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Concentration, Distribution and Comparison of Total and Bioavailable Metals in Top Soils and Plants Accumulation in Zanjan Zinc Industrial Town-Iran

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Abstract

Heavy metal contamination of metal-mined soils is a widespread problem in parts of Zanjan province. The province located in North West of Iran is highly polluted by heavy metals due to the presence, improper utilization of its mineral resources notably Lead and Zinc, and also the development of a number of related industries. Soils are basically polluted by Pb, Zn and Cd and their concentrations in top soils are very high exceeding European and USEPA standards. The main objective of this study is to evaluate heavy metals concentration and bioavailable fractions of heavy metals and accumulation of such toxic metals in native plants growing naturally on the polluted sites. The information obtained from this study is of great value to obtain bioavailability of the toxic metals and their potential harmful effects for plants, animals and humans.

Keywords: Anthropogenic contamination; Heavy metals; Soil–plant transfer; Hyper accumulating plants; Zanjan- Iran.

1. Introduction

Heavy metal contamination of soils is widespread and there is a risk of transfer of toxic and available metals to agricultural crops, animals and humans [1,2]. Heavy metals are natural constituents of the Earth crust and a number of these elements are biologically essential at trace levels and play an important role in human health [3,4]. The potential risk for the environment and population due to soil heavy metals arising from metallic mining has been well described [5,6]. Heavy metals can induce toxicity in wildlife if the soil level reaches critical values; also plant accumulation in above-ground tissues can result in an increase of metal accumulation in top-soil, via leaf deposition,

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or can create an exposure pathway for metal introduction into the food chain [7,8]. On the other hand, plants living in metalliferous soils can have exceptional properties which make them interesting for phytoremediation techniques [9]. In contrast with rural areas, soils in urban environments, particularly in parks and gardens, have a direct influence on public health not related with production of food. This is due to that they come easily in contact with humans and are transferred to them, either as suspended dust or by direct contact [10,11]. Two main sources of heavy metals in soils can be considered: the natural pedo-geochemical background, which represents the heavy metal concentration inherited from the parent rock [12] and anthropogenic contamination, which can be directed via wastes [13], compost [14], sewage sludge [15], or may diffuse via aerosol deposition [16].

The total heavy metal contents can indicate the extent of contamination, but is not usually an accurate indication of the phyto-toxicity; therefore many recent studies investigated the bioavailable heavy metal fractions of mine soils [17,18] and evaluated the phyto-toxic risk for human receptors. However, the determination of heavy metal fractions is a more complex task than the determination of the total contents of heavy metals [19].

Plants living in metalliferous soils can have exceptional properties which make them interesting for phyto remediation [9]. Thus proper management of plants may significantly contribute to restoring the natural environment. Phytoremediation was initially proposed as an environmental cleanup technology for the remediation of metal contaminated soils [20,21]. The identification of metal hyper accumulator plants demonstrates that such plants have the genetic potential to clean up contaminated soils. Phytoremediation has recently become a subject of public and scientific interest and a topic of many recent researches [22,23]. The ability of selecting species of plants, which are either resistant to heavy metals, or can accumulate great amounts of them, would certainly facilitate reclamation of contaminated areas [24,25]. Phytoremediation is a cost-effective technology for environmental cleaning if native plants were applied in each polluted areas. New studies are still necessary to find new accumulator plants for using in different climates and natural conditions.

Angoran area of Zanjan province located in North West of Iran has a large metalliferous site and has been considered as a traditional mining region since antiquity. There are still large reserves of lead (Pb) and zinc (Zn) in the area. Both mines and smelting units within the province present a risk of contamination of soils, plants, surface and ground water by dissemination of the particles carrying metals by wind action and/or by runoff from the tailings. Heavy metal contamination in Zanjan province has also been previously reported in the vicinity of Lead and Zinc mining and smelting sites [26-29]. Transportation of concentrated ore by trucks for about 100 kilometers from Angoran to Zinc Industrial Complex is another anthropogenic source of metals contamination especially along the roads.

The first aim of this study was to evaluate heavy metal content and bioavailable fraction of toxic metals. Assessment of plant accumulation of these trace elements in plants that were grown in the polluted sites of the Zinc Industrial Complex in Zanjan province located in North-West of Iran.

2. Materials and Methods

2.1. The study site

The research was conducted in Zinc Industrial Complex (36° 66’ N, 48° 48’ E). The Zinc Specialized Industrial Complex was established in 1996, with a current consumption of about one million tons of raw ore and a production of 0.19 million tons of Zn per year. The tailings from the industrial complex estimated to be about 2.5 million tons by now is containing a variety of toxic elements, are damped in the vicinity of the complex and are exposed to wind and rains, contributing to soil, surface and ground water contamination.

Soils and plants were sampled in the surroundings of the Industrial complex between Augusts to September 2009 (Fig. 1). Samples of references were also collected from an unaffected area about 10 kilometers away from the industrial complex.

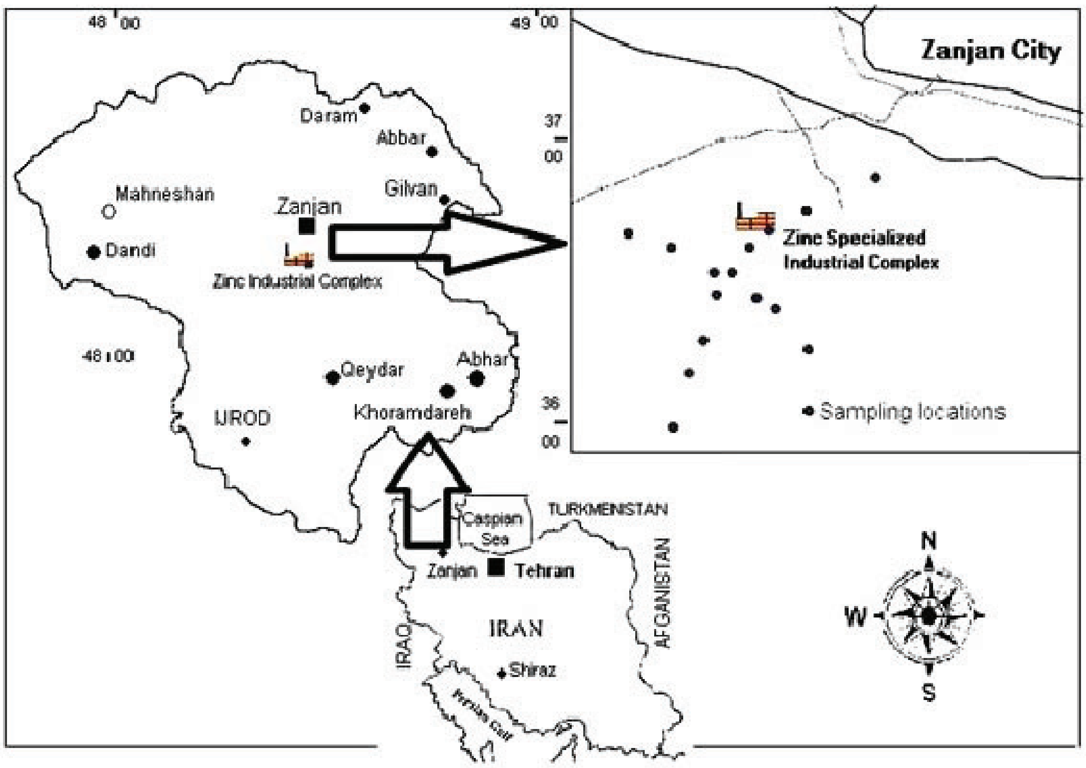

Fig.1. Location map of the studied area indicating sampling points

Soil samples were collect from the surface of the soil (0-30 cm deep) and preserved by using the methods of soil analysis [30]. From each sampling points, four soil samples were gathered and mixed properly to obtain a composite sample mixture. The soil sampling spots were cleared of debris before sampling [31]. Each composite soil samples were placed in cellophane bags [27], labeled then taken to the laboratory for pre-treatment and analysis. The sampling tools, were washed with soap and rinsed with distilled water after each sampling [32,33], shoots of 5 plant species and a 15 soil samples were also collected, as well as the soil below the plants (top 0–30cm soil layer).

2.3. Soil and plant analysis

In the laboratory, bulk soil samples were spread on trays and were air dried at ambient conditions for two weeks. The samples were then grounded by mortar and pestle, sieved through a 2 mm mesh, and oven-dried at 50 ◦C for about 48 hours. The samples were then stored in polyethylene bags and re-homogenized before being used. The soil samples were digested using the 11466 ISO standard methods -the aqua regia digestion method [34]. 3 g of soil was placed in a 100 ml round bottom flask with 21 ml of concentrated HCl (35%) and 7 ml concentrated HNO_3 (65%). The solution was kept at room temperature overnight before a water condenser was attached and the solution heated to boiling for 2 hours. 25 ml of water was added down the condenser before filtration of the mixture through using a Whatman (No. 42) filter. The filtered residue was rinsed twice with 5ml of water and the solution was made up to 100ml. the bioavailable content of metals were determined [35], 10g of soil was added in 20 mL mixture of 0.005

mol L−1 DTPA and 0.01 mol L−1 CaCl2 and 0.01 mol L−1triethylamine (pH 7.3), shaken for 2 h and then filtered through using a Whatman (No. 42) filter.

Plant materials were washed thoroughly with tap water and then rinsed with de-ionized water and dried at 50 ◦C for 7 days. Dried plant tissues were ground into fine powder. For acid mineralization of plant tissues, 10ml of mili-Q water, 3ml of HNO_3 and 2ml of H_2O_2 were added to 0.5 g dry weight (DW) of tissue and digestion was performed at 1500 Pa and 125◦ C in an autoclave. The extract was filtered and diluted to 25 ml. The metals (Zn, Pb and Cd,) in the plant extracts were also analyzed by atomic absorption spectrometry (AAS). Three analytical replicates were measured for each sample. Data with replicates were presented as mean-standard error and difference test was made using SPSS 14. The pH and EC (solid: distilled water=1:5) of the soil samples were also measured by with pH and EC meters (Metrohm, Germany).

3. Results and discussion

3.1. Total heavy metal in soils

Table1 illustrates the metal concentrations in the studied area. Comparing the results with standards range (table 2), shows that the concentrations of heavy metals in the studied area are higher than standards. However the heavy metal concentration in our study is lower than other countries standard ranges. Summary statistics for the analyzed elements in all the studied samples are presented in Table 1. Cadmium has the lowest mean concentration (0.94 mg/kg), while the highest contents are for Zn (606.2 mg/kg). This, along with the gradual decrease in available metals with distance from the complex, points out that zinc industry is most possibly the major source for the enrichment of heavy metal in the topsoil. The extremely high metal levels in tailings made them a potentially hazardous source of soil contamination. The means and standard deviations of soil pH were similar. Soil pH averaged 7.83 (from 7.51 to 8.20) indicating a neutral nature. Electric conductivity (EC) in samples was varied in different sites.

Table 1. Total metal concentrations in the topsoil of Industrial Complex in Zanjan-Iran.

Site	pH	EC(µs.cm^{-1})	Total metal (mg.kg^{-1})		
			Pb	Zn	
1	7.77	3439.52	210.00	3066.6	3.85
2	7.51	12886.04	630.00	1560.0	18.50
3	8.20	15352.68	218.93	890.0	12.60
4	7.68	3144.33	446.86	881.0	8.20
5	7.86	3608.08	62.00	496.3	0.56
6	7.93	5117.85	46.16	340.0	1.16
7	7.92	30121.70	99.30	256.5	0.28
8	7.91	1160.08	15.00	211.5	0.43
9	7.74	5117.85	10.23	171.9	0.16
10	7.91	867.78	4.10	186.6	0.16
11	7.94	395.85	11.06	156.2	0.16
12	7.77	10536.02	25.73	295.3	3.33
13	7.91	867.78	14.60	281.0	0.94
14	7.65	957.20	9.50	146.4	1.10
15	7.82	859.40	10.20	153.4	0.45
Avg.	7.83	6295.48	128.51	606.2	3.46
Max.	8.20	30121.70	630.0	3066.2	18.50
Min.	7.51	395.85	4.10	146.4	0.16
Median	7.86	3439.52	35.95	281.0	0.94
STDEV	0.16	8094.83	191.07	786.7	5.47

Mean, standard error (S.E.), median and range (n = 15).

Table 2. Maximum level of heavy metal concentrations in different countries.

Heavy Metal	German	England	Japan	Canada	Normal Range
Pb (mg kg^{-1})	500	100	400	200	0.1-20
Zn	300	300	250	400	3-50
Cd	2	3	-	8	0.1-1

Source: [23].

3.2. Bioavailable heavy metal content in soils

Table 3 show that Bioavailable heavy metal content in soils is less than total metal content (table 3). With increasing total heavy metal content in soils increased the bioavalaible content of metals but no significant correlation between total and bioavailable heavy metal content.

Table 3. Bioavailable heavy metal content in the topsoil of Industrial Complex in Zanjan-Iran.

Site	Bioavailable heavy metal (mg.kg^{-1})			Site	Bioavailable heavy metal (mg.kg^{-1})		
	Pb	Zn	Cd		Pb	Zn	Cd
1	16.35	21	0.55	11	0.6	24.31	nd
2	30.2	198	9.92	12	3.16	1.62	0.84
3	43.2	86	2.62	13	3.56	11.28	0.01
4	107	158	1.88	14	1.43	0.42	nd
5	4.62	46	0.17	15	1.54	0.49	nd
6	6.34	100.01	0.51	Avg.	14.98	46.91	2.07
7	1.9	14.8	Nd	Max.	107	198	9.92
8	0.94	41.01	Nd	Min.	0.6	0.26	nd
9	1.42	0.42	Nd	Median	3.16	21	0.7
10	2.46	0.26	Nd	STDEV	28.32	61.95	3.29

3.3. Heavy metal phytoaccumulation

Plants that were more popular and more available at this area were collected and analyzed for their heavy metal accumulation capacities. The scientific names, their classification and determinations of the heavy metals in plant shoots are given in table 4. As is shown in the table, some of these plants act as a good metal accumulator. Results showed that the amounts of heavy metals in studied plants in the studied area are more than blank sites (Table 4). N. mucronata was, however, the best Pb and Cd accumulator plant (92, mg/kg). The same results were declared by Chehregani [27] in Angoran area about 130 kilometers away from the studied area and also by Movafagh et al [36] within the study area. However Levels of Pb, Zn and Cd in topsoil and plants close to this area are higher than standard range. Almost entire soils close to the tailing dumps and an overwhelming portion of the soils affected by surface drainage exceeded the toxic concentration in soils for at least one metal (Zn), posing an important environmental risk.

Table 4: Total metal concentrations in native plants growing in the studied area.

Site	Alhaji cameloron			Amaranthus-retroflexus			Hultemia persica			Noea mucronta			Onosma kotschyi		
	Pb	Zn	Cd	Pb	Zn	Cd	Pb	Zn	Cd	Pb	Zn	Cd	Pb	Zn	Cd
1	3.23	70.03	0.22	3.92	53.44	0.23	1.02	10.06	0.18	36.35	283.66	0.74	0.62	39.85	0.18
2	9.1	35.44	1.19	9.8	27.94	1.23	3.03	5.92	1.1	92.73	143.99	1.75	1.87	19.46	1.1
3	3.1	17.3	0.88	3.71	14.75	1	1.24	2.34	0.75	37.44	87.34	2.41	0.58	8.94	0.74
4	6.92	17.22	0.47	6.7	13.96	0.5	2.71	2.68	0.39	73.2	79.76	1.42	1.45	8.12	0.4
5	1.35	9.03	nd	1.02	6.87	nd	0.36	1.32	nd	12.03	38.87	nd	0.23	4.62	nd
6	0.92	8.4	0.08	0.91	5.87	0.1	0.31	1.16	nd	9.08	34.86	0.23	0.18	4.01	nd
7	1.7	8.18	nd	1.76	4.76	nd	0.67	0.82	nd	18.09	31.22	nd	0.33	3.84	nd
8	0.31	7.97	nd	0.33	4.55	nd	0.06	0.8	nd	2.39	32.33	0.08	-	-	-
9	0.12	6.93	nd	0.29	3.98	nd	0.04	0.63	nd	1.92	27.39	nd	0.12	3.33	nd
10	0.06	7.22	nd	0.1	4.07	nd	0.02	0.69	nd	0.89	28.34	nd	0.01	3.35	nd
11	0.13	6.58	nd	0.32	3.8	nd	0.04	0.61	nd	2.04	26.93	nd	0.03	3.2	nd
12	0.33	8.28	0.203	0.45	4.89	0.21	0.23	0.92	0.18	6.02	35.74	0.79	0.07	3.9	0.19
13	0.11	4.03	nd	0.29	4.83	nd	-	0.89	nd	-	35.11	nd	-	-	-
14	0.87	6.13	0.08	-	-	0.09	0.04	0.61	nd	1.87	23.82	0.24	nd	3.1	nd
15	0.74	6.4	nd	0.13	3.4	nd	0.04	5.59	nd	1.92	24.73	nd	0.15	3.27	nd
Avg.	1.93	14.61	0.45	2.12	11.55	0.48	0.7	2.34	0.52	21.14	62.27	0.95	0.47	8.38	52
Max.	9.1	70.03	1.19	9.8	53.44	1.23	3.03	10.06	1.1	92.73	283.66	2.41	1.87	39.85	1.1
Min.	0.06	4.03	0.08	0.1	3.4	0.09	0.03	0.61	0.18	0.89	23.82	0.08	0.01	3.1	0.18
Median	0.87	8.18	0.22	0.68	4.83	0.23	0.27	0.92	0.39	7.55	34.86	0.76	0.21	3.9	0.4
STDEV	2.69	17.2	0.43	2.94	14.42	0.46	1.03	2.75	0.4	29.13	69.55	0.83	0.6	10.5	0.4

4. Conclusions

The concentrations of heavy metals (Cd, Pb and Zn) in topsoil and plant's samples analyzed in the studied area are found to be higher than standards. Almost entire soils close to the tailing dumps and an overwhelming portion of the soils affected by surface drainage exceeded the toxic concentration of such metals, posing an important environmental risk. This, along with the gradual decrease in concentration of these elements in soil by increasing distance from the tailings, indicates that anthropogenic sources, namely the Zinc Industrial Complex is most possibly the major source for the enrichment of heavy metals in topsoil. Extremely high metal levels are encountered near the tailings from the industry which is dumped in open space at the vicinity of the industrial complex.

Determination of bioavailability of heavy metals in soils also shows that there is a direct correlation between the bioavailable content and the total concentration of these metals in topsoil. By decreasing the total amount of heavy metals in the topsoil or increasing distance from the industry, the bioavailable content of heavy metal in plants also show a sharp decrease and show the same results for plants accumulation of this elements. Among the native plants grown in the studied area, N. mucronata was found to be a good hyperaccumulator plant for Pb, Zn, and Cd in this site. The amounts of heavy metals were decreased in polluted soils under the effect of N. mucronata and we suggest the species, as an effective accumulator, for phytoremediation of heavy metal polluted soils in the studied area.

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