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CONCENTRATION OF SOME HEAVY METALS (CU, ZN, FE, MN, PB, CD AND NI) IN ARABLE LANDS OF MOGHA

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ABSTRACT

Heavy metal contamination of soil and plants was widely studied in different countries of the world. According to the conducted studies, heavy metals enter the food chain through uptake and accumulation in soil and water has negative influences on physiological and metabolic activities of living organisms. Principally the first step in evaluation and measurement of pollutants is identification of their sources. Therefore, this study was conducted during 2008 in Moghan, Iran, with 131 samples of arable land, non-arable land and irrigation water of 9 places in Moghan. Soil samples were dried and sieved in laboratory. Then, prepared samples were extracted and determined their concentration of Cu, Zn, Fe, Mn, Pb, Cd and Ni using Atomic Absorption Spectrometer. The results showed that there was statistically significant difference ($p=0.01$) between arable land, non-arable land of different areas in term of metals mentioned. Concentration of heavy metals was more in arable lands than non-arable lands. The accumulation of Cu, Zn, Fe, Mn, Pb, Cd and Ni in arable lands was 5, 3.5, 10, 14, 3, 20, 5 times more than those of non-arable lands, respectively. It can conclude that increasing pollution and decreasing soil fertility may be attributed to irregular use of pesticides and fertilizers on arable lands and the use of contaminated irrigation water.

Key Word: *Heavy Metals, Soil, Fertilizers, Pesticides, Pollutions*

INTRODUCTION

Increase in population growth over the last 20 years, then, the growth in food demand and need, has caused human to raise cultivated land on the one hand, and on the other hand increase yield per unit area through the use of new techniques, agricultural machinery, chemical fertilizers and pesticides (Shiykhizadeh, 1998). Heavy metal contamination in soil and water is a major concern because of reduction in yield quantity and quality and their toxicity and threat to Sustainable agricultural production and human life (Begum *et al.*, 2009). Based on definition, heavy metals are metals possessing a specific gravity of more than 5 g/cm³ in their standard state. Heavy metals entering the food chain through uptake and accumulation in time in soils and could impose a harmful effects on physiological activities of plants (e.g. photosynthesis, gaseous exchange, and nutrient absorption), determining the reductions in plant growth, dry matter accumulation and yield (Suciu *et al.*, 2008). There are known sixty heavy metals. Heavy metals such as Cadmium (Cd), Chromium (Cr), Cobalt (Co), Lead (Pb), Mercury (Hg) and Nickel (Ni) through uptake that are later used for consumption have a great threat to human health. Three of the mentioned metals, Cd, Pb and Hg, are toxic in any concentrations (Bradl, 2005).

Heavy metals are potentially toxic to plants, animals and humans if contaminated soils were used for crop production, due to heavy metals get accumulated in vital organs to threaten crop growing and human health (Razo *et al.*, 2004). Many researchers have conducted studies throughout the world and reported estimations of heavy metal concentrations (Zhai *et al.*, 2008; von Braun *et al.*, 2002). Every 1000 kg of "normal soil" contains 200 g chromium, 80 g nickel, 16 g lead, 0.5 g mercury and 0.2 g cadmium, theoretically (IOCC, 1996).

Heavy metals concentration in cultivated crops mostly depends on agricultural, environmental and geochemical factors (Grant *et al.*, 1998). Result obtained from alkaline lands under sugar beet cultivation showed that the rate of reduction yield was 25% if leaf cd content reaches 150 $\mu\text{g gr}^{-1}$ (Hakimi and Alimoradi, 1998).

Research Article

Management practices of agriculture play an importance role on Heavy metals concentration (Spiegel *et al.*, 2009). Application of phosphate fertilizers by farmers in northern paddies of Iran increased cadmium levels in soil at a rate of 15.5 % (32 mg/kg) within two years (Kavosi, 2003). The annual consumption of phosphate fertilizers in Iran considers 800 tons and if the concentration of cadmium in imported phosphate fertilizers assumes 100 mg kg⁻¹, then, generally more than 80 kg of cadmium annually enter the arable land that is too high and dangerous rate (Malakoti and Khani, 2000).

Moghan considers as one of the main parts of agricultural in Iran in which grow a variety of strategic and industry products. Unfortunately, in recent years the interest \rightarrow agricultural users, regardless of environmental issues and sustainable development of agriculture solely to gain more profits in a short time use the irregular consumption of agricultural inputs. This study was therefore aimed at evaluating the distribution status of heavy metals in arable and non-arable land and comparison between them.

MATERIALS AND METHODS

Study Area

Moghan is located in the Ardabil province of Iran (by the longitude of 39° 42' to 49°25'E, latitude of 47°25' to 48°25'N and 1400 m in elevation) (Fig. 1). This area, which is referred to Moghan plain, encompasses a total area of 300 to 350 thousands hectare. A utilization scheme of Aras river water resource has been implemented in 90 hectares. Common crop of Moghan are wheat, cotton, sugar beet, alfalfa, corn and cash, soybeans, oats, sesame and peanut. Also, rice is grown in lands with good drainage. Pear, apple, peach and hazelnut are among the horticulture crops grown in this area. The main fertilizers contain phosphate fertilizers, liquid fertilizers, and urea applied in corn and cash crops.

Due to the large extent, the different types of crop rotation, modern agriculture life in different parts of this area, and the classification of agricultural organization In terms of agricultural services, the study area was divided into 9 parts.

Sampling

131 samples (117 samples of crop-land, 9 samples of non-crop land and 5 samples of irrigation water) (Table 1) were prepared at a depth of 0 - 30 cm.

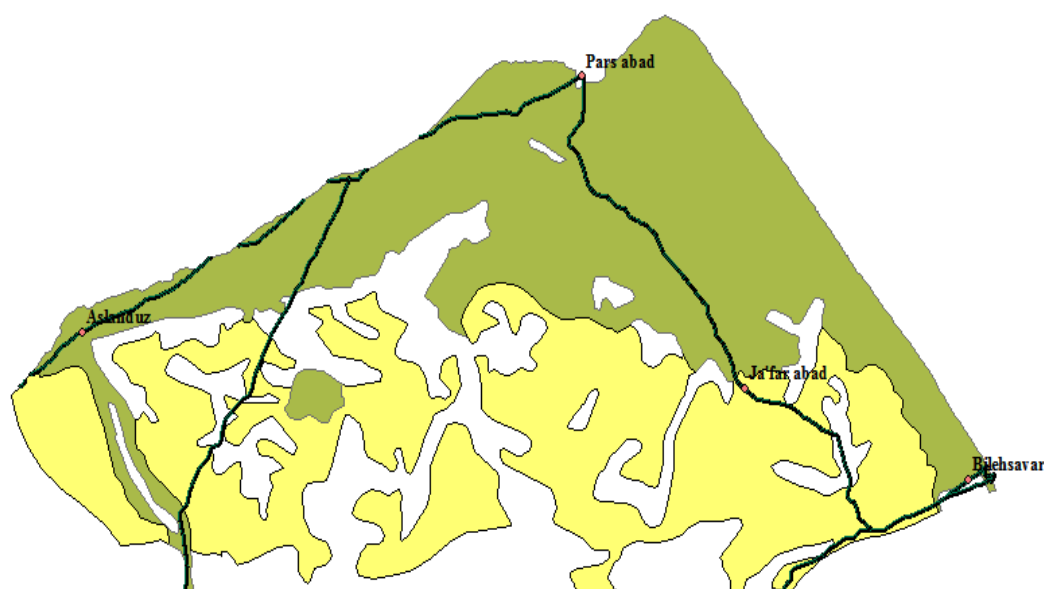


Figure 1: Geographic areas included into the study (green areas are irrigated crops; yellow areas are rainfed crop and non-farming area).

Research Article

The soil samples were passed through a 2 mm sieve before extraction. The surface sediment samples were collected using an Ekman grab sampler. Each sediment sample was air-dried in the laboratory at room temperature and was passed through a 2 mm sieve before extraction.

Table 1: Sampling locations

Locations	Crops grown	Fertilizers applied
1 Firoozabad	Wheat, corn, canola	urea, phosphate, and liquid fertilizers
Tazeh kan old and new, Abasabad, Takaleh	Wheat, corn, canola	urea, phosphate, and liquid fertilizers
3 Ozonghoei	Wheat, corn, canola	urea, phosphate, and liquid fertilizers
4 Ghosha ghashlagh	Wheat, corn, canola	urea, phosphate, and liquid fertilizers
5 Takchi	Wheat, corn, canola	urea, phosphate, and liquid fertilizers
6 Oltan	Wheat, corn, canola	urea, phosphate, and liquid fertilizers
7 Ajirlo, Parsabad	Wheat, corn, canola	urea, phosphate, and liquid fertilizers
8 Moghan agriculture research center fields, Moghan agroindustrial company	Wheat, corn, canola, cash crop	urea, phosphate, liquid fertilizers, sulfur and micro elements
9 Jafarabad	Wheat, corn, canola	urea, phosphate, and liquid fertilizers

The concentrations of seven of the elements (Mn, Ni, Cu, Zn, Fe, Cd, and Pb) were determined using Lindsay and Noral. Briefly, About 20 g of each sieved samples were weighed and placed on Erlenmeyer flask. Then, 40 ml of DTPA was added to it. The mixture was stirred on a rotary shaker 1500 rpm for 2 h. Samples was extracted using Whatman No. 42 filter paper. Water samples were taken from inlet and outlet water into/from the field. The concentrations of the heavy elements were determined using an Analyst™ 800 atomic absorption spectrophotometer (AAS) (Perkin Elmer Instruments, USA) with either an acetylene flame (Cu and Zn) or an argon non-flame (Co, Ni, Mn, Cd and Pb) after preparation of the calibration standards.

Statistical Analysis

Statistical analysis was carried out using statistical analysis system SPSS. Analysis of variance (ANOVA) followed by calculation of means that were compared using Duncan < 0.05 was used to compare of different groups of samples. Mean comparison was carried out using t student between crop and non-crop lands.

RESULTS AND DISCUSSION

Significant differences were found among different locations regarding accumulation in heavy elements (Table 2). Mean Comparison of different locations showed that the highest amount of Cu, Zn and Pb were related to location 7 (with 6.4, 3.3 and 3.598 mg kg⁻¹, respectively). The lowest amount of Cu (2.34 mg kg⁻¹), Zn (0.674 mg kg⁻¹) and Pb (1.452 mg kg⁻¹) were found in locations 2, 5 and 5, respectively (Table 3). High concentration of Cu, Zn and Pb in location 7 as compared to all other locations may be due to the planting of vegetable, cash and crops in these areas. Excessive and uncontrolled use of chemical pesticides containing Cu compounds and other toxins is prevalent in this location and might also have an effect on the concentration of Cu. Cu is also found in the form of cu sulfate (Karimian, 1991).

Studies conducted in location 2, which posse low concentration of Cu, Shows that agricultural soils of this region are young and was brought under the irrigation network after soils of locations 6 and 7. Agriculture in this area is still in its traditional form and second crop is underdeveloped as well.

Table 2: Analysis of variance of the studied elements in arable lands of Moghan

Source of variations	Df	Mn	Fe	Zn	Cu	Ni	Cd	Pb
Between Locations	8	700.994**	**18.585	**5.111	**30.911	**1.068	**2.082	**3.068
Within Locations	108	68.228	5.073	0.936	2.380	0.153	0.014	0.102

Research Article

The results also suggest that farm lands located near the road posses higher level of Cu as compared to farm lands located away from the road due to more vehicle traffic and travel. Smith (1997) Claimed that contamination levels o Cu affected by the distance from the road. So lands surrounding the road are much more contaminated by Cu.

The results of the samples analysis revealed that the highest ratios of Fe (7.433 mg kg^{-1}) and Mn ($33.837 \text{ mg kg}^{-1}$) was found in area 6, while the smallest ratios of Fe (3.243 mg kg^{-1}) and Mn ($15.236 \text{ mg kg}^{-1}$) was observed in location 5 (Table 3). Acceptable concentration of Fe in soil is 2.5 to 4.5 mg kg^{-1} (Malakooti, 1995). Thus, accumulation of Fe in the studied soils is rather excessive. Obviously, Fe ratio is gradually increased in the lands applied Fe sulfate fertilizers and other fertilizers containing Fe. Hakimi and Alimoradi (1998) reported that concentration of heavy elements in in the field soils irrigated with contaminated water was 53.46 % higher than that of the field soils irrigated with normal water. In general, the present study showed that the Fe ratio was high in the fields with agriculture advanced techniques and crop rotation. Low Fe concentrations in regions 1, 2, 3, 4 and 5 can be attributed to the new intensive farming of these regions.

The highest mean Cd (1.791 mg kg^{-1}) and Ni (4.462 mg kg^{-1}) concentrations was detected in regions 5 and 8, respectively, The minimum values of Cd (0.857 mg kg^{-1}) and Ni (3.629 mg kg^{-1}) was also related to location 2. These results show that heavy metal pollution in Moghan includes very high Mn concentrations. Allowable amount of Mn concentration in soils is 1 to 2 mg kg^{-1} (Malakooti, 1995). With regard to, over the past 30 years, it has just been considered amount of phosphorus in the decomposition of phosphate fertilizers and no control was existence on Cd concentrations, consequently, significant ratios of Cd has been entered to Farm and Garden lands of Iran by using phosphate fertilizers.

Table 3: mean of studied elements at different location (mg/kg)

Locations	Mn	Fe	Zn	Cu	Ni	Cd	Pb
1	12.945 d	4.947 bc	1.039b	2.876bc	3.772c	0.862d	2.409c
2	18.285c	4.483bc	0.880b	2.344c	3.629c	0.857d	2.242c
3	16.988cd	3.801c	1.040b	2.749c	3.714c	0.854d	2.310c
4	25.089b	4.675bc	0.989b	4.084b	3.756c	1.019c	2.254c
5	15.236cd	3.243c	0.674b	2.394c	4.016bc	1.014c	1.452d
6	33.837a	7.433a	1.184b	6.152a	4.229b	1.740a	3.174b
7	25.813b	5.996b	3.296b	6.382a	4.271ab	1.690a	3.589a
8	28.517b	5.975b	1.355b	5.499a	4.462a	1.791a	2.335c
9	30.842ab	3.614c	1.531b	3.964bc	3.903bc	1.353b	2.331c
Mean	22.847	5.159	1.33	4.049	3.903	1.175	2.495

Results showed that statistically significant difference ($P < 0.01$) in the evaluated elements concentration was found between crop and non-crop lands in all areas. The Cu concentration of location 7 has increased from $1.0061 \text{ mg kg}^{-1}$ in non-crop lands to 6.382 mg kg^{-1} in crop lands. The obtained higher mean concentration of Cu in the crop lands (5 times that of non-crop lands) might be due to excessive and uncontrolled use of chemical pesticides containing Cu compounds. The concentration of Cu was significantly higher in crop lands as compared to the desirable level of agriculture lands (0.2 to 0.8 mg kg^{-1}) (Malakooti, 1995). Among the non-crop lands, the highest concentration of Cu was revealed Fr location 2 (1.218 mg kg^{-1}), while, the lowest Cu ratio (0.094) was observed in location 6 (Table 3). Presently, excessive and uncontrolled use of phosphate fertilizers neutralizes negative impacts and poisoning of Cu, but we will confront with more problems in the future with the continuing increase in the use of pesticides containing copper and phosphate fertilizer.

The Zn concentration of location 7 has increased from 0.749 mg kg^{-1} in non-crop lands to 3.296 mg kg^{-1} in crop lands. Irregular application of some agriculture inputs especially phosphate fertilizer and Zn

Research Article

sulfate can induce the heavy elements contamination of soil and plant. Mean concentration of Zn in the non-crop lands was 0.0186 to 0.749 mg kg⁻¹ (Table 4).

Table 4: Statistical analysis of elements rates in crop land and non-crop land in the studied areas (mg kg⁻¹)

Locations	Mn			Fe			zn			cu		
	Non-crop land	Crop land	T Calculated	Non-crop land	Crop land	T Calculated	Non-crop land	Crop land	T Calculated	Non-crop land	Crop land	T Calculated
1	2.48 0 b	12.9 45a	**11.59	1.11 2b	4.94 6a	**11.54 0	0.07 1b	1.03 9a	**18.96 4	0.91 3b	2.88 a	**4.89
2	4.66 b	18.2 85a	**6.62	1.70 5b	4.48 2a	**5.924	0.49 2b	0.87 9a	**5.441	1.21 8b	2.34 a	**3.32
3	4.31 2b	16.9 88a	**4.86	0.51 8b	3.80 0a	**6.813	0.03 6b	1.04 0a	**11.48 4	0.20 19b	2.75 a	**4.89
4	5.44 5b	25.0 89a	**19.76	0.80 2b	4.67 5a	**12.44 9	0.10 5b	0.98 9a	**14.19 9	1.01 2b	4.08 a	**19.38
5	4.23 4b	15.2 36a	**2.97	0.79 4b	3.24 2a	**4.061	0.04 2b	0.67 4a	**13.73 7	1.02 b	2.39 a	**3.11
6	2.26 8b	33.8 37a	**12.71	0.62 8b	7.43 3a	**7.785	0.64 8b	1.18 4a	**9.784	0.09 4b	6.15 a	**12.4
7	3.10 4b	25.8 13a	**6.8	1.06 4b	5.99 6a	**5.203	0.74 9b	3.29 6a	**2.022	1.00 61b	6.38 a	**6.75
8	4.15 2b	28.5 17a	**5.09	0.45 0b	5.97 4a	**6.100	1.01 8b	1.35 5a	**11.78 0	1.00 42b	5.49 9a	**12.0
9	5.23 3b	30.8 41a	**8.37	0.57 0b	3.61 4a	**4.820	1.53 1a	0.09 1b	**2.600	1.01 1b	3.96 4a	**5.13

Table Continuous

Locations	Ni			Cd			Ni		
	Non-crop land	Crop land	T Calculated	Non-crop land	Crop land	T Calculated	Non-crop land	Crop land	T Calculated
1	0.329b	3.772a	**42.357	0.0249b	0.862a	**60.498	0.712b	2.408a	**28.084
2	0.664b	3.629a	**27.972	0.069b	0.8566a	**47.147	0.884b	2.241a	**23.930
3	1.102b	3.713a	**22.097	0.011b	0.8536a	**21.703	0.623b	2.309a	**19.821
4	0.875b	3.756a	**49.292	0.035b	1.0192a	**89.255	0.379b	2.254a	**33.978
5	1.033b	4.016a	4.016a	0.029b	1.014a	**15.936	0.379b	1.451a	**9.407
6	0.829b	4.229a	**32.728	0.089b	1.739a	**87.715	0.167b	3.173a	**27.081
7	1.074b	4.271a	**28.766	0.015b	1.690a	**18.284	0.967b	3.597a	**27.479
8	0.766b	4.461a	**26.177	0.084b	1.791a	**64.924	0.0656b	2.335a	**33.292
9	1.041b	3.902a	**14.964	0.0247b	1.352a	**6.184	0.653b	2.330a	**6.515

The concentration of Fe in the crop and non-crop lands was detected 5.159 and 0.849 mg kg⁻¹, respectively. The Fe concentration in areas 6 has increased from 0.628 mg kg⁻¹ in non-crop lands to 7.433

Research Article

mg kg⁻¹ in crop lands. Among the non-crop lands, the maximum (1.705 mg kg⁻¹) and minimum (0.450 mg kg⁻¹) Fe concentration was found in locations 2 and 8 (Table 4).

Mean concentration of Mn in the crop and non-crop lands was 22.847 and 3.988 mg kg⁻¹, respectively. High ratios of Mn (5.445 mg kg⁻¹) was observed in parts 4, while, low Mn level of Mn (2.268 mg kg⁻¹) was found in parts 6 (Tables 3 and 4).

The concentration of Pb in location 7 has increased from 0.9686 mg kg⁻¹ in non-crop lands to 3.598 mg kg⁻¹ in crop lands. This is may be due to high application of pesticides and fertilizers in arable lands. The uppermost mean Pb concentration (0.884 mg kg⁻¹) was detected for location 2 among the non-arable lands, in contrast, the lowest mean concentration of Pb (0.0656 mg kg⁻¹) was related to location 8 (Table 4). The total mean concentration of Pb was found 2.495 and 0.537 mg kg⁻¹ for arable and non-arable lands, respectively (Table 3 and 4).

The Cd concentration of arable lands in location 8 (1.791 mg kg⁻¹) was 20 times that of non-arable lands (0.084 mg kg⁻¹) (Table 4). In fact, location 8 had the most Cd concentration. The total mean concentration of Cd was 1.175 and 0.0391 mg kg⁻¹ for arable and non-arable lands (Table 3 and 4). Kuperman and

Crreiro (1997) reported that phosphorus fertilizers contain the impurity of heavy elements, contaminating soil, reduce microbial activity and sometimes absorb by plants and enter to the food chain of animals. According to Alloway (2002) the relative proportion of phosphorus fertilizers in soil contamination was estimated 54-58 % and the remaining contamination has been attributed to atmosphere deposit and sewage sludge. Thus, optimum application of phosphorus fertilizers plays a critical role in reduction of soil contamination. Rezaei and malakoti (2002) stated that the Cd concentration in the soil of the produced phosphate of Senegal, Togo, Marrakesh, Tones possessed greater Cd concentration as compared to soil of the produced phosphate of Russia, Jordan, Syria, and Iran. Thus, it is suggested that the manufactured countries should be considered in the time of shopping of phosphate soil and phosphate fertilizers. Furthermore, genetic manipulation of crop is one of the most important strategies to prevent Cd accumulation and its entering to food chain of animals. Irrigated water is another source for soil pollution.

The concentration of Ni in arable lands of location 8 (4.462 mg kg⁻¹) was 5 times that of non-arable lands (0.766 mg kg⁻¹) (Table 4). Some of the common phosphate fertilizers contain high concentration of As, Ur, Pb, Cd and Ni (Raven and Loeppert, 1997). The highest (1.102 mg kg⁻¹) and lowest (0.326 mg kg⁻¹) Ni concentration of non-arable lands was detected in locations 3 and 1, respectively (Table 4). The mean concentration of Ni was 3.903 and 0.855 mg kg⁻¹ for arable and non-arable lands, respectively (Table 2 and 3). Motashirzadeh, (2003) found that phosphates can be used to minimize poisoning in soils containing considerable ratio of Ni. Ni phosphates formed have low solubility and reduce Ni concentration of soil solution. Irrigation water of Moghan region provided from Aras River and the mentioned river contaminate heavy elements because of the industrial sewage. Evaluation of mean concentration of the studied elements in Moghan region indicates that the mean concentration of Cu, Zn, Fe, Mn, Pb, Cd and Ni was 1.192, 0.933, 0.864, 0.996, 1.639, 0.623 and 1.349 mg kg⁻¹, respectively. Results showed that the concentration of Cu, Fe and Cd was higher than allowable level of irrigation water, thus it should be noticed that the ratio of these element not be increased through fertilizers and pesticides.

Totally, the present study revealed that the mean concentration of heavy elements in arable lands was higher as compared to that of non-arable lands and significant increase in elements ratio originated from uncontrolled application of fertilizers and pesticides. Thus, application of the agriculture inputs must be controlled to prevent more pollution.

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Research Article

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