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EVALUATION OF SOME HEAVY METALS CONTAMINATED SOILS AROUND THE SHAHID SALIMI POWER PLANT, NEKA, MAZANDARAN PROVINCE, IRAN

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Abstract. One of the most important problems threatening the health of natural resources and, in turn, the food safety of societies is environmental contamination. Heavy metals are considered as the environmental pollutants. The entry of heavy metals into the soil is done through the atmospheric sources and mostly via melting plants, oil refineries and power plants. Due to the mazut consumption in some seasons, power plants are considered as a threat to the soil. This study was conducted with the aim of evaluating contamination of some heavy metals including copper, zinc, cadmium, lead, and nickel in the soils around the Shahid Salimi power plant, Neka located in Mazandaran province, north of Iran. One of the greatest threats is the possible contamination of cultivated paddy by pollutant elements. A number of 50 samples from the soil around the power plant were taken from a depth of 0–20 cm within the form of a regular grid and the concentration of the corresponding metals was measured in each of them. The mean background concentration of copper, nickel, lead, zinc, and cadmium was 36.2, 339.8, 90.8, 13.8, and 0.20 mg·kg, respectively. The maximum mean contamination factor belongs to nickel, lead, copper, zinc, and cadmium, respectively. The frequency of the obtained contamination evaluation classes indicates that the majority of the analyzed samples have a medium level of contamination. Copper, nickel, and lead belong to the class of very high contaminants. By comparing the concentrations of the heavy metals of studied region with quality standard of Iranian soil resources, presented by the Depart-

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ment of Environment Protection of Iran, it was observed that the concentrations of cadmium, zinc, and copper have been significant at the level of 5% based on the standards determined by the agency for agricultural uses, environmental standard and groundwater level. In other words, they do not have conflict with the determined standard at any of the three levels.

Keywords: background concentration, contamination factor, heavy metals, Mazandaran province, soil contamination

INTRODUCTION

The devastation and environmental contamination are among the tangible signs of unstable activities of today's societies and one of the products of industrialization of the human society. One of the most important problems threatening the health of natural resources and, in turn, the security of societies is environmental contamination (Kebata-Pendias and Pendias 2001). When the soil becomes contaminated, it can be transferred to other parts of the environment, jeopardizing the human health either directly or indirectly (Zhang *et al.* 2007). Wide farming lands under consumption of chemical fertilizers, regions around large and industrial cities, factories, mines, and main roads are among the most important regions in which the concentration of heavy metals is high and in most cases – toxic (DeMeeus *et al*. 2002).

One of the main reasons for scientists' growing interest in soil formation and its contamination is the long period needed to form the soil, such that for formation of only 1 cm of fertile soil 700–1,000 years is required (Borzin *et al.* 2015).

Bhuiyan *et al.* (2010) studied heavy metals contamination in agricultural soils using contamination factor, geo-accumulation and contamination load indices. The results indicated significant enrichment of soil with titanium, manganese, zinc, lead, arsenic, iron, strontium, and antimony metals, resulting from entrance to soil through coal mining activities. Yongming *et al.* (2006) investigated contamination with urban debris using normal enrichment factor and cluster analysis in Shian, China. They attributed the origin of silver and magnesium to residential and commercial sources, the origin of chromium, copper, lead, zinc, and antimony to industrial sources and traffic, and arsenic and the manganese origin – to soil making processes.

The results of the research by Esmaeili *et al.* (2011) in lands of Zanjan town indicated that 70% and 100% of these regions are facing zinc and copper toxicity, respectively. They reported the maximum level of total zinc found in the lands around factories, lead and zinc mines, and steel factory.

Azimzadeh and Khademi (2013) examined enrichment and distribution of heavy metals in the soils of Mazandaran province using contamination factor and contamination load index. Results showed that the concentrations of lead, zinc, and copper were mainly affected by human activities, while nickel was mainly controlled by natural factors such as parent material and agricultural activities. Mousavi (2011) investigated the spatial distribution of copper, chromium, antimony, and arsenic in the superficial soils of Hamedan province using geostatistical methods. Their results indicated that the studied elements mostly had an earthborn origin. Moreover, the study by Barati *et al.* (2012) showed that the concentration of chromium, cobalt, and nickel in the soils of Hamedan is dependent on parent materials. Borzin *et al.* (2015) studied some heavy metals contamination of superficial soils of Hamedan province using contamination indices. They found that the concentrations of nickel, lead, copper, and zinc were influenced by natural factors including parent materials, but agricultural activities can cause progressive increase in these elements in soil due to overuse of manures and chemical fertilizers.

Shahid Salimi power plant of Neka is known as one of the largest and most important power plants in the country with the nominal power capacity of 2214 megawatt (MW). It is located offshore of the Caspian Sea, 22 km away from the north of Neka, Mazandaran province. The main and subsidiary fuels sequentially are natural gas and mazut (heavy and low quality fuel oil) (Farabi 2009).

Studies on the emission factor for sulfur dioxide from the chimney of the Shahid Salimi power plant indicated that the output SO_2 concentration from the chimneys under normal working conditions was 2.8 times larger than the standard output limit (86 $g \cdot gj^{-1}$), and in its maximum state, it increased three times the allowable limit. The level of the output (NO_x) concentration from the chimneys was 2.5 (135 g·gj) and 2.8 times greater than the maximum standard output level under normal working conditions and the maximum state, respectively (Power Research Center, 1996).

Considering the gas deficit in Mazandaran and high consumption of mazut fuel by the Shahid Salimi power plant, especially in the second half of the year, and also the high level of water table in the region along with the frequency of agricultural lands and intensive gardening around the Neka power plant, preservation of the quality of water and soil resources would become a matter of discussion in studies. Consumption of mazut fuel causes entrance of a large volume of toxic gases to the air and, in turn, conversion to acidic rain, contaminating the soil. The aim of this research is to compare the concentration of copper, nickel, lead, zinc, and cadmium in the soil around the Neka power plant.

MATERIALS AND METHODS

The studied region

The geographical position of Neka power plant is 36°50'N and 53°15'E. The region is located 20 km away from Sari, Mazandaran province and in the north of Neka (Fig. 1). The mean ten-year (2005–2015) temperature is 17°C and the mean ten-year precipitation is 669.6 mm.

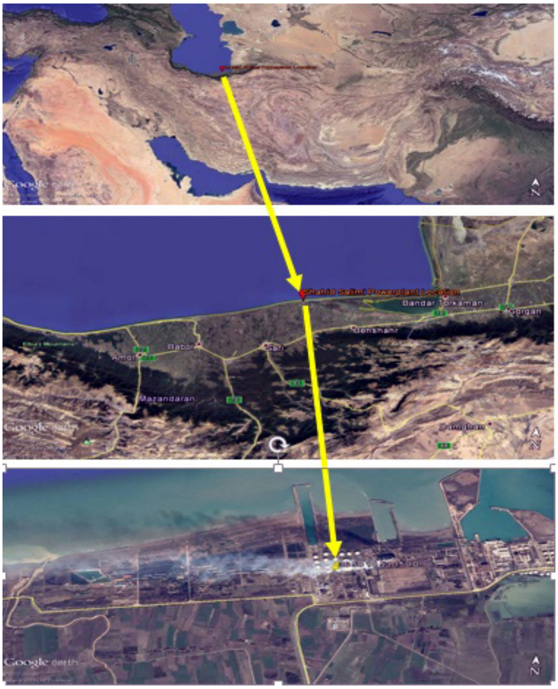


Fig. 1. The location of the Shahid Salimi power plant in Iran

Sampling and experimental equipment

Sampling was done in a regular network form with distances of 400 × 400 m grid, using user layer in the geographical information system (Arc GIS 9.3). The position of 50 points was determined for the sampling and totally 50 samples were taken from a depth of 0–20 cm of the soil. Further, according to Fig. 2, samples were also taken from the major parent materials in the studied region including conglomerate and sandstone to measure the total concentration for heavy metals. The samples were stone milled and passed through the 2-mm sieve and then transferred to the laboratory for experimental analysis.

The samples were oven dried at 105°C for 24 h. They were then beaten and passed through a 30-mesh sieve and then re-dried in the oven. Next, 0.2 g of the dried sample was weighed in a microwave Teflon tube with the accuracy of ±0.00001 using an analytical balance (Sartorius BP 210 D). To prevent corrosion, 2 ml of hydrofluoric acid and 5 ml of nitric acid were added to the samples using a plastic pipette. The samples were kept at room temperature for 1 h and then transferred to microwave for digestion.

Following completion of the microwave program and samples cooling, 0.8 g of boric acid was weighed in a plastic volumetric flask, to which 20 ml of deionized water was added. The samples were added to the flask and following

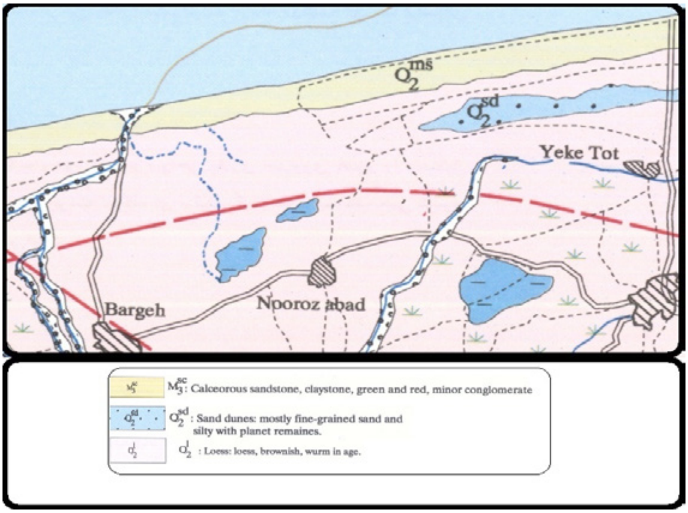


Fig. 2. The geological map of the studied region with a scale of 1:500000 (adapted from Organization of Geology of Iran)

complete dissolution of the soil, it was brought to 100 ml. To read the metals by Atomic Absorption Device (AAnalyst-700), according to the instructions, the standards related to each metal were developed. The device was then calibrated and the level of zinc, copper, lead, nickel, and cadmium was read in terms of mg·L. The concentration of the metal in the weight of the solid sample was calculated as equation 1 (*The Standard for the Quality*…, 2016):

$$C = \frac{Gs \times V}{W} \qquad (1)$$

Where:
C – metal concentration in the solid sample (mg·kg)
Gs – the metal concentration in the metal solution resulting from digestion (mg·L)
V – the dilution volume (100 ml)
W – the dry weight of the sample (0.2 g) (*Standard Methods*… 2005).

Calculation of the background concentrations

Contamination of heavy metals in the environment can be easily evaluated by metal concentration test (Zhang *et al.* 2007). To determine the extent of soil contamination with heavy metals in a region, the concentration of the metals in that region should be compared against a known standard. The best type of comparison is comparison against the available standards for that region, as different geological and climatic conditions around the world create different concentrations (Ye *et al.* 2011, Blaser *et al.* 2000). In this study, to calculate the background concentration, the geometrical mean of the concentration of the heavy metals in the soil of the studied region was calculated by equation 2. As has been shown in equation 2, the geometrical mean (GM) is the mean natural logarithm of a set of data (X_1, X_2, ..., X_n) which is eventually returned using exponential conversion (Gilbert 1987). In this study, *X* refers to the concentration of the studied element.

$$GM = \exp\left(\frac{1}{n}\sum_{i=1}^{n} \ln x_i\right) \quad (2)$$

Calculation of the contamination factor

The SPSS software was implemented in order to estimate the context concentration, pollution factor and pollution load index. Hakanson contamination factor (Hakanson 1980) is obtained by equation 3:

$$C_f = \frac{Mx}{Mb} \quad (3)$$

In this equation, *Mx* represents the concentration of the element in the sample and *Mb* is the concentration of the same element in the reference material (parent material). In this study, the Hakanson classification for contamination factor was used for evaluation of contamination of the heavy metals. Table 1 showed the evaluation of the contamination with heavy metals based on the contamination factor (Hakanson 1980).

Table 1. Evaluation of the contamination of heavy metals based on contamination factor (Hakanson 1980)

Severity of pollution	Variation rang of CF
Low pollution	$CF < 1$
Medium pollution	$1 \le CF < 3$
High pollution	$3 \le CF < 6$
Very high pollution	$6 \le CF$

RESULTS AND DISCUSSION

The statistical description of the concentration of heavy metals

Table 2 summarizes the statistical properties of the concentration of the heavy metals of all analyzed samples. The mean concentration of copper, nickel, lead, zinc, and cadmium is 36.16, 339.82, 90.76, 13.78, and 0.203634 mg·kg, respectively.

Table 2. Summary of the statistical status of the total concentration of the studied heavy metals in terms of mg·kg

	Cu	Ni	Pb	Zn	Cd
Number	50	50	50	50	50
Mean	36.16	339.82	90.76	13.78	0.203
Median	30.39	292.50	78.34	16.92	0.201
Mode	8.10	195.00	25.84	8.69	0.160[a]
Std. deviation	24.27	265.59	54.96	5.66	0.028
Variance	589.39	70540.03	3021.38	32.06	0.001
Skewness	0.204	0.162	0.318	-0.263	0.252
Std. error of skewness	0.337	0.337	0.337	0.337	0.337
Kurtosis	-1.617	-1.673	-1.371	-1.728	-0.816
Std. error of kurtosis	0.662	0.662	0.662	0.662	0.662
Minimum	6.00	19.44	15.20	4.50	0.160
Maximum	69.50	700.00	180.00	20.02	0.260

Background concentrations

The natural background concentration of copper, zinc, nickel, lead, and cadmium has been estimated as 36.16, 13.78, 339.82, 90.76, and 0.20 mg·kg, respectively. Table 3 provides the natural background concentration of heavy metals in different countries (Carlon 2007, Chen *et al.* 1991, Azimzadeh and Khademi 2013) along with their range on a global scale (Kabata-Pendias and Pendias 2001, Azimzadeh and Khademi 2013) as a comparison. The inequality and difference between the natural background of heavy metals in the studied region and presented countries can also be seen in Table 3.

Table 3. The background concentration of heavy metals in terms of mg·kg in the studied region, some countries, and on a global scale

Element	Concentration	Lithuania	Belgium	China	Global scale
Cu	36.16	11	17	22.6	13–24
Zn	13.78	62	36	74.2	45–100
Ni	339.82	9	18	26.9	12–34
Pb	90.76	40	15	26	22–44
Cd	0.20	0.8	0.2	0.097	0.30–0.70

The results regarding degradation of parent materials are provided in Table 4.

Table 4. The total concentration of heavy metals in parent materials in the studied region environmental assessment of heavy metals

Mother rock	Cd	Pb	Ni	Zn	Cu
Conglomerate & sand stone	0.22	12.8	23.4	4.2	8.4

Table 5 summarizes the statistical status of contamination factor of the studied heavy metals.

Table 5. A summary of the statistical status of contamination factor and contamination class of the studied heavy metals

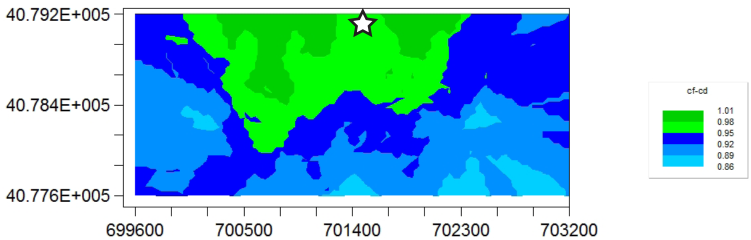
Element	Mean	Mini-mum	Maxi-mum	Skew-ness	Kurto-sis	% pollution			
						Low	Moderate	High	Very high
Copper	4.3048	0.71	8.27	0.204	-1.617	20	22	22	36
Zinc	3.2828	1.07	4.77	-0.263	-1.728	-	48	52	-
Nickel	14.5224	0.83	29.91	0.162	-1.673	6	20	6	68
Lead	7.0913	1.19	14.06	0.318	-1.371	-	26	24	50
Cadmium	0.9256	0.73	1.18	0.252	-0.618	70	30	-	-

Table 6. The calculated values (mg·kg) of the soil contamination standard by the Department of Environmental Protection of Iran

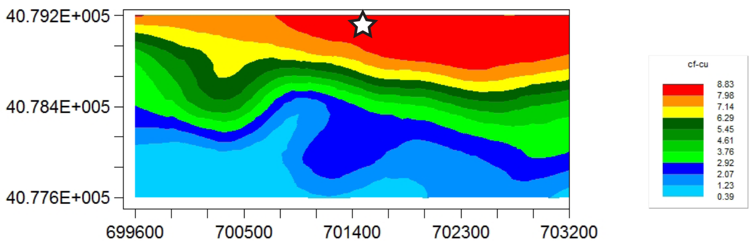
Elements	Agriculture	Environmental protection	Ground water protection
Copper	200	63	1,500
Lead	75	300	300
Zinc	500	200	3,000
Nickel	110	50	600
Cadmium	5	3.9	20

Figure 3 outlines the Kriging maps of the distribution of the contamination factor of copper, nickel, lead, zinc, and cadmium.

a)



b)



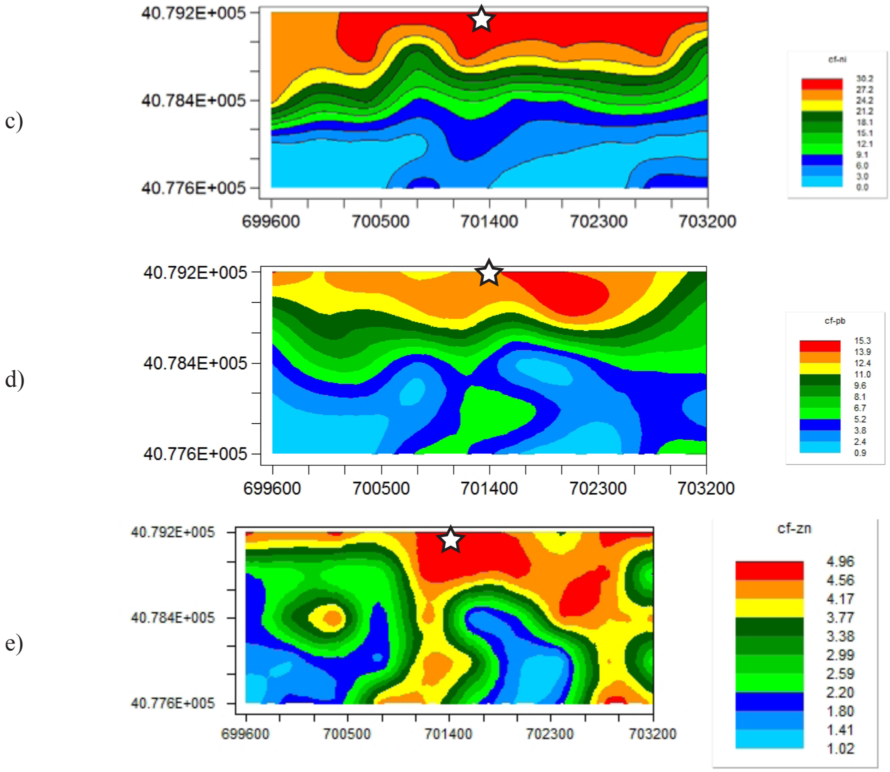


Fig. 3. Distribution map of the contamination factor of heavy metals:
a) cadmium b) copper c) nickel d) lead e) zinc
☆=location of the power plant

The maximum level of the contamination factor was observed for nickel, which, however, diminishes as we move farther away from the power plant. In GS+ software, the best model was chosen for each metal with the minimum RSS and maximum R2 values and the Kriging maps associated with the pollution factor distribution of the studied area and that of the pollution load index, were provided as well. The Kriging map of PLI is depicted in Figure 4. Using PLI distribution map, the regions with a high probability of environmental risk of heavy metals are illustrated as well.

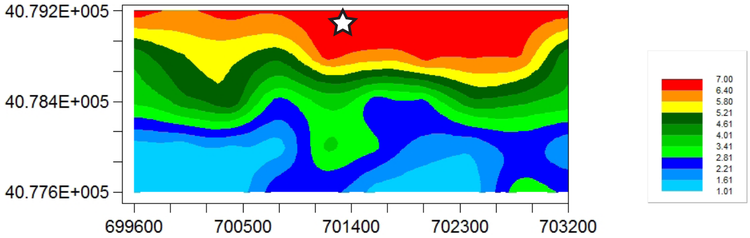


Fig. 4. Distribution map of the pollution load index in the studied region (around Shahid Salimi power plant)
☆ = location of the power plant

As can be seen from Figure 4, the downstream regions of the area, which include the agricultural lands, indicate the lower risk level in relation with the studied heavy metals. Evaluating the heavy metals of iron, manganese, zinc, copper and lead in Isfahan Region, Dankoub *et al.* (2012) observed that the PLI value in the urban regions and industrial zone of Isfahan steel factory is greater than in the lands under cultivation or with no cultivation.

Table 6 shows the quality standard of Iran's soil resources for the studied heavy elements which has been represented by the Department of Environmental Protection of Iran. By comparing the desired heavy metals' concentrations in the studied region achieved via SPSS with these standards, it was observed that the concentration of cadmium, nickel, zinc and lead is significant at the 5% level with the standards determined by the department of environment for the agricultural use, environmental standard, and groundwater level and there is no contradiction with the determined standards at any of the three levels.

Among the studied elements, the maximum mean values of the contamination factor are dedicated to nickel, lead, copper, zinc and cadmium, respectively, and this indicates the influence of the human activities, including mazut consumption, indiscriminate use of agricultural toxins and chemical fertilizers in the variations of the elements. As can be seen in Table 5, among the contamination classes, the medium contamination class has the largest frequency in the collected samples, while copper, nickel and lead belong to the very high contamination class. By investigating the soil contamination of Mazandaran province using the contamination factor, Azimzadeh and Khademi (2013) illustrated that most of the analyzed samples have medium concentration class in terms of lead, zinc, copper, cadmium and nickel contamination.

Figure 3 provides the Kriging maps of the distribution the contamination factor of nickel, lead, zinc, copper and cadmium. As can be seen, the maximum level of contamination factor of nickel, lead and copper in the studied region is in the proximity of the power plant with the contamination intensity diminishing with distance from power plant. It is probable that the mazut burning by the power plant and the proximity of the studied area to the road have resulted in higher concentration of nickel and lead. Moreover, excessive use of manure and chemical fertilizers and chemical pesticides in agricultural lands may have led to the increased concentration of copper and zinc in the soil. Rodriguez Martin *et al.* (2006) investigated the level of heavy metals in the agricultural soils of Abro Area in Spain using multivariate and geostatistical analyses. They indicated that chromium and nickel are controlled by parent materials, while cadmium, lead, mercury, copper, and zinc are influenced by human activities. Moreover, the mean concentration of copper was high in olive farms and vineyards, which was due to the usage of chemical fertilizers and soil fertilizing materials in these regions. Having examined the lead accumulation rate in the agricultural lands of Hamedan province, Yeganeh (2012) indicated that without considering atmospheric subsidences, manures and weathering of parent materials account for 14 and 85% of the total lead introduced into agricultural lands, respectively. The study by Taghipour *et al.* (2011) on the investigation of the source of heavy metals in part of Hamedan province, indicated that in the studied region, the concentration of chromium, nickel and cobalt is controlled in relation with parent materials (shale stones). Also, the copper concentration is jointly controlled by human activities and parent materials, whereas the concentration of input lead changes with human activities. The level of the input lead concentration has been greater in urban regions as compared to the other ones. Facchinelli *et al.* (2001) examined the concentration of heavy metals and their controlling sources in northern Italy by implementing the multivariate analysis and geographic information system (GIS). Their results indicated that chromium, cobalt, and nickel are controlled by the effect of the parent materials in the studied region which include ultra-alkaline stones. In addition, the concentration of copper, zinc and lead changed with human activities.

CONCLUSIONS

Considering the assessment classes of the contamination factor, most of the samples taken from the studied region have a medium contamination class. The distribution map of the contamination factor of heavy metals in the studied region indicated that in the vicinity of the power plant, contamination is higher than in other regions, and the concentration of the elements in the region is influenced by natural factors and human activities. As for weathering, which is a natural process, no special measure can be provided. Hence, by decreasing the mazut consumption in the power plant, lowering consumption of manures and chemical fertilizers, as well as using clean and renewable energies such as solar and wind powers, the status of heavy metals can be controlled in the region.

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