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The impact of municipal waste disposal of heavy metals on environmental pollution: A case study for Tonekabon, Iran

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Abstract. Municipal solid waste disposal is considered as one of the most important risks for environmental contamination which necessitates the development of strategies to reduce destructive consequences on the ecosystem as related especially to heavy metal accumulation. This study investigates heavy metal (i.e., As, Cd, Co, Cr, Cu, Mn, Ni, Pb, Zn) accumulation in the Tonekabon region, NW of Iran that is related to city waste disposal and evaluates the environmental impact in the Caspian Sea coastal region. For this purpose, after performing field studies and collecting 50 soil specimens from 5 sites of the study area, geochemical tests (i.e., inductively coupled plasma mass spectrometry, atomic absorption spectroscopy and x-ray fluorescence) were conducted on the soil specimens collected from the 5 sites (named as Sites A1, A2, A3, A4 and A5) and the results were used to estimate the pollution indices (i.e., geo-accumulation index, normalized enrichment factor, contamination factor, and pollution load index). The obtained indices were utilized to assess the eco-toxicological risk level in the landfill site which indicated that the city has been severely contaminated by Cu, Mn, Ni, Pb and Zn. These levels have been developed along the stream towards the nearshore areas indicating uptake of soil degradation. The heavy metal contamination was classified to range from unpolluted to highly polluted, which indicated serious heavy metal pollution in the study area as related to municipal solid waste disposal in Tonekabon.

Keywords: environmental contamination; municipal waste; heavy metal; leachate; Tonekabon

1. Introduction

Solid waste (burial, surface discard, open dumps, landfills, sanitary landfills, incinerators, etc.) excretion is one of the main problems for urbanization in various countries. The final destination of all municipal solid wastes is through discarding by burial as waste-disposal or landfilling. The main concern of municipal solid waste disposal is leachate contamination which overshadows large areas (Azarafza *et al*. 2015, Azarafza and Asghari-Kaljahi 2016). The environmental impact

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produced by municipal solid waste disposal and leachate pollution has received special attention in recent decades which involves the earth, air and water supplies (Met *et al*. 2005, Akgün *et al*. 2015, 2017, Met and Akgün, 2015, Yal and Akgün 2013, 2014, Chen *et al*. 2016, Li *et al*. 2016, Wong *et al*. 2016). Researchers have conducted a number of studies about the environmental aspect of municipal solid wastes and leachate contamination all over the world (Calvo *et al*. 2005, European Commission 2012, 2017, Azarafza and Mokhtari 2013, Uyan 2014, Yuan *et al*. 2015, Ghazifard *et al*. 2016). This fact reflects the global challenge for the governments and civilizations to design engineered landfills (USEPA 2007). Although many advances have been made in the design of sanitary landfills and although regulatory programs have been established for the management of municipal solid waste disposal, in developing countries, the traditional burial path (i.e., open-dumping or unsanitary waste disposal) method, which is associated with high eco-toxicological risks is practiced. Open-dump sites are the dominant source for heavy metal contamination which is a serious threat for environmental pollution (Kanmani and Gandhimathi 2013). Unsanitary waste disposal promotes environmental pollution in a variety of ways, including surface expansion, leachate generation, uptake of soil degradation, deep slug penetrations (layered soils), etc., where leachate plays a much more effective role in spreading pollutants, which in cases of groundwater contamination, can reach several kilometers (El-Fadel *et al*. 1997). Leachate migration from open-dump sites by seepage to ground/surface waters transfers heavy metals and when combined with the human food chain (vegetation or animals), may cause the ‘pollution magnification’ phenomenon (Vasquez *et al*. 2013, Muller *et al*. 2015, Lenz *et al*. 2016, De Pauli *et al*. 2018). The most problematic heavy metals identified in municipal solid waste leachate can be classified as cadmium (Cd), chromium (Cr), copper (Cu), nickel (Ni), lead (Pb), and zinc (Zn) which are transportable in aquatic conditions (Kanmani and Gandhimathi 2013, Jaishankar *et al*. 2014, Fernandes *et al*. 2014) and hence, may lead to serious threats to ecosystems, human health and the environment since they are not biodegradable (Hong *et al*. 2002). Leachate is produced based on organic wastes (e.g., discarded food, plants, carrions, etc.), chemicals (e.g., detergents, hygienic, disinfectant, solvents, washing powders, etc.) where a high volume of domestic consumption is involved (Samuding 2009) under soil and waste layer pressures, temperature and microorganism activities. This production is essentially associated with precipitation/rainfall that permeates through the waste and soil layers which results in leachate migration and groundwater pollution. In the migration path, soil by absorbing pollutants attempts to trap and degrade materials so that the concentration of the pollutant decreases. With the continuous flow of leachate, the soil adsorption capacity is reduced leading to an increase in the contamination radius and a decrease in the defensive barrier capacity of the soil (Mandal and Sengupta 2006). Leachate, due to its migration continuously, pollutes the environment and may transport the heavy metals to fairly far distances. The main heavy metal sources in waste dumps are related to incinerator ashes, mine/industrial/hospital wastes, household hazardous substances (e.g., batteries, paints, sprays, dyes, cosmetics, inks, etc.) and disposed electronics (Kanmani and Gandhimathi 2013). However, by filling the soil capacity and reaching groundwater, the heavy metals expand much more than the soil, and the pollutant multiplies and is discharged into the environment (Wuana *et al*. 2016, 2017, Samadder *et al*. 2017, Riahi *et al*. 2017, Tameh *et al*. 2017).

This study investigates the heavy metal transfer around the municipal solid waste local dump area in Tonekabon city and traces the heavy metal migration to the Caspian Sea nearshore area. This study was conducted on samples collected from 5 different sites related to piezometric wells and sediments bored by farmers, the Regional Water Organization (RWO) and the ABFA bureau. The present study has sampled and examined 50 specimens for waste composition, heavy metal

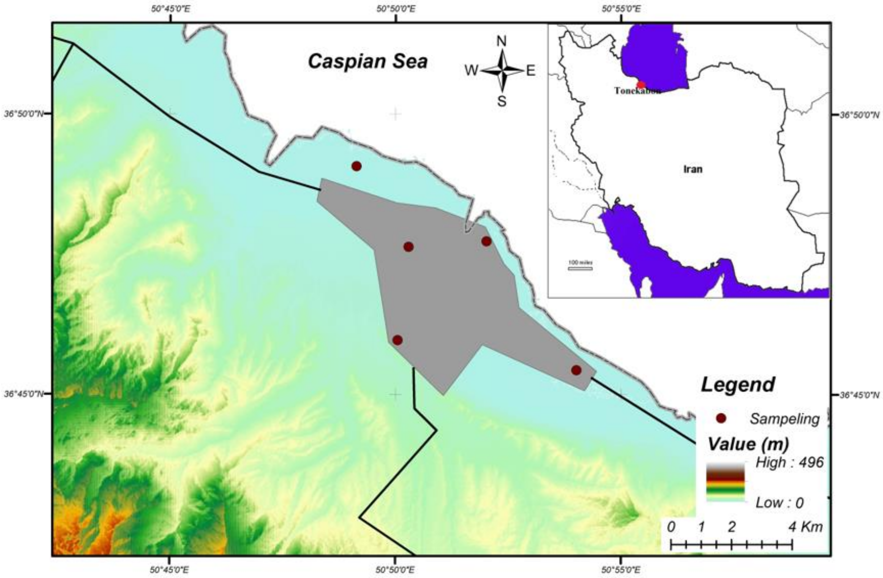

Fig. 1 Location map of the study area

content and concentration in the region. The heavy metal concentration was determined by Inductively Coupled Plasma mass spectrometry (ICP), Atomic Absorption Spectroscopy (AAS) and X-Ray Fluorescence (XRF).

2. Description of the study area

Tonekabon (formerly known as Shahsavar) is the capital city of the Tonekabon County which is located in the Mazandaran province, northern Iran. According to the 2016 census, the population of the Tonekabon County was 166,132, while that for the city was 55,434. The city is located on the southern coast of the Caspian Sea and the Cheshmeh-Kileh River cross of Tonekabon that discharges into the Caspian Sea. Tonekabon is the second largest municipality in western Mazandaran and the fifth populated city in the entire province. Climatologically, it has a moderate and humid climate in the north and cold weather in the south. The average recorded annual temperature in the city is 16℃; average annual rainfall is 1100-1500 mm and annual frost prevails approximately 20 day per year (Iran Meteorological Organization 2019). High rainfall as well as limited temperature variations, access to the main river and proximity to the shore has caused the rise of the groundwater level as close as to the ground level (in several locations the groundwater is about 1 m deep), which presents an increased risk of pollution (Azarafza and Ghazifard 2016). The geographical layout of the study area is shown in Fig. 1. In terms of the geological setting, the city and the county are established on Quaternary sediments and in the southwestern part of the region, Jurassic formations (Shemshak, Dalichai and Tiz-kuh formations) have been identified (Aghanabati 2007). Well-bedded gray to pale-gray limestones with shale, massive biothermal limestone with orbitoline volcanic based pyroclastic rocks, sandstones and cherts are the main geological units of the rocky outcrops (Darvishzadeh 2015). Fig. 2 presents the geological map of the study area. As seen in Fig. 2, the sedimentary deposits, minute elevation changes and plain

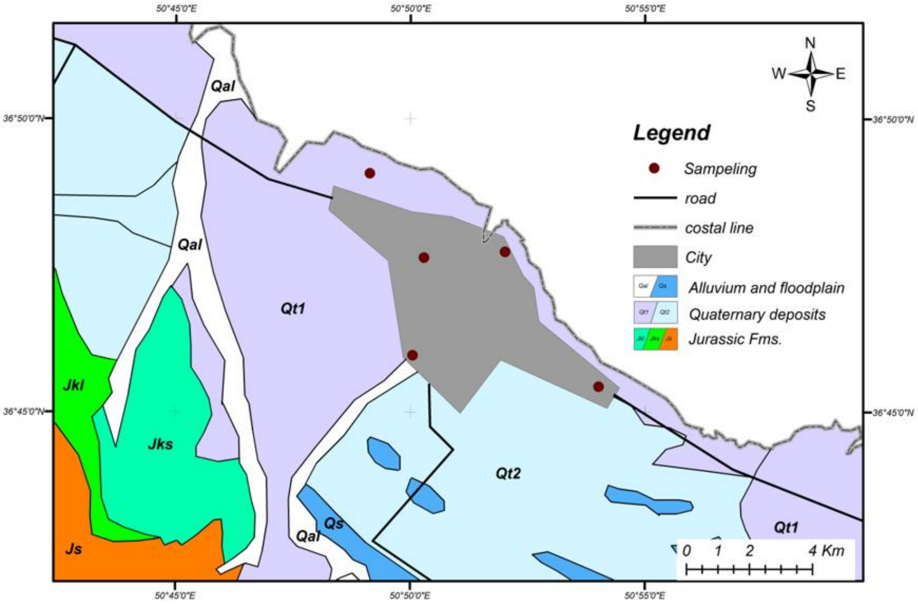

Fig. 2 Geological map of the Tonekabon region

fields are the most important advantages of the city for landfill site selection and construction (Ghazifard *et al*. 2016). On other hand, the high groundwater level is regarded as the biggest disadvantage. Unfortunately, the city does not possess a sanitary landfill and waste disposal is performed by discarding through traditional dumping. As far as the geology is concerned, Tonekabon is located on the coastal plain of the Caspian Sea which is covered by recent alluvium. Sedimentary and alluvial formations (including water network, drainage pattern and river basin in the study area) are considered as the most important geological formations that possess groundwater aquifers. Rainfall in almost all of the seasons along with severe climate change and humid weather conditions enhance surface and subsurface migration of pollutants.

In regards to the geotechnical aspects, the sediments in the study region are categorized as consolidated clayey soil which can be described as SM to CL based on the Unified Soil Classification System (USCS). But high groundwater level, the presence of suitable sediment layering along with flood-plain sediments (i.e., sandy gravel, sandy silt and gravely sand) that possess high permeability has led to the occurrence of pollution in the area at a higher rate. The soil plasticity properties are quite variable with unconfined compression strength (UCS) values ranging from 8 to 25 kPa. In general, the soil structure is durable and has good stability, but the most important issue in the pollution diffusion is related to high soil permeability as well as high water table.

3. Materials and methods

In environmental assessment, several computational indices are utilized based on contaminant element type, contamination intensity and emissions which are used to compare, evaluate, monitor and manage the environmental impact of the threat (Hakanson 1980). Evaluation of heavy metal concentration is commonly presented by various indices such as land geo-accumulation index, GI, normalized enrichment factor, EF, contamination factor, CF along with pollution load index, PLI (Liu *et al*. 2009, Mendil *et al*. 2010, Varol 2011). The GI (which in some cases is referred to as I_{geo}) is identified as the ratio of the concentration of the heavy metals to the geochemical background concentration which is presented by Eq. (1). GI is mainly categorized into seven classes, namely, 'class 0/GI^0' as unpolluted; 'class 1/GI^1' as unpolluted to moderately polluted; 'class 2/GI^2' as moderately polluted; 'class 3/GI^3' as moderately to heavily polluted; 'class 4/GI^4' as heavily polluted; 'class 5/GI^5' as heavily to extremely polluted; and 'class 6/GI^6' as extremely polluted (Bhuiyan *et al*. 2010, Varol 2011, Rashed *et al*. 2018).

$$GI = \frac{log_2[\,C_{metal}]}{1.5[C_{background}]} \tag{1}$$

The EF factor is generally used to evaluate the anthropogenic heavy metal pollution variation as presented by Eq. (2) (Sakan *et al*. 2009). Sakan *et al*. (2009) suggested that if EF is smaller than the critical state (< 1), then there is no enrichment; if EF is between 1 and 3, then there is minor enrichment; if EF is between 3 and 5 then there is moderate enrichment; if EF is 5-10 then there is moderately severe enrichment; if EF is 10-25 then there is severe enrichment; if EF is 25-50 then there is very severe enrichment; and if EF is > 50 then there is extremely severe enrichment (Morillo *et al*. 2002, Varol 2011).

$$EF = \frac{[C_{sample}]}{[C_{background}]} \tag{2}$$

The Contamination Factor (CF) represents the sample contamination rate for heavy metals which is represented as the amount of heavy metal that is measured relative to that in the nature and in the sample. Eq. (3) shows the CF relation as suggested by Hakanson (1980). The scholar states that CF < 1 represents low; 1 < CF < 3 represents moderate; 3 < CF < 6 represents considerable; and 6 < CF represents very high contamination (Varol 2011). In general, the mean concentration of each element in natural grassland is considered as the natural background concentration (Bhuiyan *et al*. 2010).

$$CF_{metal} = \frac{[C_{metal}]}{[C_{background}]} \tag{3}$$

The PLI, which is also referred to as the Tomlinson pollution load index is utilized to quantify the risk of infection and to obtain the potential heavy metal pollution. The advantage of PLI over other indices is that PLI estimates the entire metal contamination risk in the studied sites. According to Tomlinson *et al*. (1980), PLI is calculated with Eq. (4) which is determined as the nth root of the nth CF and classified in two classes. If PLI < 1, this situation represents no metal pollution and if PLI > 1, this situation represents metal pollution. It should be noted that, PLI = 1 is a critical situation and needs to be carefully investigated.

$$PLI = \sqrt[n]{CF_1 \times CF_2 \times CF_3 \cdots \times CF_n} \tag{4}$$

To identify contaminated areas or areas exposed to heavy metal pollution, distribution maps for contamination intensity and pollution indices have been prepared for the study area. In preparing such maps, various field studies and sampling have been performed. The 50 reagent samples were taken from the 5 sites (piezometric wells and marginal sediments) which were bored in the past by

Table 1 Locations of the sampling sites in the Tonekabon region

Sites	Coordinates	MASL	Description
A1	36º50'13.31"N – 50º50'21.61"E	4 m	A1 is located 281 m from Caspian Sea coastal line. Geologically, it is composed of recent alluvium. A1 represents the nearest location to the Tonekabon landfill.
A2	36º49'22.86"N – 50º51'28.36"E	5 m	A2 is located in the central city and is 977 m to the Caspian Sea coastal line, and 1.23 km to the city's main river. Geologically, it is composed of recent alluvium. A2 represents wastewater discharge containing heavy metal from machinery and human activity that is discharged into the river.
A3	36º49'4.06"N – 50º53'4.76"E	1 m	A3 is the nearest location to Caspian Sea in the city and is in the sandy coastal line.
A4	36º48'29.24"N – 50º51'30.83"E	4 m	A4 is located 400 m to the main river of the city and is the nearest location for the discharge of wastewater containing heavy metals from industrial activities in the city.
A5	36º47'51.82"N – 50º54'52.29"E	3 m	A5 is the located in the Azadi township in the city and is close to the Islamic Azad University. A5 is at a distance of 314 m to Caspian Sea coastal line.

farmers, RWO and ABFA. Due to the shallow groundwater level, surface samples could be extended to deeper sections. The collected samples were subjected to geochemical tests (i.e., ICP, AAS, XRF) and then synthesized. These tests aided to determine the concentration of the heavy metals where the results were evaluated with the aid of extrapolation performed in a GIS environment to obtain the pollution indices and the eco-toxicological risk maps. In addition, statistical analysis was used to extrapolate the results to the entire region.

4. Results and discussion

4.1 Geochemical tests

For the basic evaluation of heavy metal contamination, initially, a field survey and sampling was performed at the 5 different sites by recovering a total of 50 specimens. Table 1 illustrates the detailed location of the sampling sites. The recovered samples were exposed to ICP, AAS, XRF tests. ICP is a type of mass spectrometry that uses inductively coupled plasma to ionize the sample. It atomizes the sample and creates atomic and small polyatomic ions, which are then detected. It is known for its ability to detect metals and several non-metals in liquid samples at very low concentrations. It can detect different isotopes of the same element, which makes it a versatile tool in isotopic labeling (Jarvis 2012). AAS is a spectro-analytical procedure for the quantitative determination of chemical elements using the absorption of optical radiation (light) by free atoms in the gaseous state which is based on absorption of light by free metallic ions (Haswell 1991). XRF entails the emission of characteristic 'secondary' or fluorescent x-rays from a material that has been excited by being subjected to bombardment of high-energy x-rays or gamma rays which is widely used for elemental analysis and chemical analysis, particularly in the investigation of metals (Margui 2013).

Table 2 Statistical analyses results for heavy metal concentration at the five sites in the study area

Sites		Heavy metal concentration (mg/kg)								
		As	Cd	Co	Cr	Cu	Mn	Ni	Pb	Zn
A1	Max	21.2	3.9	187.9	78.3	896.8	1211.4	206.2	545.4	1457.6
	Min	3.3	1.1	41.6	36.5	208.2	376.6	87.3	129.1	277.1
	Mean	12.2	2.5	114.7	57.4	552.5	794.0	146.7	337.2	867.3
	S.D.	12.6	1.9	103.4	29.5	486.9	590.9	84.0	294.3	834.7
A2	Max	9.6	2.2	102.7	86.9	592.6	720.3	113.6	399.6	134.7
	Min	2.3	0.8	36.0	71.7	96.8	544.0	36.6	159.4	61.9
	Mean	5.9	1.5	69.3	79.3	344.7	632.1	75.1	279.5	98.3
	S.D.	5.1	0.9	47.1	10.7	350.5	124.6	54.4	169.8	51.4
A3	Max	8.8	3.0	39.7	97.4	238.6	540.2	104.4	259.4	168.8
	Min	3.7	1.6	22.5	30.3	61.0	174.2	29.1	56.5	14.5
	Mean	6.2	2.3	31.1	63.8	149.8	357.2	66.7	157.9	91.6
	S.D.	3.6	0.9	12.1	47.4	125.5	258.8	53.2	143.4	109.1
A4	Max	5.6	4.8	25.5	162.6	342.5	288.4	117.9	220.2	300.7
	Min	1.1	2.0	12.7	50.5	136.0	172.1	89.6	55.4	107.4
	Mean	3.3	3.4	19.1	106.5	239.2	230.2	103.7	137.8	204.0
	S.D.	3.1	1.9	9.0	79.2	146.0	82.2	20.0	116.5	136.6
A5	Max	6.0	1.2	14.1	189.7	282.8	244.7	173.0	191.2	349.6
	Min	3.3	0.3	7.7	25.9	111.7	89.1	102.3	63.2	21.5
	Mean	4.6	0.7	10.9	107.8	197.8	166.9	137.6	127.2	184.5
	S.D.	1.9	0.6	4.5	115.8	120.9	110.0	49.9	90.5	230.5

The statistical analyses performed on the results of the geochemical tests are presented in Table 2 which represents significant variations in the heavy metal concentrations at the sites. The heavy metal concentration variations were as follows: As, 21.2-1.1 mg/kg; Cd, 4.8-0.3 mg/kg; Co, 187.9-7.7 mg/kg; Cr, 189.7-25.9 mg/kg; Cu, 896.8-61.0 mg/kg; Mn, 1211.4-89.1 mg/kg; Ni, 206.2-29.1 mg/kg; Pb, 545.4-55.4 mg/kg and Zn, 1457.6-14.5 mg/kg. According to the results of the measurements, the highest recorded heavy metal concentrations were related to site A1 which is the nearest location to the Tonekabon landfill. The second location is the A4 site which is related to the industrial activities in the city. Due to the proximity of Site A1 to the city landfill, the heavy metals concentration is high which indicates leakage through the landfill. In addition, since A1 is only 281 m from the Caspian Sea coastal line, this most probably indicates that the pollution extends to the coastal environment. Table 3 presents the statistical assessment of the sediment physicochemical properties in the study area.

4.2 Contamination indices

In order to evaluate the contamination indices, the land Geo-accumulation Index (GI), normalized Enrichment Factor (EF), Contamination Factor (CF) and Pollution Load Index (PLI)

Table 3 Statistical evaluation of the sediment physicochemical properties in the Tonekabon region

Sediment	Parameter	Max	Min	Mean	S.D.
A1	pH	8.3	7.0	7.6	0.6
	Calcium carbonate (%)	58.4	12.1	35.2	23.1
	Organic compound (%)	4.4	0.1	2.2	2.1
	CEC (Cmol/kg)	159.5	2.9	81.2	78.3
	Coarse-grained (%)	26.4	7.8	17.1	9.3
	Fine-grained (%)	54.0	22.2	38.1	15.9
A2	pH	7.9	7.1	7.5	0.4
	Calcium carbonate (%)	43.0	9.9	26.4	16.5
	Organic compound (%)	7.3	1.2	4.2	3.0
	CEC (Cmol/kg)	133.2	17.1	75.1	58.0
	Coarse-grained (%)	43.7	33.8	38.7	4.9
	Fine-grained (%)	51.0	6.3	28.6	22.3
A3	pH	8.2	7.0	7.6	0.6
	Calcium carbonate (%)	75.3	1.6	38.4	36.8
	Organic compound (%)	5.9	0.8	3.3	2.5
	CEC (Cmol/kg)	179.4	23.9	101.6	77.7
	Coarse-grained (%)	22.9	7.0	14.9	7.9
	Fine-grained (%)	42.4	7.7	25.0	17.3
A4	pH	8.3	7.1	7.7	0.6
	Calcium carbonate (%)	36.7	7.3	22.0	14.7
	Organic compound (%)	3.6	0.1	1.8	1.7
	CEC (Cmol/kg)	167.2	36.6	101.9	65.3
	Coarse-grained (%)	74.6	7.6	41.1	33.5
	Fine-grained (%)	36.5	14.9	25.7	10.8
A5	pH	7.6	7.6	7.6	0.01
	Calcium carbonate (%)	52.2	3.7	27.9	24.2
	Organic compound (%)	4.4	0.3	2.3	2.0
	CEC (Cmol/kg)	122.5	9.4	65.9	56.5
	Coarse-grained (%)	51.5	11.2	31.3	20.1
	Fine-grained (%)	32.2	5.5	18.8	13.3

which are presented in Tables 4 to 6 were determined. According to Table 4 which was related to the CF and PLI indices, the highest CF for all metals was measured at the A1 site which receives municipal leachate discharge from the Tonekabon waste disposal open-dump site. The second highest value is related to the A4 site which receives metallic discharge from the Tonekabon industrial activities. The calculated CFs indicated that the Cu, Pb, Co and Zn concentrations were high at the A1 and A2 sites. Cd, Co, Cu and Zn concentrations were > 6 in Site A1 and Co, Cu and Zn concentrations were > 6 in Site A4 which denotes a fairly high contamination for these heavy metals. The As, Ni, Pb concentrations in Site A1 and Pb concentration in Site A4 varied from 3 to

Table 4 The CF and PLI indices for heavy metal measurements in the Tonekabon region

Sites	CF									PLI
	As	Cd	Co	Cr	Cu	Mn	Ni	Pb	Zn	
A1	3.75	2.39	9.22	1.79	21.12	1.11	3.27	5.68	7.69	1.56
A2	1.85	1.36	6.81	1.21	19.78	0.71	2.59	3.29	4.94	1.51
A3	1.25	1.19	5.79	1.38	13.70	0.98	2.63	3.45	5.52	1.48
A4	2.66	2.37	7.93	1.88	34.65	1.05	2.98	4.80	6.73	1.59
A5	1.07	1.14	4.45	1.65	12.67	0.66	2.25	3.19	4.12	1.46
Max	3.75	2.39	9.22	1.88	21.12	1.11	3.27	5.68	7.69	1.59
Min	1.07	1.14	4.45	1.21	12.67	0.66	2.25	3.19	4.12	1.48
Mean	2.41	1.76	6.83	1.54	16.89	0.88	2.76	4.43	5.90	1.53
S.D.	1.11	0.58	1.89	0.27	7.24	0.19	0.40	1.08	1.43	0.05

Table 5 The GI index for heavy metal measurements in the Tonekabon region

Sites	GIs								
	As	Cd	Co	Cr	Cu	Mn	Ni	Pb	Zn
A1	1.21	0.91	2.22	0.31	1.18	0.62	0.97	4.81	2.11
A2	-0.24	0.55	-1.73	-0.17	-0.25	-0.31	0.22	3.66	1.15
A3	0.33	0.34	-1.52	-0.20	-0.18	-0.15	0.25	2.74	0.86
A4	-0.76	-0.07	2.09	0.27	0.89	0.24	0.31	3.99	2.32
A5	0.43	0.80	-0.87	-0.04	-0.17	-0.23	0.27	2.65	0.38
Max	1.21	0.91	2.22	0.31	1.18	0.62	0.97	4.81	2.32
Min	-0.76	-0.07	-1.73	-0.20	-0.18	-0.23	0.22	2.65	0.38
Mean	0.22	0.42	0.24	0.05	0.50	0.19	0.59	3.73	1.35
S.D.	0.76	0.39	1.82	0.22	0.64	0.38	0.32	0.89	0.81

Table 6 The EF index for heavy metal measurements in the Tonekabon region

Sites	EFs								
	As	Cd	Co	Cr	Cu	Mn	Ni	Pb	Zn
A1	3.09	2.55	7.91	0.33	11.17	2.25	3.65	5.25	6.11
A2	2.81	2.11	2.45	0.27	4.53	5.13	2.88	4.63	6.52
A3	1.29	1.75	1.65	0.12	3.32	3.81	2.15	3.75	6.38
A4	2.51	2.58	4.25	-0.17	30.63	3.60	3.32	5.89	5.87
A5	1.12	1.63	1.40	-0.04	5.07	2.65	1.68	2.99	4.25
Max	3.09	2.58	7.91	0.33	30.63	5.13	3.65	5.89	6.52
Min	1.12	1.63	1.40	-0.17	3.32	2.65	1.68	2.99	4.25
Mean	2.10	2.10	4.65	0.08	16.97	3.89	2.66	4.44	5.38
S.D.	0.86	0.41	2.73	0.20	11.72	1.09	0.81	1.16	0.94

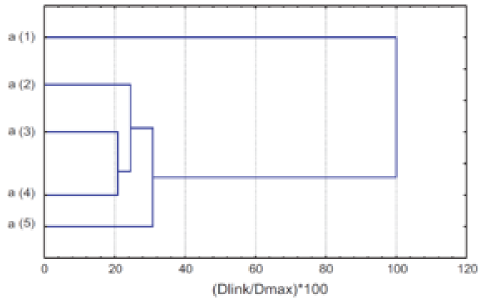

Fig. 3 Dendrogram for clustering the studied sites

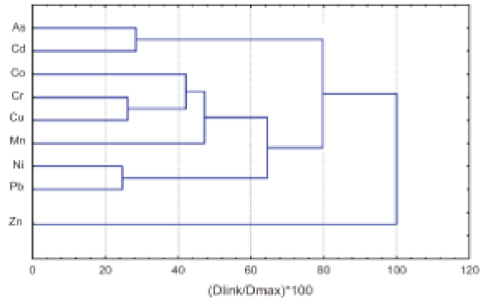

Fig. 4 Dendrogram for clustering the heavy metal contamination

6, which denotes considerable heavy metal contamination at these sites. On other hand, the PLI value ranged from 1.48 to 1.59; leading to a mean value of 1.53 for the entire sites. Tables 5 and 6 present the GI and EF results for metals studied at all sites in the Tonekabon region. The GI value for heavy metals in several sites was less than zero which indicates that these sites are not polluted by these metals. In several sites, the GI value was approaching 1, which indicates that these sites are unpolluted to moderately polluted. In the A1 and A4 sites, the GI index was highly variable and higher than the other sites which implied moderate to high pollution.

4.3 Eco-toxicological risk assessment

According to the environmental assessment results of heavy metal distribution conducted for the study area, the variation of Cu, Mn, Ni, Pb and Zn is high and the city is seriously contaminated. For the stream evaluation of pollution migration in the stream, the spatial variability analysis was applied to the study area's sediment quality data-set which is illustrated as dendrograms in Figs. 3 and 4. These figures were clustered by spatial variability analysis to group the analyzed parameters and sampling sites as $(D_{link}/D_{max}) \times 100 < 35$ and $(D_{link}/D_{max}) \times 100 < 80$, respectively. For establishing a relationship between the heavy metal contamination and sources, the Pearson correlation matrix of the heavy metals at all sites were prepared as presented in Table 7. Based on the estimated correlation of As, Cd, Cu and Zn with Pb, it was determined that Pb did not show significant correlation with Zn. Positive correlations were obtained with As ($R^2 = 0.354$), Cd ($R^2 = 0.549$), Co ($R^2 = 0.711$), Cr ($R^2 = 0.368$), Mn ($R^2 = 0.633$), Ni ($R^2 = 0.428$), and Zn ($R^2 = 0.307$) with Cu. In order to determine the heavy metal concentrations in the sediments, sediment samples that were recovered from the studied site were tested (A1 to A5) where Table 8 presents

Table 7 Pearson correlation matrix for the heavy metals in the entire study area

Element	As	Cd	Co	Cr	Cu	Mn	Ni	Pb	Zn
As	1	0.252	0.229	0.147	0.354	0.188	0.263	0.314	0.169
Cd	0.0252	1	0.422	0.362	0.549	0.258	0.220	0.178	0.131
Co	0.229	0.244	1	0.372	0.711	0.119	0.153	0.285	0.366
Cr	0.147	0.362	0.372	1	0.368	0.404	0.311	0.257	0.232
Cu	0.354	0.549	0.711	0.368	1	0.633	0.428	0.213	0.307
Mn	0.188	0.258	0.119	0.404	0.633	1	0.498	0.366	0.128
Ni	0.263	0.220	0.153	0.311	0.428	0.498	1	0.450	0.199
Pb	0.314	0.178	0.285	0.257	0.213	0.366	0.450	1	0.212
Zn	0.169	0.131	0.366	0.232	0.307	0.128	0.199	0.212	1

Table 8 Statistical analysis for heavy metals in the Tonekabon region

Element		As	Cd	Co	Cr	Cu	Mn	Ni	Pb	Zn
N	Valid	50	50	50	50	50	50	50	50	50
	Missing	1	1	1	1	1	1	1	1	1
Mean		15.31	69.07	19.36	69.50	17.17	25.11	18.02	27.96	73.51
S.D.		6.08	19.54	8.13	18.89	27.66	11.25	8.12	14.97	20.20
Variance		42.31	657.69	117.289	588.98	22.44	158.41	112.25	88.64	691.44
Range		33.00	25.00	42.00	17.00	29.00	14.00	25.00	33.00	35.00

Table 9 The maximum permissible heavy metal concentration for water quality (based on WHO, USEPA and EC guidelines)

Quality guidelines	As	Cd	Co	Cr	Cu	Mn	Ni	Pb	Zn
EC (1998)	0.01	0.005	0.05	2	0.2	0.05	-	0.01	0.1
WHO (2004)	0.01	0.003	0.05	2	-	0.4	0.07	0.01	-
USEPA (2009)	0.01	0.005	0.1	1.3	0.3	0.04	-	0.015	5
This work	0.03	0.017	0.09	1.525	0.354	0.278	0.103	0.014	0.169
Class	High	High	Low	Moderate	High	Moderate	High	Moderate	Moderate

the correlation for each heavy metal in the Tonekabon region. Hierarchical classification systems are the most common approaches to categorize heavy metal concentrations for water quality as presented by the U.S. Environmental Protection Agency, USAEP (2006, 2009), World Health Organization, WHO (2004) and the European Community, EC (1998). These classifications were used herein to provide the maximum permissible heavy metal concentrations in the studied area for water quality (Table 9). By considering the variations of the pollution indices, the potential risk to the environment was evaluated for each heavy metal in Tonekabon. As a result, As, Pb, Mn, and Zn provided more than 57% of the environmental risk-ability.

5. Conclusions

Environmental contamination is one of the main concerns in many countries which leads to the to development and application of a variety of operating instructions. This study investigated the heavy metal (i.e., As, Cd, Co, Cr, Cu, Mn, Ni, Pb, Zn) accumulation in the Tonekabon region as related to city waste disposal to evaluate the environmental impact on the Caspian Sea coastal area. For this purpose, after the field studies and sampling (i.e., 50 soil specimens were recovered from the 5 sites) were performed at the study area, geochemical tests were conducted on specimens (i.e., inductively coupled plasma mass spectrometry, atomic absorption spectroscopy and x-ray fluorescence) and the results were used to estimate the pollution indices (i.e., the geo-accumulation index, normalized enrichment factor, contamination factor, pollution load index). The obtained indices were utilized to prepare the eco-toxicological risk maps. According to the results of the study, the eco-toxicological risk level in the landfill site and the city was high due to serious contamination by Cu, Mn, Ni, Pb and Zn. These levels have been developed along the stream to the nearshore areas indicating uptake of soil degradation. The results represented a serious threat of heavy metal pollution in study area as related to municipal solid waste disposal in Tonekabon.

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