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Health risk assessment of lead contamination in soil, drinking water and plants from Marrakech urban area, Morocco

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Abstract
The aim of this study is to investigate lead contamination in food chain and evaluate the consequent health risks to local residents in three different sites in the Marrakech urban area, compared to a rural reference region far from any source of lead contamination. The following three urban sites that have been selected to have different potential routes of lead exposure: a) old unimproved water pipes (the Medina); b) agricultural land irrigated from untreated urban wastewater (El Azzozia); and c) a mining site (Drâa Lesfer region) were considered in this study. Samples were collected from three compartments: drinking water, soils and plants (edible part). The levels of lead contamination in these compartments were measured. Transfer factors of lead from soils to plants and the eventual health risk of this metal were calculated. The results showed that lead concentration in drinking water of all sites was below the drinking water safety limit. However, soils and plants from mining site were heavily contaminated as compared to the other sites. Consequently, the oral intakes of lead from local plant foods may pose a high health risk to local residents in the mining site and in the wastewater irrigation sites.

Keywords: Lead contamination, health risk, drinking water, soil, plants.

Introduction
The undesirable health effects caused by low-level exposure to lead, particularly in children (the most sensitive target group), have been extensively studied and documented [1;2]. Environmental lead exposure can come from a wide variety of sources including air, water, food and housing. Lead contamination in the soil can usually be attributed to one of the three main processes: industrial activities such as mining and smelting processes, agricultural activities such as the use of insecticide and municipal sewage sludges, and finally, urban activities such as the combustion of gasoline containing the anti-knock additives tetraethyl- and tetramethyl-Pb, and uncontrolled disposal of lead containing materials such as paints [3]. Furthermore, plants can take up lead from the soil and under certain conditions high levels can be accumulated in the leaves and other edible parts of the plant [4]. Heavy metals in soils can be sequestered into a number of fractions including the metal sorbed to clays, hydrous oxides and organic matter, and metal within the matrix of soil minerals [5]. Plants cannot normally access the lead from all of these fractions and so measurements of total soil metal are not necessarily a reliable predictor for bioavailable metal and therefore cannot be used for evaluating which soils pose a risk for crop production [5;6]. So far there was numerous studies have been undertook to understand the relationship between concentrations of extractable metal from soil and metal in plants, and therefore models for risks assessment were developed [7;8]. Lead concentrations in urban soil are influenced by anthropogenic activity and are therefore likely to be much greater than those found in soil from rural areas. Drinking water can also be a source of exposure to lead due to its release from the internal surface of the lead pipes [9]. Moreover, water is clearly fundamental to sustaining any city or society and is a commodity that increasingly needs to be absolutely managed. A whole understanding of the lead contamination cycle is hence regarded as crucial.
The objective of this study is to assess the lead contamination levels in soil, drinking water and plants of three different sites in Marrakech region of Morocco. The factors controlling the heterogeneous distribution of lead in soil, water and plants are also discussed.

2. Materials and methods

2. 1. Sampling sites

The sampling sites were located in regions of Marrakech city. Three regions together with one a reference region were outlined. The monitoring regions were as follow: Medina region (RMd), an old water pipe site; El Azzozia region (RE), lands irrigated from untreated wastewaters; Drâa Lesfer region (RD), a mining site and finally a reference site (RR), that is not exposed to lead contamination. All sampling sites are shown in the Fig. 1. The water, soil and plant samples were collected during September 2009 and June 2011.

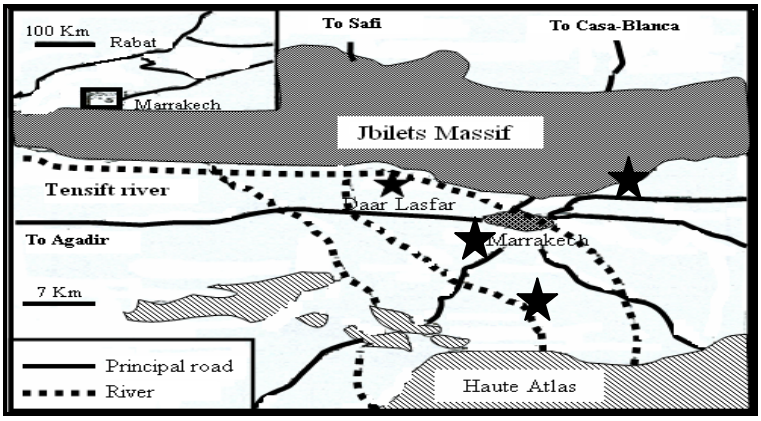

Figure 1. Localisation of sampling site in Marrakech region.

2. 2. Water samples

The water samples were stored in polyethylene bottles, pre-washed with nitric acid (1%). The temperature of each sample was measured at the sampling sites. Conductivity (µS/cm) and pH were measured in situ. The samples were maintained at 4°C until the analyses were carried out. Chemical analyses including oxidizability O_2 (mg/l), hardness ($CaCo_3$, mg/l), chlorides (Cl^-, mg/l), ammonium (NH_4^+, mg/l), nitrate (No_3^-, mg/l), nitrite (No_2^-, mg/l), sulfates (SO_4^{2-}, mg/l), phosphates (PO_4^-, mg/l), potassium (K^+, mg/l), sodium (Na^+, mg/l) and calcium (Ca^{2+}, mg/l). Water samples was filtered and analyzed directly. The physicochemical parameters of the analyzed water samples are presented as the mean of twenty individual values ± the corresponding standard deviation.

2. 3. Soil samples

Soil samples were collected from selected agricultural fields. Soils at the three locations were randomly sampled from the upper horizon (0-20 cm) and bulked together to form one composite sample (different soil samples were taken in the same manner from different sites). After transportation to the laboratory, soil was air-dried and sieved through a < 2 mm mesh, and then sealed in paper envelopes until analysis.

2. 4. Plant sampling and identification

Only the most abundant species were sampled (Table1). All plants were mature and appeared healthy and did not show the presence of parasites. The plants were washed with tap water and rinsed with distilled water to remove airborne pollutants. To reduce water content, the edible parts of the vegetable samples were weighed and air-dried for a day. Dried sample were powdered using a pestle and mortar sieved and then sealed in paper envelopes until analysis.

Table 1: Plant species* collected from the study area.

Species	Common name	Family	Order
Olea europaea	Olive, African olive	Oleaceae	Lamiales
Zea mays	Corn, maize	Poaceae	Poales
Triticum turgidum	No common name	Poaceae	Poales

*Latin and common names and taxonomic classification were obtained from the United States Department of Agriculture. National Resources Conservation Services (http://palnts.usda.gov/)

Digestion of soil and plant samples

For each samples, three powdered samples from each site (0.5 g) were accurately weighed and placed in crucibles, three replicates for each sample. The soil samples, was gradually warmed to 450°C. After cooling, hydrofluoric acid (HF) and perchloric acid ($HClO_4$) were added to the residue, and the mixture was heated to dryness. Hydrochloric acid (HCl) was added and heated to redissolve the residue. The solution was thereafter brought to 50 ml volume with distilled water.

1 g of plant samples powders were weighed into beakers (100 ml), and treated with 10 ml concentrated HNO_3 (ultrapure 65%). The beakers were covered with watch glass, and the suspensions were heated to 130°C for 1 h. A total of 4 ml 20% H_2O_2 were added in four aliquots of 1 ml each. After cooling to the room temperature, the suspensions were filtered and the filtrates were collected in 50 ml flasks. The filtrates were diluted with distilled water to 50 ml.

2. 5. Samples analysis
The metal analysis of samples (Pb) was carried out by using UNICAM atomic absorption spectrophotometer (AAS).

2. 6. Data analysis
Calculation of transfer factors
The transfer factor (TF) is an index of the ability of the vegetable to accumulate a particular metal with respect to its concentration in the soil substrate [10;11;12], was calculated for each metal species as follow:

$$TF = \frac{\text{Metal concentration in plant tissue}}{\text{Metal concentration in soil}}$$

Calculation of oral intake of metals from vegetables
The daily intake of metals (DIM) was determined using the equation:

$$DIM = \frac{C_{metal} \times C_{factor} \times D_{food\ intake}}{BW_{average}}$$

C_{metal}, C_{factor}, $D_{food\ intake}$ and $BW_{average}$ represent the heavy metal concentrations in plants (mg/kg), conversion factor (fresh vegetable weight into dry vegetable weight), daily intake of vegetables and average body weight, respectively. The conversion factor 0.085 was used to convert fresh green vegetable weight to dry weight, as described by Rattan [13]. The average daily vegetable intake for adults and children was considered to be 0.345 and 0.232 kg/person/day, respectively, while the average adult and child body weights were considered to be 55.9 and 32.7 kg, respectively [14;15].
Calculation of health risk index of metal contamination of vegetable
The risk index for the locals through the consumption of contaminated vegetables was defined as a quotient between the estimated exposure to daily metal intake (DIM) from soil through food chain and reference dose (*RfDo*) for Pb [16]. Therefore risk index was calculated as follow:

$$Risk\ Index = \frac{DIM}{RfDo}$$

RfDo represents safe levels of exposure by oral for lifetime [17;18]. The HRI under 1 means the exposed population is assumed to be safe.

2. 6. Statistical analysis
The data were statistically analyzed and performed using the SPSS12.0.1 software package for Windows, Release 12.0.1 (2003). Chicago, IL: SPSS Inc.
Analysis of variance (ANOVA) was carried out in order to determine the statistical significance. The level of significance was set at $P < 0.05$.

3. Results and discussion

3.1. Drinking water characteristics
In all drinking water samples examined in the present study, the values set in accordance with safety limits. However, electrical conductivity, total hardness, calcium and nitrites exceeded greatly these limits. The highest concentration of ammonium (0.52 mg/l) and phosphorus (0.56 mg/l) were found in R.E waters which exceeded slightly the safety limits, whereas regarding nitrites, nitrates, chloride, sulfates, sodium, potassium, calcium and lead, the highest values are shown by drinking waters from the mining site (Table 2). The concentration of chloride in drinking waters from the mining site exceeded slightly the standard value, but it is 5 to 7 times higher than the concentrations found in R.E and R.Md water samples with the respective values of 52.54 and 37.63 mg/l. Calcium is known to occur naturally in water due to its passage through mineral deposits and rock strata and contribute to its total hardness. Drinking waters from mining site exhibited the highest concentration of calcium (237.2 mg/l) and the highest value of total hardness (772.6 mg/l).
The highest conductivity values were detected in RE waters (mean value 1059.05 µS/cm), followed by those determined in R.Md waters (805.55 µS/cm) and the mining site waters (217.95 µS/cm).

3.2. Soils characteristics
Table 3 summarizes the physicochemical and metal characteristics of soil samples in R.D, R.E an R.R. The pH of R.D and R.E ranged from 8.43 to 9.23; values which are higher than the pH of the reference soil (7.2). The concentration of organic matter in the studied soils varies widely within sites and ranged from 1.16 to 5.24 %.
The highest values of electrical conductivity and salinity were found at mining site with the respective values of 450 µS/cm and 1.44 g/l. The most calcareous (17.37 %) soil was found at R.E, which exhibits also the highest concentration of organic matter (5.24 %). Lead concentration in soils was variable, but in general decreasing

from R.D soils to the R.E soils and ranged from 113 to 127 µg/g (Table 3). In all soils the lead concentration was considerably higher the concentration in the reference soil (37 µg/g).

Table 2: Physicochemical analysis of drinking water samples collected from the study area.

	R.Md	R.D	R.E	R.R	F	*P* value
pH	7.45 ± 0.19	7.41 ± 0.16	7.56 ± 0.12	7.49 ± 0.12	0.741	0.548
E.C (µS/cm)	805 ± 3.33	218 ± 3.9	1059 ± 53	248 ±16.69	892.785	0.0001
O_2 (mg/l)	4 ± 0.22	4.29 ± 0.12	3.85 ± 0.07	3.7 ± 0.29	7.325	0.005
T.H (mg/l)	332 ± 4.16	773 ± 8.56	454.6 ± 1.01	137.5 ± 5.57	9260.538	0.0001
Cl^- (mg/l)	38 ± 7.35	264 ± 0.61	52.54 ± 1.21	71.85 ± 2.07	2986.990	0.0001
NH_4 (mg/l)	0.15 ± 0.04	0.25 ± 0.05	0.52 ± 0.06	> 0.0003	95.013	0.0001
NO_3 (mg/l)	0.02 ± 0.02	9.26 ± 1.65	8.88 ± 0.19	0	158.177	0.0001
NO_2 (mg/l)	0.17 ± 0.03	0.29 ± 0.02	0.19 ± 0.01	0	151.217	0.0001
SO_4 (mg/l)	76.5 ± 0.75	110 ± 1.08	96 ± 0.88	63 ± 2.68	698.804	0.0001
PO_4 (mg/l)	0.02 ± 0.01	0.28 ± 0.03	0.56 ± 0.01	0.005 ± 0.003	1049.198	0.0001
Na^+ (mg/l)	17.4 ± 1.15	24.3 ± 2.16	21 ± 2.6	16.38 ± 0.47	16.053	0.0001
K^+ (mg/l)	2.74 ± 0.23	5.63 ± 0.32	5 ± 0.19	3.1 ± 0.37	97.212	0.0001
Ca^{2+} (mg/l)	116.7 ± 7.37	237 ± 2.57	166 ± 1.8	78.9 ± 0.93	1132.180	0.0001
Pb (µg/l)	3.35 ± 0.69	5.3 ± 3.56	5 ± 2.25	0.93 ± 0.65	3.454	0.051

EC: Electrical Conductivity. TH: total hardness.

Table 3: Main analytical characteristics of soil samples collected from the study area.

	R.D	R.E	RR	F	*P* value
pH	8.64 ± 0.11	8.4 ± 0.15	7.2 ± 0.03	198.033	0.0001
E.C (µS/cm)	450 ± 0.08	410 ± 0.11	250 ± 0.06	5.929	0.023
Salinity (g/l)	1.44 ± 0.08	1.31 ± 0.03	0.8 ± 0.03	188.972	0.0001
CT (%)	16 ± 0.67	17.4 ± 0.26	12 ± 0.62	105.792	0.0001
O.M (%)	1.16 ± 0.08	5.24 ± 0.15	1.6 ± 0.03	2084.730	0.0001
Pb (µg/g)	127 ± 9.06	113 ± 4.90	37 ± 2.50	250.751	0.0001
FP	1.27	1.13	0.37	----	----

O.M.: Soil organic matter.

3.3. Lead concentrations in the collected plants

Table 4 summarizes the Pb concentrations in the edible part of (*Olea europaea*, *Zea mays* and *Triticum turgidum)* grown in the same soil samples in R.D and R.E compared with soils in R.R.

Table 4: Concentration of lead in plants collected from the study area.

	R.D	R.E	R.R	F	*P* value
Olea europaea	10.7 ± 1.92	8.4 ± 0.93	6.7 ± 0.48	7.680	0.011
Zea mays	8.9 ± 0.73	7.6 ± 0.70	7.4 ±0.62	5.681	0.025
Triticum turgidum	8.55 ±0.41	8.1 ± 1.29	7.3 ± 0.49	2.315	0.154

It can be clearly observed that the concentrations of Lead in edible part of plants are higher in R.D and R.E than in R.R. However, the concentrations of lead in R.D is highest in all plants analysis and in R.E is the lowest, which are similar with the distribution trend of concentrations in soils; indicating that the concentrations of lead in different plants are associated with the concentrations in soils.

3.4. Transfer factor

The TF is a factor of the ability of plants to accumulate a particular toxic metal with respect to its concentration in the soils substrate. Based on data in tables (3 and 4), transfer factor was calculated. According to the results in Table 5, the values of TF in R.Mn and R.E were significantly different and were less than 1.

Table 5: Lead transfer factors for plants grown in contaminated soils.

	Transfer factor		
	Olea europaea	*Zea mays*	*Triticum turgidum*
R.D	0.08	0.07	0.07
R.E	0.07	0.07	0.07

3.5. The daily intake of metals and human health risks

The daily intakes of metals in plants in regions of Marrakech are investigated and their human health risks for local consumers are simultaneously calculated in table 6.

The pH values of analyzed waters are slightly higher than 7 and ranged from 7.41 to 7.56. It is to be noted that water should be preferably slightly alkaline in order to assure protection of pipe work and metallic fittings from corrosion. The obtained values of physicochemical parameters indicate that all drinking waters are enriched with salt that occurs either naturally or due to human activity. Regarding lead, for all analyzed water samples, concentrations of Pb, stay below the recommended maximum concentration in drinking water according to those of WHO [19].

The lead concentrations in soils were significantly different among regions and the comparisons for Lead between regions showed a significant pollution gradient. Lead concentrations in soils from R.D and R.E were highly elevated compared to the baseline values [19] and R.R. The most seriously contaminated region is R.D with (127 µg/g). A substantial fraction of the metals in the soils are potentially plant-available [20; 21; 22].

The results of lead concentrations in edible part of plants growing on contaminated soils are in agreement with previous studies showing elevated level of lead in soils and edible part of plants [23; 24]. The above reported results demonstrate that the plants grown on soils with elevate level of lead are generally contaminated with this toxic metal, which pose a major health risk [25]. Results from present and previous studies [26; 27; 28; 20] demonstrated that the food crops grown on contaminated soil threatened health for the local inhabitants.

The results showed also, that the plants differ widely in their ability to accumulate the metal, as demonstrated in table 4. It was found that among the three plants (*Olea europaea*) accumulated the highest concentrations of Pb (10.7 µg/g), while (*Triticum turgidum*) accumulated the lowest concentrations of Pb (7.3µg/g) in their edible part.

Table 6: Daily oral intake of metals (mg) and health risk index (HRI) for individual Pb caused by the consumption of tree selected vegetables grown in soils of mining region and El Azzozia region.

Species	Individuals		R.D	R.E
Olea europaea	Adults	DIM	5.35 E-3	4.41 E-3
		HRI	1.53	1.26
	Children	DIM	6.15 E-3	5.07 E-3
		HRI	1.76	1.45
Zea mays	Adults	DIM	4.67 E-3	3.99 E-3
		HRI	1.33	1.14
	Children	DIM	5.37 E-3	5.58 E-3
		HRI	1.53	1.31
Triticum turgidum	Adults	DIM	4.49 E-3	4.25 E-3
		HRI	1.28	1.21
	Children	DIM	5.16 E-3	4.88 E-3
		HRI	1.47	1.40

There were no apparent differences among the three plants regarding their respective transfer factors, suggesting that these plants have similar uptake and translocation ability for Pb in soils. We can also conclude that, it is much difficult for Pb to transfer from the soils into the edible parts of the plants, however, soils and plants are still severely contaminated with Pb. Nevertheless, the uptake of soils metal by plants depends on their bioavailable amount rather than the total concentrations and plants physiological processes [15]. Our results suggest that we have in these regions a low transfer of Pb from the soils to the plants (edible part).

Laughlin *et al.* [29] propose that total soils concentrations are not a good predictor of metal bioavailability to plants. However, high lead content in edible part of plants in our results, recorded to the contaminations by dust. Li *et al.* [24] suggest also that plants and crops can uptake toxic metals through their roots from contaminated soils and even leaves can absorb toxic metals deposited on the leaf surface. For these reasons more research should be done to complete this first investigation.

The DIM values for Pb were high when based on consumption of plants both in R.D and R.E, also, the values of DIM from plants grown at R.D and R.E, have exceeded the Rfd levels of Pb and have a hazard effect on human's health especially in R.D. The values of HRI of studied Pb were higher than 1, both in R.D and R.E,

indicating that the inhabitants of these regions are experiencing relatively high health risk. The results showed that the residents of R.D especially children, are at high risks of health effect.

Conclusion

Lead is a very toxic metal in humans and previous research has shown that the food chain is the main pathway of lead transfer from the environment to human.

In order to observe the transfer of environmental lead and its risk on health, it is important to estimate the level of contamination by detecting the route of exposure to the humans.

The results of this study show that the concentration of lead in water was low and does not represent a health risk. However, concentrations of lead in soils and plants, especially in the mining region, were in most cases higher than those in the El Azzozia region.

This preliminary environmental risk assessment shows that irrigation with urban wastewaters in El Azzozia region and contamination of soils and plants with mining wastes in mining region could lead to the high health risk in humans residing in these areas.

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