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A solid phase extraction procedure for the determination of heavy metals in street dust from Dammam, Kingdom of Saudi Arabia and Estimation of the health risk

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Abstract

A relatively rapid, accurate and precise solid phase extraction procedure is developed for the determination of Fe, Mn, Zn, Cu,Pb and Co in street dust samples. Quantitation is performed by flame atomic absorption spectrometry (FAAS) . The proposed method is based on the retention of the metal ions on DowexMarathon C, a strong acid cation exchange resin. The precision and accuracy of the proposed procedure wereevaluated by comparison with certified reference material (BCR 701). To best of our knowledge, there is no any study for separation and pre-concentration of heavy metals using Dowex Marathon C resin as a solid phase extraction. This method was applied to the determination of the analytes in street dust samples collected from Dammam city, capital of the Eastern Province and fifth largest city in Saudi Arabia. The results showed that the dust samples contained significant levels of the studied metals (except Cd), in comparison with the control values. In order to evaluate the contamination by heavy metals and to study their effect on the human health, contamination factor, enrichment factors, Pollution Load Index, and modified contamination degree were calculated. The models used in present study to evaluate exposure risk of adults and children to heavy metals in street dust are based on models according to US Environmental Protection Agency (USEPA) . Health risk analysis indicates that there is probably no risk to health from oral ingestion, dermal contact with dust particles and inhalation of dust particles from the air of street dust.

1. Introduction

Heavy metals are classified as one of the most broadly spread pollutants in the environment. Due to their high stability, they tend to accumulate in the environment and cause problems for humans, plants, and animals [1]. Several studies around the world have investigated the effects of heavy metals on human health, especially on the health of children. Dust is an important medium through which human bodies can be exposed to toxic substances (e.g., heavy metals). This could be attributed to the fact that the fine dust particles can accumulate in the human body directly through inhalation; but also by ingestion and absorption after dermal contact [2-7]. Street dust consist of particulates from vehicle exhaust, particles falling from the air, house dust, soil dust, and aerosols carried by air and water [8,9]. Street dust significantly affects the contribution of pollutants in several environmental media due to its movement via air and water from one place to another. Moreover, the level of heavy metals in street dust can provide valuable information about pollution levels in urban and industrial areas. Suspended particles of metals can be adsorbed to or absorbed by road dust. The metals in road dust mainly originate from the Earth’s crust or from anthropogenic sources (e.g., vehicles and industrial exhaust emissions, corrosion of metal, brake and tire wear) [10,11]. Controlling the level of heavy metals in street dust has become an essential goal for researchers around the world, particularly in urban areas. Therefore, several studies were carried out to determine the concentration of heavy metals in street dust samples from different countries around the world. For example, relatively high concentrations of some heavy metals have been found in soil and street dust samples collected from different places in Jordan; 58.8–94.8, 1.8–84.9, 15.4–136.9,1.7–6.5 and 2.1–314.1 mg kg^{-1} for Fe, Cu, Zn, Ni and Pb, respectively [8, 12–15]. This is due to high anthropogenic and industrial activities. Also, similar observation was noticed in different places in Near East and North Africa regions. Such as , in Oman, the mean concentrations of lead, zinc, copper, nickel and chromium in indoor dust were; 108 ± 65, 753 ± 1162, 108 ± 91, 130 ± 125 and 34 ± 14 mg kg− 1, respectively [16] in Bahrain, the mean values in street dust were 742, 67, 1.5, 9.6, and 12 mg/kg, for Pb, Zn, Cd, Cr, and Ni respectively [17]. Comparable results have been found in Iraq [18], Egypt [19] and Nigeria [20]. These results are expecting since there is no regulations about the use of heavy metals have been adopted in these countries. In addition, significant levels of some heavy metals, (0.4–2800 mg kg^{-1}), have been found in Tehran [21], Turkey [22-24] and Pakistan [25]. All these levels are associated with intensive use of fertilizers and different human activity. In addition, high concentrations of some selected heavy metals were detected in the Asia region, such as Hong Kong (8.6–6800 mg kg^{-1})[26], Malaysia (2.3–3456 mg kg^{-1})[27, 28]and china (12–6783 mg kg^{-1}) [29]. These levels of heavy metals were 5-10 times higher than that in Europe countries. This is can be explained due to the growing of industrial activities in Asian countries. In contrast to the majority of Asian countries, Europe region showed a strict approach to combating heavy metals pollution from a very stage of time. This is resulted in a progressive decrease of heavy metals in European environment. For example, the levels of some heavy metals that have been found in Greece was (0.1–169 mg kg^{-1}) [30], Spain (43.8–110 mg kg^{-1}) [31], Poland (8–125 mg kg^{-1}) [32] and the United Kingdom (0.14–233 mg kg^{-1}) [33, 34].Moreover, very low levels of some heavy metals were found in street dust in Canada (2.7–372 mg kg^{-1})[35]. In Saudi Arabia, a few studies have been conducted to determine the level of heavy metals in street dust [36–41]. Turner et al. found high levels of some heavy metals; 9590, 32.40, 77.31, 230.0, 320.0 for Fe, Pb, Cu, Mn and Zn respectively in the street dust of Dhahran City (a neighbor city to Dammam). However, similar studies have not previously been conducted in the region of Dammam. In summary, the main aims of the current study are: a) developing a simple, selective and rapid solid phase extraction procedure by using DowexMarathon C (DMC) resin for the extraction and preconcentration of heavy metals, b) applying the proposed method for the determination of some heavy metals in street dust in Dammam, c) comparing heavy metal levels in the studied with other data worldwide and, d) estimation the potential health risk to children and adults via ingestion, inhalation and dermal contact to street dust.

2. Sampling and Methods

2.1. *Area description and sample collection*

Dammam is the capital of the Eastern Province of Saudi Arabia, and the fifth largest city in Saudi Arabia. It is located on Arabian Gulf Coast at the geographic coordinates of 26°25′33″N,50°6′51″E (Figure 1). It has a human population of around 900,000 inhabitants (2014 estimate), and covers an area of approximately 2800 km^2. Dammam is one of the most oil-rich regions in the world. This is a developing area, and it is considered a major place of employment in the Kingdom of Saudi Arabia (KSA). It contains many workplaces including provision of oil, smelters, steel and non-steel industries, preparation of construction materials, and furniture making. Dammam has a hot desert climate. The area within 40 km of this city is covered by lakes and rivers (62%), oceans and seas (22%), shrub lands (13%), and built-up areas (4%).

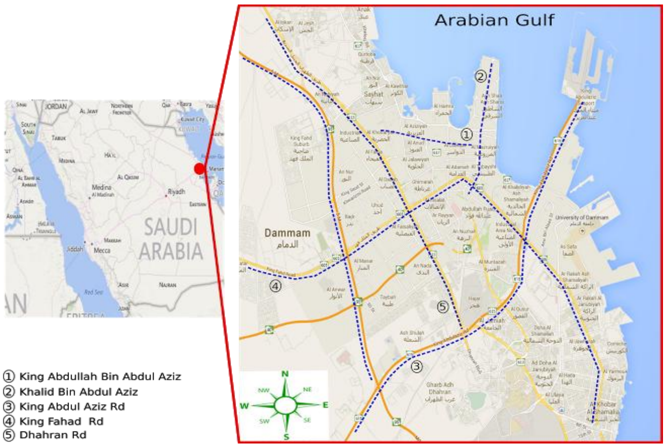

Figure 1: Map of Dammam showing locations (modified from Google maps).The geographical coordinates of the city are 26°25′33″N,50°6′51″E. With permission of Google Map

During a year, the temperature typically varies from 10 to 45°C, and is rarely below 6°C or above 47°C.There is virtually no rainfall. Five main streets (King Abdullah Bin Abdul Aziz, King Khalid Bin Abdul Aziz, King Abdulaziz Road, King Fahd Road, and Dhahran Road) were chosen as sample sites (Figure 1). The sampling was done in March at the end of spring 2014. Fifty samples (three parallel samples for each sampling site) were collected in the main streets of Dammam by gently sweeping an area of about 2 m^2 adjacent to the curb of the streets. Samples were collected of the street into a clean plastic dustpan with a brush, and then transferring about 300 g of the dust to a polyethylene bag for transport to the laboratory [42]. The samples so collected were stored in polyethylene containers, protected from sunlight, and stored at 4°C until they were analysed.

2.2. *Preparation for analysis*

In the laboratory, the dust samples were placed in a desiccator for 24 h, sieved through a 100-mesh stainless steel sieve and then oven dried at 100°C overnight. Samples then were placed in plastic tubes, sealed with parafilm and kept in the freezer until analysis. All the concentrations reported in the current study are on a dry weight basis.

2.3. *Materials*

Deionized water (>18 MΩ-cm at 25°C) was produced using an ELGA OPTION 4 water purifier. Nitric acid (65%), hydrochloric acid (37%) and hydrogen peroxide (H_2O_2, 30%) were obtained from Merck (Darmstadt, Germany). Dowex Marathon C, a strong acid cation exchange resin (DMC) was purchased from Sigma Aldrich (Australia) and it was used as solid phase extractant. The BCR-701 certified reference material for dust analysis was purchased from Sigma Aldrich (UK).

2.4. *Instrumentation*

The total concentration of selected heavy metals (Fe, Pb, Cu, Mn, Zn, Co, and Cd) was analysed using flame atomic absorption spectrometry (Shimadzu Corp., Japan, AA-6200) with a system double-beam, equipped with hollow cathode lamps. The spectral range extended from at least 180 to 900 nm. Quality control was based on the use of standard metal solutions and duplicate analysis (for the fraction soluble in water). The condition standards for the determination of metals are presented in Table 1.

Table 1: Condition standards for atomic absorption spectrometry of heavy metals

Heavy Metals	Wavelength (nm)	Atomization (℃)	FTS[a] (l/min)	Sensitivity (ppm)	DL[b] (µg/g)
Fe	248.3	2450	2.0	0.05	0.006
Pb	217.0	2433	2.2	0.01	0.001
Cu	324.8	2850	2.2	0.04	0.004
Mn	279.5	2800	2.0	0.02	0.015
Zn	213.9	2750	1.8	0.01	0.008
Co	240.7	2400	1.8	0.09	0.009
Cd	228.8	2630	2.0	0.08	0.008

[a] FTS = flow of test solution; [b]DL = detection limit

2.5. *Analytical procedure*

For dust digestion, 2g (dry weight) of the sieved sample and 70 mL of concentrated HNO_3 were transferred to a two-necked round-bottomed flask (250 mL). The mixture was refluxed at 100°C for 3 h. During the heating process, 1 mL of H_2O_2 was slowly added through a dropping funnel. The reaction was stirred at 100°C for 30 min. The condenser was removed and then the solution was evaporated to dryness using a nitrogen stream. The dry residue was dissolved in 25 mL of conc. HNO_3, and then the pH of the solution was adjusted to 4.0 with 10 mL of CH_3COOH/CH_3COONa buffer solution. For extraction of heavy metals, the aqueous solution was passed through the DMC solid phase extraction column. The flow of the sample and eluent solution through the column was gravitationally performed at a flow rate of 2.0 mL min^{-1}. After being completed the passing of the sample solution, the column was washed with a small amount of deionised water. Then, the retained metal ions were eluted from the column by the aid of 25 mL of 3 mol L^{-1} HNO_3. After the evaporation was continued to dryness, the final volume of the residue was completed to 3 mL with 0.5 mol L^{-1} HNO_3. The metal ion concentrations in the eluted solution were determined by flame atomic absorption spectrometry.

3. Results and Discussion

3.1. *Effect of pH*

The pH of the solutions in the solid phase extraction is one of the important parameters for quantitative recoveries of the analytes [43]. The effect of the pH on the recoveries was investigated on the pH range of 1.00-10.0. Maximum recoveries (> 95 %) were achieved in the pH 4.0 with no improvement being observed after that value (Figure 2).

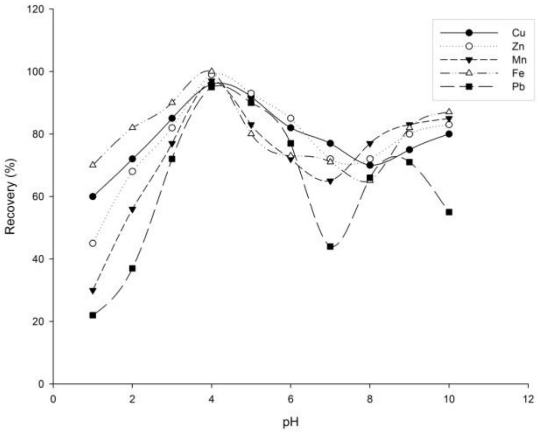

Figure 2: Effect of pH on the recoveries of the analyte ions (n=3).

3.2. *Effect of type, concentration and volume of eluents*

For the elution of the heavy metals adsorbed on the resin, dilute acid solutions having various concentrations and volumes were assessed. Different elution solutions were used for desorption of the trace metals from the resin. It was found that 25mL of 3mol L^{-1} was sufficient for complete elution of the metal ions studied. Therefore, this amount of solution was used as eluent for subsequent work (Table 2).

Table 2: Effect of kind, volume and concentration of HCl and HNO_3 solutions on the recovery of the analytes (sample volume: 25mL, pH=4, n=3)

Concentration and type of eluent	Volume (mL)	Recovery (%)[a]					
		Fe	Cu	Mn	Zn	Co	Cd
3mol L^{-1} HNO_3	25	99±1	100±1	97±2	98±2	90±1	-
3mol L^{-1} HNO_3	10	94±2	90±1	88±2	93±1	85±1	-
2mol L^{-1} HNO_3	25	82±1	78±2	85±2	84±1	77±2	-
2mol L^{-1} HNO_3	10	81±2	75±2	77±1	71±2	64±2	-
1mol L^{-1} HNO_3	25	53±1	48±2	56±1	61±1	39±2	-
3mol L^{-1} HCl	25	42±2	23±1	28±2	35±2	26±1	-
2 mol L^{-1} HCl	25	29±1	31±2	17±2	23±2	17±2	-
1 mol L^{-1} HCl	10	25±1	32±2	28±2	29±1	22±1	-

[a] Average ± standard deviation.

3.3.*Amount of the resin*

The effect of the amount of the resin on adsorption of the metals was studied under the optimised conditions (pH 4.0, eluent: 25 mL of 3 mol L^{-1} HNO_3, sample and eluent flow rates: 2 mL min^{-1}). The recovery values of the analytes were gradually increased by increasing the amount of the resin up to 1.25g, but no improvement was obtained after that amount. On the other side, the recovery of the metal ions decreased with the increasing amounts of the resin beyond 1.25 g due to the insufficient eluent volume and so the glass column was filled with 1.25 g of the resin (Figure 3).

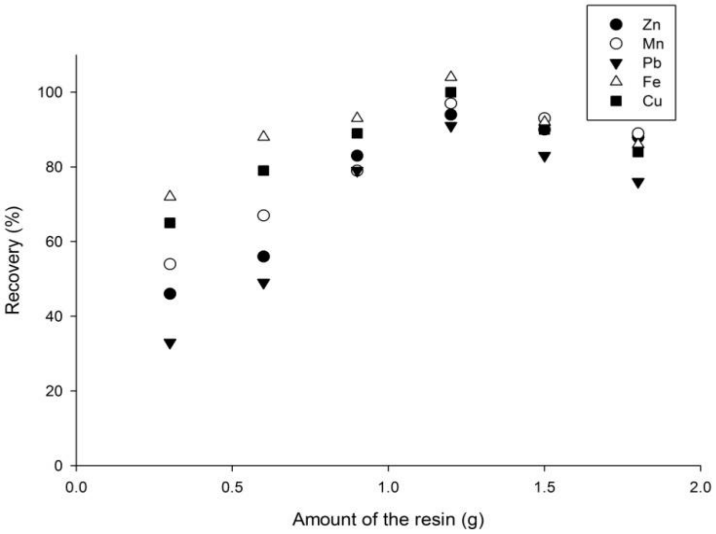

Figure 3: Effect of amount of the resin on the recoveries of the analyte ions (n=3).

3.4. *Heavy metals in street dust*

The obtained values of heavy metals in dust samples (based on dry weight (mg/kg dw) are compared with the maximum permissible levels (MPC), set by World Health Organization (Table 3). In some previous studies, the soil concentration of most heavy metals met or exceeded permissible levels [44]; whereas we found that the mean concentrations of all the heavy metals were less than their maximum permissible concentration.

Table 3: Levels of heavy metals in street dust samples from Dammam (mg/kg) comparing with MPC

Metal	Mean	Range	Median	SD	MPC(mg/Kg)[b]
Fe	8168	8115	4728–9494	1280	50000
Pb	65.17	64.12	25.74–72.25	13.60	100
Cu	71.64	70.92	3.23–152.1	47.34	100
Mn	161.9	105.2	81.02–163.3	33.13	2000
Zn	79.13	78.01	15.45–103.5	33.03	300
Co	6.120	5.311	1.810–9.341	6.120	50
Cd	n.d.[a]	n.d.	n.d.	n.d.	3

[a] n. d.; not detected

[b]: the maximum permissible levels set by World Health Organization (WHO).

The heavy metal levels obtained in this work were compared with the results obtained in other Saudi cities, and in some other countries (Table 4). For over all data, Fe showed the highest concentration of all the selected metals with a mean value of 8168 mg/kg. The level of Fe in the dust is highly variable from place to place. This is due to its highly variable natural abundance in soil [45]. This fact is noticeable in the mean Fe concentration obtained from Dhahran City (similar region as Dammam), which was higher than the results from this study [40]. In contrast, the mean Fe concentration obtained from a study in Amman City (different region) was lower than the results obtained from this study [13]. More detailed comparison between the results obtained here and in other reported studies is shown in Table 4. The mean concentration of Pb was 65.17 mg/kg. This value is significantly higher than the values obtained from Riyadh (Table 4)[37,38]. Also, the level of Pb in this study is more than in recent studies in many cities, such as Jeddah, Toronto, Tehran, Mumbai, and Kuala Lumpur (Table 4) [1,21,38,46,47]. The presence of Pb in this area is related to traffic, which is highly in Dammam compared with the other cities reported [48].The average concentration of Cu (71.64 mg/kg) is lower than that in Riyadh, and higher than the value obtained in Dhahran [36,40]. In turn, the value in Dammam is significantly lower than those obtained in Toronto, Madrid, and Amman [1,2,13] (Table 4). The different concentrations of Cu in dust samples have been associated with anthropogenic activities (brake housing dust and crushed brake pads) [48]. The mean concentrations of Mn, Zn, and Co were 101.9, 79.13, and 6.12mg/kg, respectively. These values are lower than reported in Riyadh and Dhahran [40]. These could be released by tire treads, tire dust, oil and traffic, fuel additives, and such differences could be attributed to the difference in population between the three cities [48,49]. Table 4 shows comparison of the results obtained in this study and in the results reported from elsewhere.

Table 4: Average heavy metal concentration (mg/kg) in street dust from different cities

Location	Year	Fe	Pb	Cu	Mn	Zn	Ref.
Dammam (This study)	2014	8168.0	65.17	71.64	161.9	79.13	
Dhahran (KSA*)	2010	9590	32.4	77.3	230	320	[40]
Riyadh (KSA)	1997	-	66.8	36.4	318.9	141.8	[39]
Riyadh (KSA)	1993	-	110	-	-	-	[36]
Jeddah (KSA)	2009	-	52.6	-	-	91	[38]
Amman (Jordan)	2003	5370.6	976	249.6	144.6	401	[13]
Toronto (Canada)	2013	48234.5	182.8	162.2	1407.2	232.8	[1]
Tehran (Iran)	2012	47935.7	257.4	225.3	1214.5	873.2	[21]
London (UK**)	1988	26000	1030	155	-	680	[35]
Madrid (Spain)	1997	19300	1927	188	362	476	[31]
Istanbul (Turkey)	2003	-	211.8	208.5	397.9	520.8	[23]
Kuala Lumpur (Malaysia)	2013	9888	144.3	137.3	243	292.6	[43]
Mumbai (India)	2014	63,524	70.4	106	1,050	234.8	[44]
Hong Kong (China)	2000	-	157	311	-	1410	[26]
Warsaw (Poland)	2000	-	158	129	-	1150	[32]
Kavala (Greece)	2009	-	386.9	172.4	-	354.8	[30]
Islamabad (Pakistan	2009	-	104	52	-	116	[25]
Birmingham (UK)	2003	-	48	466.9	-	534	[33]

*Kingdom of Saudi Arabia** United Kingdom

3.5. *Validation of the extraction method*

To confirm that the proposed extraction method is suitable for its intended use, it was validated by comparison with certified dust reference material BCR701. Six 2g (dry weight) subsamples of BCR 701 were analysed using the procedure described above (Section 1.5). According to student-t-test calculations, the concentrations of the selected heavy metals recovered during the analysis were very close to the certified values shown in Table 5. Because the calculated t-values were less than the table t-value (critical) at n= 6% and 95% confidence level (value of 2.57), no significant differences were present between the obtained and certified values.

Table 5: Determined and reference values of extractable heavy metals on BCR 701

Element	Obtained value (mg/kg± S.D.)[a]	Certified value (mg/kg ± S.D.)	Calculated t	Table t at95% CL[b]
Fe	8168±72	8172±55	1.73	2.57
Pb	65.17±8.3	61.23±6.7	0.89	2.57
Cu	71.64±8.2	73.11±8.8	1.2	2.57
Mn	161.9±34	163.2±22	1.21	2.57
Zn	79.13±17	82.24±13.60	0.87	2.57
Co	6.120±2.2	5.842±1.4	0.76	2.57
Cd	2.45±0.09	-	-	-

[a]Reported as mean (mg/kg)±RSD(%); N = 6; [b]CL =confidence level

3.6. *Correlation coefficient of heavy metals*

The coefficients of correlation between selected heavy metals are given in Table 6. Significant correlations were found between Fe, Mn, and Co. This indicates that Mn and Co are released together with Fe from the Earth's crust, or from anthropogenic sources at the same rate. These results were in good agreement with other published data [50,51]. It is noteworthy that the Pb, Cu, and Zn were strongly coupled, which indicates that these metals are emitted from the similar anthropogenic sources (vehicles, traffic, industry) or from other sources at the same rate [52,53]. Weak correlations were found for the following element pairs: Pb-Mn, Pb-Co, Zn-Mn, Zn-Co, Cu-Mn, and Cu-Co. These results are closely in agreement with published data [54]. These indicate that Co and Mn on one hand, and Pb, Zn, and Cu on the other hand, are emitted from different sources, or from the similar sources at different rates. Generally, traffic and industrial activities that take place in this area are potential sources of heavy metals.

Table 6: Coefficients of correlation between heavy metals

	Fe	Pb	Zn	Mn	Cu	Co
Fe	1					
Pb	0.51	1				
Zn	0.47	0.59	1			
Mn	0.79	0.15	0.23	1		
Cu	0. 50	0.80	0.73	0.30	1	
Co	0.79	0.40	0.34	0.69	0.37	1

3.7. *Enrichment factor*

The enrichment factor (EF) model is a double normalization model in which each element in the studied samples that was based on standardization of the measured elemental composition is compared with the elemental composition from the crust [55]. The EF calculated for heavy metals related to the crustal composition depends on the background value for each element. The elements commonly considered reference materials are Al, Sc, Ba, and Fe [56,57]. In this research, Fe levels in the crust were used as a reference for EF calculation since soil is considered the major source of Fe in aerosols, in accordance with:

$$\mathrm{EF} = \frac{(\mathrm{CMe}\ /\mathrm{CFe}\ )_{\mathrm{sample}}}{(\mathrm{CMe}\ /\mathrm{CFe}\ )_{\mathrm{crust}}} \quad (1)$$

where $(\mathrm{CMe/CFe})_{\mathrm{sample}}$ is the concentration ratio of the metal and Fe in the sample and $(\mathrm{CMe/CFe})_{\mathrm{crust}}$ is the concentration ratio of the metal and Fe in the crust. Based on this analysis, the five contamination categories proposed by Sutherland [58] are calculated and presented in Table 7.

Table 7: Enrichment factor classification

EF values	Designation of quality
EF < 2	Deficiencyto mineral
EF = 2–5	Moderateenrichment
EF = 5–20	Significantenrichment
EF = 20–40	Veryhighenrichment
EF > 40	Extremelyhighenrichment

Enrichment factors for the selected heavy metals in street dust are shown in Table 8.

Table 8: Crustal average enrichment factor for street dust samples

Metal	Fe	Pb	Cu	Mn	Zn	Co
EF	1.0	18.0	9.8	0.9	5.3	2.5

The EF values recorded for heavy metals in samples followed the order Pb > Cu > Zn > Co > Fe ≈ Mn. The highest EF values recorded for Pb followed by Cu then Zn. This indicates that these metals are emitted from different sources and not only from the Earth's crust [59,60]. The metals with lower EF values (Co, Mn, and Fe) appear to have originated mainly from crustal sources, with minimal anthropogenic input [61].

3.8. *Pollution assessment methodology*

Statistical analysis of the heavy metal levels in street dust is an essential step in basic environmental studies, because it serves as a basis for predictions, and for designing new experiments [53]. To apply these results further, the study was continued to include determination of the contamination factor (CF), pollution load index (PLI), and modified contamination degree (mCd) of the heavy metals in street dust samples from Dammam [62].

3.8.1. *Contamination factor*

The contamination factor (CF) is calculated according to Varol M.[63]. CF is the quotient obtained by dividing the concentration of each metal by its background according to:

$$\mathbf{CF} = \frac{\mathbf{C_{metal}}}{\mathbf{C_{background\ value}}} \qquad (2)$$

where C_{metal} is the metal concentration in street dust and $C_{background}$ refers to the background concentration of that metal.

3.8.2. *Pollution load index*

The pollution load index (PLI) of a place is calculated by obtaining the n-root of the n-CFs for all selected metals [49]. The PLI is governed by the following mathematical Equation [50]:

$$\mathbf{PLI} = \sqrt[n]{\mathbf{CF_1 x CF_2 x CF_3 x \ldots x CF_n}} \qquad (3)$$

where n is the number of metals and CF_1 to CF_n indicate the contamination factors calculated for the first metal to the nth one. A PLI value of >1 indicates pollution; < 1 means no pollution [64].

3.8.3. *Modified contamination degree*

The modified contamination degree (mCd) is the overall degree of contamination, calculated using the modified and generalized Hakanson equation [65]. According to this equation, mCd is defined as the sum of all contamination factors (CF) for a given set of pollutants, divided by the number of pollutants analysed, as follows:

$$\mathbf{mCd} = \frac{\sum_{i-1}^{i-n} \mathbf{CF}}{\mathbf{n}} \qquad (4)$$

where n= number of analysed elements; i = the element. The modified contamination degree is interpreted according to the classification presented in the following Table 9

Table 9: Modified contamination degree classification

mCd value	Designation of quality
mCd< 1.5	Very low degree of contamination
1.5 ≤ mCd< 2	Low degree of contamination
2 ≤ mCd< 4	Moderate degree of contamination
4 ≤ mCd< 8	High degree of contamination
8 ≤ mCd< 16	Very high degree of contamination
16 ≤ mCd< 32	Extremely high degree of contamination
mCd ≥ 32	Ultra-high degree of contamination

The CF, PLI, and mCd values were calculated, and the results are given in Figure 4.
The CF values recorded for the metals occurred in the order CFPb>CFZn>CFCo>CFCu>CFFe>CFMn. These results show that the CF values for Pb and Zn were >1. This could be attributed to the influence of anthropogenic inputs of these two metals. The values of PLI and mCd were 1.1 and 1.82, respectively. Both values were < 1, indicating that there was no appreciable input from anthropogenic sources [66].

3.9. *Potential risk to human health from the selected metals in street dust samples*

The human health risk models developed by the United States Environmental Protection Agency (US EPA) were employed to explore the potential health hazards of heavy metals in street dusts [52]. Currently there is no agreed limit for acceptable maximum risk levels in Saudi Arabia. We therefore adopted the US EPA model and their threshold values to assess the potential human health risk posed by heavy metals in this study. Human beings could be exposed to heavy metals from dust through the following pathways: (1) direct ingestion of dust particles, (2) dermal contact with dust particles, (3) inhalation of dust particles from the air. The formulas to calculate dose received through each different exposure pathways and the detailed explanation for all the parameters are listed in Table 10 [66].

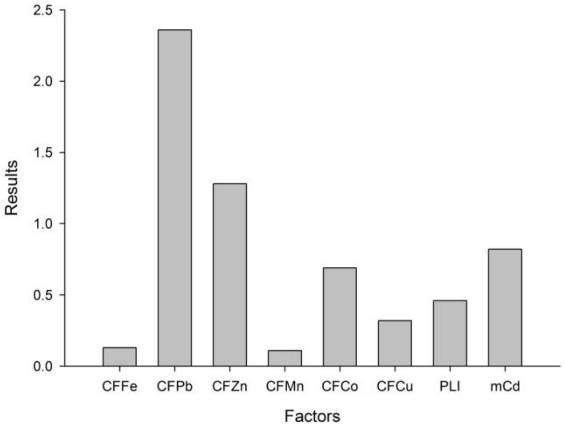

Figure 4: CF, PLI, and mCd values for street dust samples.

Table 10: Defining equations of daily intake via various exposure pathway[a]

Exposurepathway	Calculation formula
Ingestion	$CDI_{ingestion} = \frac{CSxIRSxEFxED}{BWxAT} xCF$
Dermal contact	$CDI_{dermal} = \frac{CSxSAxAFxABSxEFxED}{BWxAT} xCF$
Inhalation	$CDI_{inhalation} = \frac{CSxETxEFxED}{PFEx24xAT}$

[a]CDI = chronic daily intake; CS = exposure point concentration (mg/kg); IRS = ingestion rate (100 mg/d); EF = exposure frequency (350 d/a); ED = exposure duration (30 a); BW = body weight (70 kg); AT = averaging time for non- carcinogens (365 x 70 d); CF = units conversion factor (10^{-6} kg/mg); SA = exposure skin area (5700 cm^2); AF = adherence factor (0.07 $mg.cm^{-2}$); ABS = dermal absorption fraction (0.03 As, 0.001 other metals); ET = exposure time frequency (24 h/d); PFE = particle emission factor (1.36 x 10^9 m^3/kg).

The average daily dose (ADD) of the selected metals and potential risk to health were calculated to assess the potential for chronic (non-carcinogenic) effects for children and adults from ingesting metal-containing street dust. The ADD ($mg/kg·day^{-1}$) values of the selected metals in dust were calculated using the following Equation:

$$\mathrm{ADD} = \frac{(\mathrm{C} \times \mathrm{C_F} \times \mathrm{IR} \times \mathrm{E_F} \times \mathrm{E_D})}{(\mathrm{BW} \times \mathrm{AT})} \quad (5)$$

where C is the heavy metal concentration mg/kg, and IR is the dust-ingestion rate (suggested level is 60 $mg·day^{-1}$ for children, 30 $mg·day^{-1}$ for adults) [53]. BW is the average body weight and is assumed to be 15 kg for children and 70 kg for adults [54,55]. EF is the exposure frequency (350 $days·year^{-1}$) [56]. ED is the exposure duration, in this study assumed to be 6 yr. for children and 24 yr. for adults [57]. AT refers to the average time (for non-carcinogens, AT= ED×365 d) and CF is the conversion factor (1×10^{-6} $kg·mg^{-1}$) [67,68].Furthermore, the potential chronic effects for individual metals are evaluated by comparing the exposure (oral dust ingestion) level over a specified time with a reference dose (RfD) derived from a similar exposure period [52,69]. Risk of intake of metal-contaminated dust to human health characterized by Hazard Quotient (HQ) and Hazard Index (HI) [70-73]. HQ is the ratio of determined 18 dose to the reference dose (RfDi) [74] . HI is the sum of more than one hazard quotient for multiple substances or multiple exposure pathways [75,76]. HI values > 1 shows that there is a chance that health risk may occur, and when HI < 1 the reverse applies [68,79]. The values of the parameters and results of HQ, HI, and ADD are listed in Table 11. HQ and HI were computed using the following equations [52,58]:

$$HQi = \frac{ADD}{RfDi} \qquad (6)$$

Where RfDi is the reference dose[54,59]. Based on calculations of exposure dose at possible exposure pathways, a hazard quotient HQ for each metal and for each exposure pathway and hazard index HI which represent the magnitude of harmful effect with total exposure pathways were yielded as follows:

$$HI = HQ_{ing} + HQ_{der} + HQ_{inh} = \left(\frac{D_{ing}}{RfD_{ing}}\right) + \left(\frac{D_{der}}{RfD_{der}}\right) + \left(\frac{D_{inh}}{RfD_{inh}}\right) \qquad (7)$$

where is corresponding reference doses for each metals and for different exposure pathway [80] is presented as the sum for each metal. The HQ values increased in the following order Co>Pb> Fe> Cu>Mn> Zn. The order was similar for children and adults. The HI for the road dust samples was found to be 0.17 for children and 0.018 for adults. The HQ and HI values were found to be<1. This indicates that there is no significant risk of chronic effects for children and adults in Dammam. The accumulation of toxic metal over time in the bodies of mammals can cause serious health problems. Therefore, the potential risk to the health of children and adults due to exposure to heavy metals in street dust could not be ignored. However, as a result of this study, it is now believed that the level of heavy metals in the street dust do not presently pose a threat to the health of children or adults (Table 11).

Table 11: Risk to health from heavy metals ingested in street dust

Element	RfDi(mg kg^{-1} day^{-1})	ADD(mg kg^{-1} day^{-1})		HQ		HI	
		Children	Adult	Children	Adult	Children	Adult
Fe	7.0×10^{-1}	2.3×10^{-2}	2.5×10^{-3}	3.4×10^{-2}	3.6×10^{-3}		
Pb	3.5×10^{-3}	1.8×10^{-4}	1.9×10^{-5}	5.2×10^{-2}	5.5×10^{-3}		
Cu	4.0×10^{-2}	2.2×10^{-4}	2.4×10^{-5}	5.5×10^{-3}	5.9×10^{-4}		
Mn	1.4×10^{-1}	3.9×10^{-4}	4.2×10^{-5}	2.6×10^{-3}	3.0×10^{-4}		
Zn	3.0×10^{-1}	2.5×10^{-4}	2.7×10^{-5}	8.4×10^{-4}	9.0×10^{-5}		
Co	3.0×10^{-4}	2.3×10^{-5}	2.5×10^{-6}	7.9×10^{-2}	8.4×10^{-3}		
Cd	7.0×10^{-1}	2.3×10^{-2}	2.5×10^{-3}	3.4×10^{-2}	3.6×10^{-3}		
						0.17	0.018

Conclusions

In this work, a simple and rapid solid phase extraction procedure, using Dowex Marathon C (DMC) was successfully developed for the extraction and preconcentration of some heavy metals in street dust samples. The method developed was validated using the dust certified reference material BCR 701. All results obtained fall within the certified value. The method developed was then applied to the determination of six heavy metals (Fe, Pb, Cu, Mn, Zn, and Co) in street-dust samples collected from Dammam City. The average concentrations of the heavy metals were approximately within the safe limits, established by the US Environmental Protection Agency (USEPA).The enrichment factors (EF) relative to Earth-crust abundance and correlation coefficients of heavy metals were calculated to evaluate anthropogenic versus natural sources. The anthropogenic character increased in the following order Fe > Mn > Zn > Cu > Pb > Co. Several statistical analyses of heavy metal levels in street dust have been done. Furthermore, an assessment of the potential risk to health has been carried out. HI values for single elements and the sum of HI value for all studied elements that exposure to population through ingestion, inhalation and dermal contact were lower than 1 for both adult and children, meaning that there are no health risk form the cumulative of these elements to both population groups. However, it should be kept in mind that the data set in this study is relatively small, results are only representative from just one city and the data did not extrapolated to reflect other cities, for example, cities with dryer environments and heavily industrialized areas. Therefore, further work is recommended to investigate the health risk of heavy metals in different areas in Saudi Arabia.

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