

Heavy Metals Pollution in Surface Soils of Jamalabad District of Lowshan in Guilan, Iran

Mohsen Mohammadi Galangash^{a*} , Pedram Hedayat^b , Ali Fazlollahi^c 

^aDepartment of Environmental Sciences and Engineering, Faculty of Natural Resources, University of Guilan, Sowme Sara, Guilan, Iran.

^bDepartment of Environment and Energy, Science and Research Branch, Islamic Azad University, Tehran, Iran.

^cDepartment of Range and Watershed Management, Faculty of Natural Resources, University of Guilan, Sowme Sara, Guilan, Iran.

*Correspondence should be addressed to Dr Mohsen Mohammadi Galangash, Email: m_mohammadi@guilan.ac.ir

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Background & Aims of the Study: Jamalabad district of Lowshan is one of the ancient industrial zones of the country with regard to having Lowshan industrial estate, Shahid Beheshti power plant, and the locality of two cement production factories. Hence, the study of some persistent pollutants such as heavy metals can be extremely valuable in terms of public health and environmental issues.

Materials & Methods: In this survey, 30 samples of surface soils were collected around Lowshan industrial estate and Shahid Beheshti power plant. After sample preparation the specimens were analyzed using ICP-OES. In the next, according to the results of statistical analyzes, Pollution Loading Index (PLI) and Contamination Factor (CF), the qualitative status of the soils in the region was evaluated.

Results: The distribution of metals was obtained according to pattern of $Si > Pb > V > Co > Ni > Cd$, respectively. The mean soil concentrations ranged within 1.33-2.08 for Cd, 32.55-49.33 for Ni, 80.12-124.76 for Pb, 45.51-66.36 for Co, 59.58-106.76 for V and 140.61-304.36 mg/kg for Si. According to the results of PLI, the soil of the area was classified as inappropriate quality.

Conclusions: The main components of cobalt, cadmium and nickel were more effective on contamination levels than other metals. According to cluster analysis, these grouping of metals can illustrate the industrial origins of pollutants. Surface soil pollution in the area, demonstrate the long-term effects of various industrial units activities in the industrial estate, power plant activities, and road transport, operation of various mines activities and the existence of cement industries, can also be effective in discharging of pollutants in the region.

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Background

The deliberate and unconscious interferences of human being in the nature have led to environmental crises and the occurrence of various illnesses. (1,2). Nowadays, among the human interference on nature, the direct and indirect effects of industrial activities on their peripheral environment have become one of the most controversial challenges in the world.

Every day, myriad amounts of hazardous pollutants from various industrial activities in industrial estates as well as combustion of fossil fuels from their units enter into water, air and soil environments (3,4) Among the various pollutants, heavy metals have a significant contribution of industrial pollution. The major concerns about heavy metals are the proliferation of their emission sources, toxicity and sustainability in the environment, so that

heavy metal pollution not only affects physical, chemical and biological properties of the soil, but can threaten human health by entering the food chain and contaminating groundwater (5,6). In recent years, bulks of studies have been implemented on the study of heavy metals in surface soils around industrial centers all over the world. Ahmadipour *et al.* (2013) studied the concentration of mercury in soils and different organs of rice in the fields around Amol Industrial Estate. The results of their study showed that high amounts of mercury from industrial estate activities have accumulated in the soil and in different organs of rice (7). The results of studies by Parizangeneh *et al.* (2010) regarding heavy metal levels in soils around Zanjan Industrial Estate revealed that heavy metals of lead, cadmium, and zinc contained in waste and industrial waste of industrial units of this estate has caused excessive accumulation of lead and zinc elements in the surrounding areas by wet and dry deposition of air pollution or industrial wastewater discharges (8). The study carried out by Conko *et al.* (2013) on the contamination of arsenic and mercury elements in soils around an industrial city in the Donets Basin in Ukraine showed that the concentrations of all studied elements were higher than their mean in soil of the region (9). Jamalabad district of Lowshan is located 5 km west of Lowshan near the two old roads and Rasht-Qazvin highway in Gilan province. Shahid Beheshti Power Plant and Lowshan Industrial Estate have the potential of transferring high amounts of heavy metals to the adjacent environment. The most important active industrial units in the region that can contribute to the discharge of heavy metals are including, metal melting and casting, mineral processing, plastics production, the production of asphalt and the refineries of motor oil (10). Output pollution load from two cement factories in the region has always contributed significantly to changes in the

chemical structure of the surrounding soils given the direction of the dominant winds.

Aims of the Study

The presence of heavy metals in the raw materials of industrial units located in Lowshan Industrial Estate, huge amounts of fossil fuels consumed in industrial units, power plants and vehicles are of the main known sources of heavy metal pollution in study area. In this study, the concentration of heavy metals of lead, silica, vanadium, cadmium, cobalt and nickel in surface soils around the Lowshan Industrial Estate Shahid Beheshti power plant and road of Rasht-Qazvin was investigated. Preliminary literature reviews show that since the establishment of these industries there has been no scientific report on the status of heavy metals pollution in the surface soils of the area. Given the agricultural activities in the region, proximity of Shahrood River, which flows to Manjil dam and the growth of rural and urban communities, the results of this study are essential for ecological values and public health.

Materials & Methods

Soil sampling

Sampling was carried out in the spring of 2017 following the initial field surveys in Jamalabad area in the vicinity of Lowshan industrial estate. 30 sampling stations were selected by random systematic method and according to Fig.1 their geographic positions were obtained using by GPS (Map62s Garmin model). A total, 30 combined samples in the depths of 0-30 cm of the surface soil were collected. Also, a control sample was taken in the opposite of dominant wind direction and at a depth of 1 meter. The samples were packaged in polyethylene bags along with labeling, placed in a Styrofoam ice box and then transferred to the laboratory (11).

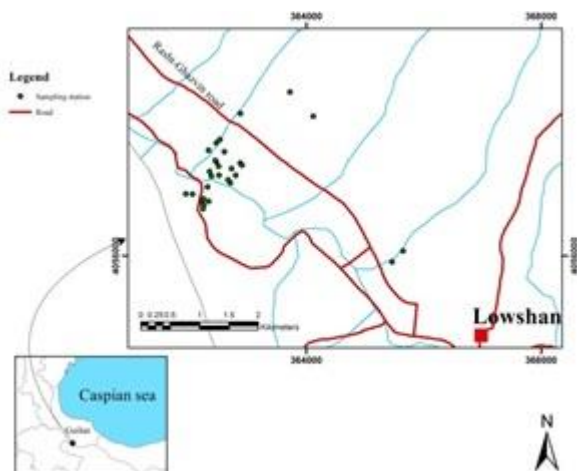


Figure 1) Sampling stations at the study area

Analysis

Sample preparation operations in the laboratory were performed with air drying for 72 hours, then passing through a 2 mm sieve to allow for large particle separation. The initial screened samples were dried in a thinner air layer and then passed through a sieve with mesh 100 (0.149 mm). At this stage, to reach the constant dry weight, the soil samples were dried in the oven for 3 hours and the temperature of 110°C and 1 gram of the samples were weighed using a digital scale with a precision of 0.0001 gram and were put inside the test tubes. In order to digest the samples, first, 1 ml of Nitric acid 65% solution and 3 ml of chloride acid 37% were added to the samples (1 to 3 ratio) and placed in ambient temperature for 30 minutes to remove their toxic fumes. The samples were

then placed in an aqueous bath for one hour at 85°C and then were heated for two hours at 120°C in the digestion reactor of CR 3200 WTW model in order for the digestion to be completed. Finally, after cooling, the samples were plated with Whatman filter paper grade 42 and dispersed in a 50-ml balloon with deionized water. Finally, the total concentration of lead, silica, vanadium, cadmium, cobalt and nickel of all extracts was read by ICP-OES (Spectro Arcos model) in the Faculty of Health of Guilan University of Medical Sciences (12). Contamination Factor (CF) and Pollution Loading Index (PLI) values were calculated to determine the potential of surface soil contamination according to equations (1) and (2), where C_{metal} is the concentration of metal in the sample, $C_{background}$ is the concentration of metal in the background or the mean concentration in the earth's crust, and n is the number of metals. The pollution load index is a simple comparative tool for assessing the quality of the site (13,14).

$$CF = \frac{C_{metal}}{C_{background}} \quad \text{Eq (1)}$$

$$PLI = \sqrt[n]{CF_1 \times CF_2 \times CF_3 \times \dots \times CF_n} \quad \text{Eq (2)}$$

Table 1) Contamination factor and Pollution Loading Index for contamination levels in soil

Quality	PLI	Level of Contamination	CF
No polluted	$PLI < 1$	Low contamination	$CF < 1$
At background level	$PLI = 1$	Moderate contamination	$1 \leq CF < 3$
Polluted	$PLI > 1$	Considerable contamination	$3 \leq CF < 6$
		Very high contamination	$CF > 6$

Statistical Analysis

The statistical analysis of data was running by SPSS software version 24. Initially, normality testes of data were carried out by Shapiro Wilk

test. One-way ANOVA test was used to determine the mean difference of heavy metals concentration between the stations. To determine the origin of the metals, the Principal

Component Analysis (PCA) and the Agglomerative Hierarchical Clustering (Ward's Sighting) method were implemented.

Results

The mean concentration of heavy metals in soil samples around the Lowshan Industrial Estate is summarized in Table 2. According to this table, the concentration pattern of metals was Si>Pb>V>Co>Ni>Cd. The results of the PCA test according to Table 3 show that there are three main components that, in total, 80.19% of variance of variables are related to these three components. From this, 30.6% of the total variance was related to first factor, 26.26% to second factor and 23.33% to third factor. Three

clusters were also obtained based on the cluster analysis tree (Fig. 2), such that cluster A contains nickel, cobalt and cadmium; cluster B contains vanadium and lead but only silica was placed in C cluster. The calculation of contamination factor index and pollution load index are given in Table 4. Regarding the results of CF index, the study area is in sever pollution in terms of Cadmium, Cobalt and Vanadium, is in high and medium pollution in terms of nickel and lead, and is in low to medium pollution condition in terms of silica, respectively. Also, the consequences of the PLI index showed that the soil quality at all stations is inadequate in terms of the heavy metal levels.

Table 2) Mean concentration of heavy metals (mg/kg±SD) in sampling sites

Station	Mean mg/kg ± SD					
	Cd	Ni	Pb	Co	V	Si
1	1.76±0.25	45.1±5.008	124.76±4.47	66.36±3.71	93.93±27.52	149.58±24.56
2	1.483±0.27	39.65±6.89	115.28±8.27	57.26±4.21	97.25±15.51	140.61±7.41
3	1.55±0.26	40.86±10.48	117.7±13.00	56.33±7.33	60.9±21.4	168.21±63.48
4	1.53±0.18	32.95±3.12	119.43±5.07	55.16±1.75	102.38±19.5	271.9±10.96
5	2.03±0.78	38.7±3.86	116.46±5.74	62.91±7.5	102.96±25.61	242.8±10.23
6	1.65±0.1	39.51±0.55	116.01±1.49	60.16±9.33	91.56±20.51	177.31±8.56
7	1.5±0.35	35.15±7.34	118.56±3.77	57.05±7.27	82.96±4.28	304.36±9.82
8	1.88±0.38	43.37±1.53	115.25±6.48	54.23±2.57	70.05±4.8	187.46±10.44
9	1.76±0.076	49.33±4.35	81.036±6.81	63.75±2.85	86.9±3.16	176.58±12.09
10	1.66±0.28	39.15±4.67	108.91±11.74	60.85±3.34	102.25±8.33	176.73±20.75
11	1.916±0.85	32.55±2.47	118.56±6.15	54.58±1.59	106.76±13.52	285.28±86.59
12	1.61±0.15	40.31±2.41	117.7±4.99	62.066±8.96	100.61±26.8	207.23±14.25
13	1.683±0.15	39.1±0.39	116.46±1.95	64.61±5.84	91.033±20.62	287.68±10.67
14	1.65±0.58	36.1±8.18	116.6±5.34	45.51±1.31	59.58±5.57	210.2±79.54
15	1.68±0.12	45.91±2.95	119.21±7.27	65.86±10.94	81.05±3.050	175.16±11.64
16	1.7±0.18	44.85±8.92	80.12±6.72	63.26±2.54	106.68±2.80	209.53±97.6
17	1.73±0.25	43.66±6.19	110.08±13.62	62.58±6.02	102.23±8.31	166.4±18.64
18	1.8±0.25	40.65±5.2	124.6±4.48	63.86±3.41	95.16±2.86	171.93±52.12
19	1.33±0.028	37.61±9.05	108.7±4.4	53.48±3.3	74.016±2.71	118.48±36.25
20	1.68±0.2	43.02±7.3	121.38±8.06	58.25±5.49	74.016±1.71	163.66±6.49
21	1.66±0.1	45.1±5.01	124.76±4.47	66.36±3.71	93.93±2.75	149.58±24.45
22	1.75±0.05	39.65±6.89	115.28±8.27	57.26±4.21	97.25±15.5	140.61±74.16
23	1.783±0.25	40.86±10.48	117.7±13.001	56.33±7.33	60.9±2.41	168.21±63.48
24	1.45±0.03	34.91±7.58	114.3±1.84	47.21±14.48	74.38±5.32	163.26±46.7
25	2.08±0.71	45.91±2.95	119.21±7.27	65.86±0.94	81.05±3.5	175.16±11.64
26	1.65±0.11	44.85±8.92	80.12±6.72	63.26±2.54	106.68±2.84	209.53±9.77
27	1.521±0.35	37.3±7.1	110.2±13.81	57.25±4.07	106.35±14.5	228.33±10.22
28	1.83±0.31	36.7±5.51	114.58±12.48	59.016±6.51	93.25±10.64	230.96±81.8
29	1.761±0.07	39.01±1.01	118.05±4.54	63.31±10.07	97.6±3.03	225.65±14.11
30	1.66±0.28	39.43±0.58	119.21±2.93	58.2±7.08	79.76±3.78	304.25±98.4
Total	1.69±0.33	40.37±6.38	113.34±21.89	59.41±7.99	89.11±27.03	199.55±88.3
Ref site	0.15	9.7	46.15	3.65	2.85	184.9

Table 3) Rotated component matrix for heavy metal concentrations using principal component (PC) analysis

Rotated component matrix			Element
PC3	PC2	PC1	
0.33	-0.13	<u>0.83</u>	Co
-0.23	0.09	<u>0.82</u>	Cd
0.00	0.86	0.05	Si
0.30	-0.72	0.55	Ni
0.86	0.16	0.07	Pb
0.62	0.49	0.38	V
1.39	1.57	1.83	Eigen values
23.30	26.28	30.60	% Total variance
80.19	56.88	30.60	Cumulate. %

Table 4) Pollution Load Index (PLI) and Contamination Factor (CF)

Stations	PLI	Mean CF						Quality PLI
		Si	V	Co	Pb	Ni	Cd	
1	1.36	0.80	32.95	18.18	2.70	4.64	11.77	Polluted
2	4.82	0.76	34.12	15.68	2.49	4.08	9.88	Polluted
3	1.36	0.90	21.36	15.43	2.55	4.21	10.33	Polluted
4	1.36	1.47	35.92	15.11	2.58	3.39	10.22	Polluted
5	1.75	1.31	36.12	17.23	2.52	3.98	13.33	Polluted
6	3.50	0.95	32.12	16.48	2.51	4.07	11	Polluted
7	1.14	1.64	29.11	15.63	2.56	3.62	10	Polluted
8	1.95	1.01	24.57	14.85	2.49	4.47	12.55	Polluted
9	2.34	0.95	30.49	17.46	1.75	5.08	11.77	Polluted
10	4.90	0.95	35.87	16.67	2.36	4.03	11.11	Polluted
11	7.45	1.54	37.46	14.95	2.56	3.35	12.77	Polluted
12	2.06	1.12	35.30	17.00	2.55	4.15	10.77	Polluted
13	1.02	1.55	31.94	17.70	2.52	4.03	11.22	Polluted
14	8.29	1.13	20.90	12.47	2.52	3.72	11	Polluted
15	8.81	0.94	28.43	18.04	2.58	4.73	11.22	Polluted
16	8.95	1.13	37.43	17.33	1.73	4.62	11.33	Polluted
17	1.04	0.89	35.87	17.14	2.38	4.50	11.55	Polluted
18	1.61	0.92	33.39	17.49	2.69	4.19	12	Polluted
19	6.02	0.64	25.97	14.65	2.35	3.87	8.88	Polluted
20	1.22	0.88	25.97	15.95	2.63	4.43	11.22	Polluted
21	9.63	0.80	32.95	18.18	2.70	4.64	11.11	Polluted
22	1.30	0.76	34.12	15.68	2.49	4.08	11.66	Polluted
23	3.17	0.90	21.36	15.43	2.55	4.21	11.88	Polluted
24	2.87	0.88	26.09	12.93	2.47	3.59	9.66	Polluted
25	2.48	0.94	28.43	18.04	2.58	4.73	13.33	Polluted
26	7.48	1.13	37.43	17.33	1.73	4.62	11	Polluted
27	8.54	1.23	37.31	15.68	2.38	3.84	10	Polluted
28	2.25	1.24	32.71	16.16	2.48	3.78	12.55	Polluted
29	4.59	1.22	34.24	17.34	2.55	4.02	11.77	Polluted
30	3.95	1.64	27.98	15.94	2.58	4.06	11.11	Polluted

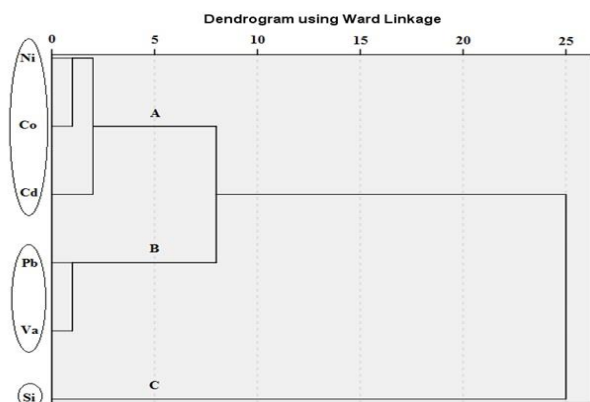


Figure 3) Dendrogram obtained by hierarchical cluster analysis for heavy metal contents (Ward method).

Conclusion

Toxicity of some heavy elements for soil microorganisms, their ability to transfer into plant organs and finally, their entry into different parts of the human food basket has led the monitoring of these pollutants in the soil became as a research priority in the scientific centers of the world. The rapid development of pollution sources and prevalence of various known and unknown diseases led to the pollutants monitoring became a serious issue in industrialized areas (15). According to the results of this study, Pb and Si metals had the highest concentrations in the surface soils around Lowshan Industrial Estate compared to other metals. Silica is known as the second most abundant element in the earth's crust, so a significant portion of this elements level can be of natural origin. The history of the cement factory in Lowshan dates back to 1957, with the aim of supplying cement for the construction of the Manjil dam. Over time, with the increase in the number of furnaces in the same factory and also construction of a new cement factory with a much higher capacity, the transfer of silica through the dust from the outlet of these industries and its deposition, the concentration of this element has been increased in the surface soil of the region. Moreover, the processes of mineral products, in Lowshan

Industrial Estate can also increase the concentration of this element in surrounding surface soils. Although the increase in silica in surface soils causes to change in the physical and chemical properties of the natural soil, nevertheless, they can be re-suspended as a result of the high winds of the region. Studies show that exposure to silica crystals, both respirable and irrespirable, can cause irreversible effects in human health, as silicosis is one of the infectious diseases caused by silica contamination (16). Among the studied elements, lead is one of the toxic pollutant enter in nature from a variety of industrial sources, such as painting, battery manufacturing, metal processing, casting and mineral operations. A large number of these industries are active around or within the industrial estate (17). Among the heavy metals, lead can be absorbed through the soil from different organs of the plant and animal and various adverse effects of lead such as neurological, cardiovascular and immune disorders were reported, also in particular, the effect of this element on the decline of IQ in children has been proven (18). Other metals Given that the results of statistical analyses show that there is a significant difference between the concentrations of all heavy metals at sampling stations with their concentration in the control sample, this is illustrated the effect of anthropogenic resources on increasing of pollution load (19,20). Multivariate statistical methods such as parsing of the main components and cluster analysis have been introduced as powerful methods for the separation of the effective sources of pollution. Based on the analysis of the main components, the elements at each component are likely to be the same in terms of controller resources (21). According to Table (3), three main components were identified that the first factor explained 30.6% of the total variance, which is positively and significantly related to cobalt, cadmium and nickel. The second factor accounts for

26.28% of the total variance, which is explained by silica and the third factor, 23.3% of the total variance, which is mainly related to vanadium and lead. On the other hand, the cluster analysis results in Fig. 2 confirmed the results from the analysis of the main components because cobalt, cadmium and nickel are in the same cluster and lead and vanadium are located in a separate cluster and silica is in a farther cluster. The presence of elements such as nickel, vanadium, and lead has been reported in various types of fossil fuels (12). In the study area, there are asphalt production plants inside the Lowshan Industrial Estate and Shahid Beheshti Power Plant that can play an important role in increasing the concentration of these pollutants in the area. In addition, industrial units located inside the Industrial Estate, including casting, motor oil recycling industries, metal and mineral industries, can affect the changes in concentration of metals in the soils of the region. Also, the existence of phosphate fertilizer plants (Jahan Phosphate) can effect on cadmium levels (20). A study by Martin *et al.* (2006) has shown that the concentration of some elements such as Cd, Cu, Pb, Zn is associated with common lithogenic and anthropogenic sources (22). The study, which was carried out by, Kariminejad *et al.* (2015) on the quality of soil around the Ahwaz mega city founded the human activities have a significant effect on the variation of nickel and chromium levels (23). In the present study, according to the CF index, the amount of Si was in low to moderate conditions, Pb was in the medium and Ni in high pollution conditions and Co, V and Cd were in severely polluted conditions. According to the PLI calculations in Table (4), all samples of soil around Lowshan Industrial Estate are of inadequate quality in terms of all heavy metals level. This result reveals that the concentration of heavy metals in the region is likely to be affected by anthropogenic sources. Road transportation, small and large scale

industrial unites, like power plants, cement factories and metal smelting are of known sources of metal pollution (14). So, the establishment of this kind of activities in the region can also be effective in reducing the environmental quality. It should be noticed that in the case of agricultural activities in the region, heavy metals may be transferred from the soil to the products and other biota through the food chain. The water table level is various from Shahroud riverside to upper land, Thus, due to the long-term industrial activities, it is always a concern that these pollutants can be penetrated to ground water sources.

Footnotes

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Conflict of Interest:

The authors declared no conflict of interest.

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