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Assessment of Heavy Metal Pollution in Soils and Crops of Industrial Sites, Isfahan, Iran

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Abstract: This study was planned to investigate the concentrations of heavy metal in soils and crops and estimate the potential health risks of metals to humans via consumption of crops grown at industrial sites (Zarrinshahr and Mobarakeh) and control site (Natanz) in Isfahan province, central Iran. The soils and food crops (wheat and rice grains and onion bulbs) were digested by acid digestion method and then were analyzed for Mn, Cu and Zn by atomic absorption spectrophotometer. The results showed that the concentration of Zn in the soils of Mobarakeh was higher than the soils of Zarrinshahr and Natanz. The concentrations of Mn in the soils of Natanz and Mobarakeh were higher than the soils of Zarrinshahr. The concentration of Zn in the wheat was significantly higher than that rice and onion crops. The concentrations of Zn and Cu were higher in wheat crop in Mobarakeh compared with other cases. Results of this study revealed that the concentrations of Zn, Cu and Mn in the soils of studied sites were below than the maximum allowable levels. The average concentration of Zn, Cu and Mn metals in rice, wheat and onion crops were below than the maximum allowable levels of WHO guideline. The estimated daily intakes of heavy metals from the crops of three sites were lower than the tolerable daily intake recommended by FAO/WHO. Consequently, these crops cannot be an important source of Zn, Cu and Mn for risk to human health.

Key word: Heavy metal, industrial region, maximum allowable levels, estimated daily intake

INTRODUCTION

Environmental pollution means undesirable changes in physical, chemical and biological qualities of air, water and soil that threaten existence and health of human beings and other creatures or restrict their activities (Markert, 1993). In recent decades, industrial and mining activities and unsuitable use of heavy metal-enriched materials in agriculture (e.g., chemical fertilizers, pesticides, sewage sludge and wastewater irrigation) are the main sources of soil pollution with heavy metals (Kuo *et al.*, 2006). Industrial residual/wastes, polluted air and crop food with these metals are the sources of heavy metal exposure to humans (Furst, 2002). Cultivation of crops for human and livestock consumption on contaminated sites can cause the uptake and accumulation of heavy metals in the edible plant parts and then exert potential risk to humans and animals health (Lim *et al.*, 2008).

Isfahan province is an industrial area in the center of Iran. The multiplicity of heavy industries in the west of Isfahan has raised the risk of the pollution of water, soil, agricultural products and the air of these areas by heavy metals. In recent decades, wastewater irrigation, sewage sludge application to agricultural lands in this region might have caused increasing

heavy metal pollution which this represents, the considerable attention for crop food production and consumer (animals and human) health. In this study wheat, rice and onion crops were selected because rice cultivation is widespread in Isfahan and wheat and rice are common foods consumed daily in Iran, particularly in the studied sites. Thus, there is an increasing requirement for studying of heavy metal concentration in food crops sampled from agricultural lands around industrial sites. The objectives of this study are to (1) Quantify the concentration of heavy metals in soil and crops grown around industrial sites of Isfahan and (2) Estimate dietary intake of heavy metals through consumption of food crops.

MATERIALS AND METHODS

Study area: The studied area were two industrial sites including Zarrinshahr (32°22' N, 51°25' E) and Mobarakeh (32°15' N, 51°18' E) sites in western area of Isfahan province and a site far-away the industrial zone as control, Natanz (33°39' N, 51°58' E). The Zarrinshahr and Mobarakeh are heavily industrialized and intensely cultivated. Winter wheat (*Triticum aestivum* L.), rice (*Oryza sativa* L.) and onion (*Allium cepa* L.) are widely grown in these three sites.

Soil and crops sampling: Soils and plants grown at the above sites were collected in June 2008. Take into consideration regional consumption practices, the food crops included wheat and rice as the staple crops and onion for home-grown vegetable. In each region, three farms were selected for sampling of each crop. For each crop, three composite samples were collected. Wheat and rice grains and onion bulbs were dried (70°C) and stored in polythene zip-bags. Dried samples were powdered and the heavy metal concentrations in these samples were determined using the method of wet mineralization (Lozano-Rodriguez *et al.*, 1995). At each sampling site, soil composite samples at 0-20 cm depth were collected by a random sampling method, with paired soil and crop samples taken. After air-drying soil samples were crushed and sieved through 2 mm sieve size for chemical analysis. The soil samples digested with nitric acid, hydrochloric acid and H₂O₂ using the Method 3050B suggested by USEPA (1996). The concentrations of Mn, Cu and Zn in the soil and crop samples were determined using Perkin Elmer Analyst 800 atomic absorption spectrophotometer.

Estimated daily intake (EDI) of heavy metals: Estimated Daily Intakes (EDI) of heavy metals (Mn, Cu and Zn) depend on both the heavy metal concentration in crops and consumption amount of the respective food crop. The EDI of heavy metals for adults was determined by the following equation:

$$EDI = \frac{C_{\text{heavy metal}} \times W_{\text{food}}}{B_w}$$

where, EDI is estimated daily intake ($\mu\text{g kg}^{-1} \text{ day}^{-1} B_w$); $C_{\text{heavy metal}}$ ($\mu\text{g g}^{-1}$ dry weight) is the concentration of heavy metals in food crops; W_{food} represents the daily average consumption of crops in this region; B_w is the body weight. The local inhabitants (60 kg in body weight) have an average consumption of 265, 187 and 35 g day⁻¹ for wheat, rice and onion, respectively. The heavy metal intakes were compared with the Tolerable Daily Intakes (TDIs) for heavy metals recommended by the FAO/WHO (2007).

Statistical analysis: For heavy metal levels in soil and crop, a one-way analysis of variance (ANOVA) was conducted to detect significant differences between the three sites. The heavy metal concentrations in food crops were subjected to two-way ANOVA with sites and crops as independent factors. Means were compared by Duncan test at $p < 0.05$. Pearson correlations between heavy metals in the soil and crop were performed using the statistical package SPSS 18 for Windows.

RESULTS AND DISCUSSION

Heavy metal concentrations in the soils: The results indicated that the concentration of Zn in the soils of Mobarakeh (162 mg kg⁻¹) was significantly higher than that of Zarrinshahr and Natanz. The concentration of Mn was the lowest in Zarrinshahr soils (498 mg kg⁻¹). However, the differences between Mobarakeh and Natanz soils were not significant statistically (Table 1). The concentration of Zn in Natanz soils (control) was lower than that of Mobarakeh. The normal range of Zn in soils is between 100-300 mg kg⁻¹ (Gilmor and Kittrick, 1979). The results show that the studied soils are not polluted with this heavy metal. The normal range of Mn in soil is 200-3000 mg kg⁻¹ (Page *et al.*, 1987) and the toxic level is 850 mg kg⁻¹ (Pais and Jones, 1997). In this study, the concentration of Mn is lower than toxic level (Table 1). Although normal range of Cu in soils is 2-100 mg kg⁻¹ (Pais and Jones, 1997), the studied soils are not polluted with Cu metal (Table 1).

Heavy metal concentrations in the crops: The concentration of Zn in wheat (40 mg kg⁻¹) was significantly higher than that of rice (30.8 mg kg⁻¹) and onion (31.7 mg kg⁻¹) crops. Duncan test showed that the concentration of Mn was highest (34 mg kg⁻¹) in wheat and lowest (4.8 mg kg⁻¹) in the onion crop (Fig. 1). The

Table 1: Concentration of heavy metals in soil samples compare with normal and critical ranges (Pendias and Pendias, 1992)

| Heavy metal (mg kg ⁻¹) | Studied sites | | | Range | |
|------------------------------------|------------------|------------------|------------------|---------|----------|
| | Zarrinshahr | Mobarakeh | Natanz | Normal | Critical |
| Zn | 116 ^b | 162 ^a | 114 ^b | 1-900 | 70-400 |
| Cu | 25 ^a | 23 ^a | 21 ^a | 2-25 | 60-125 |
| Mn | 498 ^b | 595 ^a | 559 ^a | 100-400 | - |

Similar letters indicate no significant difference among the studied sites at $p < 0.05$

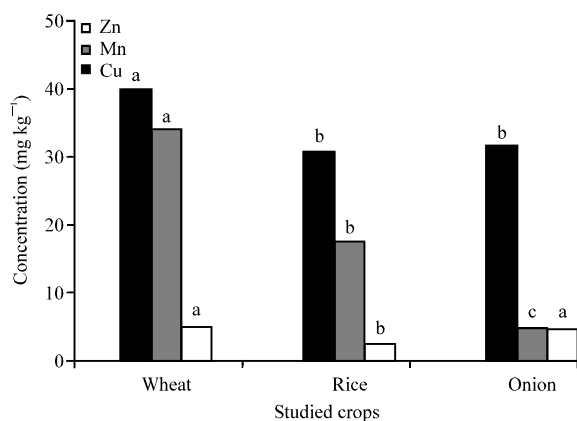


Fig. 1: Concentration of heavy metal in the crops. For each metal, means ($n = 3$) followed by the same letter are not significantly different at $p < 0.05$

concentration of Cu in wheat and onion (4.5-5 mg kg⁻¹) was significantly higher than that of rice crop (2.4 mg kg⁻¹, Fig. 1). Zhuang *et al.* (2009) found that rice grain grown in the Dabaoshan mine area, South China accumulated 5.3-7.5 mg kg⁻¹ Cu and 18-43 mg kg⁻¹ Zn. In Hamedan province, Iran, Cheraghi *et al.* (2009) reported that the concentration of Cu and Zn in the vegetables grown in an area fertilized with wastewater were several times higher than that of control area. In Zanjan, Iran, Eslami *et al.* (2007) showed that some plants were contaminated at high levels of heavy metals that were beyond the levels given by WHO and FAO for human consumption. In the agricultural lands around the steel industrial complex (Isfahan province, Iran), Rahmani and Rezaei (2007) concluded that in vegetable plants, the concentration of Mn and Zn were in normal range. Khairiah *et al.* (2009) found that the concentrations of heavy metals in both soils and plants from the Sungai Wangi Plantation at Sitiawan, Perak, Malaysia were significantly low.

The means comparison by Duncan test showed that the concentrations of Zn and Cu in wheat crop were highest in Mobarakeh site compared to other cases (Table 2). Al-Khateeb and Leilah (2005) concluded that plants grown at the region with high industrial activities accumulated higher concentrations of heavy metal than the region with light industrial activities.

The concentrations of Cu in rice in comparison to other crops were significantly lower (Table 2). The averages Zn concentration in rice and wheat crops is less than the maximum allowable levels of WHO standard. The WHO (1993) has proposed a maximum level of 60 mg kg⁻¹ Zn in these crops. The average concentration of Zn in wheat grains of studied sites were 38.3 mg kg⁻¹. Similar to Zn, the averages Cu concentration in rice and wheat crops are less than the maximum allowable levels of FAO/WHO (Codex Alimentarius Commission, 1984) standard that has proposed a maximum level of 10 mg kg⁻¹ Cu in these crops. The average concentrations of Cu in wheat, rice and onion crops in the studied sites were 4.8, 2.4 and 5.3 mg kg⁻¹, respectively. The onion had lower levels of Zn and Cu than the maximum permissible value (60 and 40 mg kg⁻¹) proposed by FAO/WHO (Codex Alimentarius Commission, 1984). The average Mn concentration in rice, wheat and onion crops was less than the maximum allowable levels of widespread foods. The average concentration of Mn in wheat, rice and onion crops in the studied sites was 34, 17.5 and 4.8 mg kg⁻¹, respectively. Pais and Jones (1997) have proposed a maximum level of 2-80 mg kg⁻¹ Mn in foods.

Table 2: Concentration of heavy metal in wheat, rice and onion of three studied sites

| Crop | Location | Heavy metal concentration (mg kg ⁻¹ DW) | | |
|-------|-------------|--|---------------------|---------------------|
| | | Cu | Mn | Zn |
| Wheat | Zarrinshahr | 4.31 ^{b*} | 32.02 ^a | 38.17 ^b |
| | Mobarakeh | 6.26 ^a | 33.71 ^a | 47.14 ^a |
| | Natanz | 4.53 ^b | 36.70 ^a | 34.33 ^{bc} |
| Rice | Zarrinshahr | 2.30 ^f | 18.83 ^b | 27.88 ^c |
| | Mobarakeh | 2.45 ^c | 15.64 ^{bc} | 31.00 ^{bc} |
| | Natanz | 2.50 ^f | 17.95 ^b | 33.61 ^{bc} |
| Onion | Zarrinshahr | 4.71 ^b | 4.60 ^f | 38.02 ^b |
| | Mobarakeh | 4.37 ^b | 5.20 ^f | 29.10 ^c |
| | Natanz | 4.60 ^b | 4.70 ^f | 28.29 ^c |

*In each column, means (n = 3) followed by the same letter are not significantly different at p<0.05

Table 3: Pearson correlation coefficients (r) between concentration of heavy metals in soils and crops

| Heavy metals in soils | Heavy metals in crops (mg kg ⁻¹) | | |
|-----------------------|--|---------------------|---------------------|
| | Zn | Mn | Cu |
| Zn | 0.694 ^{**} | 0.572 ^{**} | 0.491 ^{**} |
| Mn | 0.431 [*] | 0.309 | 0.341 |
| Cu | -0.153 | -0.316 | -0.005 |

*p<0.05; **p<0.01. n = 27

Table 4: Estimated dietary intake (EDI) of heavy metals via consumption of crops at the sites relative to the tolerable daily intake (TDI)

| Location | Crop | EDI (µg kg ⁻¹ day ⁻¹ b.wt.) | | |
|--|-------|---|--------|---------|
| | | Cu | Mn | Zn |
| Zarrinshahr | Wheat | 19.04 | 141.42 | 168.58 |
| | Rice | 7.17 | 58.69 | 86.89 |
| | Onion | 4.71 | 4.60 | 38.02 |
| Mobarakeh | Wheat | 27.65 | 148.90 | 208.20 |
| | Rice | 7.64 | 48.74 | 96.62 |
| | Onion | 4.37 | 5.20 | 29.10 |
| Natanz | Wheat | 20.01 | 162.10 | 151.62 |
| | Rice | 7.80 | 55.94 | 104.75 |
| | Onion | 4.60 | 4.70 | 28.29 |
| TDI ^a (µg kg ⁻¹ day ⁻¹ b.wt.) | | 500 | NA | 1000.00 |

^a(FAO/WHO, 2007), NA is used when nutritional or toxicological reference value has not been proposed for the element

Relationships between heavy metals of soils and crops:

Pearson coefficients of correlation analysis indicated that there was significant correlation between the concentrations of Zn in the soils with Zn in the crops in the studied areas (Table 3). Uptake of heavy metals by plants was usually increased with increasing the concentrations of heavy metals in the soils (Udosen *et al.*, 2006).

Estimated daily intake (EDI) of heavy metals through the crops:

Comparisons between Estimated Daily Intake (EDI) with Tolerable Daily Intake (TDI) for Mn, Cu and Zn are listed in Table 4. The trends of EDIs for heavy metals in wheat, rice and onion were in the order of Zn>Mn>Cu, with intake from wheat being greater than from rice and onion for all heavy metals.

These results are agreed with the findings of Zhuang *et al.* (2009) who showed that the trends of EDIs in rice grains were in the order of Zn>Cu. In the three sites, the average metals EDIs of food crops were far below the TDI limits.

CONCLUSION

The present study provides data on heavy metal pollution in soils and food crops in industrial sites, Isfahan, Iran. Results of the current study showed that only the concentration of Zn in the soils of Mobarakeh was significantly higher than that Natanz region. The results revealed that the concentrations of Zn, Cu and Mn in the soils of studied sites were below than the maximum allowable levels. The mean concentrations of Zn, Cu and Mn in rice, wheat and onion crops were below than the maximum allowable levels of standards. It is concluded that the crops grown in these sites are not a health hazard for human consumption.

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