ORIGINAL ARTICLE

Trace metals in topsoils near the Babylon Cement Factory (Euphrates River) and human health risk assessment

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Abstract Metals were studied in topsoils surrounding a cement plant near the Euphrates River, Iraq. Bulk concentrations of $SiO₂$, $Al₂O₃$, CaO, MgO, Na₂O, K₂O, Fe, Ni, Cu, Zn, Cd, Pb, pH, organic matter, clay, sand, and silt were analyzed. The results indicate that the soils in the area are primarily alkaline with an average pH of 8.8; the texture is sandy loam. The CaO percentages were found to be high (31.9 wt% average). Soil levels of Pb, Zn, and Cd levels close to the cement plant are higher than the values reported in the literature. An enrichment factor calculation suggests that Ni, Cu, Zn Cd, and Pb have anthropogenic sources and exhibit a significant level of contamination. Principal component analysis identified Pb, CaO, Zn, and Cd as the signature geochemical characteristics that are associated with the cement factory. Moreover, most of the affected soils exhibit a NW–SE trend, which coincides with the prevailing winds in the study area. This pattern is indicative of dry deposition as the primary mechanism for metal accumulation. The hazard index $(HI_{Ni-Zn-Cd-Pb})$ was

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found to be 0.619 for cumulative metals, representing the highest value reported for health risk related to impacted soils by cement industry.

Keywords Cement factory · Metals · Soils · Human health risk - Principal component analysis

Introduction

Global cement consumption has been progressively rising, reaching 3,585 Mt in 2011 and 3,736 Mt in 2012 (The Global Cement Report, 10th Edition). The environmental effects of the cement industry are related to all stages of the cement process. Emissions from cement industry activities are known to provide a large contribution of particulate matter (PM) to the atmosphere and to the surrounding soils via both wet and dry deposition (Al-Khashman and Shawabkeh [2006\)](#page-8-0). Despite the global importance of cement plants, there are few published studies regarding the extent of pollution caused by this industry (Al-Omran and Maghraby [2011](#page-8-0); Saralabai and Vivekanadau [1995](#page-8-0); Zerrouqi et al. [2008](#page-8-0); Al-Khashman and Shawabkeh [2006](#page-8-0); Ibanga et al. [2008](#page-8-0); Bermudez et al. [2010](#page-8-0)); datasets on environmental levels and the associated health risks of the cement industry are very scarce (Schuhmacher et al. [2004,](#page-8-0) [2009](#page-8-0)). A previous study on soil samples near a cement factory in southern Jordan reported that the highest concentrations of Pb, Zn, and Cd were measured in the soil that was closest to the cement factory (Al-Khashman and Shawabkeh [2006](#page-8-0)); the same elements were affected by cement plant activities in Córdoba City, Argentina (Bermudez et al. [2010](#page-8-0)) and in Saudi Arabia (Al-Omran and Maghraby [2011](#page-8-0)). In arid regions, dry deposition is the dominant deposition process (Grantz et al. [2003\)](#page-8-0), and the

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Fig. 1 Location of sampling points in the vicinity of the cement factory

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particles emitted from cement plants can enter the soil and affect its physicochemical properties. Furthermore, natural processes, such as erosion, soil resuspension, and subsequent wind transportation of particulate matter to more sensitive environments, should be examined in more detail. Surveys on the concentrations and distributions of soil contaminants in soils surrounding cement plants are important for planning management strategies that reduce the risk associated with this mining activity in arid zones.

Iraq is considered the world's largest cement importer, importing 10.5 million tons in 2012 (The Global Cement Report, 10th Edition). However, the presence of highquality natural limestone (high percentage of $CaCO₃$) and its location near the surface in Iraq promote low-cost mining activities, representing a potential for growth in the

Table 1 Statistical summary for the major physical and chemical properties of analyzed soils in the study area

	Maximum	Minimum	Average	SD
Fe (mg kg^{-1})	415	97	307	91.3
Ni $(mg kg^{-1})$	163	36	112.8	35.2
Cu $(mg kg^{-1})$	53	9	23.6	10.1
Zn (mg kg ⁻¹)	132	29	63.8	29.6
Cd $(mg kg^{-1})$	0.280	0.020	0.103	0.066
Pb $(mg kg^{-1})$	141	21	92.1	36.1
$SiO2 (wt\%)$	41.6	20.7	32.1	8.6
Al_2O_3 (wt%)	8	4.2	6.6	1.7
CaO (wt $\%$)	60.5	21	31.9	19.1
$MgO(wt\%)$	5.4	2.7	4.3	1.2
$Na2O (wt\%)$	1.8	0.3	0.9	0.6
$K2O (wt\%)$	0.8	0.2	0.6	0.3
LOI $(\%)$	22.2	4.7	16.8	8.2
OM $(\%)$	0.8	0.2	0.3	0.06
pH	10.1	8.1	8.8	0.9
Clay $(\%)$	23	13.2	16.9	4.5
Sand $(\%)$	71.5	46.3	54.9	11.4
Silt $(\%)$	33.9	15.3	27.5	8.3

SD standard deviation

Table 2 Chemical composition of soils impacted by cement industry worldwide

cement industry. An even distribution of cement plants in Iraq reflects the wide availability of raw materials; however, there are not studies on the possible environmental effects of the industry in arid climates. In this case study, a multivariate statistical method (i.e., principal component analysis) was used to evaluate the pollution caused by a cement factory located near the Euphrates River. The primary goals of this study were: (1) to evaluate the pollution level caused by the cement industry in surrounding soils in an area with no additional industrial air emission sources and (2) to conduct a human health risk assessment that considers a soil ingestion exposure path. To our knowledge, this study represents the first attempt to evaluate the extent of the environmental effects that are related to the recently growing cement industry in Iraq.

Materials and methods

Site and soil sampling

The Babylon Cement Factory is located in Babylon Governorate, Al-Mussaib District, Al-Sadda Township (Fig. [1](#page-1-0)). The plant began manufacturing normal cement and resistant cement salts in 1957. The Babylon Governorate covers a total area of $5,119 \text{ km}^2$ and hosts a population of 1,820,700. The prevailing winds in the study area are typically oriented in an NW–SE direction, i.e., directed toward population centers. The cement factory is surrounded by agricultural activities that consist primarily of cultivated lands with major irrigation to the east and southeast and desert grazing and marginal agricultural to the west of the Euphrates River (Fig. [1](#page-1-0)). Topsoil samples were collected around the area of the cement factory at a depth of 5-15 cm (according to the work procedures in the Iraqi Commission for Geological Survey). Twenty topsoil samples were collected from eight transects surrounding the Babylon Cement Factory (Fig. [1](#page-1-0)). The collected samples were stored in plastic bags.

Al-Khashman and Shawabkeh [\(2006](#page-8-0))

^b Al-Omran and Maghraby ([2011\)](#page-8-0)

^c Sielaff and Einax [\(2007](#page-8-0))

 d Schuhmacher et al. [\(2004](#page-8-0)) (calculated concentrations of pollutants in soil as emission products of cement plant)

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Fig. 2 Enrichment factors for Ni, Cu, Zn, Cd, and Pb in the studied soils

Sample chemical analysis

Samples were oven dried for 4 h at 60 \degree C to a constant weight (modified from Bermudez et al. [2010](#page-8-0)), sieved through a 200-mesh sieve (75 um) and stored for physical and chemical analysis. The soil pH was determined in a soil paste extract using a pH meter according to Sparks et al. [\(1996](#page-8-0)). The particle size distributions were analyzed following Gee and Bauder ([1996\)](#page-8-0). The percentage of organic matter (%OM) was determined by combustion of the samples at 500 °C for 4 h (Peltola and Aström 2003). The soil samples were digested with a mixture of HCl–HNO₃ (1:3) and filtered $(42 \mu m)$ before being analyzed with an optical emission spectrometer (Perkin Elmer, Optima 2100 DV) at the Department of Chemistry, Baghdad University. The method accuracy was evaluated by analyzing certified reference standard materials and was found to be better than ± 10 %.

Enrichment factor

The soil enrichment factors (EF) were estimated to assess the contamination level and the possible anthropogenic effects in soils surrounding the Babylon Cement Factory. The following equation was used in this study to determine the individual EFs:

$$
EF_i = [C_i/C_{\text{Fe}}]_{\text{Soil}} / [C_i/C_{\text{Fe}}]_{\text{EarthCrust}},
$$

where EF_i is the enrichment factor of element *i*, $C_i/C_{\text{Fe}}|_{\text{soil}}$ is the concentration ratio of element i to Fe in the soil and $[C/C_{Fe}]_{UC}$ is the concentration ratio of element *i* to Fe in the upper continental crust (Rudnick and Gao [2003](#page-8-0)). The local geochemical background was not considered in this study, because the study area is surrounded by agricultural activities and most soils are affected by these anthropogenic activities. Paterson et al. ([1996\)](#page-8-0) proposed Fe as an acceptable normalization element. Moreover, four contamination categories are recognized on the basis of the enrichment factor: $EF < 2$ represents soils with minimal enrichment or are uncontaminated, $EF = 5-20$ corresponds to substantial enrichment, $EF = 20-40$ represents very high enrichment, and $EF > 40$ corresponds extremely high enrichment (Paterson et al. [1996](#page-8-0)).

Data analysis

Factor analysis and derivate methods have been used in geochemical applications to identify pollution sources and natural versus human contributions (Chen et al. [2005](#page-8-0)). Principal component analysis (PCA) was performed to identify both the metals that are associated with the cement factory and the affected soil samples. The number of significant principal components for interpretation was selected based on the Kaiser criterion, which consists of retaining factors that have an eigenvalue exceeding 1 (Manly [1994\)](#page-8-0) and that provide a total explained variance of at least 70 %. This method allows for the identification of a group of chemical elements that are associated with the cement plant. PCA analysis was performed using XLSTAT software.

Human health risk assessment

Risk assessment for non-carcinogenics (hazard quotient, HQ) was estimated based on the Integrated Risk Information System (IRIS) of the United States Environmental Protection Agency (US EPA [2009](#page-8-0), [2013](#page-8-0)). Human exposure was calculated using the maximum and average metal concentrations in the study area. Human exposure via an oral pathway was considered according to the following equation:

$$
ADD = [C \times IngR \times EF \times ED]/[BW \times AT],
$$

where C is the mean metal concentration (mg kg^{-1}) in the soil sample. Conservative estimates of soil ingestion rates, IngR, were chosen for adults $(100 \text{ mg day}^{-1})$ and children $(200 \text{ mg day}^{-1})$. An average body weight, BW, of 60 kg for adults and 16 kg for children was considered in this study. Moreover, the exposure frequency, EF, was assumed to be 350 days year^{-1}, while the exposure duration, ED, and the averaging time, AT, were 6 years and 2,190 days, respectively. The noncancer toxic risk was determined by calculating the hazard quotient, HQ , where $HQ = ADD/$ RfD and RfD is an estimate of the daily exposure of the human population (including sensitive groups) that is likely to be without an appreciable risk of deleterious effects during a lifetime. Therefore, $HO \leq 1$ suggests that adverse health effects are unlikely, whereas $HQ >1$ suggests that adverse health effects are possible. Moreover, $HQ > 10$ suggests a high chronic risk for adverse health effects. The HQs can be added to determine that hazard index (HI) and to estimate the risk of mixing contaminants; therefore, the HQ for each metal at a specific location was added to determine the hazard index (HI). The US EPA has not established an RfD for Pb; therefore, the RfD used in this study was $3.5E-03$ mg kg⁻¹ day⁻¹, which was calculated from the provisional tolerable weekly Pb intake limit

Fig. 3 Spatial distribution of Cd, Cu, Ni, Pb, and Zn in soils surrounding the cement factory. The concentrations are in mg kg^{-1} . The cement factory area is highlighted with a white square

Table 4 Factor loadings of each variable, variance, and explained and cumulative variance of the PCA

	F1	F ₂	F ₃
Fe ₂ O ₃	0.381	0.073	-0.922
pH	-0.883	-0.469	-0.036
OM	0.165	0.863	-0.478
Clay	-0.033	0.952	-0.305
Sand	-0.619	-0.786	0.002
Silt	0.721	0.662	0.204
SiO ₂	-0.568	0.508	0.647
Al ₂ O ₃	-0.878	0.443	-0.182
CaO	0.843	-0.455	-0.288
MgO	-0.979	0.185	-0.084
Na ₂ O	-0.964	-0.215	-0.154
K_2O	-0.635	0.726	0.264
LOI	-0.784	0.601	0.156
Pb	0.985	-0.099	0.144
Cd	0.851	0.023	0.525
Zn	-0.106	-0.308	0.946
Ni	0.790	0.519	0.326
Cu	0.087	0.994	0.061
Eigenvalue	8.901	5.925	3.174
Explained variance (%)	49.451	32.914	17.635
Cumulative variance $(\%)$	49.451	82.365	100.00

Bold values are factor loadings of the principal components

(25 mg kg⁻¹ body weight⁻¹) according to the FAO/WHO (Food and Agriculture Organization of the United Nations/ World Health Organization) recommendations. The RfD values for the studied metals were 0.0005, 0.30, and 0.02 for Cd, Zn, and Ni, respectively, according to IRIS (US EPA [2009](#page-8-0), [2013\)](#page-8-0).

Results and discussion

Descriptive statistics

Descriptive statistics for the physical and chemical properties of the studied soils are summarized in Table [1,](#page-2-0) including minima, maxima, means, and standard errors of the means. The textural analysis indicates that the soils range from sandy to loam. The maximum percentages of sand, clay, and silt are 71.5, 23, and 33.9 %, respectively; the minimum percentages are 46.3 , 13.2, and 15.3 %, respectively. The soils are calcium enriched with a maximum CaO content of 60.5 wt%; the average CaO content is 31.9 wt%. The alkaline nature of the studied soils is revealed by pH values that range between 8.1 and 10.1. Table [2](#page-2-0) shows reported values from the literature for affected soils near cement plants around the world. According to this table, the Pb, Ni, and Cu contents in the samples from this study are the highest values reported in soils that have been affected by cement industry activities.

Correlations and source identification

Table [3](#page-3-0) shows the Pearson correlation matrix for the studied metals. Significant positive correlations were found for the following relationships: sand pH (0.91) , Na₂O pH (0.957), Ni–silt (0.980), SiO₂–K₂O (0.901), MgO–Al₂O₃ (0.957), Na2O–MgO (0.918), LOI–Al2O3 (0.926), LOI– MgO (0.866), LOI–K₂O (0.975), Pb–CaO (0.833), Cd–Pb (0.911), and Cd–Ni (0.855). The LOI–Al₂O₃, LOI–MgO, LOI– $K₂O$, and Ni–silt positive correlations may be indicative of rock alteration processes (geogenic). The Cd–Pb, Cd–Ni, Pb–CaO, and Ni–silt relationships are related to cement production emissions. Figure [2](#page-4-0) shows the enrichment factors (EFs) for the analyzed soils with significantly enriched levels of Ni, Cu, Zn, Cd, and Pb. The significantly higher EFs indicate that the metals are derived from anthropogenic sources. Additionally, the high correlation between CaO and pH indicate that the pollution originated from the cement factory. The spatial distribution of the studied metals in the soils is shown in Fig. [3](#page-5-0). Cd and Cu exhibit a similar distribution, i.e., higher levels along the southeastern side of the studied area. Pb and Zn exhibit a bulls-eye spatial pattern with higher concentrations surrounding the cement factory area, which gradually decrease moving away from the factory. In general, most elements are enriched along the southern and southeastern sides of the studied area.

Indicators of the cement pollution were identified using principal component analysis (PCA). In this study, the three principal components explain 100 % of the total variance of the dataset. However, only the first two components were used for interpretation because they represent 82.37 % of the total variance. The first component, i.e., Factor 1 (F1) describes 49.45 % of the total variance. Positive scores (Table 4) are related to the contribution of Pb, CaO, Cd, Ni, and silt, which are likely to reflect the geochemical signature of cement dust in soils. Figure [4](#page-7-0) shows the projection of the first two factors; the analysis differentiates at least three associations: (1) an association in the negative plane of the F1 axis it is formed by K_2O , LOI, SiO_2 , Al_2O_3 , and MgO, which are characteristic elements of soils (geogenic); (2) an association in the positive plane of the F1 axis that opposes the first association is represented by $Fe₂O₃$, Cd, Pb, CaO, silt, and Ni, which are indicators of pollution emitted from cement industry activities; and (3) a group of elements formed by clay,

Fig. 4 Graphical representation of the first two factorial planes of the PCA

Fig. 5 Projection of the sample soil variables on the F1–F2 factorial plane

Table 5 Reference doses and cancer factors of the principal studied metals and human health risk due to emissions from the Babylon Cement Factory

organic matter (OM), and Cu, which is possibly related to local agricultural activities.

The chemical compounds and samples were projected onto the F1–F2 factorial plane to understand their distributions according to the factorial axes. Figure 5 shows the projection of the samples and the group of metals that are related to the cement industry (i.e., Cd, Fe, Pb, Zn, and Ni). Samples with a geographic location restricted to the eastern side of the Babylon Cement Factory are correlated with the group of studied metals. This spatial distribution is related to the prevailing wind direction (NW to SE). Although the transport processes of particulate matter are complex, the application of PCA and mapping are useful tools to determine the most prominent environmentally affected areas.

Human health risks

The non-carcinogenic risks for the local population due to the exposure to metals in soils surrounding the Babylon Cement Factory were evaluated. One exposure route was considered in this work, i.e., soil ingestion. The hazard index (HI) for the maximum concentrations of Cd, Pb, Zn, and Ni is 0.619, with HQ_{Pb} exhibiting the highest value (0.5) (Table 5). Based on average concentrations, HI_{Ni-Zn} Cd–Pb due to oral exposure is 0.405, while a value of 0.619 is found using the maximum concentrations. Schuhmacher et al. (2004) (2004) reported that $HI_{Ni-Zn-Cd-Pb}$ is 0.0006, which is considerably lower than estimated HIs in this study. To our knowledge, there are no previously published risk assessment studies on this topic to provide a constructive comparison. The current environmental exposure to metals associated with the studied soils does suggest that health risks are higher for the individuals living in the vicinity of the Babylon Cement Factory. However, additional studies on the Pb bioavailability are necessary in this area, because Pb exhibited the highest HQ value (0.504) and also lead is considered as one of the most toxic metals for humans (Biasioli et al. [2006\)](#page-8-0).

Conclusions

PCA is a useful tool to deduce which pollution elements are produced by the cement industry in an arid environment and to detect which soil samples are affected by mining activities. CaO, Pb, Cd, Ni, Zn, and Fe were associated with cement production. Concentration mapping and the PCA results show a dominant NW to SE pollution trend in the soils (downwind of the cement plant). The Babylon Cement Factory has affected the surrounding soils with potentially harmful metals; the enrichment factors suggest extremely high pollution levels in the area that largely exceed published metal levels from soils surrounding other cement factories. The estimated hazard quotient for each studied metal and the cumulative hazard index (HI_{Ni-Zn-}) $_{\text{Cd-Pb}}$) indicate that there is no significant health risk to the population. However, further studies to evaluate the bioavailability of Pb in soils are important because HQ_{Pb} has a contribution of 0.5 to the estimated HI. This study must be considered as a preliminary evaluation of the effects caused by a cement factory in Iraq. Further investigations should include short- and long-range transport of resuspended soils in the area.

Conflict of interest We declare that we have no financial and personal relationships with other people or organizations that can inappropriately influence our work. Opinions in the paper do not constitute an endorsement or approval by the funding agencies and only reflect the personal views of the authors.

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