalioglu et al. 2000):

– *Exchangeable and bound to carbonates* Trace metals are adsorbed on the sediments or on their essential components namely clays, Fe and Mn hydrated oxides, and humic acids. The adsorption of trace metals is related to changes in water ionic composition which probably affects sorption–desorption processes. It is known that the carbonates of sediment contain significant trace metal concentrations and the concentrations are sensitive to changes of pH.
– *Reducible or bound to Fe and Mn oxides* It is well known that Fe and Mn oxides are present as cement, concretions, or nodules between particles or only as a coating on particles. These oxides bind the trace metals and have strong scavenging efficiency for trace metals, but they are thermodynamically unstable under the anoxic circumstances.
– *Oxidizable or bound to organic substances* The trace metals may be associated with various forms of organic material such as living organisms, detritus, or coatings on mineral particles. The complexation and peptization characteristics of the natural organic substances are well known. The organic substances may be broken up freeing the soluble trace metals in the natural waters under oxidizing conditions.
– *Residual* The residual solid contains mainly primary and secondary minerals which occlude the trace metals within their crystal structures.

In Marrakech most of the dumps have been operated since 1987 by the Urban Community, to bury its municipal waste; it was selected based on the criteria that do not meet the requirements imposed by environmental protection and waste control that are developing at Morocco (Hakkou 2001). The landfill site is located on the right bank of the river "Oued Tensift", on the national road "to Safi". It extends over an area of 14 ha and includes only one equipment as a fence 2 m high (urban district of Marrakech, June 2006). The dump of Marrakech is an uncontrolled discharge. Waste is deposited anarchically in the site without compaction or covering layer. Emissions of greenhouse gases and also nauseating odors are a source of nuisance for neighboring populations. They present risks to health and contribute to the degradation of water quality of the groundwater and the Oued Tensift. The present work consists of making an evaluation of heavy metals (lead, cadmium, copper, zinc, chromium, and arsenic) in the soil and the sediments of the final discharge of Marrakesh. The sequential and simple extractions were done to determine the risks of environmental pollution of these metals.

Materials and methods

Sampling

The municipal solid wastes from the Marrakech city are disposed in this landfill. Samples were taken from the soils (S1, S2, S3, S4, S5) and sediments (SD) coming from the decomposition of fermentable wastes that were collected from various localities of discharge from Morocco.

All the samples were air-dried, then passed through a 2-mm sieve before analysis and stored at 4 °C in polypropylene bottles. The use of air-dried materials in this study, does not present a problem, because the sediment samples were collected in oxic conditions (Kersten and Forstner 1986; Rapin et al. 1986).

Physical and chemical characteristics

Chemical properties such as pH, cation exchange capacity, organic matter, conductivity, total nitrogen, and limestone total of the concerned soils and sediments are also analyzed:

- *pH measurement* The pH was determined in a solution of 10 g of waste in 25 mL of distilled water. After 30 min of agitation with the help of a magnetic agitator, the solution was left to rest for 2 h and the pH was measured afterwards with a pH meter, using the electrode-type CRISON pH 25 (norm ISO 10390, NF-X31-117).

- *Cation exchange capacity* (*CEC*) The CEC is the maximum amount of cations that 100 g of dry soil can absorb. It was determined using the method of ammonium acetate CH_3COONH_4 (1 M, pH 7). Thirty milliliters of 1 M CH_3COONH_4 were added to 5 g of soil. The suspension was shaken for 2 h and then centrifuged (15 min, 6000 rpm). After centrifugation and filtration, the filtrate was transferred into a 100-mL flask and two other volumes of 30 mL ammonium acetate were added successively after 30 min of agitation and centrifugation. The final filtrates were completed to 100 mL with ammonium acetate solution.

- *Organique matter* (*OM*) The content of OM was determined by calcination of the sample at 550 °C. A mass of 10 g was charred at 550 °C for 4 h in the electric oven of type Nabertherm controller P 320.

- *Electrical conductivity* (*EC*) Measurement of the EC was performed on the extracts' salts of the samples. The extraction method is based on the displacement of the salts by stirring a suspension of the soil sample for 2 h. The suspension is left to stand before the conductivity measurement. The measuring device is a conductivity meter LF 330/SET of WTW brand.

- *Total nitrogen* (*NTK*) was determined by the Kjeldahl method.

- *Total limestone* The carbonates were determined according to AFNOR X 31-103. The method consists in solubilizing the carbonate ($CaCO_3$) and the sample is attacked with concentrated hydrochloric acid solution. The volume of CO_2 released is measured using the Calcimeter Bernard.

Single extractions

Total concentration of metals [cadmium (Cd), copper (Cu), zinc (Zn), chromium (Cr), and lead (Pb)] in the soil and sediment was determined by acid attacks using AFNOR method AFNOR X 31-151 which consists in the mineralization of soil and sediment samples; this operation is done by the calcination of 0.5 g of soil (finely crushed) in a muffle oven at 450 °C for 2 h. The obtained residue is dissolved in a beaker Teflon with 10 mL of hydrofluoric acid 50 %, and dried into dryness on a sand bath. The dissolution of the residue is made by 7.5 mL of hydrochloric acid and 2.5 mL of nitric acid for 2 h with lime. The resulting solution is adjusted to 10 mL by distilled water and kept in polyethylene pipe, then analyzed by inductively coupled plasma atomic emission spectrometry (ICP-AES).

Sequential extractions

A sequential extraction procedure for determination of the speciation of extractable heavy metals, proposed by (BCR) (Ure et al. 1993), has been applied to soils and sediments, based on the successive attacks of the samples by specific reagents on every fraction: Exchangeable and bound to carbonate fractions, the reducible fraction (metals bound to hydrated oxides of iron and manganese), oxidizable fraction (metals bound to organic matter), and the residual fraction. The heavy metals' contents were determined in the four fractions with the help of an ICP-AES. This method was chosen among several procedures because it was checked for selectivity, reproducibility, and repeatability of the different steps (Leleyter and Baraud 2006; Leleyter and Probst 1999) and it was commonly used in literature (Bur et al. 2009; N'guessan et al. 2009).

Sequential extraction was performed using the four-stage procedure (Table 1); for the exchangeable and acid soluble fractions (F1), about 1 g sample was extracted at room temperature with 40 mL of 0.11 M CH_3COOH (quality from PROLABO) during 16 h. For the reducible fractions (F2), residue from (F1) was extracted at room temperature with 40 mL of 0.1 M $NH_2OH\cdot HCl$ (quality from FLUKA) was extracted at pH 2 for 16 h. The

Table 1 Extractants used at each extraction step and the extraction phase of soil and sediments in the sequential extraction procedure

Extraction steps	Reactive/concentration/pH	Soil and sediment phase
1	Acetic acid CH_3COOH (0.11 mol/L), pH 2.85	Exchangeable, water and acid soluble (e.g., carbonates etc.)
2	Hydroxyl ammonium chloride NH_2OH_HCl (0.1 mol/L), pH 2	Reducible (e.g., iron/manganese oxides etc.)
3	Hydrogen peroxide H_2O_2 (9.8 mol/L) ammonium acetate CH_3COONH_4 (1 mol/L), pH 2	Oxidizable (e.g., organic substance and sulfides etc.)
4	Regal water	Residual (insoluble matter into other reagents)

extraction of the oxidizable portion (F3) was done by adding to the residue from (F2), 10 mL of 8.8 M H_2O_2 (pH 2) (quality from Riedel–de Haen). After 1 h, the mixture was heated at 90 °C for 1 h. And another amount of 10 mL of 8.8 M H_2O_2 was added and heated again at 90 °C during 1 h. The mixture was then cooled, 50 mL of 1 M CH_3COONH_4 was added and agitated for 16 h at room temperature. The residual fraction (F4) was extracted by regal water. After each extraction, the mixture was centrifuged (20 min, 10,000 rpm) and then the supernatant was filtered through a 0.45-μm membrane filter.

We are dedicated to determine the contents of metals which have a high toxicity, namely Pb, Cd, Cu, Zn, and Cr. The contents of heavy metals in the supernatants of the four fractions were determined by ICP-AES. The contents are expressed in mg/kg of dry matter. Our results are compared with those given by the AFNOR NF U 44-041.

Chemical analysis

Elemental analyses of the digests are carried out using (ICP-AES). The quality control of ICP-AES analyses was assessed by the analysis of blank reagents and calibration standards, prepared with commercially available solutions. Accuracy of ICP-AES measurements was determined with various certified reference materials (Rousseau et al. 2009).

Statistical analysis

The descriptive statistical parameters were calculated with the commercial statistics software package SPSS version 19.0 for Windows. Pearson's correlation coefficient analysis, principal component analysis (PCA), and cluster analysis (CA) are the most common multivariate statistical methods used to identify the relationship among heavy metals in environmental studies and their possible sources (Franco-Uría et al. 2009; Lu et al. 2010). In the study, PCA was performed with Varimax rotation with Kaiser Meyer-Olkin normalization (KMO =0.46). Clustering and calculations were performed using the Ward's method and by the Euclidean distances (Franco-Uría et al. 2009).

Results and discussion

The disparity of the results of soil samples and (SD) show the heterogeneity of the waste type (organic, medical, industrial…) (Kolédzi et al. 2011). The pH of the soil is a parameter which influences adsorption, the retention, and the movement of heavy metals in the ground (De Matos et al. 2001). As the organic acids are degraded, the pH increases to an almost neutral level, buffered by the bicarbonate system (Bozkurt et al. 1999). The pH of the samples is slightly alkaline except that of (SD) which is acidic. This alkalinity may be due to certain elements present as ions called exchangeable base (Ca^{2+}, Mg^{2+}, Na^+, and K^+), which increases the pH of the medium (Bodjona et al. 2012). It can also refer to bacterial hydrolysis of nitrogen with the production of ammonia (NH3) associated with protein degradation and decomposition of organic acids in the massif.

This observed pH is characteristic of the soil rich in OM. Also, the pH depends on the content of carbonates, therefore the soil is supposed to contain a significant content of $CaCO_3$ and $MnCO_3$. The alkaline pH increases the capacity of adsorption of oxides, manganese, and iron hydroxides which become goods and strong natural adsorbent (Bozkurt et al. 1999). Metals are thus adsorbed or coprecipitated. The OM content is low compared to those found in the literature; in fact our values are less than 59 % cited by ADEME (1999). But (SD) presents a peculiarity with high contents of OM (69.61 %) and nitrogen (5.2 %). This is probably due to intense farming activity in the region engendering waste rich of OM. The OM of the soil has an important role in the mobility of the metallic cations by complexation reactions which modify the accumulation and the toxicity of heavy metals. Some works (Bjerre and Schierup 1985) showed that the transfer of Cd is lower in soils with high OM content. Indeed, the increase of the organic load is accompanied by an increase in the (CEC) of the soil and reducing the metal transfer toward plants. What proves a relatively high CEC (17 meq/100 g) in the sample SD (Table 2).

Table 2 Characteristics of the studied soil and sediment

Samples	pH	C.E (mS/cm)	OM (%)	C.T (%)	NTK (%)	C.E.C (meq/100 g)
S1	7.70 ± 0.03	3.13 ± 0.05	11.29 ± 0.08	12.64 ± 0.03	0.21 ± 0.02	12.49 ± 0.22
S2	7.65 ± 0.02	4.83 ± 0.02	13.98 ± 0.30	11.47 ± 0.28	1.83 ± 0.15	15.04 ± 0.26
S3	7.76 ± 0.05	2.45 ± 0.03	14.30 ± 0.24	9.56 ± 0.12	3.15 ± 0.04	13.49 ± 0.56
S4	7.91 ± 0.03	2.27 ± 0.25	9.14 ± 0.05	4.41 ± 0.08	1.31 ± 0.07	11.80 ± 0.23
S5	7.50 ± 0.04	3.96 ± 0.04	5.92 ± 0.75	6.49 ± 0.95	1.60 ± 0.37	6.78 ± 0.39
SD	6.06 ± 0.07	1.85 ± 0.33	69.93 ± 7.68	2.86 ± 1.14	26.17 ± 0.62	17.05 ± 0.77
ST	7.74 ± 0.02	0.19 ± 0.03	5.65 ± 0.37	0.16 ± 0.07	0.44 ± 0.07	10.70 ± 2.96

Total content of metals

The total extracted fractions comprise both the residual and the non-residual portion of that fraction bound to silica. Table 3 shows that Cu, Zn, Pb, Cd, and Cr contents are equal to 425–526, 574–1134, 321–356, 0.72–4, and 99.69–576 ppm, respectively. These levels are far above the average concentrations in the limit values (150 ppm for the Cu, 150–300 ppm for Zn, 50–300 ppm for Pb, 1–3 ppm for Cd, and 2.677 ppm for Cr) (Kouame et al. 2006). The value obtained for Cr lies in the range of the average concentration of limit values. The soil is heavily polluted with Cd, Pb, and Zn that are part of the most dangerous industrial and municipal waste (Hasan 2007).

The concentrations of heavy metals in discharge of Marrakech (Table 4) are higher than those of discharge in literature like Al Ain (Howari 2004), Akouédo (Kouame et al. 2006), Sydney and Mall (New Jersey) (Suh et al. 2004). This difference in contents is probably due to the beginning of migration of the metals contained in the soil toward the depth of the discharge. For both samples of soil and sediment, Zn contents are very high. These results are in agreement with those of (Aulin and Neretnieks 1997) who estimate that the concentrations in Zn are 5–127 times higher in landfills than in the natural soil. These high contents are due to its use in numerous applications (electronic, chemical, electricity, pharmaceutical products, medical equipment, cosmetics, etc.) (Malayeri 1995). Except the Cr content in soil samples (S1 and S5, Table 2),

all the tenures of heavy metals are above the threshold recommended by the standard AFNOR NF 44-041 U. These high contents may be due to the heterogeneous nature of household waste which is the source of metal pollution (Kolédzi et al. 2011), related to the rejection of materials that may contain Pb Cu, Cd, Zn, Cr, etc. Although these contentsare higher than the norm, it is still insufficient to pronounce on the state of discharge pollution by these elements, since the total concentration of a potentially toxic element provides little information about the actual toxicity (Elass et al. 2003). To better assess the pollution due to these metals in the landfill, it is important to proceed with their sequential extraction to determine the chemical form in which each element is present and therefore predict their probable mobility in soil.

Sequential extraction

Splitting Cd, Pb, Cr, Cu, and Zn in the composite soil (obtained by homogenization of five soils S1, S2, S3, S4, and S5), sediment (SD) of the landfill, and witness soil is performed by BCR method. This method has enabled us to identify four fractions: the fraction bound to carbonates (F1), the fraction bound to metal (oxy) hydroxides (F2), the fraction bound to organic matter (F3), and the residual fraction (F4). Results are shown in, Fig. 1.

The distribution of heavy metals in various fractions (Fig. 1) is the same in the soil samples and those of sediments. In the exchangeable and acido-soluble fraction (F1),

**Table 3** Contents of heavy metals in soil and sediments in ppm

Samples	Cu	Zn	Pb	Cd	Cr
S1	445.89 ± 0.61	547.23 ± 0.25	344.78 ± 6.25	0.72 ± 0.02	99.69 ± 0.28
S2	425.50 ± 0.51	621.00 ± 2.00	348.8 ± 5.12	1.00 ± 0.15	108 ± 3.60
S3	500.72 ± 15.04	1001.09 ± 1.53	356.28 ± 4.17	3.88 ± 0.35	572.9 ± 1.00
S4	540.00 ± 3.05	1134.00 ± 2.80	330.0 ± 2.80	4 ± 2.00	576 ± 1.00
S5	445.89 ± 0.05	559.23 ± 0.23	364.78 ± 5.35	0.97 ± 0.04	99.82 ± 0.23
SD	526.72 ± 15.04	1001.09 ± 1.53	321.28 ± 0.17	3.88 ± 0.35	572.90 ± 1.00
ST	0.20 ± 0.06	0.60 ± 0.26	0.50 ± 0.25	0.10 ± 0.00	0.20 ± 0.06
Norme NF U 44-041	100	300	100	2	150

Table 4 Comparison of the heavy metal concentrations in soil of discharge in Marrakech (Morocco) with those of literatures (Kouame et al. 2006)

Discharge sites	Cu	Zn	Pb	Cd	Cr	Ref
Marrakech	425–526	574–1134	321–356	0.72–4	99.69–576	–
Akouédo (Côte d'Ivoire)	20–369.7	18.6–1163	10.3–1500	1–11.5	27.7–125	Kouame et al. (2006)
Al Ain (United Arab Emirates)	53.3	117	13.7	0.043	19.1	Howari (2004)
Mall (New Jersey)	27–424	13.2–1008	–	0.55	6–1260	Suh (2004)
Sydney Australia	–	–	78–167	–	–	Suh (2004)
Limit values	50–140	150–300	50–300	1–3	2677	Norme NF U 44-041

Fig. 1 Major fractions of heavy metals (Pb, Cd, Cu, Zn, and Cr) obtained by sequential extractions of soils and sediments using different solvents. (F1: exchangeable and bound to carbonates fraction, F2: reducible fraction, F3: oxidizable fraction, and F4: residual)
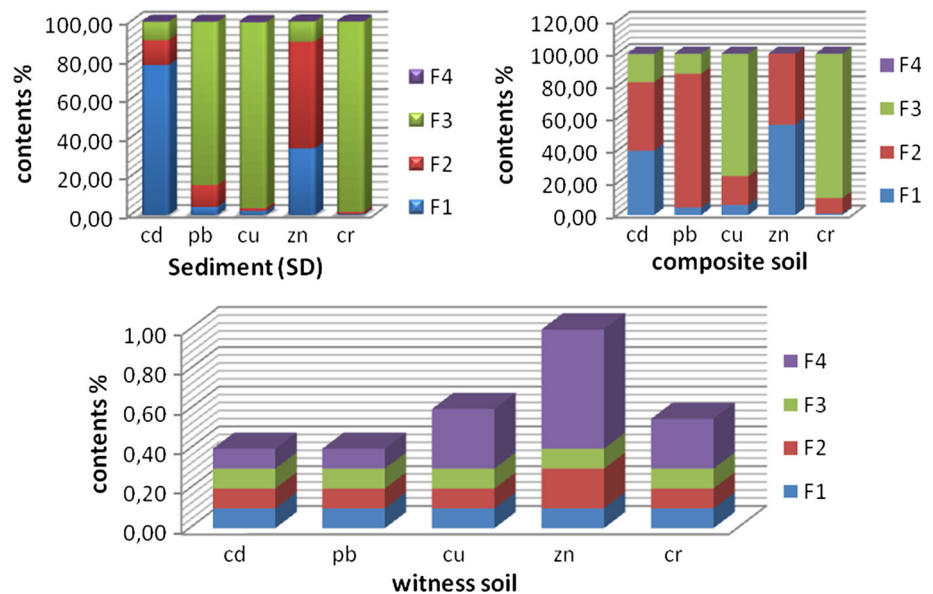
the Pb is present in 40 %, the Cd in 5 %, the Cu in 8 %, the Zn in 58 %, and the Cr is almost nonexistent in the samples of soils and sediments. The strong presence of the lead and the Zn in F1 is due to the fact that these two elements are often strongly adsorbed by carbonates and oxides and therefore have a high affinity vis-à-vis these fractions. Often, the reactions of dissolution/precipitation of carbonates favor trapping metallic ions in crystal forms (Blanchard 2000), this can be the cause of the strong presence of these elements in this fraction F1. Pb, Cd, and Zn are in high proportion in the reducible fraction (F2), respectively 43, 83, and 42 %. The disposition of Cd and Zn in F2 fraction constitutes serious environmental problems because of their high mobility (Yobouet et al. 2010). The Cu and Cr are plentiful in the oxidizable fraction (F3). The abundance of the Cu in F3 is due to the stability of the complexes formed by its ions with the OM of the soil by the association between the metallic cations and the functional groupings of humic substances. The classification made by Alloway (1995) relative to the stability of the complexes formed between the metal cations and the functional groups of the humic substances ($Cu^{2+} > Fe^{2+} > Pb^{2+} > Ni^{2+} > Co^{2+} > Mn^{2+} > Zn^{2+}$) confirms the strong presence of Cu in the oxidizable fraction. The basic pH of the samples would probably also resulted in the dissolution of OM and the consecutive formation of organometallic complexes (Chaignon 2001). Since, variations of pH especially in the presence of organic and inorganic ligands have a considerable influence on the mobility of heavy metals.

The strong presence of Cr (90 %) in the oxidizable fraction have a very high risk to the environment and human health, because the Cr^{3+} is oxidized to Cr^{6+}, which is more mobile and more toxic (Hamilton and Wetterham

1988). Trivalent chromium (Cr^{3+}) is relatively little reactive and less toxic because of its slow kinetics of ligand exchange. Furthermore, the modification of the degree of oxidation of the ligands or the elements being bound with the metal, indirectly influences the solubility of heavy metals. Under reducing conditions, the sulfates are reduced to sulfides which gladly trap the chalcophile elements such as Zn, Pb, Cd, etc. (Deneux-Mustin et al. 2003).

All the studied metal elements are almost nonexistent in the residual fraction (F4). The absence of the metals studied in the residual fraction shows the risk of pollution of these elements in the environment, since the residual fraction contains metals which are unlikely to be released under normal environmental conditions.

The metals present in the soil matrix, behave differently according to their position in the different fractions. In some soil compartments, for example the oxidizable and residual fractions, metals are tightly bound, making them difficult to mobilize. On the other hand in other fractions which are exchangeable and acid-soluble (F1) and reducible (F2), metals are weakly adsorbed and thus can be easily mobilized.

However, quantifying the portion of metals contained in F1 and F2 supposedly mobilized in the samples of soil and sediment, allows estimating the risk of immediate pollution. This portion is very high for Pb, Cd, and Zn, respectively 83, 88, and 100 %. This estimate lets us to say that Pb, Cd, and Zn have a very high risk of pollution at the final Marrakech dump. A metallic element retained on the surface of a material (physisorption, complexation, precipitation, chemisorption) will be dissolved more quickly and therefore present a greater risk of toxicity if it is inserted into the crystal lattice of the material (Benard 2003).

Table 5 Pearson's correlation matrix for the heavy metal concentrations and soil properties

	pH	C.E (mS/cm)	MO (%)	C.T (%)	NTK (%)	C.E.C (%)	Cu (mg/kg)	Zn (mg/kg)	Pb (mg/kg)	Cd (mg/kg)
C. E (mS/cm)	0.136	1								
OM (%)	−0.964**	−0.169	1							
C.T (%)	0.322	0.775*	−0.26	1						
NTK (%)	−0.976**	−0.207	0.992**	−0.348	1					
C.E.C (%)	−0.53	−0.037	0.71	0.132	0.631	1				
Cu	−0.252	0.56	0.346	0.476	0.318	0.3	1			
Zn	−0.262	0.235	0.419	0.188	0.404	0.422	0.903**	1		
Pb	−0.121	0.771*	0.171	0.676	0.137	0.164	0.948**	0.74	1	
Cd	−0.337	−0.134	0.504	−0.128	0.511	0.459	0.678	0.919**	0.441	1
Cr	−0.344	−0.172	0.516	−0.133	0.52	0.477	0.659	0.907**	0.416	0.998**

* Levels of significance: $P < 0.05$ (two-tailed)

** Levels of significance: $P < 0.01$ (two-tailed)

Descriptive statistics

Pearson's correlation analysis

Obtained correlation coefficients are presented in Table 5 as the linear correlation matrix. From this table, the heavy metals Cu, Pb, and Zn are positively correlated among themselves. Content of Cr is correlated with Zn and Cd. No correlation is observed between Cd and studied metals except Zn. According to Suresh et al. (2011) and Suresh et al. (2012), if the correlation coefficient between the metals is higher, metals have common sources, mutual dependence, and identical behavior during the transport. The absence of correlation among the other metals suggests that the contents of these metals are not controlled by a single factor.

Correlation analysis was conducted on heavy metal concentrations and all physicochemical parameters. Table 5 shows intensively significant correlations which were observed between (Zn, Pb, and Cu, $r > 0.9$), (Cd, Cr, and Zn, $r > 0.9$) and a significantly positive was also detected between Cd and Cr, $r = 0.998$.

A significantly positive correlation at $P < 0.05$ was found between the Pb–C.E ($r = 0.771$). On the other hand, a highly positive correlation was found between OM and NTK ($r = 0.992$), C.E and C.T ($r = 0.775$, $P < 0.05$). pH has a significantly negative correlation with OM and NTK at the 0.01 probability level (Fig. 2).

Multivariate statistical analysis results

Principal component analysis

PCA is an effective method to determine human impacts on a spatial scale (Facchinelli et al. 2001). In this study,
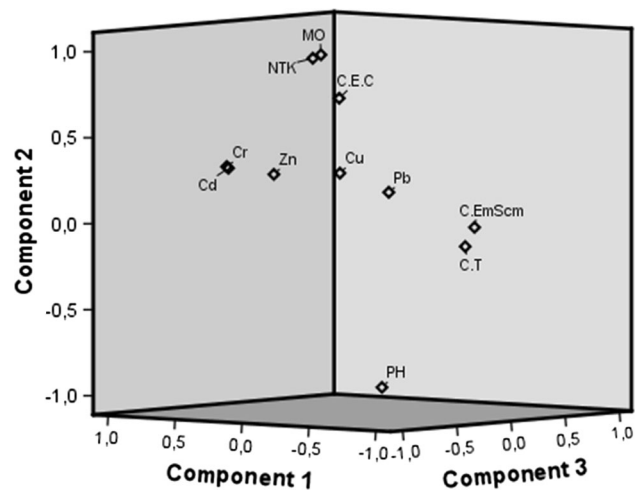
Fig. 2 Loading plot of PC1, PC2, and PC3

using PCA (VARIMAX rotation mode) we identified three principal components (PC) for total metal concentrations and soil characteristics, representing 92.33 % of the total variance of the original dataset before and after rotation (Table 6). In addition, before applying PCA results to interpretations, Kaisere–Meyere–Olkin (KMO) and Bartlett's sphericity tests were employed to examine the validity of PCA (Zhou et al. 2007). The first principal components (PC1) explains 32.77 % of the total variance and loads heavily on Cu, Zn, Cd, and Cr. PC 2, characterized by pH, OM, and NTK, explains 32.24 % of the total variance. PC3 is loaded by Pb, CT, and CE, accounting for 27.32 % of the total variance. The relations among the heavy metals based on the three factors are illustrated in Fig. 3 in three-dimensional space.

Table 6 Total variance explained and matrix of principal components analysis (significant loading factors are remarked in bold)

Component	Initial eigenvalues			Extraction sums of squared loadings			Rotation sums of squared loadings		
	Total	% of variance	Cumulative (%)	Total	% of variance	Cumulative (%)	Total	% of variance	Cumulative (%)
1	5.393	49.030	49.030	5.393	49.030	49.030	3.604	32.766	32.766
2	3.286	29.872	78.902	3.286	29.872	78.902	3.547	32.244	65.010
3	1.477	13.431	92.333	1.477	13.431	92.333	3.006	27.323	92.333
4	0.676	6.144	98.477						
5	0.139	1.260	99.737						
6	0.029	0.263	100.000						

Metal	Component matrix			Rotated component matrix		
	PC1	PC2	PC3	PC1	PC2	PC3
pH	**−0.667**	**0.522**	**−0.473**	−0.083	**−0.964**	0.077
C.E (mS/cm)	0.112	**0.842**	0.438	−0.069	−0.081	**0.950**
OM (%)	**0.791**	**−0.489**	0.364	0.252	**0.964**	−0.071
C.T (%)	0.050	**0.856**	0.331	−0.041	−0.191	**0.899**
NTK (%)	**0.773**	**−0.533**	0.319	0.262	**0.946**	−0.134
C.E.C (%)	**0.665**	−0.209	0.288	0.258	0.701	0.105
Cu	**0.797**	**0.573**	−0.034	**0.699**	0.216	**0.655**
Zn	**0.883**	0.320	−0.336	**0.919**	0.218	0.319
Pb	**0.614**	**0.756**	0.129	0.488	0.104	**0.846**
Cd	**0.861**	−0.019	**−0.501**	**0.957**	0.272	−0.053
Cr	**0.858**	−0.045	**−0.503**	**0.951**	0.283	−0.077

Extraction method: principal component analysis. Rotation method: Varimax with Kaiser normalization. Rotation converged in five iterations

Fig. 3 Dendrogram results from Ward method of hierarchical cluster analysis for 11 elements on the basis of similarity
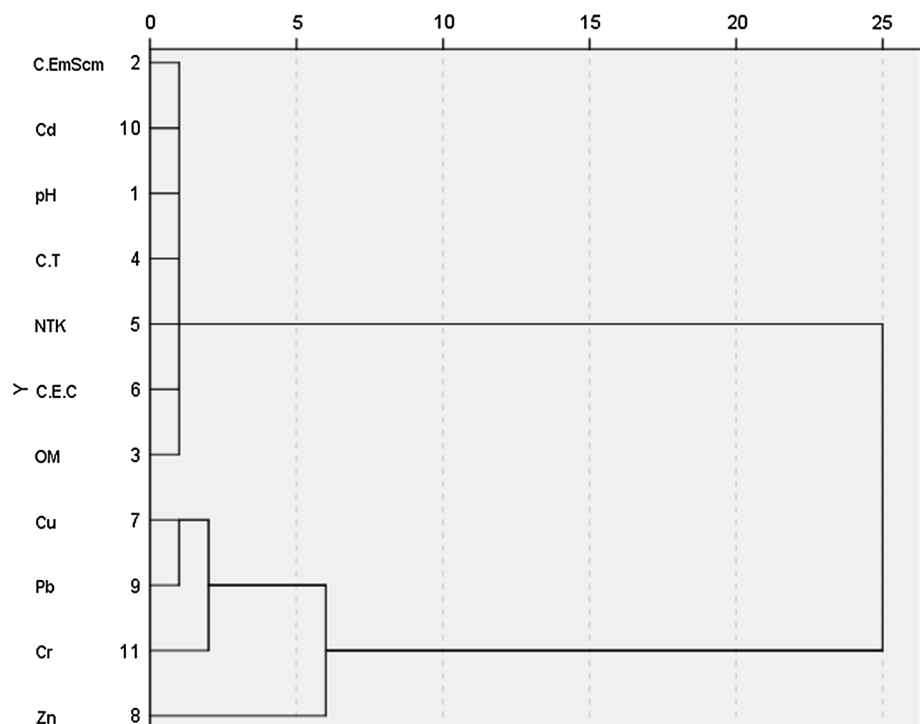
Hierarchical cluster analysis

CA is a multivariate technique, whose primary purpose is to classify the objects of the system into categories or clusters based on their similarities, and the objective is to find an optimal grouping for which the observations or objects within each cluster are similar, but the clusters are dissimilar from each other. The similarity of objects is quantified by distances in the multivariate space. The graphic representation of those distances is performed using dendograms where the magnitude of distances between two objects is represented by the vertical length of lines that connect both objects. The hierarchical clustering was enforced on the standardized data applying Ward's method. The results of hierarchical clustering for the studied heavy metals are presented in Fig. 3. In this dendrogram, all 11 parameters are grouped into three statistically significant clusters. Cluster 1 consists of the parameters such as C.E, Cd, pH, CT, NTK, CEC, and OM; Cluster 2 consists of Cu–Pb–Cr; (3) Zn.

Conclusion

Through the various levies points of the soil samples and sediments at the final Marrakech discharge, we were able to know the evolution of physicochemical parameters and make an assessment of present heavy metals. It appears that the results differ from one sample to another considering the heterogeneity of the waste. Moreover, we found an alkaline pH in all samples except those of (SD) and the OM contents were rather high. This engendered strong accumulation of Cu and Cr in the oxidizable fraction. We noted that the increase of the organic load comes along with an increase in the (CEC) of the soil through the results of physicochemical parameters. Except for the content of Cr in soil samples (S1 and S5), all heavy metal contents are superior to the threshold recommended by the AFNOR standard NF U 44-041.

The results of the sequential extraction allowed finding an important proportion of Pb, Cd, and Zn in the fractions where they are easily mobilizable. This estimate allows us to say that these three elements have a very high risk of pollution at the final Marrakech discharge; this study on the final Marrakech dump allows envisaging a rehabilitation procedures of the landfill in order to preserve a healthy environment.

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