LEVELS OF METALS IN SOILS OF AIT AMMAR IRON MINE, MOROCCO: HUMAN HEALTH RISKS

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Abstract: The concentrations of metals were determined in soil samples collected in Ait Ammar (Oued Zem, Morocco). The mean Cd, Cr, Cu, Fe, Pb and Zn contents in the mining topsoil samples were: 2.12, 135, 34.9, 214, 9.13 and 90.8 mg kg^{-1}, respectively. Human health risks developed from metal ingestion, dermal absorption and inhalation of soils were also evaluated. For non-carcinogenic risks, united hazard index (HI) values for children surpassed the safe level (HI=1) for Cr (13.1). Values for HI in adults (1.74) also surpassed the safe level for Cr. The HI values for Pb and Cd for children were 0.69 and 0.68, respectively. Cancer risk due to Cr surpassed the tolerable range (1E-06 to1E-04) for children (1.05E-03) and for adults (1.42E-04). Cancer risks due to Pb and Cd were within acceptable ranges for both children and adults. Furthermore, oral ingestion of soil particles contributed more highly to both carcinogenic and non-carcinogenic risk from Cr than either dermal absorption or inhalation in both children and adults.

Keywords: Metals; Ait Ammar iron mine; Inhalation; Dermal; Ingestion; Risk assessment

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Introduction

Mining is one of the actually bases of heavy metals in the ecosystem, and the process itself presents serious potential sources of pollution.[1] Heavy metal pollution has been a fundamental problem in the surrounding area of abandoned mine sites. These heavy metals have a potential to pollute topsoil. They can be dispersed and collected in plants and animals, and taken in by human beings as consumers. Human health risk assessment has been employed to define if exposure to a chemical, at any dose, could cause an increase in the incidence of adverse effects to human health.[2] In residential areas, surplus accumulation of heavy metals in topsoil can immediately threaten the safety of exposed inhabitants via ingestion, inhalation and dermal contact.[3]

The possible toxicity of pollutants is determined by the speciation of the elements implicated. In risk assessment, oral exposures are characteristically specified in terms of the external dose or intake, instead of in terms of absorbed dose or uptake. Intake is characteristically described as the method by which an element crosses the outer exposure surface of a human without passing an absorption barrier, while uptake is the method by which an element crosses an absorption barrier into human or animal.

Risk assessment practices are well advanced and recognized in the USA. Lots of examinations have accepted human risk assessment methods by considering exposure scenarios of metal intake through polluted soil.[2] Risk assessment processes have mainly concentrated on urban areas, [4, 5] industrial areas, [6] petrochemical plants [7] or areas of mining activities.[8]

Heavy metal exposure can be severe in infants and young children because of their rapid growth capabilities. The children's exposure is higher

when compared to adults because of their playing activities, licking objects which may be polluted and hand to mouth habit.[9]

The human health risk models including carcinogenic and non-carcinogenic risks developed by US EPA have proved successfully and adopted worldwide. Human health risk assessment (HQ and HI) studies on various exposure ways in urban and industrial environments have recently been given great importance.[10] The adverse health effects through life can be assessed by utilizing threshold RfD value. The chances of severe health effects will be lowest if the average value of average daily dose (ADD) is inferior to that of the reference dose (RfD) and the chances will be higher if the average value of ADD is higher than that of RfD.[11]

The human health risk assessment has been suggested by USEPA and numerous scientists have utilized it for the evaluation of exposure rate of metals on human health.[12, 13]

The present study focused on evaluation of the human health risks due to selected metals exposure through contaminated soil located nearby abandoned iron mine. The study area (Ait Ammar mine site) is known by the presence of high levels of metals in soil.[14] These elements may affect the health of residents in the Ait Ammar village via their entry into the food chain of domestic livestock (cow and sheep), and the consumption of muscle, liver and kidney tissue from animals grazing over the mining area.[15] Through the present study we have investigated: (1) the contamination levels and dispersion patterns of metals in soil samples, and (2) characterization of the potential health risks in adults and children via the exposure pathways of soil ingestion, inhalation and dermal absorption.

Material and Methods

Surface soil was collected at the site of Ait Ammar iron mine (33° 04' N; 6° 38' W), which is located in the Khouribga Province, Morocco. The region's climate is Mediterranean arid to semi-arid.[14] Four sampling transects (T1, T2, T3, and T4) were selected based along the direction of iron deposits. Five sampling sites were selected along each transect, with the most distance point being 300-600 m from the first transect point (Figure 1). So, five sampling rounds (R1, R2, R3, R4 and R5) were determined based along the distance of iron deposits (e.g. R1 contained T11, T21, T31 and T41).

Figure 1. Location map of the study area and topsoil samples.

At each point, 2000g of soil was taken manually from the upper most 0-20 cm layer. Each sample was composed of five subsamples collected around the point, which was pooled in the field. Soil at Ait Ammar area present a relatively heterogeneous composition, varying in texture and color (brown to black). In addition, one reference site (REF) (6° 34' 2'' W; 32° 49' 34'' N) was selected. This site of fallow land was located about 27 km south of the mining site. Five subsamples from the REF site were mixed and treated in the same manner as the transect samples. In the laboratory,

apportion of each sample was ground to 2 mm and kept for basic soil properties and metal content analyses.

Along each transect, the topography varied significantly on a small scale but no important changes in terms of vegetation cover were observed. The vegetation was sparse and dominated by *Eryngium ilicifolium* and *E. triquetrum*. Today most of the area is barren ground or sparsely vegetated (nothing has been left of the mine with the exception of some concrete ruins), and it is utilized as a grazing area for livestock possessed by the inhabitants of the nearby small Ait Ammar village.

The concentrations of metals (Cd, Pb, Cr, Cu, Zn, and Fe) in soil were measured after their digestion in HNO_3, HF and HCl.[14] These acids were ACS reagent grade from Sigma Aldrich (Steinheim, DE). Briefly, 2 mL of concentrated HNO_3 were added to 150 mg of each soil sample, and mixed. The samples were then heated at 100°C until dryness. After this, 3 mL of concentrated HF were added to the Teflon vessels and heated at 140°C for ≥15 h in closed vessels. After cooling, the vessels were opened and heated to dryness at 110°C. Concentrated HNO_3 (2 mL) was added and heated at 110°C to dryness. This step was repeated five times to ensure the evacuation of excess HF, since traces of HF in the sample solution would quickly deteriorate the nebulization system. HCl (25 mL) was then added, and the closed vessels were heated for 2 h at 100°C. After cooling and filtration, all samples were analyzed for Cd, Cr, Cu, Pb, Zn and Fe. The concentrations of the metals were determined by inductively coupled plasma-atomic emission spectrometry (ICP-AES, Jobin Yvon ULTIMA 2) (The National Centre for Scientific and Technical Research (NCSTR), Rabat, MA). The accuracy and quality of quantitative determinations of these elements were verified by the use of standards corresponding to precise single elements of 1000 ppm. In

addition, the CNRST certified ISO 9001 quality assurance system and Good laboratory practice (ISO 17025) approach was applied throughout. Detection limits were (ppm): Cd 0.002, Cr 0.004, Cu 0.004, Zn 0.002, Pb 0.006 and Fe 0.006.

Risk assessment followed a multi-step method,[16] which included data assemblage and assessment, exposure evaluation, toxicity calculation, and risk description. In this analysis, Cd, Cr, Cu, Pb and Zn were classified as potential hazardous elements with particular reference to human health. In accordance with the toxicological profiles[17] of these agents, all have toxicological health effects in humans, and some are carcinogenic (Cd, Cr and Pb induce both non-carcinogenic and carcinogenic risks).[18, 19]

Contact of humans with heavy metals in mining soils may occur through three major pathways:[20] (a) direct oral ingestion of elements ($ADD_{ingestion}$); (b) inhalation of suspended particulates produced from soil ($ADD_{inhalation}$); and (c) dermal absorption of heavy metals in particles adhered to exposed skin (ADD_{dermal}). Both non-carcinogenic and carcinogenic risks of these exposure pathways were considered. In the phase of exposure assessment, a particular method characteristic for human exposure to soil in mining areas was applied, acquiring principally precaution of the non-carcinogenic hazard exposure for children. The carcinogenic risk was estimated for the lifetime exposure, valued as the probability of a single individual developing cancer over a lifetime as a consequence of total exposure to the potential carcinogen. The dose expected (average daily dose, ADD) through each of the three exposure routes considered was analyzed employing:

$$ADD \text{ ingestion} = \frac{C \; X \; IngR \; X \; EF \; X \; ED}{BW \; X \; AT} \; X \; 10^{-6}$$

$$ADD \text{ inhalation} = \frac{C \ X \ InhR \ X \ EF \ X \ ED}{PEF \ X \ BW \ X \ AT}$$

$$ADD \text{ dermal} = \frac{C \ X \ SA \ X \ SAF \ X \ ABS \ X \ EF \ X \ ED}{BW \ X \ AT} \ X \ 10^{-6}$$

The ADD for each agent and exposure pathway was consequently divided by the equivalent reference dose to yield a Hazard Quotient (HQ, or non-cancer risk):

$$HQi = \frac{ADD}{RfDi}$$

The definitions of symbols, used values of particular variables and parameters are shown in Tables 1 and 2. For carcinogens (Table 2), the dose (Cd, Cr and Pb) was multiplied by the corresponding factor to produce a level of excess lifetime cancer risk:

$$Risk = ADD * CPF$$

Although interactions between some metals might result in their synergistic, additive or antagonistic manners,[21] it was supposed that all the metal risks were additive, therefore it was possible to calculate the cumulative non-carcinogenic hazard expressed as the Hazard Index (HI):

$$HI = \sum_{i=1}^{n} HQi$$

and carcinogenic risk expressed as the total cancer RISK:

$$Total \ risk = \Sigma Risk = Risk \ ing + Risk \ inh + Risk \ dermal$$
$$= ADD \ ing * CPF \ ing + ADD \ inh * CPF \ inh$$
$$+ \frac{ADD \ dermal * CPF \ ing}{ABS \ Gi}$$

Table 1. Definitions of the parameters for the human health risk assessments.

Symbol (units)	Definition
ABS_{GI}	Gastrointestinal absorption factor
C (mg kg^{-1})	Concentration of metal in soil
ADD_{ing}, ADD_{inh}, and ADD_{derm}	Chronic daily intake or dose contacted through oral ingestion (mg kg^{-1} d^{-1}), inhalation of (mg m^{-3} for non-cancer, and µg m^{-3} for cancer), and dermal contact (mg kg^{-1} d^{-1}) with soil particles, respectively
CPF_{ing} (mg kg^{-1} d^{-1})$^{-1}$	Chronic oral potency factor
CPF_{derm}	Chronic dermal slope factor, = CPF_{ing}/ABS_{GI}
RfD (mg kg^{-1} d^{-1})	Chronic reference dose
BW (Kg)	Body weight expressed
EF (d y^{-1})	Exposure frequency expressed
ED (y)	Exposure duration expressed
SA (cm^2)	Skin surface area available for daily contact expressed
LT	Life time
AT (d)	Average time
SAF	Skin adherence factor for soil
IngR (mg d^{-1})	Ingestion rate expressed
InhR (m^3 d^{-1})	Inhalation rate expressed
PEF (m^3 kg^{-1})	Particle emission factor
ABS dermal	Dermal absorption factor

Table 2. Values of the variables for the estimation of human exposure.

Variables	Value	References
BW	60 for adult and 15 for children	16
EF	350	22
ED	24 years for adults and 6 years for children	23
SA	5700 for adult and 2800 for children	23
LT	65 years	6
AT	For non-carcinogenic (ED X 365 days/year) and for carcinogenic (LT X 365 days/year)	22
SAF	0.07 mg/cm^2/h for adults and 0.2 mg/cm^2/h for children	23
IngR	100 for adults and 200 for children	23
InhR	20 for adults and 7.6 for children	8
PEF	1.36 x10^9	23
ABS dermal	0.001 (for all metals)	3, 8, 20
RfD_{ing}	Cu=4E-02; Cr=3E-03; Pb=3.5E-03; Cd=1E-03 and Zn=3E-01	24
RfD_{derm}	Cu=1.2E-02; Cr=6E-05; Pb=5.25E-04; Cd=1E-05 and Zn=6E-02	20
RfD_{inh}	Cr=2.86E-05 and Cd=1E-05	20, 22
ABSGI	Cu=1; Cr=0.013; Pb=1; Cd=0.025 and Zn=1	17
CPF_{inh}	Cr=4.2E+01; Pb=4.2E-02 and Cd=6.3E-01	6
CPF_{ing}	Cr=5E-01 and Pb=8.5E-03	22

Generally, the higher the HQ value is above unity (1), the greater the level of concern; Thus HQ ≤ 1 proposes unlikely adverse health effects, whereas HQ > 1 proposes the probability of contrary health effects. In general, the excess cancer risks lower than 10^{-6} are considered to be negligible, and cancer risks above 10^{-4} are considered unacceptable by most international regulatory agencies.[16, 25] The value 10^{-6} is also considered the carcinogenic target risk by the USEPA.[17]

Statistical analyses were performed in PRIMER 5 (Primer-Eltd, Plymouth, UK). Similarities were found using non-metric multidimensional scaling (MSD).The similarity matrix was found with normalized Euclidean distance similarity of the metal concentration values converted as log(x+1).

Results and Discussion

Total contents of metal in the topsoil of the study area are presented in Table 3.The mean values of metal contents in the soils from mining areas follow a decreasing order as: Fe >>> Cr > Zn > Cu > Pb > Cd. Surprisingly, concentrations in the reference soil (REF) were not inferior to those from the mining site in a number of cases. For Cd, Cr and Zn, the REF soil had higher concentrations than the mining site soils in almost all transects and rounds. The REF site contained lower concentrations of Pb and Fe than the mining sites.

Multi-dimensional scaling (MDS) analyses indicated that samples from the mine area were clearly separated (Figure 2). The plot of the MDS analysis of the metal concentrations does not reveal a clear disconnection between the soil samples (Figure 2a, b) and no gradient could be determined. This could be linked to natural processes of soil ageing and system recovery, since mining activities stopped 51 years ago.[26] In fact, our results suggest that the distance (round) and direction (transect) had little effect on the metal contents. Nevertheless, the concentrations of Zn, Cr, and Fe were generally above some USA soil screening values (Table 3). In addition, except for Cr and Fe, all metals were below the ranges quantified

by other authors[27, 28] in different Moroccan abandoned mines. For this study, the stress level applied to this study evaluated by MDS is 0.09 (Figure 2), indicating that the two-dimensional representation is valid.

Table 3. Total metal concentrations in the soils of Ait Ammar mining site (mg.Kg^{-1}) (Mean ± SD, n=5 for transect (T) and n=4 for round (R)).

|	Cd	Cr	Cu	Zn	Pb	Fe
T 1	1.04 ± 0.364	128 ± 51.5	36.4 ± 13.3	95.1 ± 31.4	10.8 ± 9.85	248.000 ± 122.000
T 2	1.20 ± 0.409	102 ± 29.7	26.9 ± 7.24	69.0 ± 29.9	11.7 ± 9.91	132.000 ± 825.000
T 3	1.46 ± 0.919	133 ± 35.9	28.7 ± 12.1	78.4 ± 57.8	3.53 ± 5.11	156.000 ± 149.000
T 4	4.80 ± 7.80	175 ± 20.7	47.9 ± 30.3	120 ± 14.7	10.54± 13.1	320.000 ± 253.000
R 1	1.47 ± 0.961	130 ± 18.2	44.9 ± 13.2	104. ± 34.0	7.23 ± 6.42	279.000 ± 691.000
R 2	1.35 ± 0.403	155 ± 43.5	38.0 ± 13.1	126 ± 36.9	20.4± 12.8	318.000 ± 935.000
R 3	0.929 ± 0.472	169 ± 44.6	48.9 ± 30.1	91.8 ± 37.1	9.51 ± 10.4	223.000 ± 108.000
R 4	0.937 ± 0.293	91.8 ± 36.9	18.6 ± 3.16	58.6 ± 38.9	4.14 ± 4.82	139.000 ± 130.000
R 5	5.93 ± 8.36	126 ± 29.5	24.2 ± 2.98	72.8 ± 22.4	4.33 ± 5.44	110.000 ± 101.000
REF	5.14	166	44.8	155	0.92	598.000
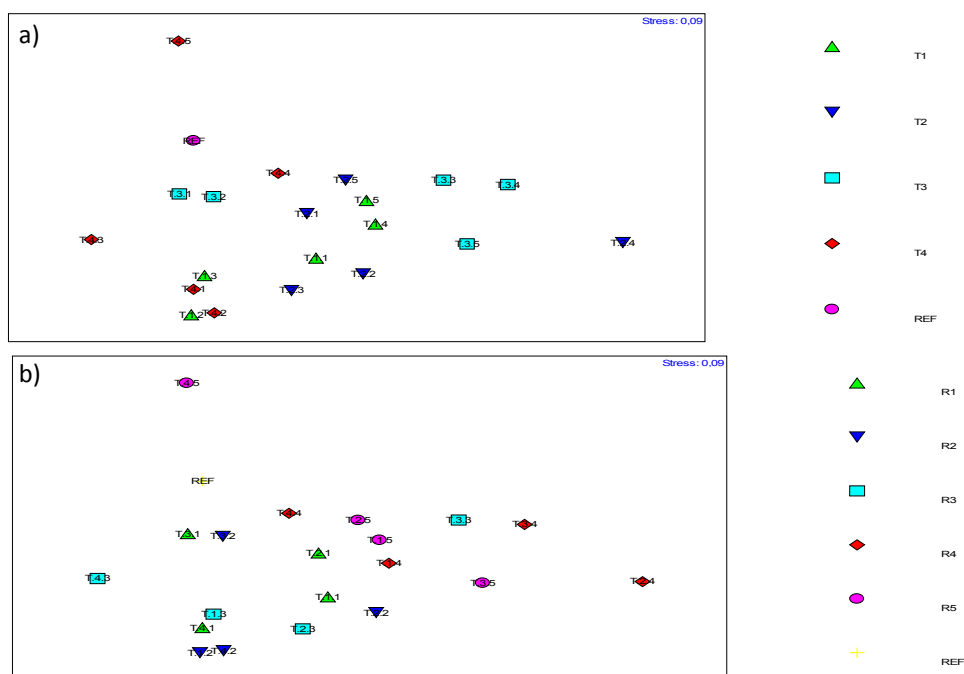
Figure 2. Non metric multidimensional scaling analysis of average metal concentrations in the soils of Ait Ammar mining area, Analysis made "a" by transect, "b" by round

Though some elements such as Fe, Cu and Zn are essential nutrients, heavy metal pollutants in contaminated soils can have a serious impact on human health. According to the human health risk assessment model for heavy metals in mining soils, both the non-carcinogenic hazard (HQ) and carcinogenic risk (Risk) of each heavy metal, and the cumulative HI and RISK of multi-pathway exposure and combined metals in mining soils of Ait Ammar were characterized.

The results of the non-carcinogenic and carcinogenic health risks due to metals exposures in mining soils via different pathways (ingestion, dermal and inhalation) are shown in Table 4. From the literature on the traditional risk assessments for metals in mining soils, sites were considered to present health risks to children and adults when HI >1 and Risk>10^{-6}.

For non-cancer effects, HQ values for children are always higher compared to adults due to higher intake rates and lower body weight. Shown by the mean values, HQ values for different routes of exposure for combined metals were HQ_{ing} (0.13) > HQ_{dermal} (0.0177) > HQ_{inh} (0.00088) and for adults HQ_{ing} (0.0162) > HQ_{dermal} (0.00316) > HQ_{inh} (0.00057). Further, ingestion of soil appeared to be the major route of exposure to mining soil that results in a health risk from exposure to Cu, Cr, Pb, Cd and Zn. This was followed by dermal contact and lastly inhalation (Table 4). Similar results have been reported for soils from the rural clusters in the Thiva area of Greece,[29] for urban soils around industrial clusters in Ghaziabad, India[6] and for street dusts in Luanda, Angola.[30] Furthermore, cumulatively, the HQ of each metal for multi-pathway exposure is Cr (0.656) > Cd (0.0349) ~ Pb (0.034) > Cu (0.0113) > Zn (0.00392) for children; and for adults Cr (0.0871) > Cd (0.00479) ~ Pb (0.00428)> Cu

(0.00142) > Zn (0.000494). The highest observed HQ value was 0.656 for Cr, while the other values were less than 0.1.

Chromium was also the only metal with an HI value greater than 1. For children, the HI values were 11.5 and 1.61 for ingestion and dermal absorption, respectively. For adults and Cr, only the HI value of 1.43 for ingestion exceeded the safe value of 1. These HI values indicate the potential for adverse non-cancer health effects for both children and adults from exposure to Cr in these soils. However, it should be noted that Cr was measured as total Cr in this study, and that the toxicity of Cr is directly dependent upon its valence state.[4] Therefore, the health implications require further investigation.

For non-cancer risk, HIs to adult and children decreased in the order of Cr > Pb > Cd > Cu > Zn for inhalation and ingestion; and in the order of Cr > Cd > Pb > Cu > Zn for dermal. The potential health risk for Zn was the least for both adult and children populations. Overall, Cr, Cd and Pb are metals of concern for children in terms of non-cancer risk.

Table 4. Non-carcinogenic and carcinogenic risk for adult and children.

			Cd	Cr	Cu	Zn	Pb
Children	Dermal	Intake HQ	7.60E-03	8.03E-02	1.04E-04	5.42E-05	6.23E-04
		HI	1.52E-01	1.61E+00	2.09E-03	1.08E-03	1.25E-02
		carcinogenic risk		1.85E-04			2.78E-09
	Inhalation	Intake HQ	7.6E-05	1.7E-03			
		HI	1.5E-03	3.4E-02			
		carcinogenic risk	4.78E-10	2.02E-06			1.37E-10
	Ingestion	Intake HQ	2.72E-02	5.74E-01	1.12E-02	3.87E-03	3.34E-02
		HI	5.43E-01	1.15E+01	2.23E-01	7.74E-02	6.67E-01
		carcinogenic risk		8.60E-04			9.92E-07

Table 4. Continued

Adult	Intake Dermal	HQ	1.35E-03	1.43E-02	1.86E-05	9.65E-06	1.11E-04
		HI	2.71E-02	2.86E-01	3.71E-04	1.93E-04	2.22E-03
		carcinogenic risk		3.30E-05			4.95E-10
	Intake Inhalation	HQ	5.0E-05	1.1E-03			
		HI	1.0E-03	2.2E-02			
		carcinogenic risk	3.15E-10	1.33E-06			9.01E-11
	Intake Ingestion	HQ	3.39E-03	7.17E-02	1.40E-03	4.84E-04	4.17E-03
		HI	6.79E-02	1.43E+00	2.79E-02	9.67E-03	8.34E-02
		carcinogenic risk		1.08E-04			1.24E-07
Children RISK			4.78E-10	1.05E-03			9.95E-07
Adults RISK			3.15E-10	1.42E-04			1.25E-07
Combined Children HI			6.97E-01	1.31E+01	2.25E-01	7.85E-02	6.80E-01
Combined Adults HI			9.60E-02	1.74E+00	2.83E-02	9.86E-03	8.56E-02
Combined Children HQ			3.49E-02	6.56E-01	1.13E-02	3.92E-03	3.40E-02
Combined Adults HQ			4.79E-03	8.71E-02	1.42E-03	4.94E-04	4.28E-03

For cancer risk, only Cr, Pb and Cd were estimated through the exposure pathway of mining soils. Shown by the mean values, the Risk of different exposures for combined metals is $Risk_{ing}$ (4.30×10^{-4}) $\gg$ $Risk_{dermal}$ (9.25×10^{-5}) $\gg$ $Risk_{inh}$ (6.74×10^{-7}) for children, and $Risk_{ing}$ (5.41×10^{-5}) $>$ $Risk_{dermal}$ (1.65×10^{-5}) $\gg$ $Risk_{inh}$ (4.43×10^{-7}) for adults. Cumulatively, the children RISK is 1.05×10^{-3} and adults RISK is 1.42×10^{-4}, these levels were higher than the range of acceptable threshold values (10^{-6}-10^{-4}). Furthermore, the children Risk of each metal for multi-pathways exposures were Cr (1.05×10^{-3}) $\gg$ Pb (9.95×10^{-7}) $\gg$ Cd (4.78×10^{-10}). Risk values for adults were Cr (1.42×10^{-4}) $\gg$ Pb (1.25×10^{-7}) $\gg$ Cd (3.15×10^{-10}). The $Risk_{Cr}$ of all samples was higher than 10^{-6}. Nevertheless, the $Risk_{Pb}$ for all samples was lower than 10^{-6}. The particularly significant carcinogenic risk level of Cr in urban road dusts has also been reported by Shi et al. (2011)[3] and Luo et al. (2012)[5].

In conclusion, the carcinogenic risks of Cr due to mining soil exposure by oral ingestion and dermal contact cannot be negligible in Ait

Ammar (exceeding the target value 10^{-6}). Carcinogenic risks for children were higher than for adults. Cr was considered as a major toxic chemical substance to human health in this mine area.

Conclusions

The present study examined the content of metals in the mining soils in Ait Ammar iron mine, Morocco. The results based on total metal concentrations were compared. Both the non-carcinogenic and carcinogenic human health risks of combined heavy metals in mining soils through oral ingestion, inhalation, and dermal contact pathways were evaluated. Cr was considered as a major toxic chemical substance to human health in this mine area. Highest risk is associated with soil particle ingestion and the non-carcinogenic health risk for children was higher than to adults. Cr cancer risk exceeds the acceptable range for children and for adults and cancer risk due to Pb and Cd were within acceptable range. Following recommendations epidemiologic investigations with a large number of participants are needed in order to evaluate the actual health effects of naturally derived contaminants to exposed population. Since all target concentrations for remediation action must be protective of human health, the framework suggested above would facilitate producing more applicable guidelines for risk assessments and defining realistic cleanup levels of mining soil contamination.

Acknowledgments

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