Research Article

Mohsen M. El-Sherbiny*, Ali I. Ismail, Mohamed E. EL-Hefnawy

A preliminary assessment of potential ecological risk and soil contamination by heavy metals around a cement factory, western Saudi Arabia

Abstract: Twenty surface soil samples (0-10 cm) and shoots of a perennial shrub *Zygophyllum coccineum* L. were collected around a cement factory on the western coast of Saudi Arabia, in order to assess concentrations of some heavy metals (Cr, Cu, Ni, Pb and Zn). The most noticeable among all heavy metals was Pb that showed an average concentration of 460.15±86.60 μg g⁻¹ followed by Cr (138.67±30.89 μg g⁻¹), Zn (54.41±43.79 μg g⁻¹), Ni (41.22±12.60 μg g⁻¹) and Cu (33.48±12.52 μg g⁻¹). Based on biological concentration factor analysis, *Z. coccineum* can be considered as an accumulator only for zinc (BCF >1).

1 Introduction

The soil is considered an important natural resource because of its capability to act as a geochemical reservoir for various contaminants, including heavy metals resulting from aerosol deposition through urban and manufacturing activities [1,2]. Soil can also act as a natural buffer and therefore can control the dispersal of chemical contaminants in the air, water and biological components [3]. The soil ecosystems worldwide are significantly influenced by rapid industrialization and urbanization [4]. Anthropogenic activities such as construction, energy production, industrial mining, fossil fuel combustion and waste disposal resulted in the uncharacteristic deposition of heavy metals in urban soil resulting in severe environmental pollution [5,6,7]. Industries involved in cement production are the chief source of environmental pollution due to the emission of dust that contains toxic chemicals, which vary according to the raw materials used [8,9]. These toxic chemicals include heavy metals that accumulate in the surrounding environment including soil [10-13]. Many of the heavy metals produced as a byproduct of cement industrial activities are known to be toxic for living organisms even in minimal concentrations [14]. The level of impact is mainly determined by its potential harmfulness, high tenacity, level of non-degradation and biological accumulation [15]. The wind and rain have a major influence on the distribution of dusts that carry heavy metals [16,17]. Other factors that influence the dispersal of heavy metals are the soil-pH and availability of calcium ions, which eventually can determine the solubility, adsorption, retention and movement of heavy metals [18,19]. Many plant species are known to be sensitive to higher concentrations of heavy metals that adversely affect their growth and physiological activities [20,21]. Higher levels of heavy metals can increase the phytotoxicity that affects human beings by bioaccumulation through the food chains [14,22].

*Corresponding author: Mohsen M. El-Sherbiny, Marine Biology Department, Faculty of Marine Sciences, King Abdulaziz University, Jeddah 21589, Saudi Arabia; Marine Biology Department, Faculty of Science, Suez Canal University, Ismailia 41552, Egypt, E-mail: oooomar@kau.edu.sa
Ali I. Ismail, Mohamed E. EL-Hefnawy, Department of Chemistry, Rabigh College of Science and Arts, King Abdulaziz University, Rabigh 21911, Saudi Arabia
Mohamed E. EL-Hefnawy, Department of Chemistry, Faculty of Science, Tanta University, Tanta 31527, Egypt

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Ecological risk assessment studies can reveal the possibility of contamination, as well as the potential impact of heavy metals on the ecology of soil [23]. Many geochemical approaches such as contamination factor (CF), ecological risk factor (ER), potential toxicity response index (RI) and geochemical index method are now widely used for evaluating the anthropogenic influence on urban soil. These indices represent the pollution degree and provide detailed information about the soil quality [24].

Rabigh is an actively growing industrial town located on the western coast of Saudi Arabia. In the south of the city center, an active cement factory with capacity of 4000 tons/day is located. The current study is mainly focused on the assessment of various heavy metals concentrations (Cr, Cu, Ni, Pb and Zn) in the surface soil near the cement factory and their potential impact on the perennial shrub *Zygophyllum coccineum* population. It further focused on evaluating the contamination level of the measured heavy metals based on different pollution indices. These results in turn can be helpful to different stakeholders such as urban development planners and environmental risk managers.

2 Material and methods

2.1 Study Area

Rabigh region in Saudi Arabia is considered as one of the most active places in terms of development activities. By having various natural resources (soils with important minerals, natural vegetation of high economic value and tourism related activities), it plays an integral part in the Saudi Arabian economy. The area of Rabigh city is about 14,000 km\(^2\) and the inhabiting population is almost 93 thousands [25]. It is located in Makkah quadrangles where the Precambrian basement rocks are covered by tertiary sedimentary rocks in the west and by Miocene to Pliocene lavas in the north. The climate is of hot and arid nature with high temperature and humidity during the summer season. The minimum temperature in the study area is normally observed during January (26˚C) and the maximum during the period between July-September (45˚C). The dominant wind direction is from west to southwestern (with a speed of about 10-30 km/h). The present study area is located around a cement factory and has a distance of 30 km south from Rabigh city center.

2.2 Sampling and analytical procedures

Sampling was carried out during January 25-30, 2018. Twenty composite soil samples and 20 plant samples (*Zygophyllum coccineum*) were collected from the area around the Rabigh cement factory. The sampling sites were selected with a grid system having an equal distance from one another (Figure 1) and it covered an area of 2.0 km\(^2\) from the active factory zone. From each site, about one kg of soil sample was collected from the surface 0-10 cm soil layer using an auger. In order to increase the accuracy, three subsamples were collected from each site and were mixed to obtain a bulk composite sample. Upon reaching the laboratory, all samples were air-dried and then sieved through <2 mm sieve. Large objects like pebbles, foreign particles, and debris were carefully removed during the sieving. The particle size distributions for soil samples were carried out through the pipette method [26]. The pH was measured in deionized water with 1:2.5 soil to solution ratio using Beckman glass electrode pH meter. Electrical conductivity (EC) was measured in soil paste 1:5 extract [27], while total carbonates were estimated gasometrically using Collins calcimeter and later calculated following the methods of Hesse [28]. In addition, the organic matter (OM) percentage in the soil samples were also determined by the titration method based on the oxidation of organic matter by K\(_2\)Cr\(_2\)O\(_7\) [28].

In order to remove the heavy metals adhered to fine soil particles, the samples were oven dried at 105˚C overnight, sieved mechanically using a 0.5 mm sieve, homogenized and then ground to 0.063 mm fine powder following the protocols mentioned by Madrid et al. [29]. Crushed soil samples were then weighed (1.00 gm±0.01) and digested using 4:1 nitric acid/perchloric acid (HNO\(_3\)).
and HClO₄ mixture in a Teflon beaker. The samples were later heated initially at 40°C for 1h and the temperature was then subsequently increased to 140-170°C up to a time of 4h until a clear solution was obtained [30]. The resultant solution after filtration is diluted with deionized water to a total volume of 50 ml. For the plant samples, shoots of Z. coccineum were collected and washed with distilled water in order to remove the attached fine sediment particles. The shoots were then homogenized after oven-drying at a temperature of 80°C. About one gram of the homogenized shoot was placed into 125 ml digestion tubes and 5 ml of concentrated perchloric acid was added to each tube. All the tubes were then heated at 120°C for 3h in a block digester and made to total volume of 50 ml [31]. The total heavy metal contents (Cr, Cu, Ni, Pb and Zn) in the soil and the plant samples were estimated with the help of an Inductively Coupled Plasma Optical Emission Spectrometer (Optima 5300 DV with an auto-sampler Model AS 93 Plus/S10, Perkin Elmer, USA). Standards were pre-prepared in order to measure the heavy metals concentration in the digested samples and the obtained values were expressed in μg g⁻¹. To ensure accuracy of the analysis, certified reference materials were used for soil and plant samples (IAEA-433, International Atomic Energy Agency and CRM-1570, National Institute of Standards and Technology Standard, respectively). The analysis was carried out in triplicates and the recoveries of the studied metals were 92.5–114.2% and 93.3–105.5% for the soil and plant reference materials, respectively (Table 1).

| Metal | Soil sample (IAEA-433) | Plant sample (CRM-1570) |
|-------|------------------------|-------------------------|
|       | Certified | Measured | Recovery (%) | Certified | Measured | Recovery (%) |
| Cr    | 136       | 131±3.1  | 96.3         | -         | -         | -           |
| Cu    | 30.8      | 28.5±2.7 | 92.5         | 12.2      | 11.1±1.1  | 91.0        |
| Ni    | 39.4      | 37.7±1.4 | 95.7         | 2.14      | 2±1.0     | 93.5        |
| Pb    | 26        | 29.7±2.6 | 114.2        | -         | -         | -           |
| Zn    | 101       | 98.2±7.6 | 97.2         | 82        | 78.4±9.2  | 95.6        |

2.4 Risk assessment

Different pollution indices were used to assess the metal pollution in this particular study namely; geo-accumulation index ($I_{geo}$), contamination factor (CF), pollution load index (PLI) and potential toxicity response index (RI).

2.4.1 Geo-accumulation index ($I_{geo}$)

For environmental pollution assessment studies, the geochemical and physico-chemical characteristics of sediments are very much crucial in order to identify the source as well as the intensity of the contamination. $I_{geo}$ is therefore used to determine the progressive variation of heavy metals by comparing the present-day metal concentrations with the geochemical background (pre-civilized background values). Geo-accumulation index, introduced by Müller [32], has been applied in most of the recent pollution studies for assessing the soil contamination by heavy metals and is calculated by the following equation:

$$I_{geo} = \log_2 \left[ \frac{C_n}{1.5 \times Bn} \right]$$

where, $C_n$ is the concentration of metal $n$ measured in soil and $Bn$ is the geochemical background value in the upper continental earth’s crust [33]. The constant 1.5 was used to account for potential variability in reference value due to the influence of lithogenic processes. In this regard, seven classes of $I_{geo}$ were categorized by Müller [34] as shown in Table (S1).

2.3 Biological concentration factor (BCF)

To find out the distribution and the level of heavy metals uptake, the bio-concentration factor is calculated by the following equation:

$$BCF = \frac{C_{shoot}}{C_{soil}}$$

where, $C_{shoot}$ and $C_{soil}$ are the heavy metal concentrations in the shoot and the soil sample respectively.
2.4.2 Contamination factor (CF) and pollution index

The contamination factor is a major tool for identifying the pollution and the contamination level in the environmental matrix. CF is considered as the ratio obtained by dividing the concentration of each metal in the sediment by the background value and is obtained by the following formula:

\[
CF = \frac{C_i}{B_i}
\]  

(3)

where \(C_i\) is metal concentration in soil and \(B_i\) is the background value, which refers to the concentration of metal in the soils when there is no anthropogenic input. According to Håkanson [35], the following criteria were applied: CF < 1 indicates low contamination; 1 < CF < 3 is moderate contamination; 3 < CF < 6 is considerable contamination; and CF > 6 is very high contamination.

The pollution load index (PLI) is the estimated geometric mean of relative concentration factors of selected heavy metal of a seemingly polluted site. According to Daud et al. [36], PLI is considered as a combined tool used to assess the amount of pollution at a site for a particular set of heavy metals. The PLI value equal to 1 describes the potential absence of pollution, whereas PLI >1 indicates the polluted nature of the site. The following equation is used for calculating the PLI:

\[
PLI = (CF_1 \times CF_2 \times CF_3 \times \ldots \ldots \times CF_n)^{1/n}
\]  

(4)

Where \(n\) = number of metals and \(CF\) = contamination factors.

The potential ecological risk coefficient \(E_r^i\) was estimated using the formula mentioned by Håkanson (1980) as follows:

\[
E_r^i = T_r^i \times \frac{C_r^i}{C^i_s} = T_r^i \times \frac{C_r^i}{C^i_B}
\]  

(5)

where \(T_r^i\) is the metals toxic response factor (Cr = 2, Cu = 5, Ni = 5, Pb = 5 and Cd = 30) and \(C_r^i\) is the contamination factor, \(C^i_s\) is the concentration of heavy metals in the sediment, and \(C^i_B\) a background value for heavy metals. The degree of \(E_r^i\) can be categorized as shown in Table (S2). The potential toxicity response index (RI) is a method for calculating the sum of different risk factors and is commonly used to evaluate the toxicity of various heavy metals in soil. Håkanson [35] described RI as the index that determines the heavy metal toxicity and the subsequent environmental response to all five risk factors (Pb, Cd, Cu, Zn and Cr) in soils. The potential ecological risk index (RI) was calculated as follows:

\[
RI = \sum E_r^i
\]  

The classification criteria for RI classes are presented in Table (S2).

2.5 Statistical Analysis

Pearson’s correlation coefficient was performed in order to determine the relationships among the physico-chemical properties of soils and the observed heavy metals concentration of each site. Descriptive statistical analysis of the studied parameters was conducted using SPSS software for Windows (version 23.0). Principal Component Analysis (PCA) was performed using factor extraction. The eigenvalue was kept being larger than 1 after Varimax rotation.

Ethical approval: The conducted research is not related to either human or animal use.

3 Results and discussion

The range of variations and the obtained descriptive statistical analysis of various physico-chemical properties of the collected soil samples are given in Table 2. The grain size analysis showed that the soil texture of the studied sites was predominantly sandy (81.0%) followed by silt and clay (14.5% and 4.5% respectively). The soil-pH fluctuated in a narrow range (7.7 to 8.5) with an average value of 8.15 that clearly indicated the neutral to sub-alkaline behavior of the examined soil samples. In case of electrical conductivity, it exhibited comparatively higher values at site 16 (20.1 dSm\(^{-1}\)), which is located adjacent to the cement factory and the lowest one obtained at site 20 (1.1 dSm\(^{-1}\)). The highest organic matter content has been observed from the sites with abundant wild plants. It ranged from a minimum of 0.5 to a maximum of 1.8% (at sites 17 and 16 respectively) with a mean value of 0.9%. The percentage of calcium carbonate in the soil samples varied between 21.4 and 67.9% at sites 11 and 1 respectively with a mean value of 0.9%. The percentage of calcium carbonate in the soil samples varied between 21.4 and 67.9% at sites 11 and 1 respectively (average: 43.9%). The study area is characterized by different geological, morphological, climatological characteristics as well as rapid population growth and urbanization. The present results showed that in the downstream of Rabigh valley,
where significant urbanization is happening, the slope varies from slight to very slight flood risk.

The total concentrations and other descriptive statistics of the analyzed heavy metals from the soil samples around the cement factory are given in Table 3 and Figure 2. The range of each heavy metal in the surface layer of the soil was: 88.33-200.00, 12.30-64.00, 18.30-68.30, 280.40-586.40 and 15.20-89.90 μg g\(^{-1}\) for Cr, Cu, Ni, Pb and Zn, respectively. It is worth mentioning that Pb displayed the highest mean concentration (460.15±86.60 μg g\(^{-1}\)) followed by Cr (138.67±30.89 μg g\(^{-1}\)), Zn (54.41±43.79 μg g\(^{-1}\)), Ni (41.22±12.60 μg g\(^{-1}\)), and Cu (33.48±12.52 μg g\(^{-1}\)) (Table 3). Chromium, copper and nickel are the most influenced heavy metals by the proximity to the cement factory (Figure 2) and sites, such as 19 and 20 clearly exhibited higher concentrations for the above mentioned heavy metals (200.0, 64.0 and 86.3 μg g\(^{-1}\) respectively). Even though the maximum concentration of lead (586.4 μg g\(^{-1}\)) was observed at site 5, there are a few sites (20, 14 and 4), which also showed higher concentrations of this metal. This may be due to the effect of pollution from both the cement factory (sites 20, 14 and 4) and the motor vehicles (at site 5). The high occurrence of lead in such environmental conditions was previously observed by Carreras and Pignata [37], Banat et al. [38], Kakareka and Kukharchyk [39], and Ogunkunle and Fatoba [40].

### Table 2: Descriptive statistics of different physico-chemical characteristics of soil samples studied around the cement factory.

| Sites | Particle size distribution (%) | pH | EC (dSm\(^{-1}\)) | %OM | %CaCO\(_3\) |
|-------|-------------------------------|----|-------------------|-----|-------------|
|       | Sand  | Silt  | Clay  |       |             |
| 1     | 78.6  | 16.8  | 4.7   | 7.7  | 2.6         | 0.9 | 67.9 |
| 2     | 89.3  | 9.3   | 1.5   | 7.9  | 12.6        | 1.0 | 58.9 |
| 3     | 96.7  | 3.0   | 0.3   | 7.8  | 9.0         | 1.3 | 29.5 |
| 4     | 79.0  | 12.0  | 9.0   | 8.2  | 1.9         | 0.5 | 61.6 |
| 5     | 76.4  | 19.7  | 3.9   | 8.0  | 4.7         | 0.8 | 38.4 |
| 6     | 65.4  | 27.2  | 7.4   | 8.4  | 1.8         | 0.5 | 49.1 |
| 7     | 66.4  | 24.6  | 9.0   | 8.0  | 8.6         | 1.6 | 33.9 |
| 8     | 63.3  | 28.4  | 8.3   | 8.1  | 3.5         | 0.5 | 30.4 |
| 9     | 91.6  | 8.2   | 0.2   | 7.9  | 14.1        | 1.5 | 33.9 |
| 10    | 94.8  | 4.7   | 0.5   | 8.4  | 1.8         | 0.7 | 48.2 |
| 11    | 75.0  | 20.9  | 4.1   | 8.4  | 1.3         | 0.8 | 21.4 |
| 12    | 73.4  | 21.5  | 5.1   | 8.4  | 1.5         | 0.7 | 65.2 |
| 13    | 85.4  | 12.2  | 2.4   | 8.1  | 17.2        | 0.8 | 64.7 |
| 14    | 72.2  | 18.8  | 9.0   | 8.2  | 2.0         | 0.9 | 48.2 |
| 15    | 90.5  | 8.2   | 1.3   | 8.5  | 1.1         | 0.5 | 22.3 |
| 16    | 70.8  | 21.3  | 7.9   | 8.0  | 20.1        | 1.8 | 28.6 |
| 17    | 66.1  | 23.9  | 10.1  | 8.3  | 1.6         | 0.5 | 58.5 |
| 18    | 94.9  | 1.8   | 3.3   | 8.3  | 1.6         | 0.9 | 30.4 |
| 19    | 97.7  | 2.2   | 0.1   | 8.1  | 2.1         | 0.6 | 56.7 |
| 20    | 92.5  | 6.1   | 1.4   | 8.3  | 1.1         | 0.6 | 29.9 |
| Minimum | 63.3 | 1.8   | 0.1   | 7.7  | 1.1         | 0.5 | 21.4 |
| Maximum | 97.7 | 28.4  | 10.1  | 8.5  | 20.1        | 1.8 | 67.9 |
| Average | 81.0 | 14.5  | 4.5   | 8.2  | 5.5         | 0.9 | 43.9 |
| Standard error | 2.6 | 2.0   | 1.8   | 0.1  | 1.3         | 0.1 | 3.5 |
| Standard deviation | 11.8 | 8.8   | 3.5   | 0.2  | 6.0         | 0.4 | 15.6 |
contrary to site 2, which was away from the direct effect of various environmental pollution, showed significant low values for most of the heavy metals (copper, nickel and zinc). Similarly, the minimum concentration of lead (280.4 μg g⁻¹) was obtained from site 13, whose location was far away from the factory. Occurrence of the higher concentrations of heavy metals, mainly in the soils north of the cement factory might be linked to different characteristics of the particular soil such as particle size, pH, electrical conductivity and organic matter content. It may also be affected by the direction of the prevailing wind in the region, which is normally north to northwest [41]. Regarding heavy metal concentrations in the shoots of Z. coccineum, results showed the following averages: Zn (16.56 μg g⁻¹±6.99) > Cr (7.43 μg g⁻¹±3.22) > Cu (6.53 μg g⁻¹±2.49) > Ni (5.47 μg g⁻¹±2.14) > Pb (1.56 μg g⁻¹±1.16).

From the current study, it is clear that, the average concentration of each heavy metal exceeded the background values suggested by Håkanson [35]. Also, the current concentration of lead is considerably higher than the values reported around cement factories as well as in many cities worldwide [13, 24, 38, 40, 57, 60-63, see Table 3) except from Nigeria by Ogunkunle and Fatoba [40]. This high Pb content of the soil might be the result of synergistic deposition from the adjacent cement factory. It is well documented that both Pb and Cu are the principal waste products of the cement production [38,39]. However, chances that the emission of such heavy metals is from the motor transport cannot be written off [42]. The cement factory in the current study is located near various major roads and motor transport activities, which can be significantly contributing to the reported high concentration. The obtaining of higher concentrations of Pb from the surface soil layer in the present study coincides with the findings of many studies [43-45]. It is highly recommended to provide proper attention in order to reduce the lead pollution owing to its negative influence on human health; such as its effect on the central nervous systems and many other disorders [46]. Proper monitoring of residents in Rabigh area can provide detailed information on the impact of such high concentrations of Pb on their health and can be useful in drawing future strategies to curb the pollution.

### 3.1 Biological concentration factor (BCF)

BCF values for heavy metals is ranked on the following sequence: Zn > Cu > Ni > Cr > Pb (Table 4 and Figure 3). Relatively higher bioconcentration factors were observed for Cu (0.58), Ni (0.31) and Zn (1.19) from the plants...
collected at site 2, while Cr (0.11) and Pb (0.01) were on the higher side from the plants collected at sites 16 and 7 respectively. Enhanced bioconcentration factors for these heavy metals in the tissues of *Z. coccineum* revealed the weak nature of particular shrub as a bioindicator for heavy metal pollution monitoring programs. The studies of Semhi et al. [11] further corroborated the same finding, who found only minimal differences of heavy metals in *Rhazya stricta* in comparison to the surrounding soil adjacent to a cement factory in Oman. Still, there are many studies pointing out the negative effect of cement dust on the growth and productivity of some wild and cultivated plants [47-49]. Even though the BCF values of Cu and Zn obtained for *Z. coccineum* in the present study is comparatively higher than those of Cr, Ni and Pb, which may only indicate the less absorption of those elements.

### 3.2 Geo-accumulation Index

The $I_{geo}$ index for Pb varied from heavily contaminated (HC) to heavily extremely contaminated (HEC) at all the sites with values varying between 3.22 (site 13) and 4.29 (site 5) (Table 5). $I_{geo}$ values of Cr and Cu in turn fluctuated...
within the status of uncontaminated to moderately contaminated level. More importantly, Zn displayed status was at an uncontaminated level (negative) at all sites (Table 5). It is understood that the proximity of an active cement factory together with the presence of an industrial city and petrochemical factory (located 15 Km north of the cement factory) are the main sources of pollution in the current study area. Also, both traffic emissions from local roads and highways, and the direction of the wind play a significant role in transferring pollutants.

### 3.3 Contamination factor and pollution load index

Results showed that the highest CF value obtained for Pb is a direct indication of the higher contamination of this metal (CF > 6), in all studied sites (Table 6). This might be due to the high synergistic deposition of heavy metals from the cement manufacturing [37-39]. Mean contamination factor indicated moderate contamination (1 < CF < 3) for Cr and Cu and low metal contamination for Zn and Ni (CF < 1). The following sequence was visible in terms of the average CF values obtained in the present study: Pb > Cr > Cu > Ni > Zn. As represented in Table 6, the PLI values were found to be high (PLI >1) in almost all the studied sites indicating the severe nature of pollution and subsequent deterioration of the sediment quality [50]. The PLI values in the present study ranged between 1.04 and 2.65 and the obtained higher PLI value might be directly associated with the higher concentrations of heavy metals in the sites, particularly at the site 15 (PLI = 2.65) and site 19 (PLI = 2.58). Since PLI obtained in the current observation is >1, all sites are considered to be polluted according to the studies of Cabrera et al. [51].

### Table 5: Averages of geo-accumulation ($I_{geo}$) of the studied heavy metals in all sites.

| Sites | Averages of $I_{geo}$ of the studied heavy metals |
|-------|--------------------------------------------------|
|       | Cr      | Cu      | Ni      | Pb      | Zn      |
| 1     | 1.58MC  | -0.78UC | 0.33UMC | 3.71HC  | -1.06UC |
| 2     | 0.78UMC | -1.61UC | -0.71UC | 3.84HC  | -2.81UC |
| 3     | 1.51MC  | 0.04UC  | 0.39UMC | 4.04HEC | -0.24UC |
| 4     | 1.16MC  | -1.12UC | 0.35UC  | 4.22HEC | -1.74UC |
| 5     | 1.20MC  | -0.44UC | 0.13UMC | 4.29HEC | -0.68UC |
| 6     | 1.72MC  | -0.09UC | 0.70UMC | 3.69HC  | -1.05UC |
| 7     | 1.08MC  | 0.45UMC | 0.34UMC | 3.81HC  | -2.18UC |
| 8     | 1.52MC  | 0.06UMC | 0.95UMC | 4.02HEC | -1.10UC |
| 9     | 0.75UMC | 0.21UC  | -0.14UC | 3.91HC  | -0.71UC |
| 10    | 1.46MC  | 0.23UMC | 0.73UMC | 4.01HEC | -0.78UC |
| 11    | 1.58MC  | 0.06UMC | 0.97UMC | 3.46HC  | -0.64UC |
| 12    | 1.30MC  | -0.78UC | 0.21UMC | 3.40HC  | -1.54UC |
| 13    | 0.93UMC | -0.48UC | 0.35UMC | 3.22HC  | -1.00UC |
| 14    | 1.79MC  | -0.57UC | 0.39UMC | 4.22HEC | -1.52UC |
| 15    | 1.66MC  | 0.36UMC | 0.88UMC | 4.12HEC | -0.77UC |
| 16    | 1.20MC  | -0.32UC | 0.04UMC | 3.96HC  | -0.41UC |
| 17    | 1.68MC  | -0.59UC | 0.25UMC | 4.10HEC | -1.11UC |
| 18    | 1.27MC  | 0.20UMC | 0.70UMC | 4.01HEC | -0.60UC |
| 19    | 1.93MC  | 0.77UMC | 0.48UMC | 3.93HC  | -1.04UC |
| 20    | 1.23MC  | -0.39UC | 1.19UMC | 4.28HEC | -0.56UC |
3.4 Potential toxicity response index (RI)

The ecological risk factor \((E^j)\) indices for Cr, Cu, Ni and Zn obtained in the study were lower than 40 (Table 7). Lead contributed significantly towards the ecological risk factor closely followed by Cd and Cu. The \((E^j)\) value for Pb ranged from contaminated to moderately contaminated in terms of ecological risk factor. The high content of Pb in surface soil samples observed in this study can be a result of the combined effects of the pollutants from the cement manufacturing. The highest RI value of 176.89 was recorded at site 20, and the lowest value (91.46) from site 13 with an average of 140.73 (Table 7). According to the standards, most of the sites in the current study placed in low ecological risk level (RI ≤ 150) except for sites 4, 5, 8, 10, 14, 15 and 20 that showed moderate ecological risk (Table 7).

3.5 Relations between heavy metals and soil characteristics

Pearson’s correlation showed negative correlation for soil-pH with both EC \((r = -0.559, P < 0.01)\) and OM \((r = -0.579, P < 0.01)\), while positive correlation with Ni \((r = 0.531, P < 0.01)\) (Table 8). EC showed positive correlation with OM

| Sites | Contamination factor | PL Index |
|-------|----------------------|----------|
|       | Cr       | Cu   | Ni   | Pb | Zn |       |
| 1     | 1.89     | 0.87 | 0.85 | 23.08 | 0.72 | 1.88 |
| 2     | 1.08     | 0.49 | 0.42 | 25.19 | 0.21 | 1.04 |
| 3     | 1.80     | 1.46 | 0.90 | 29.09 | 1.27 | 2.44 |
| 4     | 1.41     | 0.69 | 0.54 | 32.99 | 0.45 | 1.51 |
| 5     | 1.45     | 1.10 | 0.75 | 34.49 | 0.94 | 2.08 |
| 6     | 2.09     | 1.41 | 1.10 | 22.83 | 0.72 | 2.22 |
| 7     | 1.34     | 2.05 | 0.86 | 24.76 | 0.33 | 1.81 |
| 8     | 1.81     | 1.57 | 1.32 | 28.58 | 0.70 | 2.37 |
| 9     | 1.06     | 1.30 | 0.62 | 26.48 | 0.92 | 1.83 |
| 10    | 1.74     | 1.76 | 1.13 | 28.49 | 0.88 | 2.44 |
| 11    | 1.89     | 1.57 | 1.33 | 19.46 | 0.96 | 2.37 |
| 12    | 1.56     | 0.88 | 0.79 | 18.65 | 0.51 | 1.59 |
| 13    | 1.20     | 1.07 | 0.87 | 16.49 | 0.75 | 1.69 |
| 14    | 2.18     | 1.01 | 0.89 | 32.82 | 0.52 | 2.02 |
| 15    | 2.00     | 1.92 | 1.26 | 30.61 | 0.88 | 2.65 |
| 16    | 1.45     | 1.20 | 0.70 | 27.42 | 1.13 | 2.07 |
| 17    | 2.02     | 1.00 | 0.81 | 30.24 | 0.69 | 2.03 |
| 18    | 1.52     | 1.72 | 1.11 | 28.46 | 0.99 | 2.41 |
| 19    | 2.41     | 2.56 | 0.95 | 26.86 | 0.73 | 2.58 |
| 20    | 1.49     | 1.15 | 1.55 | 34.35 | 1.02 | 2.48 |
| Minimum | 1.06 | 0.49 | 0.42 | 16.49 | 0.21 |       |
| Maximum | 2.41 | 2.56 | 1.55 | 34.49 | 1.27 |       |
| Average | 1.67 | 1.34 | 0.94 | 27.07 | 0.76 |       |
| Standard error | 0.08 | 0.11 | 0.06 | 1.14 | 0.06 |       |
| Standard deviation | 0.37 | 0.50 | 0.29 | 5.09 | 0.27 |       |
indicating the influence of high salinity on the organic particles due to the disruption of soil micro-aggregates thereby increasing the solute concentration of organic compounds as mentioned by Morrissey et al.\[52\]. On the other hand, there were negative correlation for EC with Cr (r = -0.626, P < 0.01), and Ni (r = -0.510, P < 0.01).

It is known that increasing soil pH can limit the binding capacity of clay compounds, leading to the reduced sorption of metals\[53\]. A negative correlation was also observed for CaCO\textsubscript{3} percentage with Cu (R = -0.456, P < 0.01), Ni (R = 0.522, P < 0.01), and Zn (R = 0.589, P < 0.01). Also, Pb did not show any correlation with other studied metals, which indicates the different origin or controlling factors of Pb in soil. Changes in the physico-chemical properties, biological activities and distribution of contaminants might have been attributed to such kind of relations\[54\]. The statistical results also showed significant positive correlation with the elemental pairs Cr-Cu (r = 0.439), Cr-Ni (r = 0.433) and Ni-Zn (r = 0.430) at a significance level of 0.05. A positive correlation, which was significant at the level of 0.01 was also obtained between Cu and Ni (r = 0.492).

Generally, a higher elemental pair correlation represents the influence of primary anthropogenic source\[55\].

### 3.6 Principal component analysis (PCA)

Principal component analysis provided the information about the possible interactions among the different

| Sampling Sites | Potential ecological risk indices for individual metal (E\textsuperscript{i}) | Potential toxicity response indices (RI) |
|----------------|-------------------------------------------------|-------------------------------------|
|                | Cr | Cu | Ni | Pb | Zn | Cr | Cu | Ni | Pb | Zn |
| 1 | 8.97/L | 4.36/L | 9.40/L | 98.10/C | 0.72/L | 121.55/LR |
| 2 | 5.14/L | 2.46/L | 4.58/L | 107.08/C | 0.21/L | 119.46/LR |
| 3 | 8.55/L | 7.30/L | 9.85/L | 123.63/C | 1.27/L | 150.60/M |
| 4 | 6.70/L | 3.44/L | 5.90/L | 140.23/C | 0.45/L | 156.71/M |
| 5 | 6.90/L | 5.52/L | 8.23/L | 146.60/C | 0.94/L | 168.18/M |
| 6 | 9.89/L | 7.06/L | 12.15/L | 97.03/C | 0.72/L | 126.85/LR |
| 7 | 6.34/L | 10.24/L | 9.48/L | 105.25/C | 0.33/L | 131.64/LR |
| 8 | 8.60/L | 7.84/L | 14.48/L | 121.48/C | 0.70/L | 153.09/M |
| 9 | 5.05/L | 6.48/L | 6.83/L | 112.55/C | 0.92/L | 131.82/LR |
| 10 | 8.23/L | 8.80/L | 12.40/L | 121.10/C | 0.88/L | 151.41/M |
| 11 | 8.97/L | 7.84/L | 14.65/L | 82.70/C | 0.96/L | 115.12/L |
| 12 | 7.38/L | 4.38/L | 8.65/L | 79.25/M | 0.51/L | 100.17/LR |
| 13 | 5.70/L | 5.36/L | 9.55/L | 70.10/M | 0.75/L | 91.46/LR |
| 14 | 10.36/L | 5.06/L | 9.80/L | 139.48/C | 0.52/L | 165.22/M |
| 15 | 9.50/L | 9.62/L | 13.83/L | 130.08/C | 0.88/L | 163.90/M |
| 16 | 6.90/L | 6.00/L | 7.73/L | 116.53/C | 1.13/L | 138.28/LR |
| 17 | 9.60/L | 4.98/L | 8.90/L | 128.50/C | 0.69/L | 152.67/LR |
| 18 | 7.22/L | 8.62/L | 12.20/L | 120.95/C | 0.99/L | 149.98/LR |
| 19 | 11.43/L | 12.80/L | 10.45/L | 114.18/C | 0.73/L | 149.58/LR |
| 20 | 7.06/L | 5.74/L | 17.08/L | 146.00/C | 1.02/L | 176.89/M |
| Average | 7.92 | 6.70 | 10.31 | 115.04 | 0.77 | 140.73 |
| Maximum | 11.43 | 12.80 | 17.08 | 146.60 | 1.27 | 176.89 |
| Minimum | 5.05 | 2.46 | 4.58 | 70.10 | 0.21 | 91.46 |
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environmental parameters and the observed heavy metals (Table 9). The PCA ordination of the soil properties and heavy metal concentrations revealed that the first two components accounted for 55.27 % of the total variance (PC1: 28.61% and PC2: 26.66%). PC1 was mainly characterized by the high loading of Soil-pH, sand along with Cr and Ni (Table 9). This can be mainly due to the impact of natural and anthropogenic sources as proposed by Möller et al. [56]. On the other hand, PC2 was dominated by soil characteristics like silt and clay. This factor implies the physical nature of the soil samples and its impact on the heavy metals. Moreover, PC3 was represented by Zn, Cu and Ni metals with total variance of 15.42%, which are commonly due to anthropogenic sources enriched in the top soils of urban soils [57]. While PC4 accounted for 9.54% of the total variance loaded with Pb. This is a clear indication of the pollutant contribution from various motor vehicle activities [58] and cement emissions [43]. The higher concentrations of Pb in the urban soils may reflect the effect of its long-term contamination in the particular soils as well as its long half-life in soils [59].

4 Conclusions

The distribution of heavy metals (Cr, Cu, Ni, Pb and Zn) in the surface soils around a cement factory in the Rabigh district, Saudi Arabia, indicated that this area has been affected mainly by cement industry and traffic emissions. The studied metals especially lead showed relatively higher concentrations at sites near the factory. From different perspectives of the current study, the average of ecological risk potential is described as a region with
moderate risk. Different multivariate analysis proved that the effect of heavy metal deposition due to the functioning of the cement factory and other anthropogenic sources like motor vehicle emissions are of minimal importance.

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References

[1] Liu Y., Su C., Zhang H., Li X., Pei J., Interaction of soil heavy metal pollution with industrialisation and the landscape pattern in Taiyuan city, China, PLoS one, 2014, 9(9), p.e105798.
[2] Nagajyoti P.C., Lee K.D., Sreekanth T.V.M., Heavy metals, occurrence and toxicity for plants: a review. Environmental chemistry letters, 2010, 8(3), 199-216.
[3] Lutts, S., Lefèvre I., How can we take advantage of halophyte properties to cope with heavy metal toxicity in salt-affected areas?, Annals of Botany, 2015, 115(5), 509-528.
[4] Kabata-Pendias A., Trace elements in soils and plants. CRC press, 2010.
[5] Martín J.A.R., Arias M.L., Corbí, J.M.G., Heavy metals contents in agricultural topsoils in the Ebro basin (Spain). Application of the multivariate geostatistical methods to study spatial variations, Environmental pollution, 2006, 144(3), 1001-1012.
[6] Taghipour M., Ayoubi S., Khademi H., Contribution of lithologic and anthropogenic factors to surface heavy metal in western Iran using multivariate geostatistical analyses, Soil and Sediment Contamination: An International Journal, 2011, 20(8), 921-937.
[7] Kabata-Pendias A., Pendias H., Trace Elements in Soils and Plants, 2nd ed., CRC Press Incorporation, Boca Raton, Florida, USA, 2001.
[8] Isikli B., Demir T., Urer S.M., Berber A., Akar T., Kalyoncu C., Effects of chromium exposure from a cement factory, Environmental research, 2003, 91(2), 113-118.
[9] Isikli B., Demir T.A., Akar T., Berber A., Urer S.M., Kalyoncu C., Canbek, M., Cadmium exposure from the cement dust emissions: a field study in a rural residence, Chemosphere, 2006, 63(9), 1546-1552.
[10] Bermudez G.M., Moreno M., Invernizzi R., Plá R., Pignata, M.L., Heavy metal pollution in topsoils near a cement plant: the role of organic matter and distance to the source to predict total and HCl-extracted heavy metal concentrations, Chemosphere, 2010, 78(4), pp.375-381.
[11] Semhi K., Al-Khirbash S., Abdalla O., Khan T., Duplay J., Chaudhuri S., Al-Saidi S., Dry atmospheric contribution to the plant–soil system around a cement factory: spatial variations and sources- a case study from Oman, Water, air, and soil pollution, 2010, 205(1-4), 343.
[12] Mandal A., Voutschkov M., Heavy metals in soils around the cement factory in Rockfort, Kingston, Jamaica, International Journal of Geosciences, 2011, 2(1), 48.
[13] Wang X.S., Magnetic properties and heavy metal pollution of soils in the vicinity of a cement plant, Xuzhou (China), Journal of Applied Geophysics, 2013, 98, 73-78.
[14] Kabata-Pendias A., Mukherjee A. B., Trace elements from soil to human. Springer Science and Business Media, 2007.
[15] Bozkurt S., Moreno L., Neretnieks I., Long-term processes in waste deposits, Science of the total environment, 2000, 250(1-3), 101-121.
[16] Schuhmacher M., Nadal M., Domingo J.L., Environmental monitoring of PCDD/Fs and metals in the vicinity of a cement plant after using sewage sludge as a secondary fuel, Chemosphere, 2009, 74(11), 1502-1508.
[17] Alloway B.J., Sources of heavy metals and metalloids in soils. In: Alloway B. (Eds.), Heavy metals in soils, environmental pollution, 22. Springer, Dordrecht, 2013.
[18] Sauve S., Hendershot W., Allen H.E., Solid-solution partitioning of metals in contaminated soils: dependence on pH, total metal burden, and organic matter, Environmental science and technology, 2000, 34(7), 1125-1131.
[19] De Matos, A.T., Fontes, M.P.F., Da Costa, L.M., Martinez, M.A., Mobility of heavy metals as related to soil chemical and mineralogical characteristics of Brazilian soils, Environmental pollution, 2001, 111(3), 429-435.
[20] Lepeuš H., Cesar V., Suver M., The annual changes of chloroplast pigments content in current-and previous-year needles of Norway spruce (Picea abies L. Karst.) exposed to cement dust pollution, Acta Botanica Croatica, 2003, 62(3), 27-35.
[21] Mandre M., Kask R., Pikk J., Ots, K., Assessment of growth and stem wood quality of Scots pine on territory influenced by alkaline industrial dust, Environmental monitoring and assessment, 2008, 138(3), 51-63.
[22] Lamb D.T., Ming H., Megharaj, M., Naidu R., Phytoxicity and accumulation of lead in Australian native vegetation, Archives of environmental contamination and toxicology, 2010, 58(3), 613-621.
[23] Fairbrother A., Wenstel R., Sappington K., Wood W., Framework for metals risk assessment, Ecotoxicology and environmental safety, 2007, 68(2), 145-227.
[24] Mugoša B., Đurović D., Nedović-Vuković M., Barjaktarović-Labović S., Vrvić M., Assessment of ecological risk of heavy metal contamination in coastal municipalities of Montenegro, International journal of environmental research and public health, 2016, 13(4), 393.
[25] Census 2010, The general authority of statistics, The general population and housing census, https://www.stats.gov.sa/en/13.
[26] Dewis J., Freitas F., Physical and chemical methods of soil and water analysis, Physical and chemical methods of soil and water analysis, 1970 (10).
[27] Bäckström M., Karlsson S., Allard B., Metal leachability and anthropogenic signal in roadside soils estimated from sequential extraction and stable lead isotopes, Environmental monitoring and assessment, 2004, 90(1-3), 135-160.
[28] Hesse P.R., A Textbook of Soil Chemical Analysis. John Murray, London, UK, 1971.

[29] Madrid L., Díaz-Barrientos E., Madrid F., Distribution of heavy metal contents of urban soils in parks of Seville, Chemosphere, 2002, 49(10), 1301-1308.

[30] Yap C.K., Ismail A., Tan S.G., Omar H., Concentrations of Cu and Pb in the offshore and intertidal sediments of the west coast of Peninsular Malaysia, Environment International, 2002, 28(6), 467-479.

[31] Cottenie A., Verloo M., Velghe G., Camerlynch R., Chemical Analysis of Plants and Soil. Laboratory of Analytical and Chemistry, State of Univ. Gent, Belgium, 1982.

[32] Müller G., Index of geoaccumulation in sediments of the Rhine River, Geojournal, 1969, 2, 108-118.

[33] Taylor S.R., McLennan S.M., The geochemical evolution of the continental crust, Reviews of Geophysics, 1995, 33(2), 241-265.

[34] Müller G., Schwermetallbelastung der sedimemten des Neckars und seiner Nebenflusse: eine Estandsaufnahmedie, Chemiker Zeitung, 1981, 105, 157-164.

[35] Håkanson L., Ecological risk index for aquatic pollution control. A sedimentological approach, Water Research, 1980, 14(8), 975-1001.

[36] Daud M., Wasm M., Khalid N., Zaidi J.H., Iqbal J., Assessment of elemental pollution in soil of Islamabad city using instrumental neutron activation analysis and atomic absorption spectrometry techniques, Radiochimica Acta International journal for chemical aspects of nuclear science and technology, 2009, 97(2), 117-121.

[37] Carreras H.A., Pignata M.L., Biomonitoring of heavy metals and air quality in Cordoba City, Argentina, using transplanted lichens, Environmental Pollution, 2002, 117(1), 77-87.

[38] Banat K.M., Howari F.M., Al-Hamad A.A., Heavy metals in urban soils of central Jordan: should we worry about their environmental risks?, Environmental research, 2005, 97(3), 258-273.

[39] Kakareka S., Kukharchyk T., Towards improvement of heavy metals emission assessment methodology from cement production in EMPE/EEA AEI Guidebook. In: Proceedings 12th Joint Teipe/Eionet Meeting, 2011, 2-3.

[40] Ogunkunle C.O., Fatoba P.O., Contamination and spatial distribution of heavy metals in topsoil surrounding a mega cement factory, Atmospheric pollution research, 2014, 5(2), 270-282.

[41] Elbsy M.S., Mlybari, E.A., Comprehensive environmental management of the construction of the marine works of the Rabigh coastal power plant project on the Red Sea, Saudi Arabia, International Journal of Environmental Planning and Management, 2015, 15(5) 144-156.

[42] Farmaki E.G., Thomaidis N.S., Current status of the metal pollution of the environment of Greece- a review. Global nest. The international journal, 2008, 10(3), 366-375.

[43] Al-Khashman O.A., Shawabkeh R.A., Metals distribution in soils around the cement factory in southern Jordan. Environmental pollution, 2006, 140(3), 387-394.

[44] Bi X., Feng X., Yang Y., Qiu G., Li G., Li F., Liu T., Fu Z., Jin Z., Environmental contamination of heavy metals from zinc smelting areas in Hezhang County, western Guizhou, China, Environment international, 2006, 32(7), 883-890.

[45] Wu G., Kang H., Zhang X., Shao H., Chu L., and Ruan C., A critical review on the bio-removal of hazardous heavy metals from contaminated soils: issues, progress, eco-environmental concerns and opportunities, Journal of Hazardous Materials, 2010, 174(1-3), 1-8.

[46] Beyersmann J., Gastmeier P., Wolkewitz M., Schumacher M., An easy mathematical proof showed that time-dependent bias inevitably leads to biased effect estimation, Journal of clinical epidemiology, 2008, 61(2), 1216-1221.

[47] Lübbek V., Pensa M., Rätsep A., Air pollution zones and harmful pollution levels of alkaline dust for plants, Water, Air, and Soil Pollution: Focus, 2003, 3(5-6), 199-209.

[48] Dziiri S., Hosni K., Effects of cement dust on volatile oil constituents and antioxidative metabolism of Aleppo pine (Pinus halepenesis) needles, Acta physiologiae plantarum, 2012, 34(5), 1669-1678.

[49] Prajapati S. K., Biomonitoring and speciation of road dust for heavy metals using Calotropis procera and Delbergia sissoo, Environmental Spectrics and Critics, 2012, 1(4), 61-64.

[50] Tomlinson D., Wilson J., Harris C., Jeffrey D., Problems in the assessment of heavy-metal levels in estuaries and the formation of a pollution index. Helgoländer meeresuntersuchungen, 1980, 33(3): 566–575.

[51] Cabrera F., Clemente L., Barrientos E.D., López R., Murillo J.M., Heavy metal pollution of soils affected by the Guadiamar toxic flood, Science of the Total Environment, 1999, 242(1-3), pp.117-129.

[52] Morrissey C.A., Bscendell-Young L.I., Elliott J.E., Assessing trace-metal exposure to American dippers in mountain streams of southwestern British Columbia, Canada, Environmental Toxicology and Chemistry, 2005, 24(4), 836-845.

[53] Fijalkowski K., Kacprzak M., Grobelak A., Placek A., The influence of selected soil parameters on the mobility of heavy metals in soils, Inżynieria i Ochrona środowiska, 2012, 15, pp.81-92.

[54] Kumar A., Khan M.A., Muqtadir A., Distribution of mangroves along the Red Sea coast of the Arabian Peninsula: Part 1. The northern coast of western Saudi Arabia, Earth Science, India, 2010, 3 (1), 28-42.

[55] Yang Z., Lu W., Long Y., Bao X., Yang Q., Assessment of heavy metals contamination in urban topsoil from Changchun City, China, Journal of Geochemical Exploration, 2011, 108(1), 27-38.

[56] Möller A., Müller H.W., Abdullah A., Abdelgawad G., Utermann J., Urban soil pollution in Damascus, Syria: concentrations and patterns of heavy metals in the soils of the Damascus Ghouta. Geoderma, 2005, 124(1-2), 63-71.

[57] Manta D.S., Angelone M., Bellanca A., Neri R., Sprovieri M., Heavy metals in urban soils: a case study from the city of Palermo (Sicily), Italy, Science of the total environment, 2002, 300(1-3), 229-243.

[58] Tokalioglu, S., Cetin, V., Kartal, S., Amberlite XAD-1180 modified with thiosalicylic acid: A new chelating resin for heavy metal contamination of urban soils: issues, progress, eco-environmental concerns and opportunities, Journal of Hazardous Materials, 2010, 174(1-3), 1-8.

[59] Yaprakali S.K., Biomonitoring and speciation of road dust for heavy metals using Calotropis procera and Delbergia sissoo, Environmental Spectrics and Critics, 2012, 1(4), 61-64.

[60] Thornton L. Metal contamination of soils in urban areas. In: Bullock P., Gregory P.J. (Eds.), Soils in the urban environment. London: Blackwell, 1991.
[61] Walker S., Griffin S., Site-specific data confirm arsenic exposure predicted by the U.S. Environmental Protection Agency. Soils in the urban environment, 1998, 106, 133-139.

[62] Li X., Poon C.S., Liu P.S., Heavy metal contamination of urban soils and street dusts in Hong Kong. Applied geochemistry, 2001, 16(11-12), 1361-1368.

[63] CCME (Canadian Council of Ministers of the Environment), Canadian Soil Quality Guidelines for the Protection of Environmental and Human Health, National Guidelines and Standards Office, Quebec, Publication No. 1299, 2007, 1-7.

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