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A Protocol for Pollution Index, Source Identification, and Spatial Analysis of Heavy Metals in Top Soil

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ABSTRACT

Introduction: This study aimed to assess a good protocol for the contamination indexes, concentration, spatial analysis, and source identification of toxic metals in top soils.

Materials and Methods: In the first step, samples were taken from top soil (30 cm) and the metals were extracted and detected with ICP-AES. In the second step, Enrichment Factor, Geoaccumulation Index, and Contamination Factor of metals were calculated to determine soil contamination degree. Furthermore, the principal component analysis and correlation between metals were conducted for source identification.

Results: Spatial analysis, as an important section of the present protocol, was performed using Arc GIS, kriging, and Moran's I models. As results of Moran's I model showed, distribution pattern for Fe, As, Cd, Cu, Ni, Pb, and Zn were random (z-scores ranged from -1.17 to 1.09), indicatingthat these elements could be emitted from different potential sources. In Moran's model, spatial autocorrelation of each pollutant could be measured based on its value and location.

Conclusion: The finding of this protocol can be used for extraction of contamination indexes, concentration, spatial analysis, and source identification of toxic metals in top soils.

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Introduction

The soil is part of environment in earth, that is largely exposed to heavy metal aggregation [1]. Soil pollution with heavy metals (HM) possibly results in contamination of rural products and causes other unhealthy impacts The soil pollution by HM is associated to nature and texture of soil, content of clay fraction, and its physicochemical quality [2]. In

the cities and villages residential regions, HM in soils can penetrate the human tissues through direct skin contact, ingestion, and breath. Consequently, they may gather in various body tissues including the kidneys, bones, and liver [3]. The main toxic heavy metal included Pb, As, Hg, Cd, Cu, and Cr. The Cu had a harmful effect on the liver and kidney role, lung cancer, and chief nervous system. Long-term contact of lead can harm the nervous system creating symptoms, for example insomnia, memory loss, and headache .The Cr affect gastrointestinal disorders and sometime may lead to death. The high dose contact to Arsenic can be damaging to the skin as well as the respiratory and cardiovascular systems .The Cd accumulation in human tissues can harm the nervous system and resulted to renal [3-6]. In several studies soil pollution was reported by high values of heavy metals; for example, in northern Colombia high values of Pb, Cd and Hg were reported [7]. In Tabriz, a industrial City of Iran, contamination with Cd, Cu, Cr, and Pb were mentioned [8]. In some cities of China, high levels of Cr, , Pb, As, Hg, and Cd [9] were found. In Zwierzyniec of Poland, contamination with lead and copper was indiacted.[1] In Van region in Eastern Turkey, contamination with Cd, As, Pb, Cr, and Hg was represented [10]. In Gebze town of Kocaeli City in Turkey, contamination with Cd, Pb, Cu, and Co was reported[11].

This study aimed to found a protocol for the contamination indexes, concentration, spatial analysis, and source identification of the toxic metals in top soils.

Materials and Methods

Study area and sampling points

The study was conducted around Lake Urmia in North-west of Iran. The region of study has about 4000 km^2 area[12]. Also the control station selected in prevented land in south of Urmia city. To select the study location, GIS was used and 32 zones were selected. Furthermore, one control point was selected from unpolluted soil in Urmia (Figure 1). The methods applied to select the study area and sampling points were performed and explained in previous studies [13, 14].

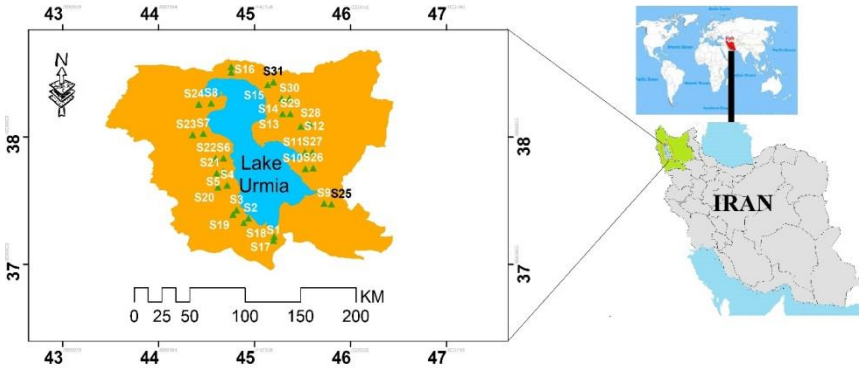

Figure 1: Geographic location of present protocol study ("S: sampling point)"

Soil sampling and chemical analysis

To conduct the study, 97 topsoil (0-30 cm) samples were collected in triplicate. Sampling was done in non-rainy days. During the sampling period, the average temperature was 16 °C.

The dry weight of each sample was about 1 kg, which was collected from three subsamples in approximately 5 meters within each sampling zone to prepare the composite [14].

Samples were packed into bags of polyethylene and moved to the soil lab. Soil samples were dried for 24 hours at 60 °C before analysis; later, they were cleaned and selected using a sieve with size100 mesh (0.15 mm) [7, 14]

Extraction of HM was done using the USEPA 1996 Technique 3050B. First 0.5 gram of each prepared soil sample was warmed (2 hour at 50 ºC)

and poured into the solution with 70 % HNO_3 (9 ml) and HCL (3 ml), and 40 % HF (1 mL).
This mixture was mineralized to digested using a Teflon high-pressure digestion vial (Applied Plastics Technology, Inc., Bristol, USA) in 170 °C for 4 h. In next step, digested solution were cooled and then were added H_2O_2 (2 mL - 30%) and concentrated HNO_3 (3 mL) into it [14]. This extraction liquid using Milli-Q water was weakened to 50 mL, and finally, by a micro-porous membrane with the pore size of (0.45 µm) filtered into bottles (PET). Also, a blank digest solution used for quality control.

In last section, HM of soil sample were detected using US EPA Method 200.7 by inductively coupled plasma-atomic emission spectrometry (ICP-AES, Model: Arcous, German),

Indexes of soil pollution

Enrichment factor (EFs)

EF was used to determine the probable pollutant origin, the impacts of unnaturally actions on the grade of soil pollution and health risk. For each metal, EF was calculated separately by formula. (2) based on the formula reccomended by Taylor [15].

$$EF = \frac{(C_n/C_{Fe})_{sample}}{(C_n/C_{Fe})_{background}} \qquad (2)$$

Where, the nth metal concentration (mg/kg) is *Cn* and Iron concentration is C_{Fe} (reference metal used for standardization in our study, mg/ kg) in the soil of experienced environment and the reference environment.

In this Eq, normaliization of a HM was used against a reference HM to recognize accumulation of HM in soil. The greatest conventional reference HM were applied in previous studies comprising Al and Fe [10, 16]. Gradation of metal pollution may be categorized into 7 groups as the rate of EF in soil: no enrichment (EF < 1); minor enrichment (1 ≤ EF < 3); moderate enrichment (3 ≤ EF < 5); moderately severe enrichment (5 ≤ EF < 10); severe enrichment (10 ≤ EF < 25); very severe enrichment (25 ≤ EF < 50); extremely severe Enrichment (EF > 50) [7].

Index of geoaccumulation (I_{geo})

The geoaccumulation (I_{geo}) index estimates the levels of HM contamination in n cities and villages soils. The I_{geo} was founded the including between the current and pre-industrial HM value [17]. This index is measured by Eq. (3):

$$I_{geo} = log_2 \frac{C_n}{1.5B_n} \qquad (3)$$

Here, C_n are the concentrations of HM evaluated in the soil samples of environment and B_n is related soil sample of the control area. The coefficient 1.5 use to evaluate usual fluctuations in contents of a given substantial in the environment and to discriminate very slight manmade influences. The l_{geo} consists of 7 groups [9]: uncontaminated ($I_{geo} \leq 0$); uncontaminated to moderately contaminated ($0 < l_{geo} \leq 1$); moderately contaminated ($1 < I_{geo} \leq 2$); moderately to heavily contaminated ($2 < l_{geo} \leq 3$); heavily contaminated ($3 < I_{geo} \leq 4$); heavily to extremely contaminated ($4 < I_{geo} \leq 5$), and extremely contaminated ($5 \leq I_{geo}$).

Contamination degree (C_{deg})

The another factors to identify soil contamination in heavy metals are the contamination factor (CF) and contamination degree (CD) [18]. The contamination factor is computed by Eq. (4) regarding value of each HM in the sampling soil point and background soil:

$$CF = {C_{meal}}/{C_{background}} \qquad (4)$$

The CF is separated into 4 groupings [10]: Low contamination (CF < 1); Moderate contamination (1 < CF ≤ 3); moderate to strong contamination (3 < CF ≤ 6) and very strong contamination (CF > 6).

Additionally, the C_{deg} is extracted using Eq (5) that considers the sigma of CF for heavy metal pollutants:

$$C_d = \sum_{i=1}^{n} C_f^i \qquad (5)$$

The C_{deg} is divided into 4 cataloging [10]: Low degree of contamination ($C_{deg} < 8$); Moderate degree of contamination ($8 < C_{deg} \leq 16$); moderate to a strong degree of contamination ($16 < C_{deg} \leq 32$); and a very strong degree of contamination ($C_{deg} > 32$).

Spatial distribution of metal elements and C_{deg}

C_{deg} maps were drawn using ArcGIS 10.1 to show the spatial distribution in assessing contamination values of the heavy metals in around Urmia Lake. To create raster layers in independent form for $C_{deg,}$ the Kriging interpolation technique was applied. Afterwards, the raster computer function was recycled to overlay each layer to create distribution map pollutants averages (Figure 2).

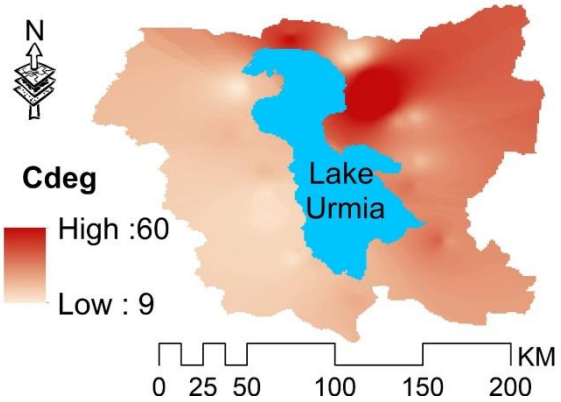

Figure 2: Spatial distribution map of soil samples' contamination with heavy metals

The regions with high and low contaminated of HM were highlighted by rane of high and low color . Based on the findings, red region, showing heavy metal concentrations was wider than the green region with low soil contamination.

Spatial autocorrelation

Global Moran's Index (Moran's I) was applied to evaluated the local variation distribution pattern (which can be as a disperse, random or clustered) of metal elements in soil samples. In this model, spatial autocorrelation of each pollutant can be measured based on its value and location. In Moran's I, the null hypothesis showed random distribution of values across the study area [19, 20]. In the spatial autocorrelation model, in addition to Morans I, z-score and P-value can be measured to evaluate significance of the mentioned Index [21]. The Global Moran's I can be calculated as follows [20, 22, 23]:

$$I = \frac{n}{S_0} \frac{\sum_{i=1}^{n} \sum_{j=1}^{n} w_{i,j} z_i z_j}{\sum_{i=1}^{n} z_i^2} \quad (1)$$

Where, (S_0) and (n) are the sum of all spatial weights and the total number of features, respectively; wij is the spatial weight between feature i and j; and zi represents the deviation of an attribute for feature i from its mean (xi – X) [23, 24]:

$$S_0 = \sum_{i=1}^{n} \sum_{j=1}^{n} w_{i,j} \quad (2)$$

Finally, the ZI-score for the statistic can be calculated as follows:

$$z_I = \frac{1 - E[I]}{\sqrt{V[I]}} \quad (3)$$

Where, E[I] and V[I] are equal to -1/(n-1) and E[I2] – E[I]2, respectively [21].

In this model, the z-scores lower than -1.65 indicated dispersed emission pattern, z-scores from -1.65 to 1.65 represent random emission, and z-scores higher than 1.65 indicated clustered emission pattern [21, 25]. According to the results of Moran's I model in figure 3, distribution patterns for Fe, As, Cd, Cu, Ni, Pb, and Zn were random (z-score ranged between -1.17 to 1.09), indicating that these elements could be emitted from different potential sources.

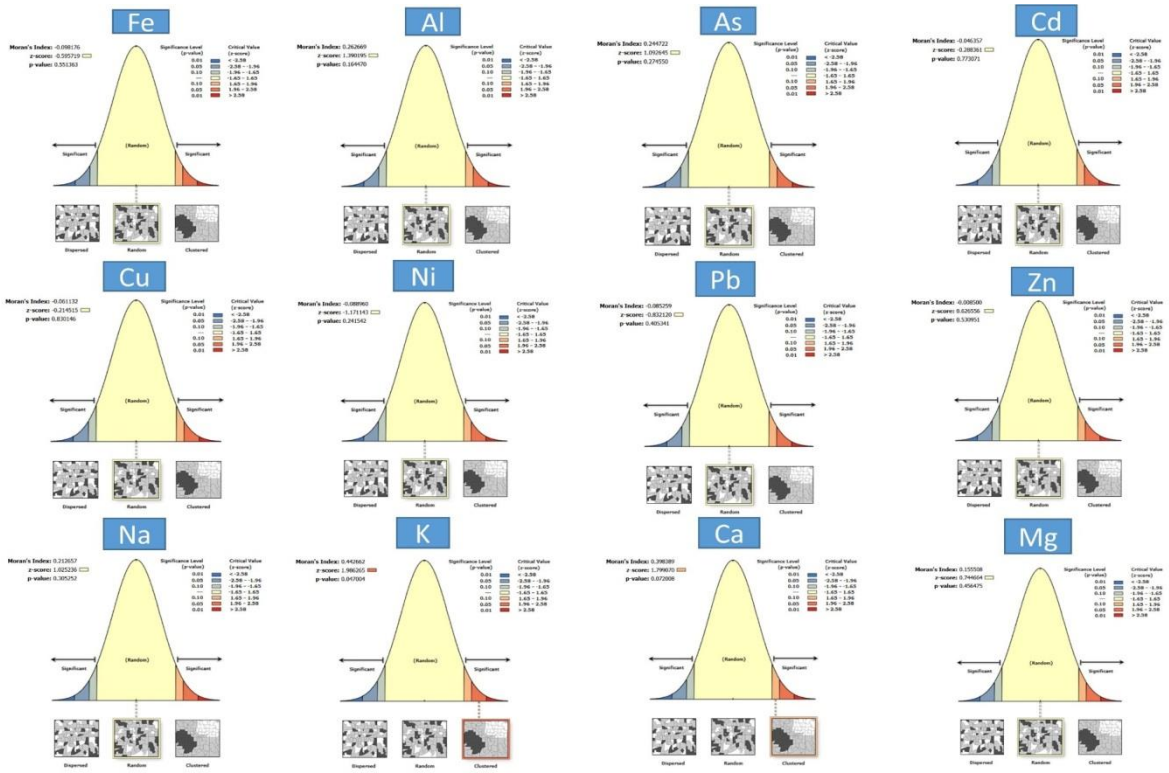

Figure 3: Spatial autocorrelation model (Moran's I) for measured metals around Urmia Lake

Descriptive statistics of the metal element concentrations

Table 1 lists the basic descriptive statistics of the metal elements' concentrations in sampled soils around Urmia Lake. The results indicated that the means of As, Cd, Cu, Ni, Pb, and, Zn content were 6, 0.4, 58, 81, 31, 129, and 390 mg/kg in sampling site top soils, respectively. Therefore, elements in the sampling sites were ranked based on their mean concentrations from highest to lowest: Zn > Ni > Cu > Pb > As >Cd.

Table 1: Statistical descriptive of metal elements in sampling soils (n: 96) around Urmia Lake (mg/kg)

Element	Fe	As	Cd	Cu	Ni	Pb	Zn
Mean	3.1%	6	0.4	58	81	31	129
Std. deviation	1.8%	1.17	0.60	77.95	174.3	59.96	199.50
Median	2.7%	5	0.26	30	40	13	84
Maximum	10%	8.1	2.7	344	743	258	888
Minimum	1.9%	3.5	0.2	20	15	8	54
C.V	0.58	0.20	1.50	1.37	2.15	1.93	1.55
Skewness	3.48	0.310	3.74	3.32	3.74	3.70	3.76
Kurtosis	11.68	-0.51	12.95	10.81	12.97	12.75	13.08

Spatial distribution patterns of the contamination rates in the soils around Urmia Lake are illustrated in figure 2. As represented, mapping pollutant values is a good graphical method for assessing the probable enrichment sources and identifying the critical points with high pollution [26, 27].

Spatial analysis showed that distribution trends for Cd, Cu, Pb, Ni, and Zn gained similarity with non-identical values. This same pattern indicates that they can be emitted from the same sources.

Source identification

To identify possible sources of HM, the principal component analysis (PCA) and spearman's correlation tests were employed. The PCA is a method suggested by the US Environmental

Protection Agency [28] to investigate the distribution of heavy metal contamination by source.

Based on the findings, two principal components were extracted with eigenvalues of higher than 1. These two principle components counted for 85.3% of the total variation among the variables.

The first PCA, factor 1, accounted for 70.8% of the total variance and consisted of Cd, Cu, Ni, Pb, and Zn as heavy metal elements. This factor represents that soil contamination may be caused by anthropogenic sources such as industries and traffic. The same results were also reported in several previous studies. In a study in urban soil of south India, based PCA analysis showed that Cu and Pb were attributed to traffic activities and Zn, Pb, and Cu had anthropogenic origin. In another study in villages of Reasi district, India, principal component analysis showed that Zn, Cu, Pb, and Cr were associated with vehicle emissions, traffic sources, and industrial sources.[3-6]

Conclusion

The findings of this protocol can be used for determining soil and dust soil contamination indexes, concentration, spatial analysis, and source identification of toxic metals in top soils.

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Conflict of interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence this paper.

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