Ecological Risk Assessment, Interpolation, and Pollution Source Identification of Toxic Elements in Soils and Leaves of the Vineyard of Malayer County

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Abstract

Grape is a strategic product in the county of Malayer. Despite the great importance and existence of polluted resources in the vicinity of vineyards in Malayer, there are few studies conducted in this regard. To evaluate the pollution level of toxic elements in these vineyards, 20 sampling stations were selected randomly and samples of garden soil and leaves of grapevine species were collected. After the acidic digestion of the samples, the concentrations of the heavy metals were measured using atomic absorption spectrometer. Then, the indices of contamination factor (Cf), geo-accumulation index (Igeo), biological accumulation coefficient (BAC), and ecological risk index (RI) were calculated. According to the results obtained for Igeo and Cf indices, the soil in the study region was moderately contaminated with copper. However, the ecological risk index and BAC of the studied region were low. To investigate the spatial distribution of copper in the studied region, the spatial distribution map was prepared. To locate the source of copper contamination and investigate the effect of various land uses on the amount of contamination, land use map (LUM) of vineyards was generated. To this end, images were downloaded from Landsat Satellite, and after the exertion of various corrections on the images based on the supervised classification method, the LUM with agricultural, residential, vineyard, brick furnace and pasture classes was prepared. The comparison of the LUM and the copper contamination map illustrated that the copper contamination was higher in the places with urban and adobe furnace land-use types.

Keywords: Vineyard pollution, Environmental pollution, Heavy metals, Land use

1. Introduction

Given the rapid growth of communities, technology, and industry, it is necessary to investigate the positive and negative effects of these sectors on each other and the environment. The contamination adversely influences human communities and the environment. It should be noted that pollution with heavy metals is of particular importance due to the fact that they are less decomposed and can easily accumulate in food chains. Additionally, they can cause contamination and damage even in low concentrations. Heavy metals originate from natural and human sources. Among the human sources, industrial activities, oil extraction, transportation, wastewater-residual wastes and the use of fertilizers, chemicals and manures can be pointed out (1).

The existence of metals in the soil might seem natural but the amounts beyond the authorized thresholds cause environmental pollution due to their uptake by plants and the subsequent entrance of them into food chains (2).

Heavy metals can be made unavailable to roots through phytoremediation and leaching but they enter plant systems more readily than getting out of them through the mentioned paths (3). Chemical fertilizers always contain heavy metal impurities. The frequent use of chemical fertilizers in the soil causes the accumulation of these pollutants (4, 5).

Many studies (6-11) have been conducted regarding the pollution of the vineyard soil with toxic elements and even the spatial distribution of the contamination in these regions as well as the pollution absorption and bioaccumulation for various varieties of grapevines. In general, the majority of these studies have dealt with the pollution by toxic elements and factors influencing the creation of pollution like the application of chemicals (pesticides, fungicides, and herbicides), use of wastewaters for irrigation and also land uses on the periphery of the studied regions.

Malayer County is one of the main regions for raisin and grape production countrywide (12). A part of this region has been designated as Globally Important Agricultural...
Heritage Systems (GIAHS) by Food and Agriculture Organization (FAO) (13). Despite the sources of pollution and the specific geographical conditions of these vineyards, as well as the nutritional importance of Malayer grapes and their products and the importance of its quality for export, it is necessary to conduct this research. This study attempts to investigate the amount of soil contamination, ecological risk, major source of pollution and the amount of pollution absorption by the vine species.

2. Materials and Methods

2.1. Studied Region

The studied region included the vineyards in the center, west, south, and southwest of Malayer County (34°20'N 48°45'E). The region has a cold and semi-arid climate. Additionally, the annual precipitation has been estimated to be 300 mm (Fig. 1)(14).

2.2. Sampling

After consecutive inspections of the studied region and investigation of the region's map, sampling was carried out during July 2017. The random sampling method was used in the present study. In total, 20 topsoil samples were collected from the depth of 0-20 cm within a 20×20 area, and 100 g of leaf sample was picked up from each grapevine species and stored in polyethylene bags. The samples were transferred to the laboratory for further analysis. It is worth mentioning that the exact location of each sample was recorded using Handheld GPS.

2.3. Analysis of the Samples

Half a gram of the dried leaf sample and soil sample was digested in a solution consisting of 65% nitric acid, 70% perchloric acid, and 72% hydrochloric acid (purchased from Marc KgaA Company, Germany) at the ratio of 3:1:1 in a digester. Firstly, it was digested for one hour at a low temperature (40°C), and then, for three hours at 140°C. In the next stage, the digested samples were condensed to a volume of 25 mL using a specific volume of double distilled water. Next, the samples were filtered using Whatman filter paper No. 1 and then the purified solution was kept in special polyethylene containers in a refrigerator. Finally, the samples were analyzed using an atomic absorption device, Analytik Jena Contraa 700. To reduce the error stemming from preparation stages and assess the concentration of the metals in each series of the digested samples, a control sample was applied.

2.4. The Applied Indices

Firstly, the mean concentrations of the toxic elements measured in the soil of vineyards in Malayer were compared with those in the global sediments, soils, the Earth’s Crust and shale (15-17). Then, to classify pollution types, indices such as contamination factor (C_f), geochemical accumulation index (I_{geo}), ecological risk index (RI), and biological accumulation coefficient (BAC) were calculated.

2.4.1. C_f

The contamination coefficient and contamination degree were, respectively, descriptions of pollution related to the studied heavy metals and the rate of contamination in the sedimentation environment. C_f is also known as Hokenson contamination coefficient (18).

\[ C_f = \frac{M_x}{M_b} \]  

(1)

Where M_x is the concentration of the element in the sample and M_b indicates the concentration of the same metal in the reference material as expressed in Table 1. The classification of CF-based contamination is given in Table 2.

2.4.2. I_{geo}

To investigate the soil contamination, contamination factor and geochemical accumulation index were employed in the current research paper. I_{geo} was introduced by Muller in 1969 (19).

\[ I_{geo} = \log_2 \left( \frac{B_n}{1.5C_s} \right) \]  

(2)

Where I_{geo} is the geochemical accumulation index or the contamination severity index of the sediments; C_s is the heavy metals concentration in sediment and B_n is the background concentration (elements concentration in shale). A coefficient of 1.5 has been used for minimizing the effect of the possible background concentration changes that are generally attributed to the petrological variations of the sediments and effects of the terrestrial factors (19). The classification of Igeo-based pollution rates is given in Table 3.

| Table 1. The Mean Concentration (mg/kg) of the Toxic Elements in Soil |
|------------------|---|---|---|---|---|
| Element | Ni | Pb | Zn | Cu | Cr |
| Concentration | 50 | 20 | 95 | 45 | 90 |

| Table 2. Classification of the Degree of Contamination Based on Pollution Factor Index (Hakanson, 1980). |
|------------------|---|
| The Amount of CF | Grade |
| 1 > CF | Low |
| 3 ≤ CF > 1 | Medium |
| 6 ≤ CF > 3 | High |
| 6 ≤ CF | Very much |
2.4.3. RI

After determining the amount of pollution in various spots, it was very important to pay attention to the idea that which region was experiencing critical conditions in terms of pollution. The ecological risk index was offered by Hokenson in 1980 and it used the toxicity of each of the heavy metals and the amounts of their accumulation in a given region to provide an overview of the riskiness of the conditions therein (18). This index has been calculated as demonstrated below:

$$RI = \sum_{i=1}^{n} E_r$$  \hspace{1cm} (3)

Where RI is the potential ecological risk for all of the metals and $E_r$ is the potential ecological risk factor of a given metal that is computed as shown in the following equation:

$$E_r = T_r \times C_f$$  \hspace{1cm} (4)

Where $C_f$ is the contamination factor and $T_r$ is the toxicity factor of the intended metal (18). $T_r$ values for nickel, copper, lead, chromium and zinc were equal to 5, 5, 5, 2 and 1, respectively (20).

The potential ecological risk values have been listed in Table 4 based on $E_r$ and RI.

2.4.4. BAC

To investigate the amount of the biological accumulation of the toxic elements in the various grapevine species, the BAC of the leaves was utilized. BAC expressed the ratio of the concentration of elements in a plant (root, leaf or fruit) and the concentration of elements in the soil (21).

$$BAC = \frac{\text{Leaf}}{\text{Soil}}$$  \hspace{1cm} (5)

2.5. Investigation of the Spatial Distribution of the Contamination

To investigate the spatial distribution of the contamination with copper in the present study, the inverse...
distance weighted (IDW) method was utilized. The method was selected based on the study goals, the properties of the existing data, the specifications of the sampling points and the prior studies for zoning heavy metal pollution in the soil (22-27). IDW is one of the most common methods used in the studies on the heavy metal-contaminated soils, which uses known points to predict unknown points. In this method, the weights are determined according to the distance of each known point from the unknown points and disregarding the position and the scattering of the points on the periphery of the estimation point in such a way that the closer points are given higher weights and the distant points are given lower weights. In fact, the points with smaller distance exert larger effects on the estimation (27). To obtain the amounts of various points, the following equations have been applied (28).

\[ W(x,y) = \frac{\sum_{i=1}^{N} \lambda_i W_i}{\sum_{i=1}^{N} \lambda_i} \]  

(6)

\[ \lambda_i = \left( \frac{1}{d_i} \right)^\varepsilon \]

(7)

Where \( W(x,y) \) is the estimated amounts in \((x,y)\) position; \( N \) indicates the number of the known points in the adjacency of \((x,y)\); \( \lambda_i \) is the weight allocated to each certain amount of \( W_i \) in \((x_i, y_i)\) position; \( d_i \) is the Euclidean distance between each of the points in \((x,y)\) and \((x_i,y_i)\) positions and \( P \) is the amount of power that is under the influence of \( w_i \) weight on \( w \). To perform copper contamination zoning, the data files were transferred to ArcGIS 10.3 and the zoning map was prepared using geostatistical analyst based on the IDW method.

### 2.6. Land Use

In order to prepare the land use map (LUM), 2017 images of UTM+ sensor were used. These images were downloaded from USGS Earth Explorer website. The entire stages of LUM preparation were carried out by ENVI 5.3 software.

In preprocessing stage, geometrical, radiometric and atmospheric corrections were performed on satellite images (29,30). Image processing techniques used statistical algorithms that changed the visual clarity attributes or the geometrical properties of the images. These corrections have been created for improving the quality of the satellite images (29-31). The preprocessed images were categorized based on a supervised classification method in which the maximum likelihood has been selected as a probabilistic model (32). In this method, each pixel was assigned to a class according to its probability value. The mean vector and covariance scales, which were obtained from the training data, were the key components of the maximum likelihood classification method (signature or region of interest) (33). The defined land uses served as the training of the classification method for the vineyard, adobe furnace, residential and agricultural land-use types. According to the field investigations and library researches, these land uses could have the highest effect on the contamination of the vineyards in the study area.

### 3. Results and Discussion

#### 3.1. Total Metal Concentration

Table 5 summarizes the descriptive statistics of the metal concentrations in the soil of the vineyards in Malayer and the leaves of the grapevine species. The mean concentrations of Cr, Cu, Ni, Pb, and Zn in the leaves of grapevine species and soil samples of vineyards in Malayer were 7.90, 3.44, 13.97, and 58.

Table 6 indicates the results of comparing the measured mean concentrations of toxic elements with the global amounts. Based on the obtained results, the concentrations of all the elements, except for copper, were below the global values; however, the mean concentration of copper in the soils of vineyards was found higher than all of the global amounts. The copper contents of the Earth’s Crust, global sediments, global soils, and shale were 50, 33, 32, and 45, respectively. The mean concentration of copper in the study area was 58.10, which was higher than all of the aforementioned values.

According to the concentration values reported by Kabata-Pendias and Pendias for copper that ranged from 13 to 24 mg/kg depending on the type of the vineyard soil (21) and considering the global values, the copper concentration in the vineyards of Malayer was higher than all of the

| Metals          | Cr      | Cu     | Ni     | Pb     | Zn     |
|-----------------|---------|--------|--------|--------|--------|
| Mean (this study)| 3.44    | 58.10  | 9.24   | 8.70   | 26.39  |
| Crust           | 100     | 50     | 80     | 14     | 75     |
| Global sediments| -       | 33     | 52     | 19     | 95     |
| Global soil     | 71      | 32     | 49     | 16     | 127    |
3.2. Contamination Indices of Toxic Elements

3.2.1. Ci Index

Table 7 presents the mean value of Ci index in the sampled points. Generally, the Ci values were in the following order for the studied metals: Cu>Pb>Zn>Ni>Cr. According to the obtained results, the soil of the vineyards was found moderately contaminated with copper among the other studied toxic elements, which took the next contamination ranks.

3.2.2. Igeo Index

The Igeo indices of the region have been summarized in Table 8 in each point for the aforementioned metals. According to the results obtained for Igeo index, some points were moderately contaminated with copper and the region was completely uncontaminated in terms of the other studied metals.

Generally, the Igeo index values were found in the following order in the study area: Cr<Ni<Zn<Pb<Cu. The high concentration of Cu in this region was not very uniform and largely differed in various points. This was reflective of the importance of investigating the spatial distribution of copper concentrations in the region and exploring the aforementioned thresholds.

3.2.3. Ecological Risk Index

Table 9 shows the results of the ecological risk index, E, As it is seen, the total risk index was 9.91.

Generally, the values of the potential ecological risk index for each of the metals were found to take the following order Cu>Pb>Ni>Cr>Zn. The highest E value belonged to copper, but it was below the global threshold, 40. Therefore, the above-mentioned metals were grouped in the low potential ecological risk index group for the study area. Furthermore, according to the fact that the total ecological risk index has been found to be below 150, as the global threshold, the region had also been classified in the low risk group. This was the reflective of the lower riskiness of the vineyards in Malayer compared to the orchards examined by Li et al (10) and Chen et al (22).

3.2.4. BCF Index

Table 10 presents the mean results for the calculation of BCF. Based on the obtained results, the uptake rates of the aforementioned toxic elements by the grapevines included in the study area take the following order: Cu>Zn<Pb<Cr<Ni.

Although the concentration of copper was higher in this region compared to the other studied metals, the grapevine examined herein exhibited less contamination with copper compared to the other metals. The highest accumulation rate of this grapevine species belonged to nickel that was found with lower accumulation and contamination in the soil of the study area. In the present study, the amount of copper transmission to the plant parts and the biological accumulation of copper were found lower in vineyards of Malayer compared with the studies performed by Beygi and Jalali (7) and Bravo et al (8) in the vineyards of the other regions.

According to the results obtained from the investigation of Igeo and Ci, the soil of the vineyards in Malayer showed moderate accumulation and low contamination with copper in this region. However, no considerable accumulation and contamination with the other toxic elements like Cr, Pb, Ni, and Zn were observed. This suggested the lower contamination of vineyards in Malayer with these heavy metals compared to the other vineyards examined in the other similar studies. However, since no contamination with copper had been documented in previous studies (12) for the soils of vineyards in Malayer, this amount of sources of copper contamination.

Table 7. The Results of Ci Index

| Metals | Pb | Zn | Ni | Cu | Cr |
|--------|----|----|----|----|----|
| Cl     | 0.435 | 0.28 | 0.18 | 1.29 | 0.04 |

Table 8. The Results of Geo-accumulation Index

| Station Number | Igeo of Cu | Igeo of Cr | Igeo of Ni | Igeo of Pb | Igeo of Zn |
|----------------|------------|------------|------------|------------|------------|
| 1              | -2.09      | -5.68      | -3.68      | -1.60      | -2.42      |
| 2              | -1.76      | -5.66      | -3.72      | -1.56      | -2.16      |
| 3              | -0.43      | -5.82      | -3.44      | -1.54      | -2.31      |
| 4              | 1.07       | -7.16      | -3.66      | -1.43      | -2.21      |
| 5              | 0.08       | -6.58      | -3.58      | -1.49      | -2.68      |
| 6              | 0.91       | -8.79      | -3.46      | -1.68      | -2.73      |
| 7              | 0.23       | -7.19      | -3.68      | -1.95      | -2.64      |
| 8              | -3.22      | -6.11      | -3.50      | -1.79      | -2.48      |
| 9              | -0.05      | -10.91     | -4.45      | -1.79      | -2.66      |
| 10             | -0.07      | 0.00       | -3.95      | -1.92      | -2.48      |
| 11             | -1.91      | -4.61      | -2.83      | -2.07      | -2.27      |
| 12             | -3.67      | -4.49      | -2.69      | -2.28      | -2.57      |
| 13             | 0.11       | -4.49      | -2.77      | -1.89      | -2.27      |
| 14             | 1.24       | -4.52      | -2.45      | -1.78      | -2.34      |
| 15             | -2.92      | -3.98      | -2.10      | -1.89      | -2.48      |
| 16             | -0.52      | -4.75      | -2.46      | -2.02      | -2.31      |
| 17             | 0.53       | -4.87      | -2.58      | -2.07      | -2.31      |
| 18             | 0.12       | -4.58      | -2.30      | -1.38      | -2.42      |
| 19             | -3.11      | -4.75      | -2.83      | -2.03      | -2.62      |
| 20             | -1.15      | -5.29      | -2.88      | -1.98      | -2.49      |

Table 9. The Potential Risk of Metals

| Metals | Cu | Ni | Pb | Cr | Zn |
|--------|----|----|----|----|----|
| Er     | 6.45 | 0.92 | 2.17 | 0.076 | 0.27 |

Table 10. Results of BCF Index

| Metals | Zn | Pb | Ni | Cu | Cr |
|--------|----|----|----|----|----|
| BCF    | 2.3 | 5.27 | 16.22 | 0.65 | 6.96 |
contamination in this short period of time could be alarming. Copper contamination has been found in the majority of the studies performed in this regard (6-11). However, the amount of copper transfer to the aerial parts of the plants and the biological accumulation of copper in the grapevine species in Malayer were lower compared to other similar studies. Among the factors influencing the contamination of vineyards, human activities could be pointed out. For example, Bordeaux mixture (Ca(OH)_2 + CuSO_4), which has been applied in the vineyards since the end of the 19th century for controlling Plasmopara viticola in many of the countries, was the cause of contamination (34).

3.3. Analysis of the Correlation Among the Metals

To investigate the relationship between the contaminating agent in the study area and the other heavy metals, Pearson and Spearman Correlation indices were used. The results of the correlation between various metals and the soil characteristics have been given in Table 11.

However, the concentration of copper in soil was positively and significantly associated with the concentration of nickel and zinc in leaf (P=0.01). In addition, there was a positive and significant correlation between copper concentration in soil and the lead content of the leaf. The low concentrations of nickel, zinc, and lead in the vineyard soil and grapevine leaves in the study area caused the reduction of copper uptake and accumulation in the leaves of the grapevines in vineyards of Malayer. The high correlation coefficients between the metals were expressive of the identical pollution source and the common control factor for these metals (35,36).

3.4. Geo-statistics

To manage the environment, it was necessary to have information about the contamination of the soil in the land with heavy metals. The use of zoning methods in these cases, especially for predicting the contamination values in regions that no sampling has been done can be very useful. Considering the fact that the soil of the study area was found contaminated only with Cu, the spatial distribution map was only prepared for copper contamination (Fig. 2).

Generally, 2-4 concentration class accounted for the majority of the area in the study area. There are centers with a high concentration of contamination in the northwest, center, and southeast of the study area as well as in the intervals between the pollution centers of the regions with low contamination. The determination of the spatial distribution of contamination enabled the investigation of the effects of various spatial factors.

3.5. Land Use

Fig. 3 demonstrates the LUM. According to the field studies, the investigation of the high-quality images available in Google Earth and validation works, the generated LUM was found to match the ground truths in the study area. Based on the obtained results, the most frequent land-use types in the vicinity of the vineyards in the northwestern and central sections of the study area were adobe furnace, residential and agricultural. Additionally, the agricultural and residential activities account for the majority of the land uses in the southeastern side of the study area.

It is evident from the comparison of the spatial distribution map of copper contamination with the LUM that the contamination centers matched some land uses. The pollution center in the northwest of the study area matched the residential and adobe furnace land-use types. Moreover, the pollution center in the center of the study area matched the residential and adobe furnace land-use types and the pollution center in the southeast of the study area matched the residential land use. In general, the contamination rate decreased with an increase in the distance from the residential sites and adobe furnaces.

4. Conclusion

The soil of vineyards in Malayer was contamination with copper. The results obtained for Cu and Pb indices were indicative of the idea that the soils were moderately contaminated with metals. It can be found out in a comparison of the interpolation map of copper contamination and the

| Table 11. Correlation Between Contamination of Toxic Elements. |
|----------------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
|                     | Cr Leaf         | Cr Soil         | Cu Leaf         | Cu Soil         | Ni Leaf         | Ni Soil         | Pb Leaf         | Pb Soil         | Zn Leaf         | Zn Soil         |
| Cr leaf             | 1               | -651**          | 1               |                 |                 |                 |                 |                 |                 |                 |
| Cr soil             | -651**          | 1               |                 |                 |                 |                 |                 |                 |                 |                 |
| Cu leaf             | 0.672**         | -212            | 1               |                 |                 |                 |                 |                 |                 |                 |
| Cu soil             | 0.155           | -277            | 0.159           | 1               |                 |                 |                 |                 |                 |                 |
| Ni leaf             | 0.089           | 0.101           | 0.577**         | 0.241           | 1               |                 |                 |                 |                 |                 |
| Ni soil             | -0.684**        | 0.921**         | -0.280          | 0.061           | 0.157           | 1               |                 |                 |                 |                 |
| Pb leaf             | 0.711**         | -0.513          | 0.500           | 0.064           | -0.077          | -0.625**        | 1               |                 |                 |                 |
| Pb soil             | 0.428           | -0.353          | 0.198           | 0.341           | -0.104          | -0.290          | 0.600**         | 1               |                 |                 |
| Zn leaf             | 0.461**         | -0.228          | 0.691**         | 0.089           | 0.637**         | -0.356          | 0.403           | 0.064           | 1               |                 |
| Zn soil             | -0.132          | 0.299           | 0.042           | 0.076           | -0.099          | 0.194           | 0.263           | 0.166           | 0.023           | 1               |

* Correlation is significant at the 0.05 level (2-tailed).
** Correlation is significant at the 0.01 level (2-tailed).
Figure 2. Interpolated Map for Contamination with Copper.

Figure 3. Land Use Map.
LUM that the contamination was higher in the places with residential sites and adobe furnaces. As can be observed in the maps, the contamination was higher in the vineyards on the periphery of Malayer and Gurab; this could be because of air pollution originating from activities in the residential regions and adobe furnaces. It was made clear in the field investigations and inquiring the farmers and sellers of the chemicals and fertilizers that the farmers were using copper-containing pesticides, which can also be another source of the contamination of the vineyard soil with copper.

Generally, the potential ecological risk index for the studied metals in the region and the total ecological risk were at a low level. Moreover, the copper accumulation in grapevine species was found to be lower in comparison with the other studied elements in the present study. This originated from the positive correlation of the physiological properties of the grapevine species with the environmental conditions, including the low concentration of the metals in the study area. Considering copper contamination, the low accumulation of the grapevine species did not cause a reduction in the product quality in these vineyards. However, the situation can be dangerous considering the fact that this amount of copper contamination has come about within a short period of time and further studies are required for managing and controlling the pollution. In these studies, the source and control method of copper contamination and product quality with respect to copper contamination as well as the grapevine properties should be investigated under various contingent conditions.

Conflict of Interests
The authors declare that they have no conflict of interests.

Acknowledgements
We highly appreciate the efforts and cooperation of Mustafa Mirshahvald, the head of the Central Laboratory, Bahar Roozbahani and Farnaz Mahmoodi lab manager of the University of Malayer.

Author’s Contribution
MP: Sampling, Sample perpetration, Investigation, Software & Writing.
SM: Methodology, Sample Analysis, Supervision, Writing – review & editing.

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