Determination of heavy metal pollutions in the atmospheric falling dust by multivariate analysis

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ABSTRACT

The purpose of this study was to assess some heavy metal (HM) concentrations in the soil and atmospheric falling dust along the Yazd highway, Yazd Province, Iran. The total concentrations of cadmium (Cd), cobalt (Co), copper (Cu), nickle (Ni), lead (Pb), zinc (Zn), iron (Fe) and manganese (Mn) in the dust and soil samples were measured using atomic absorption spectrophotometry after digestion with acid. The relationship between HMs in the falling dust was determined using correlation coefficients, principal component analysis and cluster analysis. The mean concentrations of HMs in falling dust were higher than those of the nearby soils, except for Fe, Pb and Zn. The highest correlation between HMs in the falling dust and soil was associated with Cd and Fe as well as Cd and Ni with the correlation coefficients, two resources were identified for HM concentrations in the falling dust. The measurement of enrichment factor exhibited that the region dust infiltration of metals on Mn (13.46), Zn (8.16) and Cu (5.21) are grouped in the severe enrichment class. Increasing industrialization and human activities lead to enter intensified levels of HMs into atmosphere. So, implementation of environmental standards and improvement of public transportation are necessary to reduce the level of pollutants entering the atmosphere.

Keywords: Enrichment factor, Falling dust, Heavy metals, Multivariate analysis.

INTRODUCTION

Dust storm is a hazardous phenomenon aggravated by climatic change and global warming in recent years. In Iran, dust storms have induced harmful influences on human societies and caused economic, social, environmental, political and security problems (Adib et al. 2018). The occurrence of this phenomenon in central areas of Iran during the recent years, has led to irreparable damages to different sections of environment, health, sanitation and finally the ecosystems (Hakimzadeh & Vahdati 2018). Due to rapid urbanization and industrialization during the past few decades, heavy metal (HM) concentrations on urban areas have reached toxic levels as a result of anthropogenic activities such as vehicle exhausts emissions, pesticide and fertilizer application, sewage sludge amendment, which release HMs into the air, water and soil (Liu et al. 2016; Peng et al. 2016). These HMs enter the environment through various human activities; affect the air quality; then by hanging and mating with dust particles, during rainfall are deposited at the surface of the earth and vegetation. Consequently, due to the wind speed or the precipitation of the heavens, they will remain in human being life cycle (Zhuanget et al. 2018). Metals like Pb, Co, Cd, Cu, Zn and Mn are dangerous pollutants which can be gathered in human body with relatively long half-life, leading to skin diseases and types of cancer in different forms (Onder & Dursun 2006). Zhuang Zhao et al. (2018) reported that the sources of lead pollution are human activities. Chen & Li (2018) used three methods to clean dusts polluted by HMs concluding that the washing dust is an affordable method. Esfandiari et al. (2018) exhibited that the input and controlling factors of these elements in the Ash tree are probably the same as the dust.

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So that, the *Fraxinus excelsior* leaf with accumulation index of 1607 mg kg⁻¹ has more ability to simultaneously absorb different metals. Hassan Farid *et al.* (2017) determined Pb levels of the street falling dust on the leaves in 29 sites in Karachi urban, concluding that Pb concentration on the leaves was high in the areas with higher number of markets such as printing, welding, soldering, and battery recycling shops.

Dust particle contains large quantities of toxic substances that pose a risk of the health of living organisms and ecosystems. Dust sources are also associated with an increase in the amount of radioactive contamination due to the high emission of dust particles in the environment. HMs may be released on a large scale by binding to those particles. They are also important due to physiological effects on humans and other living organisms, even at low concentrations (Hakimzadeh 2014; Wan *et al.* 2016).

One of the most important air pollutants in Yazd City is suspended particles, from the industries close to the urban along with some HMs, which can cause pollution of environment. Hence the lack of urban garden as well as percapital green space along with establishing pollutant industries in the Yazd-Ardakan plain, have led to many problems in this area. Therefore, in order to develop green space and establishing forest parks, the green belt design has been studied and implemented in the western part of Yazd. The purpose of this study is to investigate some of HMs in atmospheric falling dust in green belt of Yazd highway and to compare it with the HM concentrations in soil.

MATERIALS AND METHODS

Study area

Yazd City is located in the Yazd-Ardakan Plain with a dry weather in the coordinates of 54° 17' E and 31° 54' N. The wind direction is dominant in the northwest for 6 months (spring and summer seasons); inside the four months (from November to February) in the southeast and in March over 24 years. The wide variety of dusty days is 59 days and the most commonplace is 60 the summer day take place inflicting tangible and intangible damage to the human beings of Yazd (fathizad *et al.* 2018).

Yazd is an important city of Iran in terms of industry, trade, tourism, the rapid growth of industries such as steel industry, the growth of vehicles, the lack of promotion of urban traffic. The desert climate of this region, exacerbates the inflow of contaminated micro flora due to lack of proper planting and vegetation cover, or vegetation loss in the western part of Yazd urban. As the western part of Yazd is one of the important transit ports and industrial towns and factories, construe of the green belt in the western part of Yazd City has been studied and implemented (Fig. 1).

Methodology

Marble Dust Collector (MDCO) was used to measure the quantity of HMs within the falling dust in the study area. The sediment collector designed for this study comprises a circular plastic container 22 cm in diameter, placed into a three-fold glass marble with an average diameter of 1.6 cm, and then on a polyethylene bases on the height of 1 cm closed and placed inside the soil.

After three months of autumn, dust samples were taken from the marble dust collector and then transferred to the laboratory. After drying the specimens at 50 to 55 °C in an oven, 1 g of dust was weighed with of 0.0001 g precision - balance. Furthermore, 7 mL of concentrated chloride-containing acid was added in each sample, followed by adding 2.5 mL concentrated nitric acid after evacuation of the vapors, and finally, adding 5 ml diluted nitric acid (0.5 mol).

After cooling the samples, 33.3 mL diluted nitric acid was added. Then the solution was passed through filter paper and the extract was reached to the certain volume. At the same time, soil samples were taken from the depth of 0 to 10 cm close to the site of the dust collector. 50 mL of DTPA solution was added to 25 g screened soil for 2 h on a shaker with 150 rpm. The solution was passed through filter paper and the extract was reached to the certain volume. (Klute 1986). The HM concentrations (Zn, Pb, Cd, Co, Ni, Fe, Mn and Cu) in a solution digested was determined by a flame atomic absorption device Analytical Jena 330 model. The pH of the examined specimens was measured using pH meter (Page 1983).

Enrichment factor index (EF): An important factor indicating the degree of human activity in disrupting the natural environment. The soil HM contamination and their potential environmental risks were studied by some authors (Liu 2010; Muyessar -Trudi 2013; Sun 2017). The inactive element is used to calculate this factor, considering the Fe in the earth's crust.

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Fig. 1. Location of the study area.

Therefore, the enrichment factor index using Eq. 1 (Ergin *et al.* 1991) was used to determine enrichment factor of various metals using falling dust.

$$EF = \frac{(C_i/C_{Fe})_{sample}}{(C_i/C_{Fe})_{background}}$$
(1)

where $(C_i/C_{Fe})_{sample}$ is the ratio of C_i to Fe concentrations on the surface soil sample, $(C_i/C_{Fe})_{background}$ is the ratio of C_i to Fe levels in the reference value (Ergin *et al.* 1991). Table 1 illustrates the severity of HMs contamination using the enrichment coefficient.

Statistical analysis

All analyses including correlation between variables and multivariate analyses were performed using SPSS software. Principal component analysis (PCA) and cluster analysis (CA) were also used to determine the relationship between HMs and their potential sources (Zheng 2012; Lu 2012; Li 2014). The PCA is widely used in various environmental studies such as soil, dust and water to determine contamination sources along with calculating the degree of human and natural resource participation (Shrestha & Kazama 2007; Zhao *et al.* 2015).

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CA is often combined with PCA to examine the results and classifying the individual parameters and variables. CA is used to obtain an organized system of observations in which groups of common features are observed (Lu *et al.* 2010). In this study, the HM concentrations were standardized through standard Z method, and Euclidean intervals were used to calculate similarities in variables. Then, hierarchical clustering was employed using the Ward method of the standardized data set.

Table 1. Classification of the enrichment factor index (EF) (Ergin et al. 1991).								
Extremely severe enrichment	Very severe enrichment	Severe enrichment	Moderate enrichment	No enrichment	Contamination level			
$40 \ge EF$	$40 \ll \text{EF } 20$	$20 \ll EF 5$	$5 \ll EF 2$	<' EF	EF			

RESULTS AND DISCUSSION

Descriptive statistics of HM concentrations in the soil and falling dust of the study area is illustrated in Table 2. The Fe, Mn and Cd concentrations in falling dust were in the order of highest to lowest, while in the case of soil, the respective order was Fe, Zn and Cd. The element averages found in this study were comparable with those of the global elemental averages (Table 2). The Mn averages in this study were multifold higher than those in other reports. The Cd contents observed in this study were multifold lower than those reported from urban settings [Nanjing (China), Hu *et al.* (2012); Lahore (Pakistan), Mohmand *et al.* (2015); Birmingham (England), Charlesworth *et al.* (2003); Zurich (Switzerland), Amato *et al.* (2011); Islamabad (Pakistan), Faiz *et al.* (2009); Rawalpindi (Pakistan), Abbasi *et al.* (2013); Hangzhou (China), Zhang & Wang (2009); Huludao (China), Zheng *et al.* (2010); Selangor (Malaysia), Latif *et al.* (2016); Newcastle (UK), Okorie *et al.* (2012); Urumqi (China), Wei *et al.* (2009); Ottawa (Canada), Rasmussen *et al.* (2001) (Table 2)]. The Pb, Ni, Cu, Co, and Zn averages in this study were multifold lower than in the other studies (Table 2).

		area	•	
Variable		Minimum	Maximum	Mean ± SD
	Cd	0.35	3.26	1.56 ± 0.91
	Co	1.17	4.19	2.60 ± 0.29
	Cu	2.40	15.43	8.63 ± 3.65
	Ni	2.13	6.01	4.04 ± 0.86
Falling dust	Pb	8.09	40.63	19.12 ± 3.92
	Zn	4.42	66.33	22.87 ± 3.98
	Fe	63.23	723000	160170 ± 2.62
	Mn	26.41	4220.83	2256 ± 12.76
	pН	7.37	8.66	8.2 ± 0.43
	Cd	0.02	0.47	0.17 ± 0.14
	Co	0.04	0.66	0.30 ± 0.07
Soil	Cu	0.33	1.81	1.36 ± 0.41
	Ni	0.08	0.39	$0.\ 18\pm0.09$
	Pb	0.83	36.70	7.34 ± 1.84
	Zn	0.26	109.14	13.38 ± 2.31
	Fe	2.55	74.54	14.52 ± 2.19
	Mn	2.47	34.06	11.38 ± 0.23
	pН	8.17	8.53	8.36 ± 0.11

Table 2. Descriptive statistics of heavy metal concentrations (mg kg⁻¹) and selected properties of dust and soil in the study

Region/City	Mean elemental concentrations (mg kg ⁻¹)						References	
	Cd	Co	Cu	Mn	Ni	Pb	Zn	-
Yazd (Iran)	1.56	2.6	8.63	2256	4.04	19.12	42.87	This research
WMZ (Pakistan)	0.42	4.89	13.5	208.5	14.4	63.9	116.4	Eqani et al. (2016)
Newcastle (UK)	1	-	132	-	26	992	421	Okorie et al. (2012)
Urumqi (China)	1.17	10.97	94.54	926.6	43.28	53.53	294.47	Wei et al. (2009)
Nanjing (China)	13.2	13.6	328	239	24.7	655	1889	Hu et al. (2012)
Lahore (Pakistan)	2.3	3	13.2	-	93 8	170.2	196	Mohmand et al. (2015)
Ottawa (Canada)	0.37	-	65.8	-	15.2	39.05	112.5	Rasmussen et al. (2001)
Birmingham (England)	1.62	-	467	-	-	48	534	Charlesworth et al. (2003)
Zurich (Switzerland)	10	-	3547	-	504	247	2183	Amato et al. (2011)
Islamabad (Pakistan)	5	-	52	-	23	104	116	Faiz et al. (2009)
Rawalpindi (Pakistan)	8.4	-	156.9	-	47.8	145.8	890	Abbasi et al. (2013)
Hangzhou (China)	1.59	20	116	510	26	202	321	Zhang and Wang (2009)
Zhejiang (China)	-	-	158	-	125	589	686	Zhu et al. (2008)
Huludao (China)	72.84	-	264	-	-	533	5271	Zheng et al. (2010)
Selangor (Malaysia)	250	-	-	-	510	430	210	Latif <i>et al.</i> (2009)
Barcelona (Spain)	3	-	1332	-	58	248	1572	Amato et al. (2011)

Table 3. Mean concentrations of heavy metals in dust of the world in comparison to Yazd

The majority of HM concentrations in the haze were significantly ($P \le 0.01$) higher than in the soil. So, road traffic and industry probably play an important role in increased HM entrances (Fig. 2). It seems that the road traffic and transportation play higher role in the entrance of Cu to the dust than industry, because copper is made by depreciation of car break insulation and oil materials burning (Wedyan *et al.* 2009). Totally, the concentration of metals such as Mn, Cu, Ni, Co and Cd in the dust can be due to human contamination such as agricultural operations, building, the environment destruction activities or vehicles and road traffic (Birmili *et al.* 2006). Wang et al. (2003) reported that the high HM concentrations in atmospheric subsidence leads to their entrances into human-made metals due to fast growth of industrialization and urban expansion. The results exhibit that the Fe, Zn, and Pb levels in the soil is higher than in falling dust. The other HM (Cd, Co, Cu, Mn and Ni) concentrations were also higher in the falling dust than in the soil, may be due to the fact that the size of the dust particles is smaller than the soil, which mainly consists of silt and clay. (Yao *et al.* 2015). In addition, human activities lead to significantly entrance of HMs to the environment. Hence, the urban and industrial regions falling dust have high levels of these elements.

Coefficients of correlation between dust and soil properties

The correlation coefficients between metals can provide useful information about the origin and ways of entering them (Facchinelli *et al.* 2001; Lu *et al.* 2010; Maisto *et al.* 2004). According to Table 4, in falling dust, there was a significant correlation between Cd, Co and Fe ($p \le 0.01$). Cd exhibited a positive and significant correlation with Co and Fe (correlation coefficient = 0.75 and 0.81 respectively). There were significant correlations between Pb and Cu as well as between Mn and Ni ($p \le 0.01$). Pb displayed positive and significant correlations with Cu, Mn and Ni (correlation coefficient = 0.79; 0.76 and 0.71 respectively). Other studies were also reported the direct correlations between HM contamination in falling dust of roadside and traffic (Addo *et al.* 2012; Werkenthin, *et al.* 2014). Positive and significant correlations ($p \le 0.01$) were found between Ni and Mn as well as between CO and Fe. In the Case of soil, according to Table 4, significant correlations were found between Pb and Cd, Co, Cu

and also Ni ($p \le 0.01$) with a correlation coefficient of 0.66, 0.97, 0.71 and 0.84 respectively. It was also true for Ni with Cd and Co ($p \le 0.01$, correlation coefficients = 0.70 and 0.97 respectively) and also between Cu and Cd as well as Co ($p \le 0.01$). Cu exhibited a positive and significant correlations with Cd and Co (correlation coefficient = 0.82 and 0.67 respectively). It was also true for Co and Cd as well as Co ($p \le 0.01$, correlation coefficient = 0.70). Nan *et al.* (2002) found high correlation between Zn and Cu as well as Zn and Pb in the soils under cultivation of wheat in china. Similar results were also reported by Rodriguez Martin *et al.* (2006) concerning to correlation between HMs in the soil.



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Fig. 2. Boxplots of dust and soil Cd(a), Co(b), Cu(c), Fe(d), Zn(e), Mn(f). Pb(g) and Ni(h) concentrations in the three study areas. (The same letters in soil or dust indicates that the means were not statistically significant at 0.05%).

Variable		Cd	Со	Cu	Mn	Ni	Pb	Zn	fe	pН
	Cł	1								-
	Ca	1	1							
	Cu	0.75	0.53 *	1						
	Mn	-0.10	0.33	0.59.*	1					
Falling	Ni	-0.10	0.33	0.39	0.71 **	1				
dust	INI DL	0.13	0.33	0.40	0.71	1	1			
uust	Pb	- 0.133	0.31	0.79	0.76	0.71	1			
	Zn	- 0.28	- 0.15	0.44	0.55 *	0.36	- 0.50 *	1		
	Fe	0.81 **	0.71 **	- 0.02	0.07	0.21	- 0.17	- 0.05	1	
	pН	- 0.52	- 0.57 *	- 0.19	0.20	0.05	0.001	- 0.05	- 0.52 *	1
	Cd	1								
	Co	0.70 **	1							
	Cu	0.82 **	0.67 **	1						
~ ~	Mn	0.19	0.37	0.32	1					
Soil	Ni	0.70^{**}	0.97 **	0.62 *	0.35	1				
	Pb	0.66^{**}	0.91 **	0.71^{**}	0.56^{*}	0.84 **	1			
	Zn	0.34	- 0.08	0.14	0.03	-0.08	-0.10	1		
	Fe	- 0.14	-0.03	-0.26	-0.52*	0.03	-0.31	0.10	1	
	pН	0.41	0.38	0.44	0.33	0.38	0.34	0.20	0.02	1

Table 4. Correlation coefficients between heavy metals and selected properties of falling dust and soil.

* Significance at 0.05, ** Significance at 0.01.

Sources of heavy metal entrances to the dust

The method of PCA was used by Varimax rotation to specify resources of heavy metal entrances to the dust. The Scree Plot is presented in Fig. 3. The results of the first to eighth principal components are also illustrated in Table 5. The factor load of each variable is also provided in Table 6 before and after rotation.

According to Fig. 3, two factors had the highest amounts of variances. Classification of variables in order to select factors are based on special values larger than one. The results exhibited that total variance between two eigenvalues was higher than 1 and these two factors comprise 80.86 % of total variances, while second factor comprise 31.15 % of total variances including Zn, Cd and Co (Table 5). The first factor comprise 49.71% of total variances and including elements such as Fe, Cu, Pb, Mn and Ni, with factor loading of 0.48, 0.08, 0.52, 0.72. 0.83, 0.91, 0.86 and 0.81 respectively (Table 6).

The results of CA for HMs in the falling dust are indicated in Fig. 4, exhibiting the two different groups which can be distinguished: 1) Fe, Co, Mn, Pb, Ni and Cu in the falling dust; and 2) Zn, Cd and Co in the falling dust.

The first group displayed a strong correlation between each other and made an independent cluster, while in the second group, Zn, Cd and Co were placed in a cluster. These results are consistent with the results of PCA and correlation coefficients. Kim *et al.* (2016) used a dendrogram of clusters using Euclidian distance, resulting in three clusters, as for the principal component score plot. Demkova & Lenka (2017) once assessing the agricultural soil contaminations in two different periods (1997 & 2015), divided the HMs into two separate clusters.



Fig. 3. C	lassificatio	on of	variable	s with a	in eigenval	ue>	1.
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Table 5. PCA values for the heavy metals in dust of the study area.									
		Initial eigen	values	Ex	traction sum	s of squared	Rotati	ion sums of so	uared loadings
Component					loadin	igs			
	Total	Variance	Cumulative	Total	Variance	Cumulative	Total	Variance	Cumulative
		(%)	(%)		(%)	(%)		(%)	(%)
1	3.977	49.716	49.716	3.977	49.716	49.716	3.94	49.246	49.246
2	2.492	31.151	80.867	2.492	31.151	80.867	2.53	31.621	80.867
3	.732	9.154	90.021						
4	.307	3.839	93.860						
5	.277	3.465	97.325						
6	.122	1.524	98.849						
7	.070	.875	99.724						
8	.022	.276	100.000						

Table 6. Factor loadings of heavy metals in dust the study area for the first two factors with an eigenvalue > 1.

Metals	Before	e rotation	After	rotation
	Factor 1	Factor 2	Factor 1	Factor 2
Fe	720	443	640	552
Cu	.830	094	.834	.039
Zn	.489	842	.617	754
Mn	.868	150	.881	010
Ni	.817	.065	.796	.194
Co	.523	.742	.399	.816
Pb	.910	246	.938	098
Cd	.087	.969	069	.971

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Dendrogram using Ward Method



Fig. 4. Hierarchical dendrogram for heavy metals in falling dust of the study area.

Table 1 and Fig. 5 exhibit that the falling dust reflects the low enrichment factor (EF) for Cd, while Pb, Co and Ni are placed in the moderate EF, and the infiltration of Mn and Cu in the severe one, which is in line with other studies such as those reported by Duong & Lee (2011) in Olsun City, South Korea. They reported that the falling dust of a highway in the city was grouped in a severe class in terms of Zn pollution, while Cu level in the dust of another highway was classified in a very severe pollution group. Norozi & Khademi (2015) reported that Zn, Co and Cu in the falling dust of Isfahan were placed in a very severe class in terms of contamination factor, while Fe, Pb, Cr, Mn and Ni in a moderate one. Janadeleh et al. (2016) reported that Ni exhibited the highest enrichment factor value among the elements, but placing in a moderate class. The results of the enrichment coefficient index of HM contamination are illustrated in Fig. 5.



Fig. 5. Enrichment factor for assessment of environmental protection.

CONCLUSION

Increasing industrialization and human activities intensify the mission of various pollutants into the environment. Air pollution has been considered as one of the most important environmental challenges because of its effect on ecosystems and human health. Heavy metals which enter the environment from many different sources such as industrial and agricultural activities, cause serious environmental risks. In order to reduce the negative impact of HMs, it is necessary to identify contaminated areas.

The aim of this study was to examine HM concentrations such as Fe, Zn, Pb, Cu, Cd, Ni, Co and Mn in falling dust and soil of Yazd Highway. The results exhibited the increasing order of element average concentrations in falling dust as follows: Cd <Co <Ni < Cu < Pb < Zn < Mn < Fe. The highest HM correlations in the falling dust and soil were recorded between Cd and Fe and also between Cd and Ni with the correlation coefficients of 0.81 and 0.97 respectively. Among soil HMs, maximum significant correlation was found to be as like as the falling dust. High correlation coefficient among the metals showed that the factors controlling the amount of these elements in the soil or dust are likely to be the same. The correlation coefficient, PCA and CA displayed that the

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sources of entrance of Cu, Pb, Mn, Ni, Cd, and Co are the same and are mostly affected by human activities such as road traffic and industry.

According to the results, it is necessary to control the quality and quantity of atmospheric pollutants resulted from industrial activities such as factories in the Yazd Industrial Area and development of public transportation in Yazd City in order to reduce the level of pollutions entering the atmosphere.

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چکیدہ

هدف از انجام این تحقیق، برآورد غلظت برخی فلزات سنگین در خاک و گرد و غبار ریزشی بزرگراه یزد–اردکان میباشد؛ پس از هضم نمونهها با اسید، غلظت کل عناصر آهن، نیکل، منگنز، کبالت، مس، کادمیم، سرب و روی مربوط به غبار ریزشی و خاک توسط دستگاه جذب اتمی اندازهگیری شدند، رابطه بین فلزات با استفاده از ضریب همبستگی، تجزیه و تحلیل مولفههای اصلی و آنالیز خوشهای تعیین گردید. نتایج بدست آمده نشان داد که میانگین غلظت فلزات سنگین به دست آمده در غبار ریزشی بیشتر از خاک بود بجز آهن، سرب و روی. بالاترین همبستگی بین فلزات سنگین کادمیم و آهن و کادمیم با نیکل به ترتیب با ضریب همبستگی ۱۸/۰ و ۱۹/۷ بدست آمد. بر اساس نتایج تجریه و تحلیل مولفههای اصلی و آنالیز خوشهای و ضریب همبستگی دو منبع برای غلظت فلزات سنگین تشخیص داده شد. نتایج فاکتور غنی شدگی نشان داد که نفوذ گرد و غبار ریزشی در منطقه برای فلزات منگنز (۱۳/۴۶)، روی (۱۸/۸) و ۱۸/۰ مید. نتایج فاکتور غنی شدگی نشان داد که نفوذ گرد و غبار ریزشی در منطقه برای فلزات منگنز (۱۳/۴۶)، روی (۱۸/۸) و ۱۸/۰)

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