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Introduction

The improper management of solid waste is a significant challenge in developing countries.1 This issue has led to the intrusion of potentially hazardous materials into the environment and contamination of the ecosystem.1 The lack of a comprehensive source separation plan can exacerbate the severity of environmental contamination.² Considering sustainable development goals, waste disposal has become a vital part of integrated solid waste management.3 Landfilling is the most common method for the disposal of various solid wastes around the world, especially in Tehran, Iran.⁴ Tehran is the capital city of Iran, and Kahrizak landfill (Aradkouh) is the main site for the disposal of 8500 tons solid waste produced per day.⁵ In Kahrizak landfill, the collected solid waste is managed with four strategies, including materials recovery facility (MRF) station, composting plants, landfilling, and incineration.⁵ About 200 tons per day of the generated waste is incinerated, approximately 15% of solid waste is recycled, less than 10% was

Health and ecological risk assessment and simulation of heavy metal-contaminated soil of Tehran landfill[†]

Shahla Karimian, Sakine Shekoohiyan (20)* and Gholamreza Moussavi

The toxic effects of heavy metals in landfill soils have become a significant concern for human health. The present study aimed to estimate the health and ecological risk associated with soil heavy metal in Tehran landfill. A total of 48 soil samples were taken from the landfill and residential area and were analyzed using inductively coupled plasma-optical emission spectroscopy. The results showed the following order for heavy metal levels in landfill soil: Al > Fe > Mn > Zn > Cr > Cu > Pb > Ni > Co > As > Cd. The investigated ecological indices showed moderate to high heavy metal pollution. The principal component analysis revealed that the concentration of Pb, Cu, Zn, Cr, and Ni in the investigated soil was mainly affected by anthropogenic activities. Although the hazard index (HI) value in children was 6.5 times greater than that of adults, this value for both landfill workers and residents of the target area was at a safe level (HI \leq 1). In the residential area, the Incremental Lifetime Cancer Risk (ILCR) value of adults (1.4×10^{-4}) was greater than children ILCR value (1.2×10^{-4}) . Monte Carlo simulation and sensitivity analysis showed input variables such as exposure duration, exposure frequency, Ni concentration, soil ingestion rate, and As concentration have a positive effect on ILCR of 41.3, 24.3, 9.4, 9.0, and 2.9% in children, respectively. These results indicate that the landfill soil and the adjacent residential area are affected by heavy metal contamination and that the current solid waste management policies need to be revised

composted, and finally, the residual components were landfilled. 5

Inefficient solid waste management, the lack of obligatory laws, and un-engineered landfills could worsen the diverse health and environmental problems.6 Leachate and air emissions are the major landfilling products and contain complex nature and highly polluted organic wastewater that damage the living organisms.7 Heavy metal pollution is a major issue in landfill sites. According to the literature review, anthropogenic activities such as waste disposal, pesticides and agricultural activities, domestic emission, burning, waste incineration, vehicle exhaust, and mining are the main sources of heavy metal pollution.8 Electronic wastes (e-wastes) are the main components of solid wastes that contain a high concentration of metals and are detected around informal e-waste recycling sites.9 Heavy metals are non-biodegradable, and10 can accumulate in the human body through ingestion, inhalation, and dermal contact exposures.6,7 The bioaccumulation of heavy metals in organic tissues disrupts the nervous system functions, cardiovascular and endocrine systems, immune systems, etc.¹¹⁻¹³ Also, depending on the heavy metal concentrations, route of exposure, and receptor sensitivity, adverse health effects ranging from acute to chronic reactions could be observed in human beings.14

Department of Environmental Health Engineering, Faculty of Medical Sciences, Tarbiat Modares University, Tehran, Iran. E-mail: s.shekoohiyan@modares.ac.ir; Fax: +98-21-82884580; Tel: +98-21-82884865

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Paper

Due to the complicated interactions of heavy metals with the environment, investigation of soil pollution in landfill has turned into an essential need. Vaverková *et al.*¹⁵ and Adelopo *et al.*¹⁶ indicated that non-engineered landfills can increase the level of metals in soil, air, and groundwater. Therefore, a continuous monitoring of landfill environment is necessary. Besides, Krčmar *et al.*¹⁷ indicated that living in the vicinity of a polluted site could have adverse health effects on the residents through the inhalation of emitted substances, consumption of contaminated products, and ingestion of polluted water and soil. For these reasons, it is essential to continuously evaluate and monitor the affected media.

Health and ecological risk assessment is an appropriate tool for assessing and quantifying the probable adverse effects of different pollutants on human health and environment.^{17,18} Calculating the risk value can help policymakers perform strategies to mitigate adverse health effects through removing the source of pollution, eliminating receptors, and disconnecting the relation between a pollution source and receptor.¹⁷ Landfill workers and the neighboring residents are highly exposed to pollutants through different exposure routes from the soil, water, and air near the solid waste dump.¹⁴ Therefore, to run an effective program for a further control of human health risk, a comprehensive health and ecological risk assessment in Kahrizak soil is needed.

The expansion of Tehran metropolis moved people closer to Kahrizak landfill. People living in this area are usually from lowincome families who pay less attention to preventive health measures. In addition, landfill workers are more exposed to environmental pollution because they are living in the landfill site. However, to the best knowledge of the present authors, there is no documented evidence of how landfills affect soil pollution by heavy metals in the residential area. For these reasons and the lack of any comprehensive study, we decided to conduct this research and estimate the health and ecological risks related to this pollution. This study aimed firstly to determine the concentration of heavy metals including arsenic (As), chromium (Cr), cadmium (Cd), copper (Cu), nickel (Ni), lead (Pb), cobalt (Co), zinc (Zn), magnesium (Mn), aluminum (Al), and iron (Fe) at 11 landfill soil sampling points and the center of the residential area attached to this site in four seasons. Secondly, it aimed to investigate the non-carcinogenic and carcinogenic health risks of heavy metals through different exposure routes for male adult landfill workers and inhabitants of the residential area. Thirdly, it aimed to show the spatial distribution of different heavy metals in the landfill using Geographic Information System (GIS). And finally, it aimed to simulate the hazard index (HI) and carcinogenic risk (CR) values using Monte Carlo simulation model.

Material and method

Study area and sampling point selection

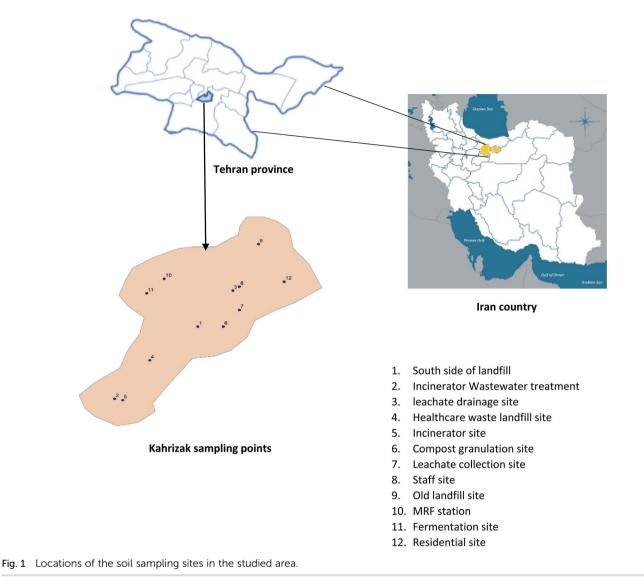
The studied area was located in the south of Tehran, Iran $(35^{\circ}27'52''N \text{ and } 51^{\circ}19'18''E)$. Kahrizak landfill accepts the wastes coming from 22 districts of Tehran and also from special centers such as hospitals and institutions. The produced wastes

in Tehran were processed in several units, including recycling, composting, incinerating, and landfilling. This center is the biggest recycling and processing facility in the Middle East. It has been operating for more than 40 years as the final destination of Tehran's municipal wastes. This center area is about 1400 ha, and admits around 8500 tons of solid wastes enters daily to this location.¹⁸ The predominant direction of wind is west to east, and the maximum, minimum, and average annual temperatures are 40 °C, -5 °C, and 17 °C, respectively. This studied area is located in an arid climate with an average annual precipitation of 250 mm and average relative humidity of 51%. The soil texture in Kahrizak is fine clayey with more than 17% of clay and 43% of slit. Due to the population growth, Kahrizak is surrounded by residential areas and industrial factories.

Entering the Kahrizak landfill for sampling required a license, and after several correspondences with the Tehran waste management organization, a sampling license was issued. After that, the sampling points were selected based on two criteria: places where laborers are working and places they used for living in the Kahrizak vicinity. In addition, the center of a residential area attached to the landfill was selected to investigate the effect of the landfill on resident health. Fig. 1 shows the location of this landfill on the Iran map and the soil sampling points. The selected points were (1) an active landfill; (2) an incinerator wastewater treatment plant; (3) a leachate drainage site; (4) a healthcare waste landfill site; (5) an incineration site; (6) a compost granulation site; (7) a leachate collection site; (8) a landfill worker's residence site; (9) a closed landfill site; (10) an MRF station; (11) a fermentation site and; (12) the center of a residential area near the landfill. In addition to the importance of the main sampling points, the determination of background heavy metals concentrations in investigated soil is challenging but necessary for calculating ecological risk indices. Therefore, the correct selection of background sampling points is essential. We chose 10 background sampling points based on wind direction (from west to east) and consultation with geologists who worked in the Kahrizak landfill. The selected points were located upstream and upwind of the landfill's elevated points and were far away from industrial areas and vehicle traffic. The distance of background locations from the active landfill was approximately 1000 m. For obtaining the natural local background concentration of heavy metals, the soil samples were collected from 100 cm below ground level.^{19,20} Ten samples of 4 sub-samples were randomly collected within a 1 m \times 1 m grid and analyzed for background heavy metal concentrations.

Soil sample collection and preparation

Due to the budget limitation, a total number of 48 soil samples were collected from 0–20 cm depth of the sampling points from September 2018 to September 2019. Soil samples were obtained using a stainless steel auger and collected in the middle of each season with a mixture of 5 subsamples. The composite soil samples were sealed in polyvinyl chloride (PVC) bags and then transferred to Tarbiat Modares University laboratory for physical and chemical analysis. The soil sample preparation steps



included air-drying at room temperature for a week, removing the stones and bulky debris by hand, grounding by a grinder, and passing through a 0.15 mm sieve. In order to remove soil humidity, the prepared samples were dried in the oven overnight and then kept in the desiccator. The prepared soil sample was digested using acids for the determination of heavy metal levels.

Chemical analysis

For soil heavy metal determination, 0.5 g of the pretreated soil samples was placed in Teflon test tubes and digested for 4 h at 220 °C using concentrated acids $(3:3:1 (v/v/v) \text{ of } HNO_3-HClO_4-HCl)$ mixtures.²¹ After cooling, the digested solution was filtered using Whatman 42 filter paper, and the final volume reached 50 mL with 1% of HNO_3 before analysis. Finally, the concentration of heavy metals, including As, Cr, Cd, Cu, Ni, Pb, Co, Zn, Mn, Al, and Fe was determined by the ICP-OES (Varian 735 model, USA). The nitrate salt of metals was used to prepare stock solutions. For metal decontamination, all glassware and plastic containers were soaked in 20% (v/v) of HNO₃ and were

washed with tap water, and rinsed with deionized water three times.

The detection limit values for As, Cr, Cd, Cu, Ni, Pb, Co, Zn, Mn, Al, and Fe were 0.5, 1, 0.1, 1, 1, 1, 1, 1, 5, 100, and 100 mg L^{-1} , respectively. The national standard soil sample was employed in each set of samples to validate the analytical procedure. The recovery rates of the national standard soil samples ranged between 87 and 101% for Cr, 89–107% for Pb, 92–108% for Cu, 97–102% for Ni, 86–105% for Zn, 95–103% for Cd, 87–102% for Al, 93–103% for Mn, 96–105% for As, and 89– 102% for Fe, respectively. Soil pH and electrical conductivity (EC) were measured immediately, and to this aim, the soil was mixed with deionized water (1 : 2.5 w/v), and pH and EC were determined in this mixture three replicates using Jenway pHmeter (3540) and conductivity-meter (Jenway, 4510), respectively.

Soil pollution assessment

For heavy metal pollution assessment in soils and sediments, different indices have been introduced such as Enrichment

Factor (EF) and Ecological Risk Index (ERI).²² These indices help provide a qualitative threshold on the ecological risk evaluation of each heavy metal.

Enrichment factor

EF is a sign of a possible source of an anthropogenic effect on heavy metal pollution. EF is measured by comparing the concentration of heavy metals in samples with a reference metal. Elements such as Al, Fe, and Mn are generally selected as a reference element for EF calculation, and Al was used as the reference metal.²³ EF was calculated *via* eqn (1).

$$EF = \frac{\left(\frac{C_{i}}{C_{ref}}\right)_{sample}}{\left(\frac{B_{i}}{B_{ref}}\right)_{background}}$$
(1)

where C_{ref} is the concentration of the reference element, B_{ref} is the background value of the soil's reference element.²³ EF values classification as follows;

- $EF \le 1 = no$ enrichment.
- $1 \le EF \le 2 = slight enrichment.$
- $2 \le EF \le 5 = moderate enrichment.$
- $5 \le EF \le 20 = significant enrichment.$

Individual and total ecological risk index

Hakanson (1980) proposed this concept to determine the ERI of heavy metals in sediment.²⁴ ERI evaluates the potential risk of heavy metals to organisms using a combination of heavy metal concentrations with their toxicological effects.²³ ERI is the sum of individual potential risk factors (E_r^i) in soils and is calculated *via* eqn (2) and (3):

$$E_{\rm r}^{\rm i} = T_{\rm r}^{\rm i} \times \frac{C_{\rm i}}{B_{\rm i}} \tag{2}$$

$$ERI = \sum_{i=1}^{n} E_{r}^{i}$$
(3)

where T_r^i represents the toxic response factor of each heavy metal and the values are As = 10, Cr = 2, Cd = 30, Cu = 5, Ni = 5, Pb = 5, Co = 2, Zn = 1 and Mn = 1. Hakanson²⁴ classified E_r^i and ERI values to determine the severity of ecological risk as follows:

• $E_r^i < 40$ and ERI < 150 represents low ecological risk.

• $40 \le E_r^i < 80$ and $150 \le ERI < 300$ represents moderate ecological risk.

• $80 \le E_r^i < 160$ and $300 \le ERI < 600$ represents strong ecological risk.

• $160 \le E_r^i < 320$ and ERI > 600 represents quite strong ecological risk.

• $E_{\rm r}^{\rm i} \ge 320$ represents an extremely strong ecological risk.

Health risk assessment

USEPA proposed a method for calculating non-carcinogenic and carcinogenic risks after chemical exposure. Three main factors in the dose-response model include the source of pollution, exposure route, and receptors.³ In this study, landfill soil heavy metals can affect landfill workers and residents through main pathways such as (i) direct soil ingestion, (ii) inhalation of dust particles through mouth and nose, and (iii) dermal absorption.²⁵ The Average Daily Doses (ADDs) as (mg per kg per day) from each exposure route should be determined through USEPA guidelines.²⁶ Direct soil ingestion (ADD_{ing-soil}), inhalation of soil particles (ADD_{inh}), and dermal absorption (ADD_{der}) for landfill adult male workers and adults and children in the residential area were calculated *via* eqn (4)–(6).

$$ADD_{ing-soil} = \left(\frac{C_{soil} \times IngR_{soil} \times EF \times ED \times CF}{BW \times AT}\right)$$
(4)

$$ADD_{inh} = \left(\frac{C_{soil} \times InhR \times EF \times ED}{BW \times AT \times PEF}\right)$$
(5)

$$ADD_{der} = \left(\frac{C_{soil} \times AF_{soil} \times SA \times ABS \times EF \times ED \times CF}{BW \times AT}\right) (6)$$

 C_{soil} is the heavy metal concentration in soil (mg kg⁻¹), IngR_{soil} is soil ingestion rate (mg per day), EF is exposure frequency (day per year), ED is the exposure duration (year), CF is conversion factor (kg mg⁻¹), BW is the average body weight (kg). Based on USEPA guideline, the mean body weight for children aged 1 to 6 was set as 15 kg,²⁷ AT is the average time (day), AF_{soil} is the skin adherence factor (mg per cm per day), SA is the exposed skin area (cm²), ABS is the dermal absorption factor (unitless), InhR is the inhalation rate (m³ per day), and PEF is the particle emission factor (m³ kg⁻¹). The values of the factors are presented in Table S1 (ESI file†). Lack of local data on exposure was one of the main limitations in our study. For solving this problem, USEPA exposure values and probability distributions were used for risk calculation and simulation.

To determine the non-carcinogenic risk or the hazard quotient (HQ) in eqn (7) and (8), ADDs is divided by the reference dose (RfD) in mg per kg per day. If there were multiple substances or exposure routes, hazard index (HI) was calculated which refers to the "sum of more than one HQ." According to the HQ or HI values, if HQ or HI \leq 1, there is no adverse human health effect, and if HQ or HI \geq 1, there is a potential noncarcinogenic risk.26 Based on the International Agency for Research on Cancer (IARC),²⁸ heavy metals such as As, Cd, Pb, Ni, and Cr are considered to have a carcinogenic effect. To estimate carcinogenic risk (CR_i) for each heavy metal or incremental lifetime cancer risk (ILCR) in eqn (9) and (10), ADDs is multiplied by the cancer slope factor (SF) in (kg day per mg). According to the USEPA²⁵ guideline, there is a negligible carcinogenic risk if CR_i or ILCR is lower than $1\times 10^{-6},$ harmful to human health if CR_i or ILCR above 1 \times 10^{-4} and there is a tolerable or acceptable carcinogenic risk if $1 \times 10^{-4} \leq CR_i$ or ILCR $\leq 1 \times 10^{-6}$. The values for SF and RfD are listed in Table S2.†

$$HQ = \frac{ADD}{RfD}$$
(7)

$$CR_i = ADD_i \times SF$$
 (9)

$$ILCR = \sum_{1}^{i} CR_{i}$$
(10)

Probabilistic health risk assessment

Monte Carlo simulation is a modeling methods used extensively for probabilistic risk assessment²⁹ and was done using Crystal ball software (version 11). This model can produce a statistical random variable from any input variable that is a point value. In Monte Carlo simulation, ILCR and HI risks are calculated several times with different random values of all inputs. Therefore, the output risk has a range of values instead of a single value. In order to ensure numerical stability, 10 000 iterations were considered. Table S1[†] shows the input values used in Monte Carlo simulation. In order to determine the effect of input variables on HI and ILCR values, a sensitivity analysis was done. The type of distribution of each variable was obtained from credible works of research and presented in Table S1.†

Statistical analysis

The results for heavy metals were presented as the mean \pm SD (standard deviation) from duplicate determinations. The normality of heavy metal in different sampling points and seasons was checked using Shapiro-Wilk and Kolmogorov-Smirnov tests in SPSS 24 software. Similarity and heavy metal concentration trends in different sampling points and seasons were measured using Mann-Whitney and Kruskal-Wallis tests. In statistical analysis, a *p*-value lower than (<0.05) was set as the significance level. In order to understand the sources of heavy metals in soils, correlation analysis was done using Pearson's correlation coefficients. Principal component analysis (PCA) was used to identify the source of soil metals. Pearson's correlation coefficients and PCA were run with Minitab (version 19). The figures were plotted by Origin 2019. The spatial distribution maps of heavy metals concentrations in different sampling points in the landfill and residential areas were prepared using the Inverse Distance Weighting (IDW) method in Arc GIS (version 10.3).

Results and discussion

Soil heavy metal concentrations in different seasons and sampling points

Table 1 indicates the average content of heavy metals concentrations \pm SD at different sampling points in the landfill and residential areas in four seasons. Sampling points no. 1-11 was located in the landfill site and no. 12 was at the center of the nearest residential area. The order of heavy metal levels at landfill sampling points was Al > Fe > Mn > Zn > Cr > Cu > Pb >

Table 1 The average values of heavy metals concentrations (mg kg ⁻¹) in four seasons in landfill sampling points and residential area	srage val	lues of	f heavy i	metals	concer	Itration	s (mg kç	\mathfrak{g}^{-1}) in f	four sea	sons in	landfill	sampli	ing poir	ts and	resider	itial area						
	As		Cr		cd	ĺ	Cu		Ņ		Pb		Co		Zn		Mn		Al		Fe	
Sampling point Mean	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD
	6.1	1.5	72.4	4.9	0.42	0.26	61.6	6.2	24.5	5.5	32.3	8.7	17.0	1.4	109.0	19.7	1150.5	98.6	79 933.3	4154.0	46 100.2	4028.6
	5.2	2.7	97.3	40.0	0.86	0.44	102.1	29.6	27.6	6.9	44.5	20.5	18.0		207.0	101.0	1254.0	169.0	70 014.8	1727.0	35 729.7	5469.8
	10.9	2.7	82.5	6.8	0.26	0.03	42.1	11.1	37.1	3.5	27.3	5.4	12.6		115.0	35.5	1096.7	226.0	58 176.3	10666.0	34 593.5	6838.3
	5.8	2.5	62.1	7.0	0.24	0.02	41.9	11.8	21.4	1.3	18.5	5.2	13.1		59.1	8.0	856.0	105.0	65 463.3	2805.0	35 722.5	4128.5
	3.9	0.6	67.3	5.4	0.28	0.04	52.5	12.4	26.1	3.1	25.8	3.8	17.6		68.1	7.0	1074.7	71.2	72 642.8	1899.0	43 719.2	1766.8
	5.3	1.2	127.5	33.0	0.38	0.10	179.4	82.7	42.9	15.5	111.5	62.8	15.5	3.1	275.0	134.0	1039.7	141.0	65 789.0	9797.0	$46\ 363.7$	5602.9
	8.4	6.1	74.3	5.1	0.32	0.12	53.3	3.4	28.3	3.3	25.0	5.7	17.6		85.4	15.8	1119.2	20.5	69898.0	7053.0	42 870.5	5704.1
	7.7	3.2	77.5	7.0	0.29	0.04	118.5	32.9	33.4	2.1	61.8	27.0	12.0		159.0	43.3	880.7	48.3	$64 \ 245.3$	1930.0	32 789.7	1421.3
	6.3	1.3	96.0	79.0	0.28	0.05	52.5	26.4	26.8	3.8	28.8	11.3	12.0	3.4	90.6	17.7	892.0	72.7	64 834.5	6173.0	32 676.2	8244.8
	8.2	4.5	65.5	4.5	0.30	0.10	43.9	11.0	31.6	5.1	26.8	6.3	10.7		77.3	10.6	798.5	52.9	59 756.8	2117.0	30542.5	1690.4
	7.2	2.4	87.8	30.0	0.35	0.12	134.8	94.2	33.8	13.1	65.1	56.8	13.1		225.0	179.0	898.2	71.8	$64\ 204$	7849.0	39 930.0	3105.2
	9.4	3.8	76.5	11.0	0.28	0.03	38.1	2.3	45.3	5.7	26.5	6.4	13.4	1.8	126.0	99.5	875.7	69.2	62 997.5	4090.0	32 537.2	1655.0

Paper

Ni > Co > As > Cd; but, in the residential area, it was Al > Fe > Mn> Zn > Cr > Ni > Cu > Pb > Co > As > Cd. The results show that the trend of heavy metal concentrations in the landfill and residential area was similar, except Ni. The average Al concentration in the landfill site (66 178 \pm 5106.6 mg kg⁻¹) and residential area (62 997.5 \pm 4090.9 mg kg⁻¹) was higher than other heavy metals. The average heavy metal levels in the landfill sites for Fe, Mn, Zn, Cr, Cu, Pb, Ni, Co, As, and Cd were 38 276.2 \pm 4363.7, 1005.4 \pm 98.1, 133.9 \pm 52.5, 82.7 \pm 20.3, 80.2 \pm 29.3, 42.5 \pm 19.4, 30.3 \pm 5.7, 14.5 \pm 2.5, 6.8 \pm 2.6, and 0.36 \pm 0.12 mg kg^{-1} , respectively. The average of heavy metals in the residential area (no. 12) indicated that the concentration of all heavy metals, except Ni and As was lower in the residential areas than the landfill; but, these values were higher than the background concentration. The quality of soil in the residential area may be affected by the open-dumping of solid waste in the landfill site, soil properties such as soil organic carbon (SOC) and pH, different solubility and transport of metals, climate conditions, and background concentration.³⁰ These findings are inconsistent with Rovira et al.31 and Rimmer et al.32 These studies reported that the landfill was not responsible for heavy metal soil pollution in Catalonia and Newcastle.

If we compare different sampling points according to the sum of heavy metal pollution, the results show that the highest polluted site matched the active landfill. The lowest contaminated site was the MRF station and the residential area. The higher heavy metal pollution in active landfill soil was due to the recirculation and accumulation of leachate on the soil surface. Decomposition of solid waste in the closed landfill increased heavy metals concentrations in these soil samples.16 Adelopo et al.¹⁶ reported that heavy metal concentration in a closed landfill was higher than an active landfill, and this result is not consistent with our findings. Heavy metal concentration in landfill soil is related to the composition of disposed waste and microbial degradation rate.16 High concentrations of heavy metals around landfill sites could be attributed to the previous mismanagement of landfill operations, such as insufficient leachate collection systems, illegal dumping of mixed wastes in unlined cells, and inappropriate separation of general and hazardous waste.33

The results of the heavy metal contents based on each sampling season shown in Table S3 and Fig. S1.[†] The Box plots show the mean, minimum, and maximum of measured heavy metals in each season. Fig. S1(a and b)† shows that the contents of heavy metals in autumn and winter was higher than summer and spring. This difference between the results could be due to the higher precipitation in wet than dry seasons. In wet seasons, precipitation increased leachate production and reduced leachate recirculation rate; this caused leachate to spread on the soil surface. In addition, a less viscosity of wet soil than dry soil enhanced heavy metals migration to long distances.³⁴ Complex meteorological parameters and predominant winds can possibly affect the distribution of heavy metals and odors in the landfill.34 Wind direction and velocity are useful in the dispersion of heavy metals downwind to residential areas. The amount of elements can increase gradually along with the direction of the prevailing wind. According to the higher

concentration of heavy metals in autumn and winter and also the higher wind speed in these seasons, wind and other meteorological parameters affect heavy metals distribution. The prevailing wind direction in Kahrizak landfill is generally from west to east, blowing particularly in the autumn and winter seasons. With a glance at the spatial distribution of heavy metals in Fig. 2, it seems that some metals are distributed in the dominant direction of the wind, but distribution patterns are not similar for all metals. Metals such as As and Ni, have a distinct distribution pattern in the prevailed wind direction from west to east. The presence of hotspots in the eastern part for metals such as Co, Fe, Cr, Pb, and Zn can be attributed to the role of wind in the accumulation of metals over time and the presence of compost site, which gradually has increased the concentration of elements in this site. Nikravesh et al.35 reported that the GIS map showed gradual increases in Pb, Zn, Cd, and Cu concentrations from the west to the east in Iran's Semnan industrial complex, which was consistent with the prevailing wind direction.

Topography will influence landfill capacity, drainage, final land use, surface and groundwater pollution control and, site accessibility.³⁶ Based on Shariatmadari *et al.*³⁷ reported that in Kahrizak landfill, there were natural terrains and artificial trenches filled with solid waste until the year 2000. Therefore, the current landfill is a flat area with little effect on the distribution of heavy metals. The pH and electrical conductivity (EC) of soil samples were determined in four seasons. The pH value range was between 6.8 and 7.8, and the highest pH value was observed in the compost granulation site. The investigated soil samples had a neutral pH, and the mobility of heavy metals in this condition was limited. The EC values ranged from 1.3 to 1.9 mS cm⁻¹, and the highest EC value was recorded in the leachate collection site.

In order to visually clarify the heavy metal distribution in all target areas, the spatial maps were prepared using Arc GIS, and the results can be seen in Fig. 2. It was found that the spatial distributions of Mn, Fe, and Al at different sampling points was not outstanding. The results showed that the heavy metals' spatial distribution at different sampling points was similar, except at sampling point no. 6. In sampling point no. 6, the Cr, Mn, Ni, Pb, Zn, and Cu concentrations were higher than other locations. The higher concentration of heavy metals at this sampling point was related to the windrow method's composting activity. The non-biodegradable nature of heavy metals helps increase the contents of heavy metals gradually during degradation and composting.38 A previous study conducted by Rupani et al.5 on the quality of the compost produced in Kahrizak landfill revealed that Pb concentration was higher than the threshold standard that has been approved by the Iran Institute of Standards and Industrial Research. These results show that the inappropriate source separation of hazardous wastes in Tehran increased the level of soil heavy metals in Kahrizak landfill over time.

The remarkable point of this study was the low heavy metal concentration at sampling point no. 4, which was due to the healthcare waste disposal site. The color of heavy metal spatial distribution at this sampling point for all the investigated

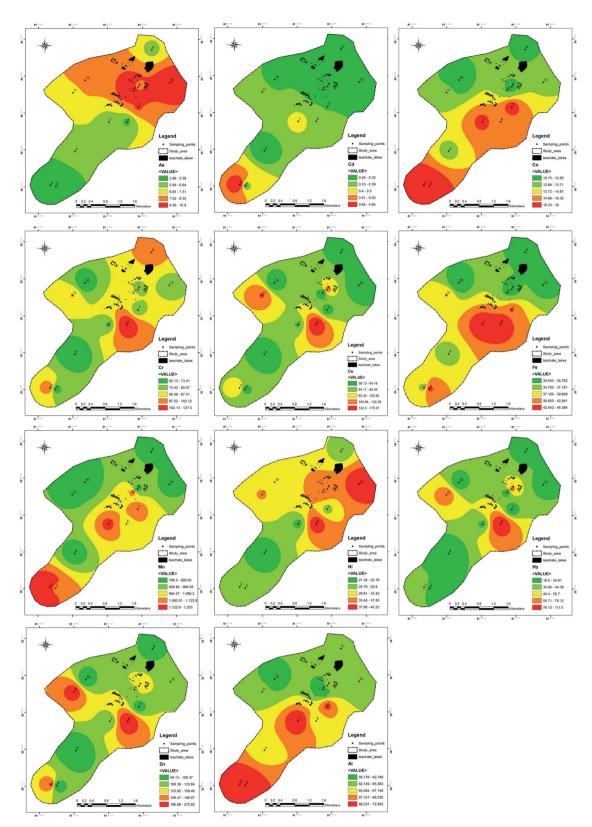


Fig. 2 Spatial distribution maps of heavy metals concentration (mg kg⁻¹) in investigated sampling points.

metals was green. The lower concentration of heavy metals in the healthcare waste disposal site was related to geosynthetic and geomembrane lining and daily covering solid waste with lime. Table S4[†] compares the heavy metals concentrations in the investigated soil, background soil and world soil. Besides, the coefficient of variation (CV) of all heavy metals in all the target areas (Table S4[†]) fluctuates between 7.7 and 75.2%, indicating

 Table 2
 Pearson correlation coefficients of soil heavy metals in the investigated area

	As	Cd	Cr	Cu	Со	Pb	Zn	Mn	Fe	Ni	A
As	1										
Cd	-0.318^{a}	1									
Cr	-0.174	0.367^{a}	1								
Cu	-0.253	0.350^{a}	0.617^{b}	1							
Со	-0.349^{a}	0.374^{b}	0.012	-0.028	1						
Pb	-0.226	0.298^{a}	0.600^{b}	0.932^{b}	-0.090	1					
Zn	-0.178	0.493^{b}	0.635^{b}	0.874^{b}	-0.033	0.883^{b}	1				
Mn	-0.300^{a}	0.451^{b}	0.172	0.015	0.642^{b}	-0.034	0.078	1			
Fe	-0.385^{b}	-0.064	-0.020	0.137	0.628^{b}	0.043	-0.047	0.486^{b}	1		
Ni	0.233	0.062	0.510^{b}	0.455^{b}	-0.108	0.488^{b}	0.571^{b}	-0.151	-0.152	1	
Al	-0.593^{b}	0.149	-0.132	-0.165	0.713^{b}	-0.280	-0.280	0.539^{b}	0.708^{b}	-0.394^{b}	1

high variations of these metals at different sampling points in Kahrizak landfill. The highest and lowest CV values belonged to Cu and Al with 75.2 and 7.7%. The wide fluctuation ranges and the high CV values of heavy metals could be due to external factors such as human activities.³⁹ Al and Fe had the lowest variation, and this result indicated that their concentrations were approximately equal to background levels. Table S4† shows the average concentrations of Zn, Pb, Cr, Ni, Cu, and Co were approximately 4.2, 4.2, 3.5, 2.7, 2.9, and 1.8 times greater than their background concentrations. This matter indicated that the excessive metal contamination in Kahrizak soil samples was due to anthropogenic activities. Ma *et al.*³ reported that the concentrations and CV values of Cd, Zn, Cu, and Pb in the landfill soil were higher than the background values.

Kolmogorov–Smirnov and Shapiro–Wilk tests were run in SPSS to determine the normality of heavy metals at the soil sampling points. Table $S5^{\dagger}$ shows that all the data were significant at the *p*-value of < 0.05. In other words, the heavy

metal concentrations in the soil samples were not normally distributed. To determine the similarity of heavy metal concentrations at different sampling points, the nonparametric Mann-Whitney U test was run. The statistical results (Table S6[†]) show all the investigated heavy metals had a significant difference (*p*-value < 0.05) at different sampling points. In order to prove the association between heavy metal concentrations at different sampling points, the Kruskal-Wallis test was run. The Kruskal-Wallis results (Table S7[†]) show that the levels of all the heavy metals at different sampling points were significantly different (p-value < 0.05). These results confirmed that heavy metal concentration varied at different sampling points due to the diversity of activities performed in Kahrizak landfill. The normality of heavy metal concentrations in four seasons was determined using Kolmogorov-Smirnov and Shapiro-Wilk tests, and the results are presented in Table S8.† The results show the distribution of the heavy metals concentrations in four seasons was not normal (p-value < 0.05);

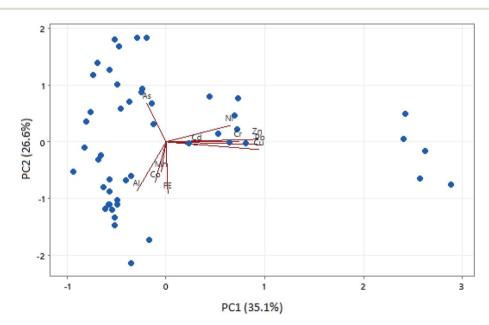


Fig. 3 Biplot of the four components influencing heavy metals variation in Kahrizak landfill soil.

but, the difference by Mann–Whitney *U* test was significant (Table S9†). The relationship between heavy metal concentrations in four seasons was investigated using the Kruskal–Wallis test and, the results (Table S10†) show the levels of all heavy metals in four seasons were significantly different (*p*-value < 0.05). The results proved the heavy metal levels were varying across four seasons in Kahrizak landfill. Sakawi *et al.*⁴⁰ reported that precipitation could be effective in the migration of soil heavy metals.

Correlation analysis and principal component analysis (PCA)

In order to reveal the source and pathway of metals in soil matrix, inter-element relationships were determined using Pearson's correlation coefficient. According to the Pearson's correlation coefficient values in Table 2, a significant strong positive correlation exists between Pb and Cu (r = 0.932, P <0.01), Cu and Zn (r = 0.874, P < 0.01) and Pb and Zn (r = 0.883, P < 0.01). A relatively weak positive correlation was found with Cd (r = 0.318, P < 0.05), Mn (r = 0.300, P < 0.05) and Co (r = 0.349, P < 0.05)< 0.05) and Cr showed to have a significant moderate positive correlation with Zn (*r* = 0.635, *P* < 0.01), Cu (*r* = 0.617, *P* < 0.01), and Pb (r = 0.600, P < 0.01). Moreover, Co had a significant moderate positive correlation with Mn (r = 0.642, P < 0.01) and Fe (r = 0.628, P < 0.01). These significant and relatively strong correlations between Kahrizak landfill heavy metals indicate that these are derived from similar sources, which mainly originated from anthropogenic activities. For more source identification and evaluation, PCA was conducted. Based on the literature⁴⁰ variables belonging to one group are highly correlated together.

The PCA results of soil heavy metal contents in sampling points are shown in Fig. 3. Three principal components were extracted. The PCA indicated three major components that explained 76.5% of the total variance. As shown in Fig. 3 and Table S11,† the rotated component matrix demonstrated that a high loading of Pb (0.951), Cu (0.943), Zn (0.928), and moderate loading of Cr (0.737) and Ni (0.648) were involved in the first component (PC1) accounting for 35.1% of the total variance. The second component (PC2) included high negative loadings of Fe (-0.908), Al (-0.870), and moderate loadings of Co (-0.705), As (0.678), and Mn (-0.531) with 26.6% of the total variance. Cadmium was located in the third component (PC3) including a high loading of -0.872 with 14.8% of the total variance. From the component grouping, PC1 and PC2 are the most important component in soil pollution. The close correlation linkages between metals in each component indicated that they might have originated from a similar source.41

Cr, Pb, Cu, Zn, Ni, and Co concentrations in Kahrizak landfill soils were higher than the background values and, the CV values of these heavy metals were relatively high (Table S4[†]). This indicated that Cr, Pb, Cu, Zn, and Ni in the investigated soil were mainly affected by anthropogenic activities.⁴² These heavy metals are released through the common part of unseparated wastes such as batteries, plastics, paints, colored glass, exhausted tires, and paper inks.⁴³ Cu and Zn are the famous elements of solid waste disposal activities, specifically related to

Table 3 Li	terature r	Table 3 Literature review of the average of heavy metals concentrati	ne averag	le of heavy	' metals co	ncentratic	h gm) snc	ons (mg kg $^{-1}$) in other countries	er countries				
Country	As	Cr	Cd	Cu	Ni	Pb	Co	Co Zn	Mn	Al	Fe	Dominant waste management practice	Reference
Delhi		0.23		0.19	0.12	0.27	I	0.14	1.0	78.7	58.1	Landfilling	46
Nigeria	2.1	29.2	1.8	168.9	16.6	83.4	3.3	1883.3	295.5	2930.7	$15 \ 091.7$	Open dumping	16
Malaysia	0.38	17.4	3.4	392.0	14.0	90.4	Ι	602.0	928.0	$12\ 261.0$	5367.0	Incinerating	47
Spain	2.2	7.24	0.32	Ι	5.92	18.6	I					Landfilling (60%)	18
Serbia	23.4	147.2	0.51	121.9	52.1	54.4	Ι	254.4				Landfilling	17
China	31.2	76.3	0.38	30.5	31.8	26.7	Ι	120.2				Landfilling + incinerating	3
Italy	5.9	84.7	0.46	68.7	73.4	39.3		127.0				Landfilling (22%) + incinerating (18%) +	48
Tehran	2.6	82.7	0.36	38.9	30.3	42.5	14.5	133.9	1005.4	$66\ 178.0$	38 276.2	Landfilling	Present study

Paper

the landfilling of e-waste, incinerator ashes, plastic, and paper wastes in the landfill site.³ Moreover, Ni and Pb are also released through treated healthcare wastes, e-wastes, and disposed of metal fragments in the investigation of Roundhill landfill by Nyika *et al.*⁴⁴ Adelopo *et al.*¹⁶ suggested that Zn is a good indicator of soil landfill pollution and could result from uncontrolled leachate discharge. Mn, Fe, As, and Al concentrations in PC2 were approximately equal to their background values (Table S4†), indicating that these metals can be originated from natural sources. The mean Co concentration in soil samples was relatively higher than the background level, but this metal was located in PC2. It was shown that in addition to a natural source, Co could be entered through an anthropogenic source such as spent lithium-ion batteries.⁴⁵

In order to determine the condition of Tehran landfill soil pollution, a comparison was made with other countries, the results of which are summarized in Table 3. Comparing the results of Kahrizak landfill with the studied countries (Table 3) revealed wide variations in metals concentration. On the other hand, the concentrations of heavy metals in different countries have wide changes, and each metal level has changed a lot in each country. This wide variation of heavy metal concentration may be related to several factors such as (1) different background levels of soil metals in various countries; (2) change of waste management policies over time; (3) use of engineered landfill or open dumping; (4) incentive and penalize regulations for waste production; (5) landfills' location. Proper implementation of source separation programs can decrease waste containing heavy metals such as paints, solvents, pesticides, paper inks, and plastics and finally reduce heavy metal pollution in landfill soils. Therefore, combining these factors complicates the possibility of precise comparing of changes in the concentration of soil heavy metals in landfill sites.

Soil pollution indicators

Enrichment factor. The results of heavy metal enrichment in sampling sites are presented in Table 4 and illustrated in Fig. S2(a).† As it can be seen, the enrichment factor for metals

including As, Cd, Co, Mn, and Fe in most of the sampling sites was at the slight enrichment level ($1 \le EF \le 2$), and Cr and Ni were at a moderate enrichment level ($2 \le EF \le 5$); but, a significant enrichment level was observed for Cu, Pb, and Zn $(5 \le EF \le 20)$. In detail, the EF value for Cu ranged between 2.9 and 13.0, in which about 67% of the sampling sites were at a moderate enrichment level. The highest enrichment factor values for Cu belonged to the composting site, fermentation unit, and landfill worker's resting site with 13.0, 10.1, and 8.8, respectively. The EF value of Pb ranged between 1.8 and 10.8, with 75% of the sampling sites having a moderate pollution and the enriched site for Pb as a composting unit. The EF value for Zn fluctuated between 1.9 and 8.6, with 75% of the sampling sites having moderate enrichment levels, and the highest level belonging to the composting site. Therefore, the composting site had the highest EF values for Cu, Pb, Cr, Fe, and Zn of other sampling points, and workers in this unit were exposed to higher risks. In most works of research, EF values lower than 2 were assumed to be the indicate a natural metal source, while EF values greater than 2 indicated an anthropogenic pollution source.¹⁶ Therefore, the high EF values for Cu, Pb, and Zn strongly suggested that metals were concentrated from the extrinsic sources, mostly from waste disposed on the landfill.

Individual and total ecological risk index. The calculated E_r^i and ERI values for the selected heavy metals in the sampling points are shown in Table 5 and Fig. S2(b, c).† As it can be seen in Table 5, ERI values for As, Cr, Ni, Zn, Mn, and Co were lower than 40, and this matter indicated that the level of pollution at this sampling point was low. The moderate ecological risk was observed for Cd ($E_r^i = 75.4$) at sampling point no. 2 (incinerator wastewater treatment plant) and, Cu was detected at sampling points no. 6, 8, and 11 due to the compost granulation site, landfill worker's residence site, and fermentation site, respectively. Besides, Fig. S2(b and c)† shows the levels of individual and total ecological risk values. The red line in both curves represents the safe mode, above which the ecological risk will start. The higher E_r^i and ERI at these sampling points was associated with the leachate accumulation and compost

Table 4	The EF values for different soil sampling points

		EF valu	ues								
Area	Sampling points	As	Cr	Cd	Cu	Ni	Pb	Со	Zn	Mn	Fe
Landfill	1	0.9	2.8	1.1	4.0	1.9	2.8	1.9	3.1	1.3	1.7
	2	0.8	3.9	2.3	6.9	2.3	4.1	2.1	6.1	1.5	1.3
	3	1.9	3.9	0.9	3.5	3.7	2.9	1.8	4.1	1.4	1.6
	4	0.9	2.6	0.7	3.1	1.9	1.8	1.6	1.9	1.1	1.4
	5	0.6	2.6	0.7	3.4	2.1	2.6	1.9	1.9	1.2	1.6
	6	0.9	5.4	1.1	13.0	3.8	10.8	1.9	8.6	1.3	1.9
	7	1.3	2.9	0.9	3.6	2.3	2.3	2.1	2.5	1.3	1.6
	8	1.3	3.6	0.8	8.8	2.9	6.1	1.5	5.1	1.1	1.3
	9	1.0	4.1	0.8	3.9	2.8	2.8	1.5	2.9	1.1	1.3
	10	1.4	3.1	0.9	3.5	3.1	2.9	1.5	2.6	1.0	1.4
	11	1.2	1.1	1.1	10.1	3.0	6.5	1.6	7.2	1.1	1.6
Residential	12	1.9	3.4	0.9	2.9	4.1	2.7	1.7	4.1	1.1	1.4

		Individu	al risk index	$\kappa \left(E_{r}^{i} \right)$						
Area	Sampling point	As	Cd	Cr	Ni	Cu	Zn	Mn	Со	ERI
Landfill	1	9.9	37.3	6.2	10.7	22.6	3.4	1.4	4.2	95.
	2	8.6	75.4	8.3	12.2	37.5	6.6	1.6	4.5	154.
	3	17.9	22.7	7.1	16.5	15.5	3.6	1.4	3.1	87.
	4	9.5	21.4	5.3	9.5	15.4	1.9	1.1	3.3	67.
	5	6.5	24.7	5.7	11.6	19.3	2.2	1.4	4.4	75.
	6	8.8	33.7	10.9	19.0	65.8	8.7	1.3	3.9	152.
	7	13.8	28.5	6.4	12.5	19.5	2.7	1.4	4.4	89.
	8	12.6	25.2	6.6	14.8	43.5	5.1	1.1	3.0	111.
	9	10.4	24.5	8.2	11.9	19.3	2.9	1.1	3.0	81.
	10	13.4	26.7	5.6	14.0	16.1	2.4	1.0	2.7	81.
	11	11.8	31.1	7.5	14.9	49.5	7.2	1.1	3.3	126.
Residential	12	15.4	24.9	6.5	20.0	14.0	3.9	1.1	3.3	89.

Table 6 Non-carcinogenic health risk values in different landfill soil sampling point in four seasons

	THQ for eac	ch metal								
Sampling points	Ni	Cu	Fe	Со	Zn	As	Cr	Pb	Cd	HI
1	$1.8 imes10^{-3}$	$2.1 imes10^{-3}$	$1.4 imes10^{-1}$	$1.2 imes10^{-3}$	$5.0 imes10^{-4}$	$9.5 imes10^{-3}$	$1.4 imes10^{-2}$	$4.4 imes10^{-3}$	$2.8 imes10^{-4}$	$1.7 imes 10^{-1}$
2	$2.1 imes 10^{-3}$	$3.5 imes10^{-3}$	$1.1 imes 10^{-1}$	$1.3 imes10^{-3}$	$9.5 imes10^{-4}$	8.2×10^{-3}	$1.8 imes 10^{-2}$	$6.1 imes10^{-3}$	$5.6 imes10^{-4}$	$1.5 imes \mathbf{10^{-1}}$
3	$2.8 imes10^{-3}$	$1.4 imes10^{-3}$	$1.0 imes10^{-1}$	$8.7 imes10^{-4}$	$5.3 imes10^{-4}$	$1.7 imes10^{-2}$	$1.6 imes 10^{-2}$	$3.7 imes10^{-3}$	$1.7 imes10^{-4}$	$1.5 imes \mathbf{10^{-1}}$
4	$1.6 imes 10^{-3}$	$1.4 imes10^{-3}$	$1.1 imes 10^{-1}$	$9.1 imes10^{-4}$	$2.7 imes10^{-4}$	$9.2 imes10^{-3}$	$1.2 imes 10^{-2}$	$2.5 imes10^{-3}$	$1.6 imes 10^{-4}$	$1.4 imes 10^{-1}$
5	$1.9 imes10^{-3}$	$1.8 imes10^{-3}$	$1.3 imes 10^{-1}$	$1.2 imes 10^{-3}$	$3.1 imes10^{-4}$	$6.2 imes10^{-3}$	$1.3 imes 10^{-2}$	$3.5 imes10^{-3}$	$1.8 imes10^{-4}$	$1.6 imes \mathbf{10^{-1}}$
6	$3.2 imes10^{-3}$	$6.2 imes10^{-3}$	$1.4 imes10^{-1}$	$1.1 imes 10^{-3}$	$1.3 imes10^{-3}$	8.4×10^{-3}	$2.4 imes 10^{-2}$	$1.5 imes 10^{-2}$	$2.5 imes10^{-4}$	$2.0 imes \mathbf{10^{-1}}$
7	$2.1 imes 10^{-3}$	$1.8 imes10^{-3}$	$1.3 imes 10^{-1}$	$1.2 imes10^{-3}$	$3.9 imes10^{-4}$	$1.3 imes 10^{-2}$	$1.4 imes 10^{-2}$	$3.4 imes10^{-3}$	$2.1 imes 10^{-4}$	$1.7 imes \mathbf{10^{-1}}$
8	$2.5 imes10^{-3}$	$4.1 imes10^{-3}$	$9.9 imes10^{-2}$	$8.3 imes10^{-4}$	$7.3 imes10^{-4}$	$1.2 imes10^{-2}$	$1.5 imes10^{-2}$	$8.5 imes10^{-3}$	$1.9 imes10^{-4}$	$1.4 imes \mathbf{10^{-1}}$
9	$2.0 imes10^{-3}$	$1.8 imes 10^{-3}$	$9.9 imes10^{-2}$	$8.3 imes10^{-4}$	$4.2 imes10^{-4}$	$9.9 imes10^{-3}$	$1.8 imes 10^{-2}$	$3.9 imes10^{-3}$	$1.8 imes 10^{-4}$	$1.4 imes 10^{-1}$
10	$2.4 imes10^{-3}$	$1.5 imes10^{-3}$	$9.3 imes10^{-2}$	$7.4 imes10^{-4}$	$3.5 imes10^{-4}$	$1.3 imes 10^{-2}$	$1.2 imes 10^{-2}$	$3.7 imes10^{-3}$	$1.9 imes10^{-4}$	$1.3 imes \mathbf{10^{-1}}$
11	$2.5 imes10^{-3}$	$4.6 imes 10^{-3}$	$1.2 imes 10^{-1}$	$9.1 imes 10^{-4}$	$1.0 imes 10^{-3}$	$1.1 imes 10^{-2}$	$1.7 imes 10^{-2}$	$8.9 imes 10^{-3}$	$2.3 imes 10^{-4}$	$1.7 imes 10^{-1}$

preparation. The landfill worker's residence site in Kahrizak landfill was located near the leachate lake, and this issue increased the concentration of heavy metals at this sampling point. Due to the high individual risk originated from Cd and Cu, it is necessary to control their discharge into the environment to reduce the ecological risk. High E_r^i and ERI values will damage landfill workers and residents living around this site. Elias *et al.*⁴⁹ investigated the ecological risk of element pollution in Abdul Rahman National Park in Sabah. The results show that the ecological risk value was 916 and indicated that the soil had a very high contamination degree.

Based on EF and ERI results, As, Cd, Cr, Cu, Pb, Zn, Fe, Co, and Ni created a moderate to high ecological risk in the landfill and residential area. Exposure to high concentrations of these soil heavy metals could hurt lungs and the respiratory system, reproductive system, DNA and kidney, cognition, and behavior disorders in children.¹⁶ These pollution indices suggest that a high concentrations of soil heavy metals could adversely affect human and ecological health. Therefore, it is necessary to estimate carcinogenic and non-carcinogenic risks on the exposed population.

Human health risk assessment

Non-carcinogenic risks. The non-carcinogenic risk for landfill workers, adults, and children in the residential area posed by heavy metals through ingestion, inhalation of dust particles, and dermal absorption exposure routes were calculated and shown in Tables 6 and 7. All HQs and HI values in both landfill and residential areas were within the acceptable range (HQs < 1). It implies that, there were no non-carcinogenic risks from the investigated elements for children and adults. The HI average value for landfill workers was 1.6×10^{-1} , which is below 1. Moreover, the calculated mean non-carcinogenic values for all the target metals for children and adults were 8.9 imes 10 $^{-1}$ and 1.4×10^{-1} , respectively, which was lower than the USEPA²⁵ guideline level (HI \leq 1). These results indicated no significant difference between non-carcinogenic risk in landfill workers and adults in the residential area. These implications emphasized that mitigation measurements should be decided to prevent a future contamination of the residential soil.

Among the 9 studied elements, the HI for both adults and children decreased in the order of Fe > Cr > As > Pb > Cu > Ni > Co > Zn > Cd. The higher HI value for Fe was originated from the

Comparison of non-carcinogenic and carcinogenic health risk values from exposure routes in residential area Table 7

		HQ vales			ILCR values		
Groups		Ingestion	Dermal	Inhalation	Ingestion	Dermal	Inhalation
Children		$7.9 imes10^{-1}$	$3.5 imes10^{-2}$	$6.2 imes10^{-2}$	$1.1 imes 10^{-4}$	$4.5 imes10^{-6}$	$1.1 imes 10^{-7}$
Adults		$9.0 imes10^{-2}$	$6.0 imes10^{-3}$	$3.2 imes10^{-2}$	$1.1 imes 10^{-4}$	$9.3 imes10^{-6}$	$2.1 imes 10^{-7}$
Children/ad	ults ratio	8.5	5.4	1.9	1.0	0.48	0.51
Children	Ingestion/dermal ratio	22.5			25.3		
	Ingestion/inhalation ratio	12.7			1027.6		
Adults	Ingestion/dermal ratio	14.3			11.9		
	Ingestion/inhalation ratio	2.9			516.7		

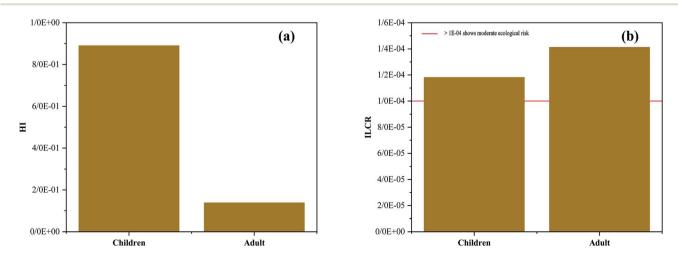
high concentration of this element in soil. The HI values for all the investigated heavy metals in the landfill and residential areas were lower than the permitted level (HI \leq 1). It indicated that there was no health threat for children and adults through soil heavy metal exposure. The non-carcinogenic risk was estimated with a high degree of uncertainty and the adverse effects of heavy metal accumulations should be considered in human body in long-term exposure.

The potential risk of non-carcinogenic in both sites followed the order of ingestion > inhalation > dermal absorption and the ingestion was the main exposure route. For example, the average HQ values for ingestion, inhalation, and dermal absorption in landfill workers were 1.1 \times 10 $^{-1}$, 4.0 \times 10 $^{-2}$, and 8.0×10^{-3} , respectively (Table S12[†]). Based on Table S12,[†] the non-carcinogenic risk created through the ingestion route in the landfill workers was 13.6 and 2.8 times greater than that of dermal and inhalation risks. These results indicated that workers should be use personal protective equipment to reduce the calculated risks. If the non-carcinogenic risk levels at different sampling points were compared together, it could be concluded that the highest HI value belongs to the composting site with 2.0×10^{-1} followed by the leachate collection site and the fermentation unit with similar HI values of 1.7×10^{-1} .

The non-carcinogenic values in children and adults are cross compared through different exposure routes in Table 7 and Fig. 4(a). Based on Table 7, Fe and Cr primarily contributed to

the HI value for children and adults. Also, the ratio of noncarcinogenic values in children to adults through ingestion, dermal absorption, and inhalation was 8.5, 5.4, and 1.9, respectively. Although the HI values for both age groups were within the permitted limit. This value in children was 6.5 times greater than that adults, suggesting that children had a greater chance of non-carcinogenic risk than adults. The higher HI value in children was related to their pica behavior and hand or finger sucking, one of the most frequent metal exposure routes for children.⁵⁰ Baltas et al.⁵¹ investigated human health risk through heavy metal soil pollution in Turkey. They reported HI values for adults and children to be 1.3×10^{-1} and 1.2×10^{-1} . respectively, and oral ingestion for both groups was the primary exposure route. Their findings were similar to our report, and children were more sensitive to the adverse health effects of heavy metals due to the higher intake of soil through their hands and mouth.

The non-carcinogenic risk associated with heavy metal pollution was simulated using the Monte Carlo model in the residential area. Presenting the data in this format made the risk better comprehensible. A cumulative distribution plot of the non-carcinogenic risk due to heavy metals exposure through polluted soil in adults and children is presented in Fig. 5(a and b). It reflects the probability distribution characteristics and the 5% and 95% percentile risk values. The 5th and 95th percentile values indicated low-end exposure and a high level of health



(a) Non-carcinogenic and (b) carcinogenic risk of heavy metals in children and adults. Fia. 4

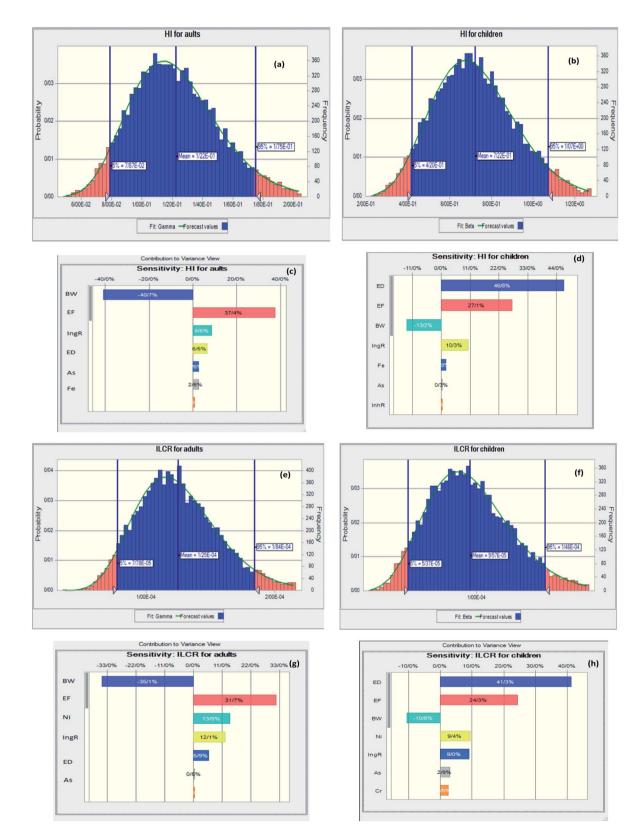


Fig. 5 Monte Carlo simulation for risk estimation (a) histogram of non-carcinogenic for adults; (b) histogram of non-carcinogenic for children; (c) sensitivity analysis for non-carcinogenic risk in adults; (d) sensitivity analysis for non-carcinogenic risk in children; (e) histogram of carcinogenic risk for adults; (f) histogram of carcinogenic risk for children; (g) sensitivity analysis for carcinogenic risk in adults; (h) sensitivity analysis for carcinogenic risk in children.

risk.50,52 The calculated mean non-carcinogenic value for all the investigated metals was 1.4×10^{-1} for adults and 8.9×10^{-1} for children, respectively, which was lower than the USEPA23 guideline level (HI \leq 1). For an adult, the 5th and 95th percentile deterministic values were 7.9 \times 10⁻² and 1.8 \times 10⁻¹; both were smaller than the upper recommended limit. Moreover, for children, the 5th percentile deterministic value was 4.2 \times 10⁻¹, which was lower than the upper recommended limit. But, the 95th percentile deterministic value was 1.1×10^{-1} , which was higher than the upper recommended limit. It is a warning that if the situation continues this way, it will threaten children's non-carcinogenic risk in future. The cumulative distribution functions (CDFs) or the probabilities of exceeding the risk of HI and ILCR in children and adults were extracted using Monte-Carlo simulation. The simulation results of HI in adults showed that there was no probability of HI exceeding 1. According to the probability distributions, the probability for HI > 1 for children was 8.4%. Besides, the values of Monte Carlo simulation for HI and ILCR in adults and children are presented in Table S14.[†] The sensitivity analysis results showed that BW posed a negative effect on HI and ILCR estimation for both adults and children. In adults, HI estimation (Fig. 5(c)), EF, ingestion rate of the soil, ED, As, and Fe concentrations with 37.4, 8.5, 6.5, 6.0, and 2.5%, respectively, were the most influential variables. Also, in children (Fig. 5(d)), ED, EF, ingestion rate of the soil, and Fe concentration with 46.8, 27.1, 10.3, and 8.0%, respectively had a positive effect on the non-carcinogenic risk.

Carcinogenic risks. For the carcinogenic risk, As, Cd, Cr, Ni, and Pb were assessed through three exposure routes in landfill workers and residential inhabitants. Table 8 shows that the CR_i values for different landfill sampling points and the results for carcinogenic risk in the residential area are presented in Table 7. The trend of carcinogenic risk for both areas was in the order of ingestion > dermal absorption > inhalation. The average values of ILCR through ingestion, dermal absorption, and inhalation for landfill workers were 1.1×10^{-4} , 9.3×10^{-6} , and 2.2×10^{-7} , respectively (Table S12†). The ingestion/dermal ILCR ratio and ingestion/inhalation ILCR ratio in landfill workers were 13.0 and 322.0, respectively (Table S12†). Soil ingestion was identified as the main exposure route for carcinogenic risks. The ILCR values for different landfill sampling point no. 1 (active landfill), 2 (incinerator wastewater treatment plant), 4 (healthcare waste landfill site), 5 (incineration site), 7 (leachate collection site), and 9 (closed landfill site) were within acceptable or tolerable risk range $(1 \times 10^{-4} \le CR \le 1 \times 10^{-6})$. The ILCR values for sampling point no. 3 (leachate drainage site), 6 (compost granulation site), 8 (landfill worker's residence site), 10 (MRF station), and 11 (fermentation site) were higher than the acceptable level (1×10^{-4}) . Therefore, landfill staff working and living at these sampling points were under extremely high carcinogenic risks.

The results showed that the ILCR value of children (1.2 \times 10^{-4}) was smaller than that of adults (1.4 \times 10⁻⁴). The ILCR values in both age groups were higher than the safe level; thus, the chance of having cancer in long-term exposure is obvious for children and adults. In the residential area, the ILCR values for children through ingestion, dermal absorption, and inhalation were 1.1×10^{-4} , 4.5×10^{-6} , and 1.1×10^{-7} , respectively. For adults, these values were 1.1 \times 10⁻⁴, 9.3 \times 10⁻⁶, and 2.2 \times 10^{-7} , respectively. On the other hand, the CR ratio in children to adults through ingestion, dermal, and inhalation routes was 1.0, 0.48, and 0.51. These values indicated that carcinogenic risk in adults was more than children. Also, Fig. 4(b) compares the carcinogenic risk in children and adults. Wang et al.53 reported that the ingestion route was the main pathway for heavy metal in agricultural soil in China, while Adelopo et al.16 reported that, in active and closed landfills, the carcinogenic and noncarcinogenic risks were in the order of dermal > ingestion > inhalation. The potential heavy metal carcinogenic risk in the landfill and residential area was in the order of Ni > Cr > As > Pb > Cd. The results showed that Ni in adults has a carcinogenic value higher than the permitted level (1.2×10^{-4}) , but this value in children (6.0 \times 10⁻⁵) was located within the acceptable carcinogenic risk level (Table S13[†]). The CR_i values for children for all the target metals were located within the acceptable carcinogen range.

The carcinogenic risk related to the heavy metal pollution was simulated using the Monte Carlo model in the residential area. Fig. 5(e and f) reflects the probability distribution

	Cancer risk (CR	_i) value for each meta	1			
Sampling points	As	Cd	Cr	Pb	Ni	ILCR
1	$4.3 imes10^{-6}$	$7.6 imes 10^{-8}$	$1.7 imes10^{-5}$	$1.3 imes 10^{-7}$	$6.3 imes10^{-5}$	$8.5 imes 10^{-5}$
2	$3.7 imes10^{-6}$	$1.5 imes10^{-7}$	$2.3 imes10^{-5}$	$1.8 imes10^{-7}$	$7.1 imes10^{-5}$	$9.8 imes10^{-5}$
3	$7.7 imes10^{-6}$	$4.6 imes10^{-8}$	$1.9 imes10^{-5}$	$1.1 imes 10^{-7}$	$9.5 imes10^{-5}$	$1.2 imes 10^{-4}$
4	$4.1 imes10^{-6}$	$4.4 imes10^{-8}$	$1.5 imes10^{-5}$	$7.4 imes10^{-8}$	$5.5 imes10^{-5}$	$7.4 imes 10^{-5}$
5	2.8×10^{-6}	$5.0 imes10^{-8}$	$1.6 imes 10^{-5}$	$1.0 imes10^{-7}$	$6.7 imes10^{-5}$	$8.6 imes10^{-5}$
6	$3.8 imes10^{-6}$	$6.9 imes10^{-8}$	$3.1 imes10^{-5}$	$4.5 imes10^{-7}$	$1.1 imes 10^{-4}$	$1.4 imes 10^{-4}$
7	$5.9 imes10^{-6}$	$5.7 imes10^{-8}$	$1.8 imes 10^{-5}$	$1.0 imes10^{-7}$	$7.2 imes10^{-5}$	$9.6 imes10^{-5}$
8	5.4×10^{-6}	$5.1 imes10^{-8}$	$1.9 imes10^{-5}$	$2.5 imes10^{-7}$	8.5×10^{-5}	$1.1 imes 10^{-4}$
9	$4.5 imes10^{-6}$	$4.9 imes10^{-8}$	$2.3 imes10^{-5}$	$1.1 imes 10^{-7}$	$6.8 imes10^{-5}$	$9.6 imes10^{-5}$
10	5.8×10^{-6}	$5.4 imes10^{-8}$	1.6×10^{-5}	$1.1 imes 10^{-7}$	8.1×10^{-5}	$1.0 imes 10^{-4}$
11	$5.1 imes10^{-6}$	$6.3 imes10^{-8}$	$2.1 imes10^{-5}$	$2.6 imes10^{-7}$	8.6×10^{-5}	$1.1 imes 10^{-4}$

Table 8 Carcinogenic health risk values in different landfill soil sampling points

characteristics, as well as the 5% and 95% percentile carcinogenic risk in adults and children. For an adult, the 5th percentile deterministic value was 7.8 \times 10^{-5} and the 95th percentile value was \sim 1.8 times higher than the upper recommended limit (1.8×10^{-4}). Moreover, for children, the 5th and 95th percentile deterministic values were 5.4 imes 10⁻⁵ and 1.5 imes 10^{-4} . The 95th percentile was higher than the upper recommended limit. Probability distributions of ILCR show the probability for ILCR > 1×10^{-4} for children and adults were 34.8 and 70.4%, respectively. According to the results, heavy metal's long-term exposure to the polluted soil increased the likelihood of carcinogenic risk and the adverse effects in the exposed population. Gaurav and Sharma⁵⁴ simulated the estimated health risk from heavy metal pollution in the industrial area using Monte Carlo simulation. The results show the risk of Cr at the 95th percentile for children and adults was 3.6 and 2.2, respectively, which was quite higher than the acceptable range.

The sensitivity analysis of carcinogenic risk in Fig. 5(g) shows the most important input variables with a positive effect on carcinogenic risk in adults were EF, Ni concentration, soil ingestion rate, ED and As concentration with 31.7, 13.9, 12.1, 5.9, and 0.5%, respectively. Fig. 5(h) shows ED, EF, Ni concentration, soli ingestion rate, and As concentration with 41.3, 24.3, 9.4, 9.0, and 2.9%, respectively, had the highest effect on carcinogenic risk estimation in children. The higher positive effect of ED and EF in sensitivity analysis for children was related to more contact with soil due to behavioral patterns. Fallahzadeh et al. 55 conducted a study to evaluate human health risk through oral ingestion of trace metals in Iran and the sensitivity analysis revealed that heavy metal level and BW had the highest positive and negative effects on cancer estimation. Comparison of Fallahzadeh et al.55 study with our results indicated that soil heavy metal pollution is an important factor in Iran and should be considered in decision-making. There was a significant carcinogenic risk associated with soil heavy metal for landfill workers and the population living near Kahrizak landfill. Heavy metals had chronic effects and could cause a health problem in long-term exposure. Therefore, it is necessary to conduct mitigation measurements in order to decrease soil heavy metal contamination in the investigated area.

Conclusion

The present study assessed the health and ecological risk arising from heavy metal contents in the landfill and residential soil of Tehran, Iran. The results revealed that the highest and lowest soil heavy metals in the landfill and residential region were related to Al and Cd. The Kruskal-Wallis analysis showed that the levels of all heavy metals at different sampling points and seasons were significantly different. The concentration of Cr, Cu, Fe, Mn, Ni, Pb, and Zn in sampling point no. 6 (composting site) was higher than other locations, which was attributed to the accumulation of heavy metals during composting through the windrow method.

Ecological indices and PCA results strongly revealed that Pb, Cu, Zn, Cr, and Ni are concentrated from external and

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anthropogenic activities, mostly from the disposal of mixed waste in the landfill. The potential non-carcinogenic risks followed the order of ingestion > inhalation > dermal absorption, but the order of exposure routes for carcinogenic risk was ingestion > dermal absorption > inhalation. The HI value for landfill workers and residents of the residential areas lay within the acceptable limit (HI < 1). It indicated that there were no noncarcinogenic risks associated with the target elements. The ILCR values for landfill workers in some locations were higher than the acceptable level (1 \times 10⁻⁴), and thus the chance of having cancer through long-term exposure was inevitable. The carcinogenic risk values of Ni in adults were above the threshold level (1×10^{-6}) , but the CR values in children for all the target metals were under the permitted level. The HI probabilistic analysis using Monte Carlo simulation showed that the higher positive effect of ED, ED, and soli ingestion rate in children was associated with more contact with soil due to behavioral patterns. These results indicate that more attention should be paid to the soil heavy metal pollution in landfills and residential areas, especially for children in Tehran.

Author contributions

Sakine Shekoohiyan was responsible for resources, conceptualization, methodology, validation, writing - original draft, writing - review & editing, funding acquisition, project administration, and supervision. The role of Gholamreza Moussavi was conceptualization, methodology, writing - original draft, writing – review & editing, project administration, and advising. Shahla Karimian roles were investigation, formal analysis, writing - original draft and review.

Conflicts of interest

We declare that the authors do not have any conflict of interest.

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References

- 1 M. Petrovic, M. Sremacki, J. Radonic, I. Mihajlovic, B. Obrovski and M. Vojinovic Miloradov, Sci. Total Environ., 2018, 644, 1201-1206.
- 2 H. Chen, Y. Yang, W. Jiang, M. Song, Y. Wang and T. Xiang, J. Air Waste Manage. Assoc., 2017, 67, 182-195.
- 3 W. Ma, L. Tai, Z. Qiao, L. Zhong, Z. Wang, K. Fu and G. Chen, Sci. Total Environ., 2018, 631-632, 348-357.
- 4 T. E. Butt, H. M. Gouda, M. I. Baloch, P. Paul, A. A. Javadi and A. Alam, Environ. Int., 2014, 63, 149-162.

- 5 P. F. Rupani, R. Maleki Delarestaghi, H. Asadi, S. Rezania, J. Park, M. Abbaspour and S. Weilan, *Int. J. Environ. Res. Public Health*, 2019, **16**, 979.
- 6 N. Ferronato and V. Torretta, Int. J. Environ. Res. Public Health, 2019, 16, 1060.
- 7 G. Li, J. Chen, W. Yan and N. Sang, *J. Environ. Sci.*, 2020, 55, 206–213.
- 8 M. Liu, Z. Han and Y. Yang, RSC Adv., 2019, 9, 21893.
- 9 C. M. Ohajinwa, P. M. van Bodegom, O. Osibanjo, Q. Xie, J. Chen, M. G. Vijver and W. J. G. M. Peijnenburg, *Int. J. Environ. Res. Public Health*, 2019, **16**, 906.
- 10 H. Huang, C. Lin, R. Yu, Y. Yan, G. Hu and H. Li, *RSC Adv.*, 2019, **9**, 14736.
- 11 Z. Wu, L. Zhang, T. Xia, X. Jia and S. Wang, *RSC Adv.*, 2020, **10**, 23066.
- 12 M. Liu, Z. Han and Y. Yang, RSC Adv., 2019, 9, 21893.
- S. Shekoohiyan, M. Ghoochani, A. Mohagheghian, A. H. Mahvi, M. Yunesian and S. Nazmara, *Iran. J. Environ. Health Sci. Eng.*, 2012, 9, 37.
- 14 Q. Wang, J. Liu and S. Cheng, *Environ. Monit. Assess.*, 2014, 187, 4178.
- 15 M. D. Vaverková, J. Elbl, M. Radziemska, D. Adamcová, A. Kintl, L. Baláková, S. Barton, J. Hladky, J. Kynicky and M. Brtnicky, *Chemosphere*, 2018, **208**, 569–578.
- 16 A. O. Adelopo, P. I. Haris, B. I. Alo, K. Huddersman and R. O. Jenkins, *Waste Manag.*, 2018, **78**, 227–237.
- 17 D. Krčmar, S. Tenodi, N. Grba, D. Kerkez, M. Watson, S. Rončević and B. Dalmacija, *Sci. Total Environ.*, 2018, 615, 1341–1354.
- 18 M. Mari, M. Nadal, M. Schuhmacher and J. L. Domingo, *Environ. Int.*, 2009, 35, 1034–1039.
- 19 A. A. Agbeshie, R. Adjei, J. Anokye and A. Banunle, *Sci. Afr.*, 2020, **23**, e00390.
- 20 R. P. Breckenridge and A. B. Crockett, *Environ. Monit. Assess.*, 1998, **51**, 621–656.
- 21 S. Ahmadi Doabi, M. Karami, M. Afyuni and M. Yeganeh, *Ecotoxicol. Environ. Saf.*, 2018, **163**, 153–164.
- 22 Y. Wang, Y. Wei, P. Guo, J. Pan, Q. Wu and N. Liu, *Mar. Pollut. Bull.*, 2016, **113**, 240–246.
- 23 M. Varol, Environ. Res., 2020, 187, 109664.
- 24 L. Hakanson, Water Res., 1980, 14, 975-1001.
- 25 A. Mohammadi, A. Zarei, M. Esmaeilzadeh, M. Taghavi, M. Yousefi, Z. Yousefi, F. Sedighi and S. Javan, *Biol. Trace Elem. Res.*, 2019, **195**, 343–352.
- 26 USEPA, *Exposure factors handbook*, Office of health and environmental assessment, Washington, DC 20460, 1989.
- 27 USEPA, Revised Human Health Risk Assessment Hudson River PCBs Reassessment RI/FS, 2000.
- 28 IARC, Some Metals and Metallic Compounds, *IARC* monographs on the evaluation of carcinogenic risks to humans. World Health Organization, Geneva, 1980.
- 29 N. Shalyari, A. Alinejad, A. H. G. Hashemi, M. Radfard and M. Dehghani, *MethodsX*, 2019, 6, 1812–1821.
- 30 C. Liu, J. Cui, G. Jiang, X. Chen, L. Wang and C. Fang, Soil Sediment Contam., 2013, 22, 390–403.

- 31 J. Rovira, L. Vilavert, M. Nadal, M. Schuhmacher and J. L. Domingo, *Waste Manag.*, 2015, 43, 168–175.
- 32 D. L. Rimmer, C. G. Vizard, T. Pless-Mulloli, I. Singleton, I. V. S. Air and Z. Keatinge, *Sci. Total Environ.*, 2006, 356, 207–216.
- 33 J. M. Nyika, E. K. Onyari, M. O. Dinka and S. B. Mishra, Orient. J. Chem., 2019, 35, 1286–1296.
- 34 Z. Sakawi, M. R. Ariffin, S. M. S. Abdullah and M. F. M. Jali, *Res. J. Appl. Sci., Eng. Technol.*, 2013, 5, 8619–8625.
- 35 M. Nikravesh, A. Karimi, I. Esfandiarpour Borujeni and A. Fotovat, *Casp. J. Environ. Sci.*, 2019, **17**, 163–174.
- 36 M. Aljaradin and K. M Persson, *Open Waste Manage. J.*, 2012, 5, 28–39.
- 37 N. Shariatmadari, A. H. Sadeghpour and M. J. Mokhtari, *Int. J. Civ. Eng.*, 2015, **13**, 126–136.
- 38 Z. Kong, X. Wang, Q. Liu, T. Li, X. Chen, L. Chai, D. Liu and Q. Shen, *J. Environ. Manage.*, 2018, 207, 366–377.
- 39 E. Mahmoudabadi, F. Sarmadian and R. N. Moghaddam, Int. J. Environ. Sci. Technol., 2015, 12, 3283–3298.
- 40 Z. Sakawi, M. R. Ariffin, S. M. S. Abdullah and M. F. M. Jali, *Res. J. Appl. Sci., Eng. Technol.*, 2013, 5, 8619–8625.
- 41 J. Marrugo-Negrete, J. Pinedo-Hernández and S. Díez, Environ. Res., 2017, 154, 380-388.
- 42 Y. Han, H. Xie, W. Liu, H. Li, M. Wang, X. Chen, X. Liao and N. Yan, Front. Environ. Sci. Eng., 2016, 10, 129–139.
- 43 Y. Y. Long, D. S. Shen, H. T. Wang, W. J. Lu and Y. Zhao, J. Hazard. Mater., 2011, 186, 1082–1087.
- 44 J. M. Nyika and E. K. Onyari, *Air, Soil Water Res.*, 2019, **12**, 1–8.
- 45 J. Zhao, B. Zhang, H. Xie, J. Qu, X. Qu, P. Xing, P. Xing and H. Yin, *Environ. Res.*, 2020, **181**, 108803.
- 46 W. Swati, P. Ghosh and I. S. Thakur, *Ecotoxicol. Environ. Saf.*, 2017, **143**, 120–128.
- 47 B. Jayanthi, C. U. Emenike, S. H. Auta, P. Agamuthu and S. H. Fauziah, *Int. Biodeterior. Biodegrad.*, 2017, **119**, 467– 475.
- 48 F. C. Bretzel and M. Calderisi, *Environ. Monit. Assess.*, 2011, 182, 523–533.
- 49 M. S. Elias, M. S. Hamzah, S. A. Rahman, N. A. A. Salim,
 W. B. Siong and E. Sanuri, *AIP Conf. Proc.*, 2014, 196–206.
- 50 X. Wei, B. Gao, P. Wang, H. Zhou and J. Lu, *Ecotoxicol. Environ. Saf.*, 2015, **112**, 186–192.
- 51 H. Baltas, M. Sirin, E. Gökbayrak and E. Ozcelik, *Chemosphere*, 2020, **241**, 125015.
- 52 E. Durmusoglu, F. Taspinar and A. Karademir, *J. Hazard. Mater.*, 2010, **176**, 870–887.
- 53 S. Wang, Y. K. Kalkhajeh, Z. Qin and W. Jiao, *Environ. Res.*, 2020, **188**, 109661.
- 54 V. K. Gaurav and C. Sharma, *Sustain. Comput. Inf. Systems*, 2019, 100310, DOI: 10.1016/j.suscom.2019.01.012.
- 55 R. A. Fallahzadeh, M. T. Ghaneian, M. Miri and M. M. Dashti, *Environ. Sci. Pollut. Res.*, 2017, 24, 24790– 24802.