

Risk Assessment of Heavy Metals Contamination in Paddy Plants Fields at Al-Mishkhab Area, Iraq

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Abstract

Heavy metals accumulated in plants influence human health. The objectives of the present study are to estimating heavy metals contamination in soil and rice plant (*Oryza saghdтива* L.), in agricultural lands of Al-Mishkhab area and assessment the health risk for heavy metals in soil and plants. Transfer factors (TF) of heavy metals from soil to variuos parts of paddy plant and its health risk were detected. Concentrations of toxic heavy metals (Cd, Cr, As, and Pb) and the micronutrients (Cu, Mn Mo, Se and Zn) were detected in the paddy field soil and plant parts by Inductively coupled plasma – Mass spectrometry (ICP-MS) technique. Results displayed that Mn and Cd are found to be accumulated more in stem than in root. The concentrations of heavy metals were found to be within allowable worldwide limits for ordinary soils, except As, Cr, Mn and Ni which were higher than the amount of uncontaminated soil. whereas heavy metals in cultivated soil are higher than those in close uncultivated land soil expect; As, Cr and Mo. Transfer of Mn and Zn from roots to stem and from stem to grain were higher as their concentrations were higher in stem than that of roots and grains. Health Index (HIs) rates for seven metals (As, Cd, Cr, Cu, Ni, Pb, Zn) of rice consuming were 1.7627 for adults and 0.9159 for children propose their adverse health effects in the near futurity.

Keywords: Paddy Plants, Health risk index, Heavy metals, Transfer factor, Al-Mishkhab - Iraq

1. Introduction

The natural and anthropogenic sources of heavy metals concentrated in soil and plants represent significance environmental contamination problems. Though, food integrity issues and harmful health risks make this one of the most serious environmental cases [1] Environmental pollution of the biosphere with heavy metals due to dense agricultural and other anthropogenic activities demonstrate critical problems for secure use of agricultural land [2].

Human health is straight affected out of intake of crops grown in contaminated soils. There is obvious evidence that human kidney dysfunction is linked with contamination of rice with Cd in breadwinner fields in Asia [3]. Indeed, in Asia, rice has been specified as one of the major sources of Cd and Pb for human beings [4]. In Japan, rice was identified to be the prime source of Cd contamination for individual [5].

Accumulation and adsorption of heavy metals in soil layer may be "due to relatively high organic matter". The plant parts that transfer heavy metals to human body are the eatable parts such as rice grain, which may thus be a threat to human health. Thus, heavy metals in the environment, then, are of large concern, because of their stability nature, bioaccumulation, and biomagnification characters causing ecotoxicity to plants, animals, and human [6].

The aims of the present study, are to estimate the heavy metals contamination in soil and rice plant (*Oryza sativa* L.), in agricultural lands of Al-Mishkhab area and to evaluate the health risk for heavy metals in soil and plants. Risk assessment was made assess the prospect risk factor for the local inhabitants exhausting rice, the essential food .

2. Study area

The study area is located in Al-Najaf governorate to the south west Iraq between latitudes ($31^{\circ} 52' 20''$ N) ($31^{\circ} 39' 54''$ N) to the north and longitude ($44^{\circ} 29' 37''$ E) ($44^{\circ} 25' 58''$ E) to the east It covers an area of 375 square kilometers.(Statistical Bulletin for the Al-Najaf Governorate.,2000).Geologically, the study area is located within the Salman Subzone which belongs to the Stable Shelf Zone covered by Quaternary deposits [7]. Najaf governorate is characterized by semi-desert climate with a long dry hot summers and a mild short winter, with annual rainfall of less than 38cm. Agriculture is dependent almost completely on irrigation. Sampling of the soil and rice plants with grains was carried out during crop season winter 2016 in order to investigate the concentrations and spatial distribution of potentially toxic heavy metals originated from the agricultural activities of the agriculture watershed. The study site and sampling locations of the study site are shown in Figure 1 and 2 .

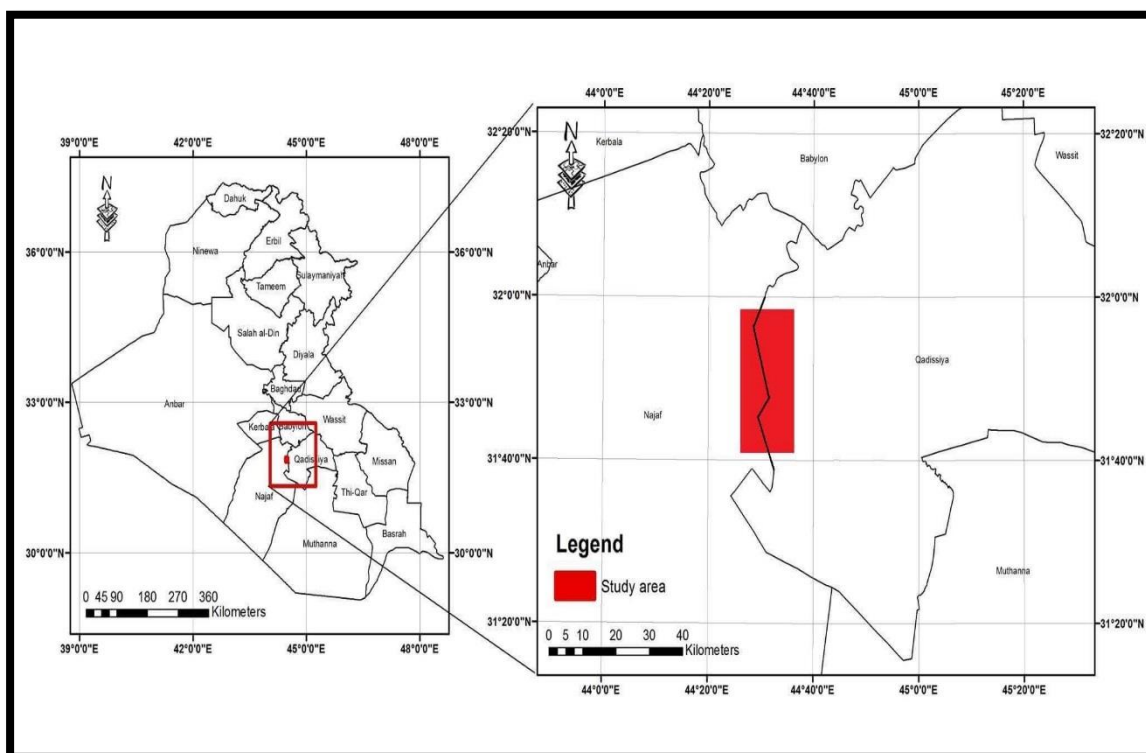


Figure 1 : Location map of the study area

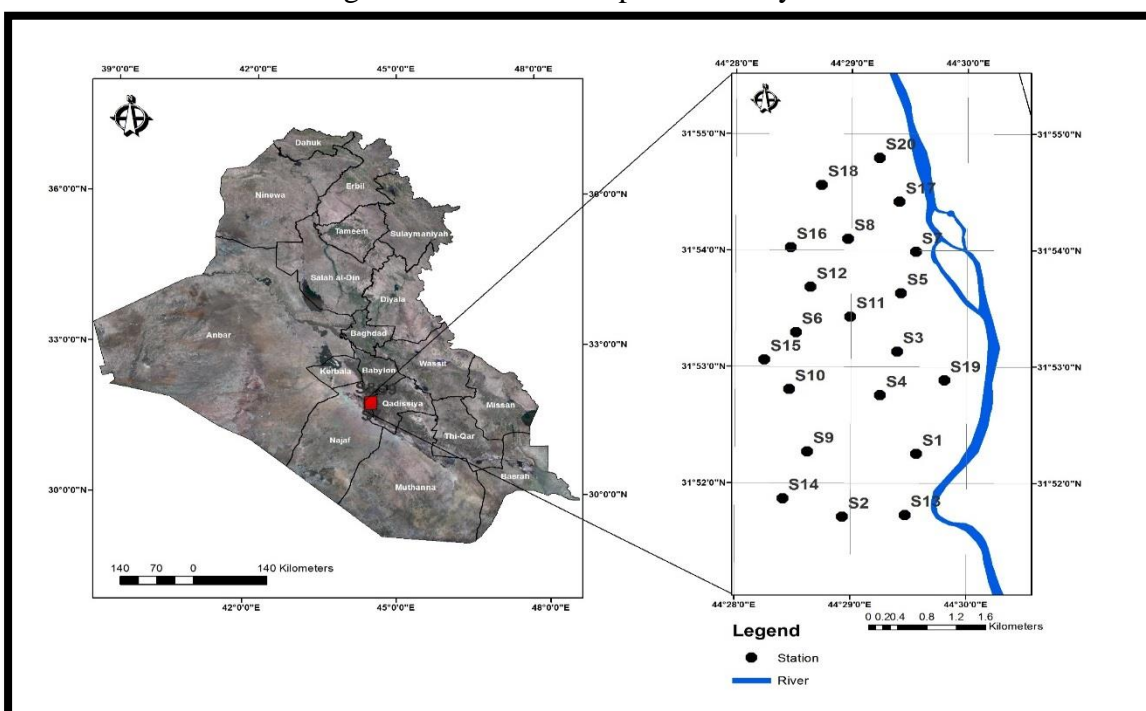


Figure 2: Location map of soil and plants samples(ARC GIS map).

3. Material and Methods

Soil samples were collected from twenty different sites of the rice fields . Out of these two were the control site where no crop cultivation. At each sampling site, a composite of soil samples was collected separately by a random selection, from each field, from surface (0–30cm soil layer) and mixed to make one composite sample . Each soil sample of about 500mg was collected from the 0–30cm layer, which represented the plough layer. Rice plant samples were collected from the corresponding soil sampling site of the paddy field for computing correlations between heavy metal concentrations of soil and plant . All soil and rice plants along with grain samples were kept in clean polyethylene bags and brought to the laboratory for analyses. Paddy crop plants were collected and washed thoroughly with deionized water. Five paddy plant was cut and separated into root, stem, and grain subsamples. All samples were oven dried at 60°C for 24 h, and the dried samples were weighed, then pulverized, and stored in Petri dishes. The soil samples were air-dried at room temperature for several days, then pulverized, and sieved through a 0.1mm stainless steel mesh. Rice grain samples were washed with deionized water and hulls were removed .

The rice grain samples without hull were oven-dried at 70 °C for 72 h and then ground with an agate mortar to fine powder [8].

For heavy metal analysis One gram each of soil and Crop sample samples were digested (wet acid digestion) with 15 ml of concentrated HNO₃ and HClO₄ in 5:1:1 ratio at 80 °C until a transparent solution was obtained [9]. The digested samples of water, soil, and Crop samples were filtered through Whatman no. 42 filter paper and the filtrates were diluted to 50 ml with distilled water. All samples were stored at ambient temperature before analysis. Heavy metals concentrations in soil, and in crop samples were estimated by ICP-MS technique in ALS Group Labs. (Spain). The precision and analytical accuracy were checked by analysis of standard reference material, GBM908-5 for soil, and NIST 1575a for plant samples. The results were found to be within the acceptable limit of certified values.

Transfer Factor (TF). Transfer factor (TF) or mobilization ratio [10] [11] was calculated to determine relative translocation of metals from soil to other parts (root, stem, or grain) of the plant species as follows:

$TF = \text{Concentration of metal in plant tissue} / \text{Concentration of metal in corresponding soil or root or stem.}$

Risk Assessment. The Health Risk Index (HRI) was calculated as the ratio of estimated exposure of rice and oral reference dose (ORD) [12]. ORDs were 0.004, 0.001, 0.04, 1.5, 0.3, 0.02 and 0.05 mg/kg/day for Pb, Cd, Cu, Cr, Zn, Ni, and As respectively.

Estimated exposure is obtained by dividing the estimated daily intake (EDI) of heavy metals by their safe limits. An index value >1 is considered unsafe for human health [13]. EDI was calculated by the following equation:

$$EDI = C \times Con \times EF \times ED / Bw \times AT$$

where C (in milligrams per kilogram) is the concentration of heavy metals in the rice, Con (in grams per person per day) is the daily average consumption of rice in the region, Bw (in kilograms per person) represents body weight, EF is exposure frequency (365 days/year), ED is exposure duration (70 years, equivalent to the average lifespan), and AT is average time (365 days/year number of exposure years, assuming 70 years in this study). The average

daily rice intake of adults and children was considered to be 389.2 and 198.4 g/person/day, respectively. [14] Average adult and child bodyweights were taken to be 55.9 and 32.7 kg, respectively, as used in many previous studies [14] [15] [16] [14,15,16].

The HI is calculated to evaluate the potential risk of adverse health effects from a mixture of chemical constituents in rice. The HI was calculated through daily average consumption of rice for a human being (adults and children) and is as follows :

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

4. Results and Discussion

The concentration of heavy Metal in Soil, it was found that, in the essential heavy metals in the paddy soil, Mn concentration ranged from 571-721 mgkg⁻¹ with mean of 646.65 mgkg⁻¹, Ni concentration ranged from 162-226 with mean of 193.35 mgkg⁻¹, Cr concentration ranged from 88-131 mgkg⁻¹ with mean of 193.351 mgkg⁻¹, Zn concentration ranged from 66-81 mgkg⁻¹ with mean of 73.85 mgkg⁻¹, Cu concentration ranged from 29.6-79.8 mgkg⁻¹ with mean of 49.22 mgkg⁻¹, concentration ranged from 10.9-17 mgkg⁻¹ with mean of 13.335 mgkg⁻¹, As concentration ranged from 7.5-13.8 mgkg⁻¹ with mean of 9.12 mgkg⁻¹, Mo concentration ranged from 0.5-0.98 mgkg⁻¹ with mean of 0.728 mgkg⁻¹, Se concentration ranged from 0.5-1.5 mgkg⁻¹ with mean of 0.68 mgkg⁻¹ and Cd concentration ranged from 0.21-0.33 mgkg⁻¹ with mean of 0.2635 mgkg⁻¹.

Among these metals, As, Cd and Cr are highly toxic, while Pb is moderately toxic and Zn, Mn, Se, and Cu are essential elements and micronutrients (Brady and Weil, 2002). "The ranking order of occurrence of the heavy metals in the paddy field soils was Mn>Ni>Cr>Zn>Cu>Pb>As>Mo>Se>Cd indicating that Mn followed by Ni was in the maximum concentrations and Cd was in minimum concentration".

The comparison of trace elements in the cultivated soil with those of worldwide limits (MAC) and other published values (A,B,C) suggest that soil samples were contaminated by As, Cr, Mn and Ni (table 1).

All trace elements in cultivated soil are higher than those in nearby uncultivated field soil expect; As, Cr, Mo are less (table 1).

The highest concentrations of heavy metals in paddy plant parts were found to be accumulated "in the roots than in other plant parts", stem, and grains with average of 256.5 mgkg⁻¹ for Mn, 25.55 mgkg⁻¹ for Ni, 13.12 mgkg⁻¹ for Cr, 17.16 mgkg⁻¹ for Zn, 19.966 mgkg⁻¹ for Cu, 2.502 mgkg⁻¹ for Pb, 20.744 mgkg⁻¹ for As, 1.058 mgkg⁻¹ for Mo, 0.3792 mgkg⁻¹ for Se and 0.1318 mgkg⁻¹ for Cd among the five sites.

Table 1, summarized the concentrations of heavy metals, show the descending order of the average contents of metals: In root Mn>Ni>As>Cu>Zn>Cr>Pb>Mo>Se>Cd. While in stem Mn>Zn>Ni>Cr>Cu>As>Mo>Pb>Se>Cd, and in rice grain Mn>Zn>Cu>Ni>Cr>Pb>As>Mo>Se>Cd.

The metal uptake was higher for the micronutrients; like Mn, most metals, Fe, Mn, Zn, and Cu, that were found amply in "the paddy plants were the micronutrients that are in demand for different enzyme actions and plays substantial functions in photosynthesis and growth of the plant [17][18]. The uptake mechanism of heavy metals contains both adsorption (from soil) and absorption (from water) and occupy place through roots [19].

Table1: Mean values of heavy metals for paddy soils compared with mean values for worldwide normal agricultural soil.

| Elements | Range | Mean of cultivated soil | Mean of uncultivated soil | Background | MAC* | TAV* | A* | B* | C* |
|----------|-----------|-------------------------|---------------------------|------------|---------|----------|-----|------|------|
| As | 7.5-13.8 | 9.12±1.365 | 11.95±2.85 | 1.8 | 15-20 | 10-65 | 4.7 | 3.8 | |
| Cd | 0.21-0.33 | 0.2635±0.0295 | 0.275±0.015 | 0.1 | 1-5 | 2-10 | 1.1 | 0.17 | 0.33 |
| Cr | 88-131 | 109.95±11.834 | 112.5±11.5 | 100 | 50-200 | 50-450 | 42 | 22 | 58 |
| Cu | 29.6-79.8 | 49.22±14.142 | 43.3±6.1 | 55 | 60-150 | 60-500 | 14 | 17 | 48 |
| Mn | 571-721 | 646.65±47.648 | 570.5±0.5 | 900 | | | 418 | 411 | |
| Mo | 0.5-0.98 | 0.728±0.1189 | 0.895±0.015 | 1.5 | 4-10.0 | 5-20.0 | 1.8 | 0.58 | 13 |
| Ni | 162-226 | 193.35±17.16 | 129.5±1.5 | 20-60 | 75-150 | 18 | 13 | 26 | |
| Pb | 10.9-17 | 13.335±1.596 | 13.5±0 | 14 | 20-300 | 50-300 | 25 | 18 | 24 |
| Se | 0.5-1.5 | 0.68±0.147 | 0.6±0.1 | 0.05 | | | 0.7 | 0.23 | |
| Zn | 66-81 | 73.85±4.973 | 70±0 | 70 | 100-300 | 200-1500 | 62 | 65 | 89 |

*Background (values are compiled from Mason and Moore) (vide Hedrick 1995) and Reimann and Caritat (1998). Given are mean values for various soils in different countries; *MAC (maximum allowable concentration); *TAV (trigger action value); *A (worldwide data after Kabata-Pendias and Pendias (1999, 2001)); *B (agricultural soil of Sweden after Eriksson (2001a) *C (agricultural soil of Japan, after Takedo, 2004)

Transfer Factor. Transfer factor is one of the main components of human exposure to toxic heavy metals through the food chain. The transfer factors (TFs) of metals from soil to root (TF_{Soil}), root to stem (TF_{Root}), and stem to grain (TF_{stem}) were calculated and given in table 3. The average transfer values of metals in paddy soils from soil to root (TF_{Soil}) were found to be in the order of .

As>Mo>Se> Cd>Cu>Mn> Zn>Pb>Ni >Cr. In the case of root (root to stem), TF_{Root} values were found in the order of Mn>Zn>Ni>Cr>Cu>>As>Mo>Pb>Se> Cd. The transfer values for stem to grain (TF_{stem}) were found in the following order of Mn>Zn>Cu>Ni>Cr>Pb>As>Mo> Se>Cd. The major components of human exposure to metals over the food chain is soil-to-plant transfer factor, that could refer bioavailability of heavy metals in interested soils. High TF values reveal more mobile/available for metals. The TFs change noticeably in the plant types even for a significant heavy metal [1] [16] The results of transfer of Mn and Zn from roots to stem and from stem to grain was higher than another heavy metals as the concentrations of these were found to be more in stem than that of roots and grains. Roots often contain more Zn than the stem parts, however the Zn might be transfer from the roots and accumulated in the plant stem parts. Cd is recognized to be comparatively mobile in plants which also transfer more from root to stem [20]. The metal

translocation process in plant species is a critical agent in determine the metal distribution in various plant tissues [21].

Table 2: Mean concentrations of heavy metals along soil and different plant parts.

| Heavy metal | Mean in soil | Mean in root | Mean in stem | Mean in grains |
|-------------|--------------|--------------|--------------|----------------|
| As | 8.58 | 20.744 | 0.73 | 0.28 |
| Cd | 0.258 | 0.1318 | 0.017 | 0.0068 |
| Cr | 103 | 13.12 | 3.776 | 1.182 |
| Cu | 43.7 | 19.966 | 2.328 | 3.038 |
| Mn | 666.4 | 256.5 | 132.68 | 45.72 |
| Mo | 0.826 | 1.058 | 0.428 | 0.238 |
| Ni | 183.9 | 25.55 | 3.836 | 2.95 |
| Pb | 13.56 | 2.502 | 0.356 | 0.778 |
| Se | 0.74 | 0.3792 | 0.0618 | 0.0684 |
| Zn | 74.6 | 17.16 | 9.68 | 16.52 |

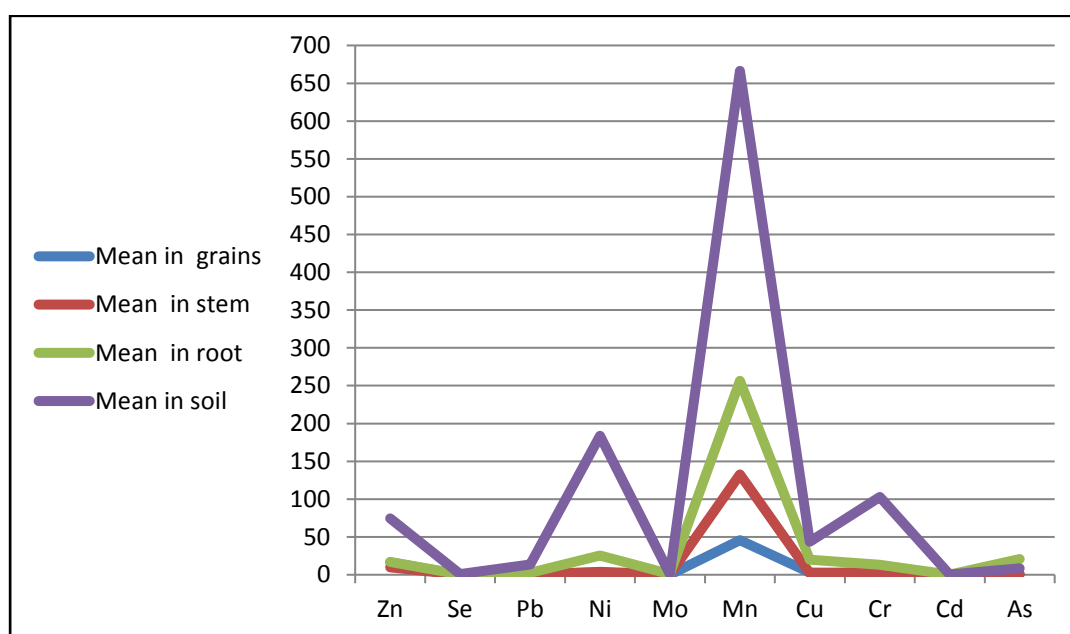


Figure 3: Distribution of heavy metals in soil, root, stem and rice grains.

Table 3: Transfer factors of the heavy metals from soil to root, root to stem, and stem to grain across five sampling sites.

| Heavy metal | TF _{soil=C Root / C Soil} | TF _{root=CSstem / C Root} | TF _{stem=C Grain/C Stem} |
|-------------|------------------------------------|------------------------------------|-----------------------------------|
| As | 2.417 | 0.03519 | 0.383 |
| Cd | 0.5108 | 0.1289 | 0.4 |
| Cr | 0.1274 | 0.2878 | 0.313 |
| Cu | 0.457 | 0.1165 | 1.3049 |
| Mn | 0.385 | 0.517 | 0.3445 |
| Mo | 1.281 | 0.4045 | 0.556 |
| Ni | 0.139 | 0.1501 | 0.769 |
| Pb | 0.1845 | 0.1423 | 2.1853 |
| Se | 0.5124 | 0.1629 | 1.1067 |
| Zn | 0.230 | 0.564 | 1.7066 |

Health Risk of Heavy Metals: One of the prime ways of human exposure to toxic heavy metals has been recognized from consumption of rice since these metals cumulative in rice grain. Table 4 showed the Estimated Daily Intake of metal (EDI) through "rice for adults and children in the survey area as the local people consume mostly rice, the essential food for the people available in the area". The EDIs of heavy metals for adults were found to be higher than those for children. This is most probably due to relatively higher quantity of rice consumption of adults compared to the children, which increased the EDIs of heavy metals. The HRIs of heavy metals through rice consumption are given in table 4. The HRI of seven heavy metals (As, Cd, Cr, Cu, Ni, Pb, Zn) for adults from rice consumption was in decreasing order: Ni > Cu > Pb > Zn > Cd > As > Cr for both adults and children. HRIs are less than 1. Thus, "the health risk of single metal exposure out of rice consumption was mostly supposed to be secure for the people of the region". However, local residents may be at hazard due to the combination of several toxic heavy metals [22]. The HRI values for rice consumption of adults and children were 1.7627 and 0.9159, respectively. This point out that adults and children may exposed poor health effects in the close future as the heavy metal cumulation along a period of time leads to biomagnifications. Actually, human beings are as well exposed to heavy metals over different foods/pathways like consumption of contaminated diet [14] [23] [24] Moreover, there may be the other sources such as dust inhalation and dermal contact [25] [26].

Table 4: Health risk assessment of heavy metals via intake of rice .

| Individuals | Element | ORD mg/kg/day | EDI mg/kg/day | HRI | HRIs |
|-------------|---------|------------------|------------------|-------------|--------|
| Adults | As | 0.05 | 0.001271387 | 0.025427733 | 1.7627 |
| | Cd | 0.001 | 0.000046704 | 0.046704 | |
| | Cr | 1.5 | 0.004226063 | 0.002817376 | |
| | Cu | 0.04 | 0.017987527 | 0.449688167 | |
| | Ni | 0.02 | 0.010531103 | 0.526555167 | |
| | Pb | 0.004 | 0.00160545 | 0.4013625 | |
| | Zn | 0.3 | 0.093051233 | 0.310170778 | |
| Child | As | 0.05 | 0.000660659 | 0.013213184 | 0.9159 |
| | Cd | 0.001 | 2.42691E-05 | 0.024269113 | |
| | Cr | 1.5 | 0.002196018 | 0.001464012 | |
| | Cu | 0.04 | 0.009346979 | 0.233674482 | |
| | Ni | 0.02 | 0.005472348 | 0.273617397 | |
| | Pb | 0.004 | 0.000834251 | 0.208562691 | |
| | Zn | 0.3 | 0.048352837 | 0.161176124 | |

5. Conclusion

The present study carried out on paddy fields of Al-Mishkhab area, Iraq, determined the accumulation of essential and nonessential heavy metals in paddy soils as well as in rice plants including rice grains). The occurrence of heavy metals in paddy field soils was in a ranking order of Mn>Ni>Cr>Zn> Cu> Pb>As> Mo>Se> Cd. Calculated concentrations of heavy metals in the paddy soils were within those of worldwide ordinary soils, except As ,Cr, Mn and Ni which were higher than the rate of uncontaminated soil . Whereas heavy metals in cultivated soil are more than those in close uncultivated field soil expect; As , Cr, Mo. "The uptake of of Mn and Zn from roots to stem and from stem to grain was more than other heavy metals as the concentrations of these were established to be higher in stem than that of roots and grains . Estimations showed that EDIs of heavy metals for adults were found to be higher than those for children , which was most probably due to relatively higher quantity intake by adults. Usually, no HRI rates were more than 1 out of rice consumption for both adults an children. The HRIs values for adults and children were 1.7627 and 0.9159, respectively, point out that both adults and children may expect several adverse health effects in the future, since continued chemical fertilizers and pesticides are applied for paddy fields, which are possibly the main origin of the cumulative toxic heavy metals .

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الخلاصة

ان الفلزات الثقيلة تتجمع في النبات مما يسبب ضرر على صحة الانسان. تهدف الدراسة الحالية الى تقييم التلوث بالفلزات الثقيلة في كل من التربة و نبات الرز المحلي (*Oryza sativa* L.) في الاراضي الزراعية لمنطقة المشخاب و كذلك تقدير الخطر الصحي للفلزات الثقيلة في التربة و النبات. تم حساب معامل الناقلية للفلزات الثقيلة من التربة ولمختلف اجزاء النبات وبالتالي تأثيراتها الصحية . تم قياس تراكيز الفلزات الثقيلة الغير اساسية (الكاديوم، الكروم، الارسنك، الرصاص و المغذيات الثانوية (النحاس المنغنيز، المولبدنيوم، السلينيوم و الزنك) في تربة حقول الرز و نبات الرز بواسطة تقنية (ICP-MS) وظهرت النتائج ان المنغنيز و الكاديوم تتجمع اكثر في الساق اكثر من الجذور. وان تراكيز الفلزات الثقيلة كانت ضمن الحدود المسموحة عالميا للتربة الطبيعية ما عدا عناصر الارسنك، الكروم، المنغنيز والنيكل التي كانت اعلى من القيم المسموحة للتربة الغير ملوثة. بينما كانت الفلزات الثقيلة في التربة المزروعة اعلى من مثيلاتها في التربة الغير مزروعة باستثناء الارسنك ، الكروم و المولبدنيوم. من الجذري الى الساق و من الساق الى الحبوب كان اعلى وذلك لارتفاع تراكيز هذه العناصر في الساق اكثر من الجذر و الحبوب. وكانت قيم مجموع معاملات الخطر الصحي لسبعة فلزات (الارسنك، الكاديوم، الكروم، النحاس،النيكل، الرصاص و الزنك) للرز المستهلك 1.7627 للبالغين و0.9159 للاطفال وهذا يقترح وجود تأثيرات صحية متوقعة في المستقبل.

الكلمات المفتاحية: نبات الرز، معامل الخطر الصحي، الفلزات الثقيلة، معامل الانتقالية، المشخاب – العراق.