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Assessment of Heavy metal concentration and their source in the groundwater near the landfill site: case study (Shiraz landfill)

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Abstract

Monitoring ground water quality around landfills is important to the environment. In this study, in order to investigate groundwater pollution, the concentration of heavy metals in groundwater around the Shiraz landfill between 2016 and 2020 was investigated in two wells and finally compared to WHO standards. In this study, concentration of heavy metals (Fe, As, Zn, Cr, Cd, Ni, Co, Pb and Cu) in groundwater of shiraz landfill was investigated for 5 years by the specialized laboratory of the Waste Management Organization of Shiraz Municipality. In this laboratory, after acidic digestion of the samples, heavy metals were analysis by using an atomic absorption spectrometer (A Analyst800, Perkin-Elmer). The results show that among the nine heavy metals measured, the concentration of Fe and Pb, in the upstream well (well No.2) was higher than the downstream well (well No.1) and the concentration of As, Zn, Cr, Cd, Ni and Co in the downstream well on was more than the upstream well. Concentration of none of the measured heavy metals was higher than the WHO recommended value for drinking water. Principal component analysis show that three factor, comprising 86.097% of the entire variance. In general, it can be concluded that the Shiraz landfill does not affect the groundwater quality around the landfill. which is probably due to the arrangements made at the Shiraz landfill to manage leachate, including the established leachate collection system and Construction of leachate storage and solar evaporation ponds.

1. Introduction

Ongoing global population growth is inextricably linked to increased waste generation. This includes household waste, demolition and building waste, chemical and hazardous waste, sludge and ash [1]. One of the main methods for disposal is landfill [2]. Landfilling is the most common and one of the least expensive waste management practices in the world [3]. Landfills, which typically receive a mix of municipal, industrial and economic waste, contain a wide variety of pollutants that affect the environment, animals and human health . Waste disposed of at landfill sites through the physical, chemical and biological absorption of nutrients releases gases and leachate into absorption with water [2]. In fact, leachate production is an outcome of landfill [5].

Leachate occurs during landfill operations and after closure. One ton of landfill waste results in about 0.2 cubic meters of leachate. However, the quantity and quality of leachate produced depends on moisture content, landfill hydrology, landfill age, weather conditions and waste stabilization temperature [6]. The leachate produced from the wastes contains various materials, including dissolved organic matter, non - soluble substances, ammonium, calcium, chloride, sodium, potassium, iron, sulfate and heavy metals such as cadmium, chromium, copper, lead, nickel, zinc and organic matter [3]. The level of leachate is more affected by the amount of rain. During the month of high precipitation, the leachate concentration will be diluted and, in other words, the leachate will be concentrated in dry periods [2].

Contact of leachate with soil, surface runoff and groundwater cause severe contamination including heavy metal pollution that can cause harm to humans and the environment [7]. At present, many technical measures, including isolation of landfill, establish the leachate collection system, drainage system and so on; have been taken to limit leachate contact [8]. Numerous studies have been conducted on the impact of landfill leachate on underground excavations in Iran [9-11]. The quantity of pollutants and pollutants per year was studied. The aim of this study was to evaluate the concentration of heavy metals in groundwater around Landfill Shiraz over a period of 5 years with using some heavy metal such as Iron (Fe), Arsenic (As), Zinc (Zn), Chromium (Cr), Cadmium (Cd), Nickel (Ni), Cobalt (Co), Lead (Pb) and Copper (Cu).

2. Methodology

2.1 Study area

Shiraz landfill is located in an area called Barmshour in the geographical position of 29' 25˙ N and 52'42˙ S, which has an average rainfall of 200 to 250 mm and an altitude of 1600 meters above sea level (Figure. 1). The general shape of this region is asymmetrical and the soil of the region is argilo-calcareous. The total area of the site is 5000 hectares, of which 40 hectares are used for landfilling, which takes place on the surface of the trenches. About 1100 tons of waste is delivered to this site daily, of which about 600 tons are recycled in the industrial separation plant. There are some industrial activity vicinity the landfill include Asphalt and sand production plant and cutting stones factory [22]. At this site, four wells were drilled to monitor and supply water to the site's green space, two of which are not in operation due to the fall. The characteristics of the wells examined are given in Table.1.

Table1. Characteristics of the studied wells

	Well Number 2	**Well Number 1**
Distance from landfill (m)	512	**733**
Well depth	300	**170**
Well situation	Upstream of the landfill	Downstream of the landfill

2.2 Sample procedure and data analysis

In this study, the concentration of heavy metals in two wells, one of which is downstream of the landfill (well No.1) and the other upstream (well No.2) of the site (figure. 1), was studied over a period of 5 years in the specialized laboratory of the waste management organization of the municipality of Shiraz. The water in each well is sampled three times monthly. A total of 30 water samples was taken from both wells. The sample was taken by glass cylinders and immediately transferred to the laboratory. In the laboratory, samples were filtered with nitrocellulose filter and then 2 ml HNO3 was added to the sample for stabilization [12]. A heavy metal that measured were included Iron (Fe), Arsenic (As), Zinc (Zn), Chromium (Cr), Cadmium (Cd), Nickel (Ni), Cobalt (Co), Lead (Pb) and

Copper (Cu). The concentration of heavy metals in water well samples was analyzed by using an atomic absorption spectrometer (A Analyst800, Perkin-Elmer), with the graphite furnace (GFAAS) method (auto sampler: AS-800; graphite tube: THGA-PE; end caps), and Zeeman background correction.

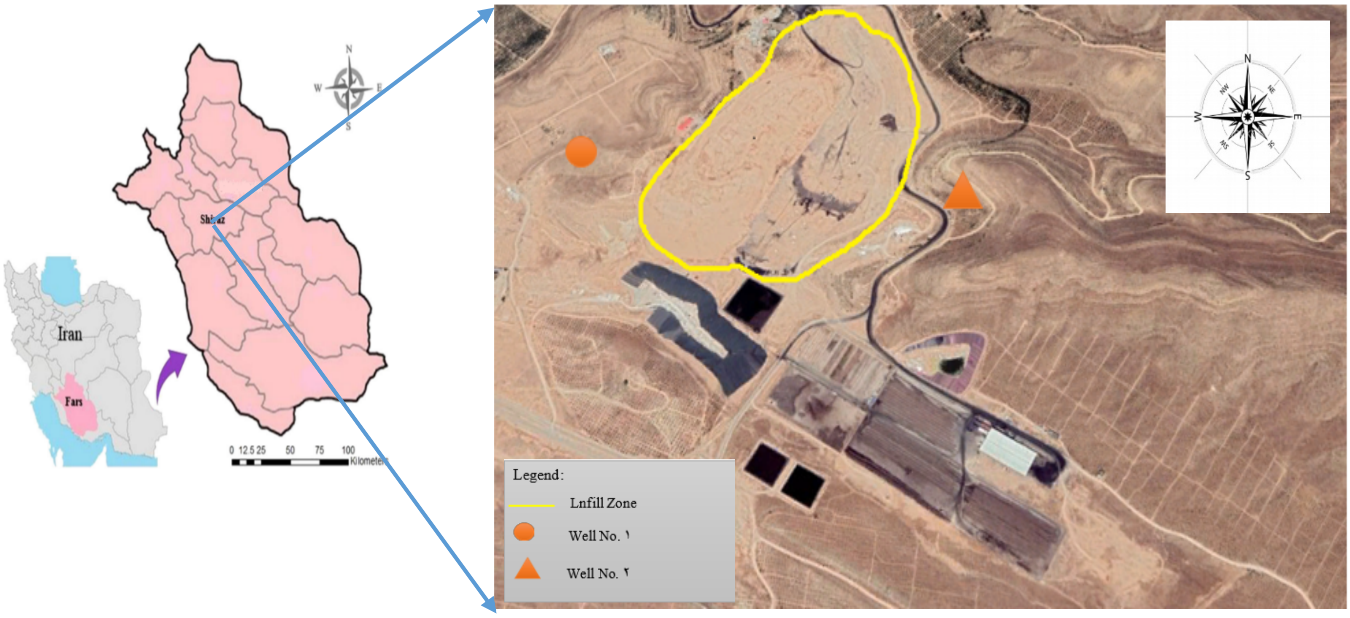

Figure 1. Location of landfill site and wells

Hollow cathode lamps were used as a radiation source to determine levels of metals [13]. Quality control and assurance include blanks, duplicate analysis and certified reference materials. For analysis of results, SPSS, and Excel software were used. The Kolmogorov - Smirnov test was used to determine the normality of the data and ANOVA test was used to evaluate the differences between the mean concentrations of heavy metals. Principal Component Analysis and Cluster Analysis were used. Also, Concentrations of heavy metals compared to the World Health Organization (WHO) drinking water standard [14].

3. Results and Discussion

3.1 Heavy Metal concentration

The concentrations of heavy metals (µg/L) in well water are reported in Tables 2 and 3. The results show that in well NO.1 the highest Fe concentration related to 2018 with mean ±SD 19. 75±0. 389 µg/L. Also, As has a high concentration in 2020 (3.02±0.26 µg/L). Zn, Cr, Cd, Ni, Co a Cu where higher concentration in 2019,2020,2017,2019,2016,2020,2020 with mean ±SD 117. 16±0. 15, 2. 15±0. 083, 0. 56±0. 025, 27. 39±0. 36, 6. 3±0. 20, 9. 39±0. 37 µg/L, respectively.

In well no2, the highest mean ±SD concentration of metals Fe, As, Zn, Cr, Cd, Ni, Co, Pb and Cu was 25. 29±0. 36, 4. 23±0. 12, 23. 29±0. 25, 1. 100±0. 100, 0. 55±0. 06, 11. 53±0. 27, 6. 3±0. 20, 3. 33±0. 10, 6. 10±0. 100 µg/L, respectively (Table. 3). Heavy metals measured during the five-year period in both wells is lower than the standard of drinking water of the World Health Organization (WHO) [14], which is probably due to the proper manage leachate in landfill site, including lining the landfill and establishing a Leachate collection system (Fig.3) and creation of leachate storage lagoon (Fig.4). While De, S (2017) in a study in Calcutta, India showed that the concentrations of heavy metals such as: mercury, lead, cadmium, chromium, iron and manganese were significantly higher than the WHO standard [5].

Table 2. Heavy metal concentration (Mean±SD; µg/L) and Anova test in the water of well No.1 in Shiraz landfill

Metals	2016	2017	2018	2019	2020	sig*	WHO
Fe							
Min	9.98	10.35	19.32	18	11.42	.001	-
Max	11.4	11.16	20.08	18.3	12.18		
mean±SD	10. 75±0. 719	10. 99±0. 625	19. 75±0. 389	18. 13±0. 152	12. 13±0. 17		
As							
Min	3.83	1.64	1.54	1.46	2.78	.005	**10**
Max	4.36	2	2	2	3.3		
mean±SD	4. 06±0. 27	1. 79±0. 18	1. 84±0. 26	1. 77±0. 27	3. 02±0. 26		
Zn							
Min	120.98	97	83.01	116.99	75.24	.000	**5**
Max	121.8	97.1	83.34	117.3	75.38		
mean±SD	1. 21±0. 42	97. 03±0. 060	83. 15±0. 16	117. 16±0. 15	75. 24±0. 13		
Cr							
Min	0.099	0.44	0.58	0.54	2.10	.046	**50**
Max	0.12	0.48	0.6	0.6	2.25		
mean±SD	0. 10±0. 01	0. 45±0. 020	0. 59±0. 010	0. 56±0. 03	2. 15±0. 083		
Cd							
Min	0.99	0.54	0.46	0.44	0.48	.007	**3**
Max	0.1	0.59	0.49	0.49	0.49		
mean±SD	0. 099±0. 001	0. 56±0. 025	0. 47±0. 01	0. 47±0. 026	0. 48±0. 005		
Ni							
Min	21.5	22.99	26.54	26.99	14.13	.001	**70**
Max	21.9	23.6	26.62	27.7	14.24		
mean±SD	21. 7±0. 20	23. 26±0. 30	26. 57±0. 043	27. 39±0. 36	14. 18±0. 049		
Co							
Min	6.1	3.12	3.08	3.4	1.39	.012	-

Max	6.5	3.25	3.21	3.6	1.43		
mean±SD	6. 3±0. 20	3. 19±0. 066	3. 16±0. 072	3. 5±0. 10	1. 41±0. 049		
Pb							
Min	0.087	1.85	1.82	1.80	3.22	.025	**10**
Max	0.1	1.92	1.9	1.9	3.43		
mean±SD	0. 095±0. 007	1. 88±0. 036	1. 89±0. 065	1. 85±0. 050	3. 33±0. 10		
Cu							
Min	8.5	6.89	4.98	7.12	8.97	.001	**2000**
Max	10	7.1	5.43	7.99	9.7		
mean±SD	9. 38±0. 78	6. 99±0. 105	5. 32±0. 300	7. 65±0. 46	9. 39±0. 37		

*P-value<0.05

Table 3. Heavy metal concentration (Mean ±SD; µg/L) and Anova test in the water of well No.2 in Shiraz landfill

Metals	**2016**	**2017**	**2018**	**2019**	**2020**	**sig***	**WHO**
Fe							
Min	12.99	9.98	23.98	24.92	24.98	.004	**-**
Max	13.1	10.1	24.07	25.1	25.7		
mean±SD	13. 03±0. 060	10. 02±0. 064	24. 03±0. 049	25. 04±0. 14	25. 29±0. 36		
As							
Min	4.12	1.95	1.83	1.65	1.85	.006	**10**
Max	4.36	2	2	2	2		
mean±SD	4. 23±0. 12	1. 97±0. 025	1. 91±0. 085	1. 78±0. 18	1. 94±0. 081		
Zn							
Min	16.98	13.98	23	16.32	18	.000	**-**
Max	17.1	14.9	23.49	16.76	18.3		
mean±SD	17. 02±0. 064	14. 29±0. 52	23. 29±0. 25	16. 54±0. 22	18. 13±0. 15		
Cr							
Min	1	0.38	0.55	0.59	0.53	.006	**20**
Max	1.2	0.46	0.6	0.6	0.6		

mean±SD	1. 100±0. 100	0. 42±0. 041	0. 57±0. 025	0. 59±0. 005	0. 56±0. 035		
Cd							
Min	0.098	0.48	0.39	0.37	0.46	.007	**3**
Max	0.1	0.59	0.49	0.49	0.49		
mean±SD	0. 099±0. 001	0. 55±0. 06	0. 45±0. 052	0. 43±0. 060	0. 47±0. 015		
Ni							
Min	6.1	9.54	11.22	7.3	8.2	.001	**70**
Max	6.5	9.67	11.73	7.7	8.5		
mean±SD	6. 2±0. 208	9. 56±0. 097	11. 53±0. 27	7. 50±0. 20	8. 22±0. 26		
Co							
Min	0.099	0.61	0.68	0.095	0.50		
Max	0.1	0.66	0.71	0.1	0.54	.035	**-**
mean±SD	09±0. 0005	0. 63±0. 026	0. 69±0. 011	0. 097±0. 00 2	0. 52±0. 20		
Pb							
Min	2	4	1.5	1.4	1.87	.006	**10**
Max	2.4	4.3	1.9	1.9	2		
mean±SD	2. 16±0. 20	4. 13±0. 152	1. 70±0. 200	1. 63±0. 25	1. 95±0. 070		
Cu							
Min	4.3	4.5	5.20	5.20	6	.000	**2000**
Max	4.8	4.7	5.24	5.46	6.2		
mean±SD	4. 53±0. 25	4. 60±0. 100	5. 2±0. 020	5. 3±0. 13	6. 10±0. 100		

Table. 4 indicated the overall mean concentration of heavy metal in well No. 1 and No. 2 in the five years. According the result of this table, Fe and Pb in well No.1 have higher concentrations than the well No.2 with Mean +SD 19. 6140±7. 41519 and 2. 5000±1. 02713 µg/L, respectively. The concentration of other metals in well No. 2 was higher than well No. 1 and only the Mean +SD concentration of Cd metal in both wells was equal (0.4320±. 19058 µg/L). Co with Mean +SD .4220±. 30037 µg/L and Cd with Mean +SD 0. 4320±0. 19058 have lowest concentration among studied heavy metal in Well No.2 and Well No.1 respectively. The results of T-test showed that there is a significant difference between the concentrations of Co, Ni and Zn at the level of 0.01.

Result of Pearson correlation test indicated in the Table. 5. The result of this test indicated that there is a significant correlation between AS and Fe, Cd and As, Ni and Co with Zn, Co and Ni, Pb with Cr,Cd and Co, Cu with Zn, Ni and Co at the 0.01 level (P-value<0.01). Also, there is a significant correlation between Co and Fe, Pb and Zn, Cu and Fe at the 0.05 level (P-value<0.05).

Table 4. Concentration (Mean +SD; µg/L) of heavy metal in two wells

Metal	**Well No.2**		**Well No.1**		**Sig**
	N	Mean +SD	N	Mean +SD	
Fe (µg/L)	15	19. 6140±7. 41519	15	14. 5840±4. 18954	**.232**
As (µg/L)	15	2. 4720±1. 05542	15	2. 7320±1. 7010	**.709**
Zn (µg/L)	15	18. 1100±3. 24527	15	98. 984±20. 38062	**.000****
Cr (µg/L)	15	.6920±. 29038	15	0. 8060±0. 83288	**.780**
Cd (µg/L)	15	.4320±. 19058	15	0. 4320±0. 19058	**1.000**
Ni (µg/L)	15	8. 8200±1. 99561	15	22 .8120±5. 32272	**.001****
Co (µg/L)	15	.4220±. 30037	15	3. 5980±1. 82986	**.005****
Pb (µg/L)	15	2. 5000±1. 02713	15	1. 8500±1. 17992	**.380**
Cu (µg/L)	15	5. 2800±0.6015	15	8. 0440±1. 89046	**.014***

*P-value<0.05
**P-value<0.01

Table 5. Pearson correlation coefficients of heavy metal from wells sample in 5 years

	Fe	**As**	**Zn**	**Cr**	**Cd**	**Ni**	**Co**	**Pb**	**Cu**
Fe	1								
As	-. 503**	1							
Zn	-0.402	0.112	1						
Cr	-0.163	0.256	-0.103	1					
Cd	0.220	-0.855**	-0.080	0.079	1				
Ni	-0.231	-0.177	0.913**	-0.240	0.144	1			
Co	-0.397*	0.226	0.916**	-0.375*	-0.264	0.824**	1		
Pb	-0.257	-0.241	-0.432*	0.497**	0.547**	-0.340	-0.590**	1	
Cu	-0.368*	0.284	0.752**	0.257	-0.127	0.472* *	0.660**	-0.286	**1**

**Correlation is significant at the 0.01 level (2-tailed).
*Correlation is significant at the 0.05 level (2-tailed).

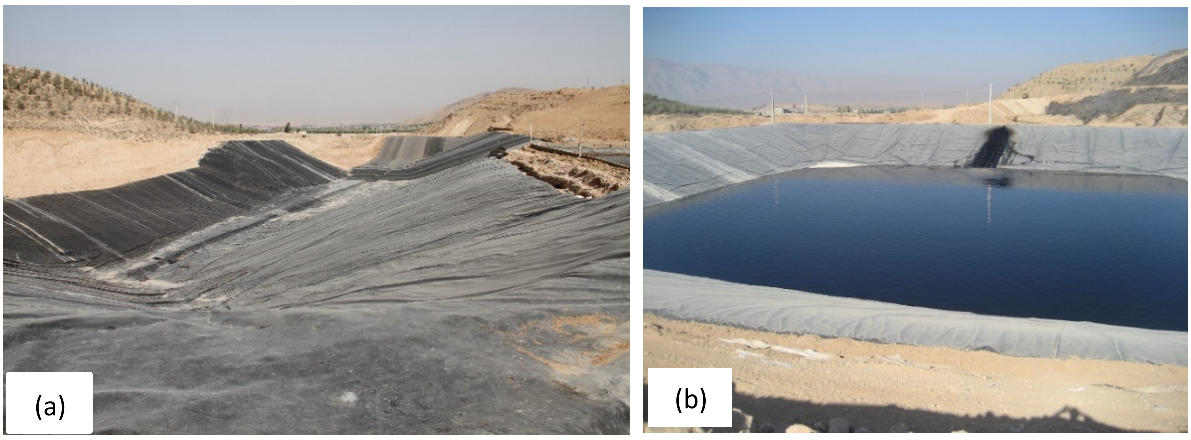

Figure 2. (a) Isolation landfill and establish a leachate collection system, (b) leachate storage lagoon

Fe:

The results of this study showed that the concentration of Fe in well No.1(19. 75±0. 389) in 2018 and well No.2 in 2020(25. 29±0. 36) was the highest (Table. 2 and 3). The Mean +SD concentration of Fe in well No.1 and well No.2 was 14.584 µg/L and 19.6140 µg/L, respectively (Table.4). Although Well No.1 is downstream from the site, the Mean +SD concentration of Fe in Well No.2 (25. 29±0. 36)is higher. Table.4 indicates that there is no a statistically significant difference in Fe concentrations in wells No.1 and No.2 (P-value>0.05). Fe is an essential metal for human body [14], the WHO has not defined a standard for Fe in drinking water. Alma et al. (2020) In a study on groundwater near Landfill in Ghazipour area of New Delhi found that with increasing groundwater distance from the Landfill site, the concentration of Fe metal reached less than 0.7 mg/l [7], which with The results of this study are consistent. High levels of Fe, Pb, Zn and Cr in groundwater near landfills and leachate can be due to toxic wastes such as battery cells, the use of aerosol cans and other substances that have a certain degree of toxicity. [15]. According to Table. 5, there is significant correlation between Fe and As (P-value<0.01), Co, Cu (P <0.05) concentrations. Of course, this relationship is a negative relationship, which means that with increasing concentration of iron, the concentration of arsenic, cobalt and copper decreases, which indicates the effect of antagonism of these metals with each other. This antagonistic effect between iron and arsenic is stronger because they are related at a significant level of 0.01 (P-value<0.01).

As:

According to the results of Table 4, the Mean +SD concentration of As in well No.1 and in well No.2 was 2. 7320±1. 7010µg/L and 2. 4720±1. 05542µg/L, respectively and there is no significant difference between the concentration of this metal in downstream and upstream well (P-value>0.05). The highest As concentration in wells No.1 and No.2 were observed in 2016 with Mean +SD 4. 06±0. 27 and 4. 23±0. 12, respectively (Tble.2 and 3). However, in the following years, the concentration of this metal has halved, which indicates that the water of this well in 2016 was probably contaminated by a source of pollutants containing As. The results of Mati, et al.(2016) study on the effect of leachate on surface and groundwater in Calcutta, India showed that the average concentration of As is below the acceptable standard of 100 µg/L for WHO [16]. Table 5 shows a negative relation between the concentration of As and Cd (Sig = -0.855). These results indicate antagonism between this metal. In groundwater containing mineral sulfide deposits and sediments from volcanic rocks, As levels may increase significantly [14]. Based on the results of correlation test in Table 5, it was observed that there is a negative significant correlation between As with Fe and Cd (P-valu<0.01). Also, this result show that, there is an antagonism relation between this metal.

Zn:

The average concentration of Zn during the five-year period in well No.1 and well No.2 was 98. 984±20. 38062 and 18. 1100±3. 24527 μg/L, respectively, and there was a significant difference between its concentration in two wells (P <0.05) (Tble. 4). This is the greatest average difference among the metals measured. Although the WHO standard for Zn is 200 μg/L and the concentration of Zn in any of the samples, whether upstream or downstream, has not reached this value (Tble.4), but the increase in downstream concentration may be due to the presence of Zn Found in landfill and spilled into groundwater . The findings of this study did not correspond to those of Akinbile et al. (2016) [17]. But that was consistent with Loizidou et al. (1993) research findings [18]. According to Table 5, which shows the correlation coefficient of heavy metals in the two wells, it is clear that there is a strong and significant correlation between Zn with Ni, Co, Pb and Cu (P-value<0.01). This correlation between Zn and Pb is negative. One of the main sources of Zn and Ni is plastics [19] and many plastics are buried in landfills without recycling [20].

Cr:

Based on the results of Table 2, it can be seen that the Mean +SD concentration of Cr in well No.1 is in a certain range in all years except in 2020(2. 15±0. 083). Also, based on the results of Table 4, it is observed that there is a significant difference between Cr concentrations in wells No.1 and 2 between different years (P-value<0.05). Based on the results, it can be seen that the average concentration of Cr in wells No.1 and 2 was 0. 8060 and .6920 μg/L, respectively (Table. 4). Also, the results of statistical analysis showed that there is no significant difference between the two wells No. 1 and 2 in terms of average Cr concentration (P-value>0.05). One of the reasons for the presence of chromium in the water sample at a distance of 100 meters from the Landfill site may be due to the slaughterhouse near the landfill site [14]. According result of table 5, there is positive relationship between Cr and Pb (P-value<0.01) and a negative correlation between Cr and Co (P-value<0.05).

Cd:

The average concentration of Cd in well No.1 and well No.2 is .4320±. 19058 μg/L (Table. 4). According to Table 4, there is no statistically significant difference between the Cd concentrations between the two wells (P-value>0.05). Electronic equipment and plastics are sources of cadmium in leachate and eventually in groundwater near landfills [19]. The WHO standard for Cd is 10 μg/L and among the measured metals, Cd has the lowest possible standard, which indicates the high toxicity of this metal. The results of De.S et al. (2017) research on the effect of leachate on groundwater showed that the concentration of Cd is very high [5]. So it does not agree with the results of this study. Also, based on Spearman correlation test (Table. 5), it is determined that there is a negative relationship between Cd with As (P-value<0.05).

Ni:

The highest average concentration of Ni in Well No.1 and Well No.2 related to 2019(27.39± 0.036) and 2018 (11.53 ± 0.27), respectively. The average concentration of Ni in well No.1 and in well No.2 was 22 .8120±5. 32272 and 8. 8200±1. 99561μg/L, respectively, and there is a statistically significant difference between the concentrations of this metal in the two wells (P-value<0.01) (Table. 4). According result of Table 4 There was a very high statistical difference between the concentration of

Ni between well No.1 and well No.2 ($P < 0.01$). Which may have been caused by the entry of nickel-containing contaminants into the downstream well. However, the World Health Organization has stated that the concentration of Ni in groundwater is usually no more than 50 micrograms per liter [14]. The main source of Ni in waste leachate is plastics [19]. Also, according to the Spearman correlation test (Table. 5), there is a strong and positive significant relationship between Ni and Zn ($P < 0.01$).

Co:

Cobalt is one of the important elements whose according Table 4 average concentrations between the two wells has a significant difference ($P < 0.05$). According to Table 4, the average five-year concentration of Co in well No.1 is 3. 5980±1. 82986µg/L and in well No.2 is only 0.422 ± 0.30037 µg/L, which is very small compared to well No.1. Also, according to Table 5, Co has a positive relationship with Zn and Ni ($P < 0.01$) and have a negative relationship with Fe and Cr ($P < 0.05$). Among these three metals, there is a strong and significant relationship with Pb and Cu, which shows that they have affected each other's concentration in well water.

Pb:

Pb is one of the metals that has a higher concentration in the upstream well (2. 5000±1. 02713) than the downstream well (1. 8500±1. 17992) (Table 4). The maximum acceptable amount of lead is 500 µg/L, more than which is unsafe for drinking. However, during five years, the concentration of these metals has not reached this amount and shows that water is not a problem in this regard (Table. 4). Contrary to the present study, Akinbile et al. (2011). Showed that the Pb concentration was higher than the standard defined by WHO [15]. According to the Spearman correlation test table (Table 5), there was a positive relationship between Pb metal and Cr and Cd ($P < 0.01$).. In the study of Maiti et al. (2016), There was a positive relationship between Pb and Cr and Cu [16]. Also, there is a negative relationship between Pb with Zn ($P < 0.05$) and Co ($P < 0.01$). Plastics, paints, paper and cardboard, and electronic compounds are sources of Pb in landfills [19]. The results obtained from the Taheri et al. (2017) show that Cu, Ni and Pb, unlike Zn, easily migrate to the end of the landfill [19]. However, the high concentration of Pb in the well above the landfill site (well No.2) probably indicates that the leachate does not penetrate into the groundwater around the landfill site.

Cu:

The average concentration of Cu in well No.1 and in well No.2 was 8. 0440±1. 89046 and 5.28 ± 0.6015 µg/L respectively (Table 4). The result of t-test shows that there is a significant difference between two wells ($P < 0.05$). Also, according to Table 5, there is a high positive relationship between Cu with Zn, Co, Ni ($P < 0.01$) and there is a negative relationship between Cu and Fe ($P < 0.05$). This high positive correlation indicates that their complexes are involved in concentration and transport in the groundwater of the region. The amount of Cu concentration measured by Gworek et al. (2016) In the study of heavy metal contamination from the landfill was consistent with the results of this study .The presence of heavy metals such as Zn, Cd and Pb may be from damaged batteries that may have been discharged and deposited in the waste disposal cell and reached the groundwater [6].

3.1. Source of heavy metals:

The results of the analysis of the main components are shown in Table 6. Based on the results of this test, it is observed that there are three main categories or components. Components 1, 2 and 3 make up 39.75, 25.36 and 2.97% of the total variance, respectively.

Table 6. Principal Component Analysis

Component	Initial Eigenvalues			Extraction Sums of Squared Loadings			Rotation Sums of Squared Loadings		
	Total	% of Variance	Cumulative %	Total	% of Variance	Cumulative %	Total	% of Variance	Cumulative %
1	3.876	43.068	43.068	3.876	43.068	43.068	3.578	39.752	39.752
2	2.121	23.565	66.634	2.121	23.565	66.634	2.283	25.366	65.118
3	1.752	19.464	86.098	1.752	19.464	86.098	1.888	20.979	86.098
4	.819	9.105	95.203						
5	.296	3.294	98.497						
6	.064	.706	99.202						
7	.054	.602	99.804						
8	.015	.161	99.965						
9	.003	.035	100.000						

Table 7 shows the results of Varimax rotation method. Based on the results of this method, it can be seen that zinc, cobalt, nickel and copper are in group 1, cadmium and arsenic are in group 2 and lead and iron are in all three groups. Chromium is only in the third group.

Table 7. Rotated Component Matrix[a]

metals	Component		
	1	2	3
Zn	.986		
Co	.914		
Ni	.895		
Cu	.782		
Cd		.957	
As		-.955	
Cr			.836
Pb	-.341	.415	.775
Fe	-.475	.354	-.550

Figure 2 shows the results of hierarchical clustering analysis. Based on the results of this diagram, it can be seen that in general, heavy metals are divided into two groups.

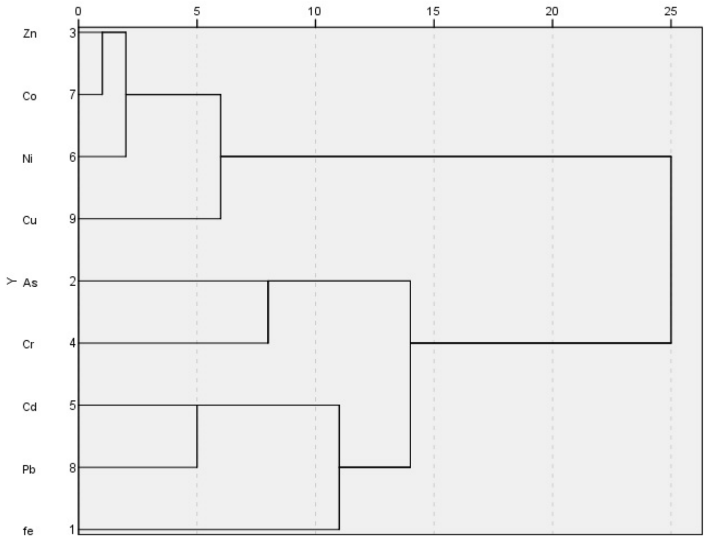

Figure 3. Results of Heavy Metal Cluster Analysis in Water Wells around Landfill, Shiraz

Based on the test results of the PCA analysis, it was found that in general, the three main categories fit the total variance. Based on the results of Warmix test, it was found that iron, cobalt, nickel and copper are in the first category, cadmium and arsenic are in the second category and chromium is in the third category. Lead and iron elements are present in all three categories, which indicates the widespread distribution of these two metals. Plastics are sources of emissions of zinc and nickel in the environment. Sources of zinc emissions also include the presence of batteries in the waste [19]. In general, the results of this analysis showed that due to the placement of these several elements in the first category, their emission sources are the same and mainly enter the stream of waste, leachate and finally groundwater from human sources. As and Cd are in two group that have common source with Fe and Pb. On the other hand, according to the positive and significant relationship between lead and cadmium (Table 4), it is indicated that this metal has a strong co-emission sources. Cr is also in the third category along with iron and lead, which due to the positive and significant relationship with Pb (Table 4), there is probably a lot in common about their sources of emissions. Slaughterhouses are among the sources of chromium emissions in the groundwater around landfills [14]. The results of cluster analysis also confirmed the results of principal components analysis. This means that based on the results of cluster analysis (Figur. 3), heavy metals in wells around Shiraz landfill were divided into two general groups, first group include Zn, Co, Ni and Co and second group include As, Cr, Ca, Pb and Fe. According result of figure 3, Pb and Cd are in the same group, which indicates the fact that the emission sources of the two metals are probably the same. The main sources for emission of Cd and Pb into the landfills are batteries, paintings, cardboard and electronic components. Zn and Ni are emitted into the; landfill by batteries and plastic [19].

Conclusion

The concentration of heavy metals in groundwater resources depends on several factors, including the type and amount of pesticides used the climatic conditions of the region, the level of aquifers and geology, etc. Also, because the movement of groundwater is very slow, it must take years after the onset of pollution to the water to be affected and contamination to appear in the well. In this study, the concentration of heavy metals in all samples was very low at five year monitoring and was less than the WHO standard. Although heavy metals are present in all samples, they will not cause any problems due to their concentration being lower than the standard [21]. Also results show that there is a significant correlation between metals that can be cause the synergism or antagonism effect. Also, the result shows that heavy metals can have a same emission source in the environment. So suggested that 4R strategy (reduce, reuse, recycle and recovery) be included in the agenda of the responsible organizations. Actually, this strategy involves actions and activities that ultimately lead to a reduction in the entry of waste into landfills. For example, if recycled and reused electronic devices or batteries as a source of heavy metals such as lead and cadmium, it can prevented from entering the this group of waste into the landfill and eventually entering the heavy metals into groundwater.

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