Assessment of Spatial Variation and Chemical Properties of Groundwater Near Municipal Solid Waste Landfill in Mashhad, Iran

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The place now used as the landfill in Mashhad (due to the increasing population and expanding city, the place used as the landfill is old) does not follow some of the environmental and socio-political standards and criteria. It makes problems include the location of the landfill site which is close to population centers where there is fertile agricultural land. As a result, there is danger of leachate leakage and pollution of groundwater and land. Therefore the area of landfill needs assessment and investigation during four seasons. With the purpose of evaluation the groundwater chemical properties in landfill of Mashhad, in northeast of Iran, groundwater samples including seven samples from wells and also one sample as evidence were taken. These samples were analyzed and studied in laboratories with ASTM method. The obtained results explained that some quantities of heavy metals elements were more than the permissible levels in water samples near the Mashhad landfill and it may be argued that samples are contaminated in relation to the heavy metals. Some indices that including the metal and heavy metal contamination index explained the water samples from wells contain heavy metal pollution. The methods were applied for water metal index to evaluate the groundwater correlation in study area for metal pollution through measured and comparison by the standard amount.

Key Words: Pollution, Groundwater, Mashhad landfill.

INTRODUCTION

Solid waste management is a widely discussed topic, including in developing countries that depend substantially on tourism as one of the main sources of income. In that context, this research investigates components of an integrated solid waste management approach in Mashhad (Iran), in their pursuit towards sustainable regional development that this research is focus on collection and transportation of solid waste as part of integrated solid waste management approach with environmental and economical issues to protect the Mashhad city as the second largest city for pilgrim (after Mecca) in the world and special situation because of high amount of population and industrial axis (after Tehran) in Iran. Leachate can pollute the groundwater if not collected and treated¹. Selection of the most appropriate method depends on local conditions. Methods for solid waste sanitary landfill differ according to geographical situation, level of ground water and amount of available soil for solid waste covering.

Most of the landfills in developing countries don't have machinery to collect leachate and monitoring systems. No monitoring is implemented in uncontrolled landfills and there is no survey on the risks of environmental and human health. The surface and ground water, soil, plants in area and air receive pollution from landfill leachate^{2,3}. Leachate organized a flow that is highly aggressive and dangerous to the environment, with a pollution exceeding that of several industrial-waste materials⁴. Johnbosco and Nnaji⁵ studied about land-use plan impact in Otmiri river to verify the environmental quality. Samples were taken from places nearest to landfill. The final results showed the values of some variables were over-passed the limitations of WHO standards. Olorunfemi *et al.*⁶ tested bio-monitoring of raw leachate from some urban waste dump sites, raw leachate was taken from three open dump sites.

The final results compare with the control. The physical and chemical characteristics demonstrated that the leachates were acidic and included toxic chemicals, presented in those

leachates were a threat for the environment and resident health in area without checked them. Emmanuel *et al.*⁷ studied the effects of pollution by bacteria in dump site. Sufficient treatment for dump site recommended decreasing health hazards. Ezekiel *et al.*⁸ searched the physical and chemical condition of Sombreiro river in Nigeria for a period of two years. The temperature value in river reported was normal, the salinity, biochemical oxygen and dissolved oxygen had clear sign of fresh water in the upper and middle of river. The mean biochemical oxygen demand value was showed that the water is not polluted. Charkhabi and Sakizadeh⁹ studied water parameters in 9 stations in all 4 continuous season on the Siahroud river. The result showed that total dissolved solid value in some parts is high. Amount of ammonium in downstream of site is high. Imoobe and Koye¹⁰ investigated impact of discharge of industrial plant on Eruvbi stream, water sample taken from 3 sample points were analyze after that parameters compared with limitation of federal environmental protection agency, amount of turbidity was more than allowable measure, amount of oxygen were the lower than minimum limits. Many elements effect on the compound of leachate such as types of waste, waste composition, the climatic condition and landfill age^{11,12}. Kumar and Alappat¹³ described leachate pollution index as a tool for quantifying pollution of landfill leachate in Hong Kong. Rezai *et al.*¹⁴ evaluated chemical pollution of groundwater (downstream) of landfill in Sanandaj, Iran. Five wells near to landfill were chosen, after six stages sampling monthly several parameters was measured. The results were compared with drinking and agricultural water standards. The result demonstrated the well's water were not suitable for drinking because amount of measured chemical parameters is high. Kumar and Allapat¹³ analyzed leachate pollution and formulated sub leachate contamination indices, the characteristics of UK's leachate is studied. The results showed that the organic parameter is more than the inorganic and heavy metals amount that can be beneficial for experts in decision making and management issues for treatment of leachate.

Produced leachates from landfill contain a number of contaminations and may have an environmental effect on the soil and surface water in area, Leachate may be very contaminated; therefore it has a risk to human health. Therefore, leachate management become a crucial issue in decision making process and needs strategy for development planning.

Kassenga and Mbuligwe¹⁵ stated the effects of solid waste disposal site on qualification of soil, river sediments, surface and groundwater in Tanzania. Sampling implemented in wet and dry season and physical, chemical and parameters such as Pb, Cd, Cr and Zn. The disposal site had found to be a P value significant ($p < 0.05$) contamination source to soil, ground and surface water in near that area. Effects of season also explained in research. Charles and Okoro¹⁶ investigated heavy metals and physico-chemical leachate characteristics of the various sites from dump site in Obehe and Ubakala, Port Harcourt. The test were related to pH, TDS, electric conductivity, COD, DO and elements of Fe, Zn, Cu, Mn, Cr, As, Cd, Pb. The results were found physico-chemical leachates characteristics to high and some acidic condition. Tay *et al.*¹⁷ determined trace metal level in water and sediment from the

Sakumo II and Muni lagoons and the Mamahuma and Gbagbla Ankonu feeder streams during one year. Moreover, temperature, pH and electrical conductivity of physical parameters had checked. The final results were described as potential sources of trace metal pollution to the Sakumo II lagoon and the Sakumo II lagoon could be explained more contaminated by trace load of metal.

EXPERIMENTAL

Study area: Mashhad is a provincial center in Khorasan Razavi and second metropolis in Iran. Mashhad is located at 36.20° latitude north and 59.35° longitude east, in the valley of the Kashaf river near Turkmenistan, between the two mountain ranges of Binalood and Hezar-masjed. The city benefits from the proximity of the mountains, having cool winters, pleasant springs, mild summers and beautiful autumns. It is divided into 4 districts, 14 villages and 660 hamlets and is considered as one of the biggest cities in Khorasan Razavi state.

In terms of its population, Mashhad has a population of nearly 3 million (2009) and an area of 29,000 hectares and it is also known for its industrial and agricultural productions. In addition, it is one of the largest religious cities in the world. According to Mashhad statistic center, more than 20 million tourists and pilgrims visit this city.

Investigating leachate of landfill and solid waste disposal in general seeking to improve environmental quality can boost the image of Mashhad, Iran towns as tourism destinations and the personal health of their residents. Significance of this research is that Mashhad is a tourism hub in Iran.

Methods: In order to scrutinize the quality of ground water supplies downstream of the Mashhad landfill, from seven wells available downstream of the current landfill solid waste site of Mashhad city, sampling was done from January 2010 to January 2011 (that is, sampling twice per week) at 8 am to 12 noon and all the samples were kept at a temperature of 4 °C (bacterial growth was low in this temperature). It is necessary to mention that because of limitation of facilities related to the test, selected elements have been measured in this study.

Due to the absence of surface water in the area during sampling, sampling was limited to regional groundwater. Seven samples of groundwater were collected. For sampling 250 mm polyethylene bottles with double caps were used. In the process of sampling the bottles were rinsed at least three times with the sample water. Steps were taken to ensure that the bottles were completely full to eliminate any air bubbles in the samples.

Acidity and electrical conductivity, temperature and sulphur hydrogen gases and carbon dioxide dissolved in water are measured in sampling site and how to measure these parameters is briefly explained. Amount of electrical conductivity (EC) for all water samples in sampling site¹⁸ with EC meter machine made by HACH. This measurement was done January 2010 - January 2011 during the four seasons in Iran. Accuracy of this machine for measuring electrical conductivity is equal to 1 µmhos/cm. Within less than 2000 µmhos and within more than 2000 µmhos is equal to 10 µmhos/cm. Amount of acidity or pH for all water samples and electrical

TABLE-1
SOME RESULTS OF AVERAGE SELECTED PARAMETERS OF GROUND WATER SAMPLES IN MASHHAD
JANUARY 2010 TO JANUARY 2011 (TWICE PER WEEK) BETWEEN 8 AM-12 NOON

Station	Coordinates	EC (μS/cm)	pH	Temp. (°C)	CO ₂ (mg/L)	H ₂ S (mg/L)	Distance from landfill site (m)
1	59°39/55'', 36°10/53''**	505	8.18	21	0.9	2.4	2500
2	59°40/54'', 36°10/40''	694	8.22	20.8	0.4	1.2	3700
3	59°41/57'', 36°10/11''	919	8.25	25/2	0.1	1.4	5450
4	59°43/2'', 36°10/41''	780	8.32	21.7	3.1	1.5	6500
5	59°42/10'', 36°12/1''	811	7.7	21.8	3.2	1.5	6000
6	59°38/38'', 36°17/6''	1585	7.19	19.8	5.2	16.2	-
7	59°36/56'', 36°19/12''	2020	7.35	20.1	5.7	14.5	-

*59°39/55'': Longitude, **36°10/53'': Latitude

Fig. 1. Map of Mashhad that clarify place of landfill Δ and wells number 1, 2, 3, 4, 5, 6 and 7, Source: Mashhad Municipality 2010

conductivity was done at the sampling site; using model pH meter machine HACH. This system's accuracy is equal to unit 0.1 for pH measurement¹⁹. Temperatures for all samples in sample sites were done with thermometer²⁰ and the two above parameters (electrical conductivity and acidity) simultaneously. This measurement with thermometer equipped EC meter was done at the water sampling site. Temperature measuring accuracy by this system was 0.1 °C based on Iranian Standard Institute (Institute of Standards and Industrial Research of Iran (ISRI)). To measure this parameter, 100 mL of pure water sample in 200 mL beaker was added with 5-6 drops of phenolphthalein solution and swirl the flask to mix and then determine this by carefully adding drops of 0.02 N NaOH, one at a time, swirling the water after each drop to ensure a complete reaction. Counting the number of drops of NaOH that is added. This action was continued until the water colour changed from colourless to light pink. A reading of the amount of sodium hydroxide used is taken at the moment the water changed colour. A relationship was then calculated according

to implemented tests for dissolved carbon dioxide in the water²¹ and used ASTM method for measuring the elements and heavy metals in laboratory.

Data analysis methods of SPSS, ANOVA, Pearson correlation matrix: If the most important purpose is investigate for fundamental aspects that are not directly clear in data groups, the factor analysis method is appropriate^{9,22}. The main purpose to apply factor analysis is to employ the calculated correlation matrix to recognize the minimum quantity of general parameters that the highest value give details or explanation for the correlation between the indicators (statistic). To realize a minor element arrangement that can be significantly explicated through the researcher, element rotation can be applied to recognize the majority probable aspects solution^{9,23}. Data was analyzed using Statistical Package for Social Science (SPSS 19.0 IBM) to assess for significance differences contained by the physico-chemical factors with one-way analysis of variance (ANOVA), where significant values ($P < 0.05$) were obtained, "A posteriori" Duncan Multiple Range Test; afterwards was related to all of means pairs to find out the variance location. Pearson's rank correlation was applied to create relations between elements in the study area of Mashhad city^{11,24}. Using UPGMA (Un-weighted Pair Grouping Method with Arithmetic-mean) software as clustering method to obtain clear shape to show all measured traits in condition of research²⁵ and Graph Pad Prism version 5 to obtain clear diagram related to SPSS parts.

Water metal index: With the purpose to evaluate the groundwater correlation in Mashhad considering metal pollution, the heavy elements concentrations were measured by the standard amount showed in Table-5.

The comparison of heavy elements concentrations with amount of maximum allowed concentration (MAC) standards, indicators for calculation the water pollution used. The index applied is named metal index (MI). The MI index at first was described by Tamasi and Cini²⁶. This index can be stated as the following equation²⁷:

$$MI = \sum_{i=1}^N \frac{C_i}{(MAC)_i}$$

where MI is the metal index, C is per factor concentration in water, MAC is the maximum allowed concentration (for per element) and the subscript i is the ith sample. The reported maximum metal concentration will compare with its relevant MAC significance. For, the worse water quality if the deter-

mined factor concentration is higher than the relevant MAC importance (for example $MI > 1$). Therefore the water cannot be used based on index.

RESULTS AND DISCUSSION

Analysis of elements characteristic in ground water of Mashhad: Mean values $\pm$ SE are from independent stations and values superscripted by different letters are significantly different by Duncan's multiple range tests ($p \leq 0.01$). The treatments were: [1] Control and [1]... [7] considered wells. Y axis shows dependent variable and X axis shows independent variables (water sampling stations).

Temperature (T): Ground water temperature in the studied area with the exception of the well no. 3 sample varies from about 19.8 to 21.8 °C. The small differences observed are related to the static level of depth and also measurement time. As for well no. 3, the water temperature is equal to 25.2 °C, despite the time difference related to the measuring and depth of water table, indicating the possibility that the water from this sample originated from another aquifer. Average temperature of all wells is between specified standard (20-30). There is no significant difference between wells except the well number 3.

Fig. 2. Average amount of temperature between wells in Mashhad landfill

Electrical conductivity (EC): The amount of electrical conductivity in the samples changed from 505 to 2020 $\mu\text{S}/\text{cm}$. The samples of well no. 1 to 5, respectively, are related to the deep available wells in the waterways downstream of the Mashhad landfill area. Their electrical conductivity from upstream to downstream waterways was shown to have increased, which is quite a natural phenomenon.

Channel water in travelling the distance from upstream to downstream, increases and adds to the ground water in the aquifer. The time the water stays in the aquifer allows for more material dissolution, causing the increase of soluble salts in the water, which has a direct relationship with the electrical conductivity of water.

For well no. 3, electrical conductivity average is 919.0092 $\mu\text{S}/\text{cm}$, as the water temperature of this well is different from the rest of the wells, probably to a different source of aquifer. Standard of electrical conductivity stated by WHO was 300 $\mu\text{m}/\text{cm}$. Electrical conductivity averages of all wells were

higher than standard amount; specially for well no. 6 and 7 well were higher than the other stations. And the all wells had significantly difference but the well number 4 and 5 had the similar condition.

Fig. 3. Average amount of electrical conductivity between wells in Mashhad landfill

Hydrogen sulphide: Table-2 showed that in all cases the hydrogen sulphide gas in varying amounts indicates ground water pollution by waste. Samples of well no. 6 and 7 show highest concentrations of hydrogen sulphide gas (average 15.6503 and 14.5147 mg/L) because of the wells being within the city and they expected impact from the adjacent sewage wells. The concentration of hydrogen sulphide gas in the rest of the wells, compared with samples of well no. 6 and 7 is considerably lower (because the wells are not affected by sewage wells). Sample from the well no. 1 showed higher hydrogen sulphide gas concentration than the others due probably to leachate leakage from the landfill, because this well is located adjacent to waterways that emanate from the landfill and in many cases inside that (the stream) leachate is outflow due to the waste; besides it is the well nearest the landfill. Fig. 4 shows the amount related to hydrogen sulphide (or sulphide) gas in different stations.

Amount of H_2S in well number 6 and 7 had significantly different with control well. The wells number of 2, 3, 4 and 5 had not significantly different ($P < 0.05$) and the well number 1 had no significantly different in 95 % level.

Fig. 4. Average amounts of H_2S between wells in Mashhad landfill

TABLE-2
AVERAGE CONCENTRATION OF SELECTED WATER QUALITY PARAMETERS COLLECTED (mg/L) OF GROUND WATER
SAMPLES IN MASHHAD JANUARY 2010 TO JANUARY 2011 (TWICE PER WEEK) BETWEEN 8 AM-12 NOON

Station		EC (μS/cm)	pH	Temp. (°C)	CO ₂ (mg/L)	H ₂ S (mg/L)	CO ₃ ²⁻ (mg/L)
0	Mean	580.6122	7.6858	20.1059	0.5034	2.0653	6.7143
	Standard deviation	3.55119	3.6831	3.49536	0.03552	0.34584	3.36139
1	Mean	505.0408	8.1816	21.0061	0.9005	2.401	5.0026
	Standard deviation	58.08418	1.20209	1.83071	0.38399	0.74936	1.09682
2	Mean	694.0082	8.2204	20.8	0.4031	1.202	5.0005
	Standard deviation	68.60147	6.7646	1.61437	0.18692	0.54678	1.07853
3	Mean	919.0092	8.25	25.001	0.2	1.401	10.0092
	Standard deviation	37.88956	0.63688	2.63167	0.12099	0.47678	1.21385
4	Mean	775.6439	8.2507	21.6391	3.4055	1.6717	9.8673
	Standard deviation	42.76036	2.49635	2.53001	1.76036	1.44967	2.7793
5	Mean	811.0265	7.7004	21.8703	3.8349	1.495	0.5007
	Standard deviation	28.51081	2.64945	2.59745	2.01759	0.30607	0.22962
6	Mean	1585.024	6.8981	20.1548	6.0982	15.6503	0.8021
	Standard deviation	710.6247	3.22835	3.15623	1.73039	2.32901	0.0325
7	Mean	2019.878	7.4716	20.7101	5.7481	14.5147	0.6047
	Standard deviation	3.57328	3.54618	3.40183	2.40785	2.78611	0.03414
Total	Mean	986.2802	7.8323	21.4109	2.6367	5.0501	4.8127
	Standard deviation	559.3623	3.50392	3.09701	2.69839	5.98781	4.05397
Station		HCO ₃ ⁻ (mg/L)	Cl ⁻ (mg/L)	SO ₄ ²⁻ (mg/L)	NO ₃ ⁻ (mg/L)	PO ₄ ³⁻ (mg/L)	Ca ²⁺ (mg/L)
0	Mean	179.7755	75.3571	97.7755	9.0612	0.051	30.1939
	Standard deviation	4.08803	3.70079	3.10812	3.62072	0.0261	3.38175
1	Mean	195.002	34.0092	65.002	9.6031	0.08	32
	Standard deviation	14.51263	3.51861	5.5004	1.32715	0.06788	6.09204
2	Mean	185.0051	68	110	17.601	0.18	44.0041
	Standard deviation	14.05985	8.35376	17.70353	4.03486	0.16164	5.69139
3	Mean	255.0041	110.0031	170.0071	16.802	0.4309	36.0265
	Standard deviation	212.7141	13.91194	21.81149	3.65048	0.25481	11.43311
4	Mean	218.3265	70.1327	121.5612	12.2876	0.3022	19.8665
	Standard deviation	2.2739	3.39386	3.55245	3.06104	0.0299	2.87005
5	Mean	240.051	73.0816	123.6224	12.694	0.2973	20.1837
	Standard deviation	3.43233	3.22578	3.22847	3.07539	0.03148	3.09421
6	Mean	349.7449	229.8367	164.7959	180.2143	0.2093	34.9898
	Standard deviation	2.86576	2.65817	3.62397	3.41389	0.02919	2.81928
7	Mean	342.3878	295.0408	207.1633	195.0816	0.3044	33.9286
	Standard deviation	3.21604	3.58093	4.53553	4.54229	0.03182	3.22442
Total	Mean	245.6621	119.4327	132.4909	56.6681	0.2319	31.3991
	Standard deviation	98.09523	86.59142	43.85673	75.89119	0.16295	9.39665
Station		Mg ²⁺ (mg/L)	Na ⁺ (mg/L)	TDS (mg/L)	Hardness (mg/L)	Alkalinity (mg/L)	
0	Mean	10.2755	99.5306	399.9082	119.6633	179.9388	
	Standard deviation	3.2988	3.5354	2.86136	3.21384	2.97001	
1	Mean	8.9082	98.8000	449	117.001	200.001	
	Standard deviation	1.69868	3.7144	13.48367	23.41285	28.2024	
2	Mean	12.0092	112.0031	651.1133	195.0041	190.0041	
	Standard deviation	2.4184	9.6253	676.8078	17.03463	31.96873	
3	Mean	7.0071	188.0010	793.0051	119.0031	265.0041	
	Standard deviation	1.57737	22.2856	21.32249	15.17004	19.70391	
4	Mean	10.0929	142.3540	603.1224	88.8776	228.0408	
	Standard deviation	2.5494	3.42710	2.99575	3.10392	3.23932	
5	Mean	10.1327	144.7878	623.9286	90.8367	239.8265	
	Standard deviation	3.05158	2.8557	3.00258	2.84911	3.26186	
6	Mean	48.3367	194.1970	1201.327	284.051	349.551	
	Standard deviation	3.1359	3.0788	2.60758	3.25029	5.53177	
7	Mean	56.0204	262.7074	1391.367	317.0102	341.602	
	Standard deviation	3.21716	3.71260	3.14721	3.63685	2.82383	
Total	Mean	20.3478	155.2976	764.0964	166.4309	249.246	
	Standard deviation	18.72945	53.9161	407.965	84.49536	63.64735	

TABLE-3
STANDARD PARAMETER IDENTIFY
BY WHO FOR LEACHATE

Parameter	WHO standards
pH	6.5-9.2 [*]
Temperature (°C)	20-30 ^a
Total dissolved solids (mg/L)	500 [*]
Electrical conductivity (μS/cm)	300 ⁺
Total hardness	50 ^a
Sulphate	200 [*]
Sodium	200 [*]
H ₂ S	NS ^c
HCO ₃ ⁻ , CO ₂	80-160 ^b
Cl ⁻	400 ^a
SO ₄ ²⁻	200 [*]
Nitrate (NO ₃ ⁻)	40 ^a
Phosphate (PO ₄ ³⁻)	5 ^a
Mg ²⁺	50 ^d
Hardness	300 [*]
Alkalinity as CaCO ₃	200-1000 ^b
Calcium	100 ^d

^{*}WHO 1997 (Ref. 28), ^aWHO 2003 (Ref. 29), ^bWHO 2006 (Ref. 30),
^c(Ref. 31), ^dNS = Not Stated, ^dWHO 2004 (Ref. 32).

CO₂: The amount of dissolved carbon dioxide in water was highly variable in the study area, showing range from about 0.2 to 6.09 mg/L. In samples 1 to 3 there is a low concentration of dissolved carbon dioxide because of the gas is consumed during the dissolution of calcium carbonate in the aquifer (ground water aquifer).

The samples well no. 4 to 7 are related to the wells located in areas an area that is under agriculture use. Here, because of relatively high carbon dioxide dissolved in the water of these wells, there is high carbon dioxide gas trapped in the soil (due to activities of microorganisms and plant roots) that cause rising concentrations of carbon dioxide in water from agricultural land that is returned to ground water from the aquifer. Wells of number 6 and 7 similar together and did not have significantly different between them and the wells number of 1, 2 and 3 had significant with control well. There is significant different between average amount of CO₂ between the control well and well no. 1, 2 and 3 with the 4 and 5 and also 6 and 7.

Fig. 5. Average amount of CO₂ between wells in Mashhad landfill

Magnesium concentrations in the studied waters vary from 7 to 56.02 mg/L and in well number 6 the average of Mg computed 48.3367. The magnesium standard concentration is measured by the amount of water sulphate, thus if the amount of sulphate is more than 250 mg/L, the amount of magnesium must be a maximum of 50 mg/L. The concentration of these cations based on the standard provided by the Institute of Standards & Industrial Research of Iran (ISIRI) 56 mg/L and the maximum allowable amount of that concentration is 50 mg/L. The importance of magnesium concentration is its effect on water hardness, so that the hardness of water is determined according to the concentration of calcium and magnesium ions. Average amount of magnesium in wells number of 6 and 7 were more than the other wells. And amount of this parameter in wells number 1, 2, 3, 4, 5 and control were according to standard. There is no significant different between well number 4 and 5 with the control one also.

Fig. 6. Average amount of Mg²⁺ between wells in Mashhad landfill

As seen in Table-2, sodium values varied between 98.8 and 262.7 mg/L. Sodium concentration in drinking water is usually less than 20 mg/L but in some areas it could exceed this amount. Currently, Health Guidelines have not provided for it but concentrations, above 200 mg/L, may give it an unacceptable taste. Of course, according to European assembly instructions from year 1984, the equivalent concentration of 20 mg/L is offered as a guide and reduces the maximum concentration from 150 to 175 mg/L. From the various samples 1, 2, 4 and 6 although these water resources are infected (by pollution) in terms of sodium. Meanwhile, it should be noted that the sodium is an effective component in agriculture. Sodium, because of two reasons is considered one of the most important parameters in irrigation water. (A) Impact on the physical properties of the soil and reducing the soil permeability and (B) another reason is the chemical impact on plants, high concentration causing the impairment, of the plant metabolism. The wells number 1 and control one have no significant different, number 4 and 5 also there is no significant different between them. Fig. 7 presents the related calculation of Na⁺ in Mashhad area. Average amount of sodium in wells number 6 and 7 were significantly different with standard and control well in level of 95 % according to statistical calculation.

Fig. 7. Average amount of Na⁺ between wells in Mashhad landfill

Calcium concentrations vary in the samples between 19.86 and 44.00 mg/L and according to the standards presented, there is no show of pollution (amount of standard is 100). Appropriate calcium range for drinking water varies between 70 and 200 (Ministry of Energy). Average amount of calcium did not have significantly different with standard. The amount of calcium in wells number 3, 6 and 7 were similar and wells number of 4 and 5 had the same condition each other.

Fig. 8. Average amount of Ca²⁺ between wells in Mashhad landfill

Nitrate concentration varies between 9.06 and 195.08 mg/L and nitrate is one of the important criteria for determining ground water pollution. Its high rate is harmful for humans and especially children. The concentration of NO₃⁻ in water should be less than 10 mg/L to be used as drinking water (Institute of Standards and Industrial Research). According to the Standards provided by the Institute of Standards and Industrial Research of Iran (ISIRI) in 2009, the maximum allowable amount of nitrate in drinking water is less than 45 mg/L nitrate ions and international standard is 40. As the chart shows, except for the first Sample, the other samples are higher than the allowed nitrate standard for drinking water. Average amount of nitrate in wells number of 6 and 7 were higher than the stated standard by WHO but the other wells were less than amount of standard; the observed contamination is very worrying because this well is exactly near agricultural product. Wells number of 1 had same condition with control well, the

wells number of 2 and 3 were the same condition and the wells number of 4 and 5 were similar together.

Fig. 9. Average amount of NO₃⁻ between wells in Mashhad landfill

According to Fig. 10 and Table-2, phosphate concentration average varies from 0.051 to 0.4309 mg/L. Phosphates, through domestic sewage are compound a detergent containing phosphate, from the agricultural sewage that passes through the land with inorganic fertilizer or through the industrial waste water and contaminates the surface water. Ground water has small amounts of phosphate unless they have been infected for some reason. According to the standard stipulated by the Institute of Standards and Industrial Research of Iran (ISIRI) in 2009, the allowable concentration of phosphate is between 0.1 and 0.2 mg and international standard is 5. Considering the source of PO₄³⁻ is in the groundwater in terms of non-contaminated geological formation and in studied practice there is no phosphate formation, so it can be concluded that ecneteixe of phosphate in the samples is probably due to the presence of the landfill is located upstream of these wells. Another possible reason could be the use of phosphate fertilizers on farms in the vicinity of the wells from which the samples were drawn. Average amount of phosphate in all the wells were the same level of standard. The well number of 1 was similar the control well, the wells number 4, 5 and 7 were similar each other and wells number 2 and 6 had the similar condition.

Fig. 10. Average amount of PO₄³⁻ between wells in Mashhad landfill

Concentrations of sulphate and chloride ions are not affected by geochemical processes, but can reduce the leachate effects on the affected water and also groundwater which has been affected by leachate. The standard extent³³ of these two ions are 250 mg/L for chloride and for sulfate 500 mg/L. Both of these ions are in accordance with the international standards. According to the standard provided by the Institute of Standards and Industrial Research of Iran (ISIRI) in 2009, sulphate (or sulfate) concentration could vary between 200 and 400 mg/L and chlorine concentration from 200 to 600 mg/L (average 400). Leachate effects can be reduced largely by transferring leachate from landfill to septic wells and/or by building a concrete floor of the landfill during its construction and creating holes to serve as leachate collection pools. The well number of 7 had different significant with standard for sulphate and higher than amount of standard. Average amount of chloride in wells number 6 and 7 were different significant with the other wells but all of the wells were less than standard amount.

Fig. 11. Average amount of SO₄²⁻ between wells in Mashhad landfill

Fig. 12. Average amount of Cl⁻ between wells in Mashhad landfill

The average amount of total dissolved solid (TDS) in control well was less than amount of standard, the well number 1 had the amount of standard (499.00) but all of the other wells were higher than the standard; especially wells number of 6 and 7.

Fig. 13. Average amounts of TDS between wells in Mashhad landfill

Average amount of hardness in wells number of 6 and 7 were higher than standard amount. For hardness parameter the wells number of 4 and 5 had similar together and the wells number of 1 and 3 similar to the control one.

Fig. 14. Average amounts of TDS between wells in Mashhad landfill

Pearson correlation related to elements characteristic in ground water, Mashhad: The relationship between physico-chemical parameters was examined using the Pearson's correlation. The correlation coefficient matrix for the water (wells) data in Mashhad is shown in Fig. 15. Strong correlations exist among pair elements of Na⁺ and H₂S ($r = 0.726$), Cl⁻ and H₂S ($r = 0.906$), NO₃⁻ and H₂S ($r = 0.961$), Mg²⁺ and H₂S ($r = 0.946$), SO₄²⁻ and Cl⁻ ($r = 0.853$), NO₃⁻ and Cl⁻ ($r = 0.965$), Mg²⁺ and Cl⁻ ($r = 0.949$), Na⁺ and Cl⁻ ($r = 0.899$), Na⁺ and SO₄²⁻ ($r = 0.928$), Mg²⁺ and NO₃⁻ ($r = 0.984$), Na⁺ and NO₃⁻ ($r = 0.808$), Na⁺ and Mg²⁺ ($r = 0.780$) with $P = 0.01$; also Mg²⁺ and PO₄³⁻, Na⁺ and Ca²⁺ with $P = 0.05$. Fig. 15 shows that the poor to negative correlation exists between some of the parameters. Negative correlation coefficient of (Na⁺, CO₃²⁻), (Mg²⁺, CO₃²⁻), (NO₃⁻, CO₃²⁻), (SO₄²⁻, CO₃²⁻), (H₂S, CO₃²⁻) and (Cl⁻, CO₃²⁻) are also significant in $P = 0.01$ level. Temperature (°C) exhibited a significant correlation with CO₂, H₂S, CO₃²⁻, Cl⁻, SO₄²⁻, NO₃⁻, PO₄³⁻, Mg²⁺ and Na⁺.

Conductivity is applied as a great quantity indicator for dissolved inorganic varieties or total concentration of ions³⁴. The EC correlated significantly with almost the elements.

	EC	pH	T(°C)	CO ₂	H ₂ S	CO ₃ ²⁻	HCO ₃ ⁻	Cl ⁻	SO ₄ ²⁻	NO ₃ ⁻	PO ₄ ³⁻	Ca ²⁺	Mg ²⁺	Na ⁺	TDS	Hardness	Alkalinity
EC μ S/cm	1																
pH	-0.064	1															
T(°C)	-.080*	0.001	1														
CO ₂ (mg/L)	.616**	-.093**	-.135**	1													
H ₂ S (mg/L)	.785**	-.093**	-.181**	.666**	1												
CO ₃ ²⁻ (mg/L)	-.461**	.074*	.224**	-.528**	-.571**	1											
HCO ₃ ⁻ (mg/L)	.541**	-0.07	0.023	.464**	.567**	-.329**	1										
Cl ⁻ (mg/L)	.881**	-.094**	-.096**	.650**	.906**	-.495**	.592**	1									
SO ₄ ²⁻ (mg/L)	.770**	-0.045	.119**	.504**	.646**	-.243**	.516**	.853**	1								
NO ₃ ⁻ (mg/L)	.856**	-.103**	-.169**	.697**	.961**	-.579**	.593**	.965**	.730**	1							
PO ₄ ³⁻ (mg/L)	.252**	0.02	.290**	.161**	0.048	.100**	.151**	.222**	.483**	.112**	1						
Ca ²⁺ (mg/L)	.132**	-0.012	-0.037	-.197**	.171**	-0.047	0.044	.196**	.123**	.204**	-0.065	1					
Mg ²⁺ (mg/L)	.841**	-.101**	-.206**	.696**	.946**	-.598**	.564**	.949**	.698**	.984**	.077*	.187**	1				
Na ⁺ (mg/L)	.827**	-0.059	.079*	.585**	.726**	-.333**	.568**	.899**	.928**	.808**	.463**	.090*	.780**	1			
TDS (mg/L)	.712**	-0.067	-0.047	.532**	.711**	-.393**	.495**	.786**	.717**	.766**	.277**	.177**	.745**	.750**	1		
Hardness(mg/L)	.777**	-.090*	-.201**	.528**	.875**	-.552**	.495**	.890**	.639**	.926**	0.027	.434**	.922**	.693**	.713**	1	
Alkalinity(mg/L)	.808**	-.090*	0.006	.680**	.837**	-.454**	.617**	.885**	.804**	.876**	.329**	0.056	.835**	.870**	.742**	.724**	1

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

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

Fig. 15. Correlation matrix for different physico-chemical parameters of groundwater samples, Mashhad

Fig. 16. Correlations between 17 characteristic for 7 wells. The strength and direction of the correlations among the different traits are indicated by the colour (red indicates positive correlations while green indicates negative correlations and the shading represents the strength of the correlation)

Fig. 17. Dendrogram generated by UPGMA clustering method of 7 stations. Of groundwater in Mashhad, based on all measured traits under leachate survey condition. Red colour refers to the high value of the studied traits while, green colour refers to the low value. The shading represents the strength of the trait, in which the bright colours have higher values than those shadows. The indicator box under the dendrogram demonstrates the number of accessions and the cutting point designates the number of clusters

Water metal index for Mashhad: The 1 value for MI is a warning threshold. The analyzed MI values are shown in a histogram (Figs. 6-33).

Findings of MI summarized in Table-5 and amount of them fluctuation between 0.080 and 2.56. The wells number 1,2 and control were under threshold line (less than 1) and also wells number 4 and 5 had the similar condition and near the threshold amount; but the wells number 6 (2.077) and 7 (2.569) were higher than the threshold amount that because of near to old landfill site.

TABLE-5 CALCULATED METAL INDEX (MI) FOR WATER SAMPLES IN MASHHAD				
Station	Ca ²⁺ (mg/L)	Mg ²⁺ (mg/L)	Na ⁺ (mg/L)	
MI 0	0.120776	0.205510	0.497653	0.823939
MI 1	0.128000	0.178164	0.494000	0.800164
MI 2	0.176016	0.240184	0.560016	0.976216
MI 3	0.144106	0.140142	0.940005	1.224253
MI 4	0.079466	0.201858	0.711770	0.993094
MI 5	0.080735	0.202654	0.723939	1.007328
MI 6	0.139959	0.966734	0.970985	2.077678
MI 7	0.135714	1.120408	1.313537	2.569659

Fig. 18. Calculated metal index for water samples in the study area (2010-2011)

TABLE-4
ANOVA WATER OF MASHHAD, JANUARY 2010 - JANUARY 2011

		Sum of Squares	df	Mean Square	F	Sig.
EC ($\mu\text{S/cm}$)	Between Groups	1.948E8	7	27832065.281	430.529	.000
	Within Groups	50165460.156	776	64646.212		
	Total	2.450E8	783			
pH	Between Groups	163.066	7	23.295	1.913	.065
	Within Groups	9450.189	776	12.178		
	Total	9613.255	783			
Temp ($^{\circ}\text{C}$)	Between Groups	1711.180	7	244.454	32.712	.000
	Within Groups	5798.933	776	7.473		
	Total	7510.113	783			
CO_2 (mg/L)	Between Groups	4133.753	7	590.536	292.348	.000
	Within Groups	1567.501	776	2.020		
	Total	5701.254	783			
H_2S (mg/L)	Between Groups	26464.405	7	3780.629	1823.161	.000
	Within Groups	1609.166	776	2.074		
	Total	28073.572	783			
CO_3^{2-} (mg/L)	Between Groups	10645.284	7	1520.755	530.849	.000
	Within Groups	2223.052	776	2.865		
	Total	12868.336	783			
HCO_3^- (mg/L)	Between Groups	3100899.055	7	442985.579	77.534	.000
	Within Groups	4433655.130	776	5713.473		
	Total	7534554.185	783			
Cl^- (mg/L)	Between Groups	5838864.506	7	834123.501	20146.896	.000
	Within Groups	32128.018	776	41.402		
	Total	5870992.524	783			
SO_4^{2-} (mg/L)	Between Groups	1420107.910	7	202872.559	1832.183	.000
	Within Groups	85924.355	776	110.727		
	Total	1506032.266	783			
NO_3^- (mg/L)	Between Groups	4500394.639	7	642913.520	53804.722	.000
	Within Groups	9272.437	776	11.949		
	Total	4509667.076	783			
PO_4^{3-} (mg/L)	Between Groups	11.082	7	1.583	126.534	.000
	Within Groups	9.709	776	.013		
	Total	20.791	783			
Ca^{2+} (mg/L)	Between Groups	45098.580	7	6442.654	207.984	.000
	Within Groups	24037.937	776	30.977		
	Total	69136.516	783			
Mg^{2+} (mg/L)	Between Groups	269034.547	7	38433.507	5292.059	.000
	Within Groups	5635.690	776	7.262		
	Total	274670.237	783			
Na^+ (mg/L)	Between Groups	2212242.477	7	316034.640	3837.968	.000
	Within Groups	63899.150	776	82.344		
	Total	2276141.627	783			
TDS (mg/L)	Between Groups	85820400.839	7	12260057.263	213.800	.000
	Within Groups	44498563.491	776	57343.510		
	Total	1.303E8	783			
Hardness (mg/L)	Between Groups	5481529.115	7	783075.588	5591.690	.000
	Within Groups	108673.158	776	140.043		
	Total	5590202.273	783			
Alkalinity (mg/L)	Between Groups	2951329.096	7	421618.442	1483.170	.000
	Within Groups	220592.332	776	284.268		
	Total	3171921.428	783			

Conclusion

Improper techniques of management for municipal solid waste caused hazards in aspects of natural environment and public health. Low performance and absence of experimental studies before schematization and weak teamwork are some factors that have affected management of solid waste. The other challenges are related to deficient system policy implementation financial limitation³⁵⁻³⁸.

The characteristics of leachate produced during the processing and disposal of waste in Mashhad show that leachate

produced from sources such as new waste, the compost heap and disposed waste have a very high degree of pollution. In that light, the concentration of measured parameters in the leachate produced in Mashhad is relatively higher compared to reported values in other countries. This issue is due to the different kinds of solid waste produced in various countries, the separation degree of waste types, waste disposal and processing technologies and methods. All these variables differ from one country to another country.

It is evident that downstream or groundwater of Mashhad landfill has been contaminated to some extent. The concentration of some elements was high when compared with standards of certain countries and WHO standards. There is no standard for soil in Iran and just for water in some area. According to Mashhad climatic and economical conditions, there are needs to set up standards and implement them in Mashhad.

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