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# Statistical Analysis of Accumulation and Sources of Heavy Metals Occurrence in Agricultural Soils of Khoshk River Banks, Shiraz, Iran

*Afshin Qishlaqi and Farid Moore*

Department of Earth Sciences, College of Sciences,
Shiraz University, P.O.Box 71454 Shiraz, Iran

**Abstract:** In this study, selected statistical methods (Discriminant analysis, ANOVA, Correlation analysis and Principal component analysis) were used to determine the heavy metal accumulation and its controlling factor and to identify the origin of these metals in soil samples collected from two sites along the Khoshk River banks, Shiraz, Iran. For this purpose, 40 topsoil samples were collected and the levels of Pb, Zn, Cr, Cd, Ni, Cu and alkaline metals (K, Mg and Ca) along with pH and organic matter content were determined in each sample. Discriminant analysis revealed that two investigated sites are different in terms of heavy metal accumulation. From the ANOVA and correlation analysis, it was found that soil organic matter is the most important factor controlling the distribution of heavy metals. Principal component analysis extracted two major components: PC1 with high loading of Pb, Ni, Cr and OM is suggested to be the result of wastewater irrigation at site A and PC2 with contribution of Zn and Cu probably due to extensive use of organic fertilizers and/or solid manure. This study concludes that statistical analysis can provide a scientific basis for monitoring the heavy metal accumulation in soil and for controlling the future soil contamination posed by human activities.

**Key words:** Statistical analysis · heavy metals · agricultural soil · Shiraz · Iran

## INTRODUCTION

The accumulation of heavy metals in agricultural soils is of increasing concern due to the food safety issues and potential health risks as well as its detrimental effects on soil ecosystems [1]. These metals have peculiar characteristics including that (1) they do not decay with time (2) They can be necessary or beneficial to plants at certain levels but can be toxic when exceeding specific thresholds, (3) they are always present at a background level of non-anthropogenic origin, their input in soils being related to weathering of parent rocks and pedogenesis and (4) they often occur as cations which strongly interact with the soil matrix, consequently, heavy metals in soils can become mobile as a result of changing environmental conditions. This situation is refereed to as “Chemical timing bomb” [2].

Sources of these elements in soils mainly include natural occurrence derived from parent materials and human activities. Anthropogenic inputs are associated with industrialization and agricultural activates deposition, such as atmospheric deposition, waste disposal, waste incineration, urban effluent, traffic emissions, fertilizer application and long-term application of wastewater in agricultural land [3-5]. Apart from the source of heavy metals, the physicochemical properties of soil also affect the concentration of heavy metals in soils. Organic matter and pH are the most important parameters controlling the accumulation and the availability of heavy metals in soil environment [6]. It is necessary then to evaluate the relationship among these parameters and heavy metal accumulation in soil.

The Knowledge of the heavy metal accumulation in soil, the origin of these metals and their possible interactions with soil properties are priority objectives in many environmental monitorings. Statistical analysis procedures, as powerful tools, can provide such knowledge and assist the interpretation of environmental data [7-9]. In recent times, the statistical methods (univariate or multivariate) have been applied widely to

**Corresponding Author:** Dr. Afshin Qishlaqi, Department of Earth Sciences, College of Sciences, Shiraz University, P.O.Box 71454 Shiraz, Iran

investigate heavy metal concentration, accumulation and distribution in soils. This is documented by a large number of reported studies which apply statistical methods to heavy metal accumulation in soils, e.g. Modak and others (1992), Arakel and Hangjun (1992), Ratha and others (1993), Chakrapani and Subramanian (1993), Ntekim and others (1993), Henburg and Bruemer (1993) and Cambier (1994) studied the behavior and distribution of heavy metals in soils using multivariate statistical methods [10]. In environmental monitoring and assessment strategies, these methods can be used to predict or estimate the variability of heavy metals and its controlling factor (s) and to highlight the influence of human activities on heavy metal contents of soils [11, 12]. Therefore, statistical analysis of heavy metals in soil can offer an ideal means through which to monitor not only the heavy metal accumulation in soil but also the quality of the overall environment as reflects in soil.

In this study, we aim to determine, by means of selected statistical methods, the most significant factor controlling spatial distribution of heavy metals and to identify the possible origins (sources) of these metals in the soil samples collected from two different sites along the Khoshk River banks in suburban of Shiraz. It is hoped that this preliminary study would provide a scientific basis for contamination control and further monitoring of the heavy metal accumulation in soils.

## MATERIALS AND METHODS

**Site description and soil sampling:** The study area is located in the eastern Shiraz (Fig. 1) where agricultural lands along the Khoshk River are considered to be affected by human activities. The surface area is 790ha of which approximately 200 ha is occupied by vegetable crops. The present study is confined to two sites along the Khoshk River banks. At each site, soil samples were collected from topsoil (0-20 cm in depth) using a hand auger. Composite samples for each site consisted of 20 subsamples (cores) of soil (total 40 subsamples). Subsamples were mixed into one composite sample for each soil and analyzed in triplicate. For statistical analyses, the samples were classified according to pH values and OM content as follows: pH values: acid (< 6.0), neutral (6.0-7.0) and alkaline (> 7.0) [13] and OM content: low content (1.3-5.3%), medium content (5.3-11.3%) and high content (11.3-20.3%).It should be noted that categorization of organic matter content is for statistical purposes and it is not conventional classification.

**Chemical analysis:** In the laboratory, the soil samples after air drying at room temperature, were sieved with nylon mesh (2 mm). The <2 mm fraction was grinded in an agate and pestle and passed through a 63 micron sieve. Selected physcio-chemical properties of these soils (OM and pH) were analyzed using standard methods. Soil pH was measured in suspension of 1:2 soil to water ratio using calibrated pH meter (Model ELE 160). Organic carbon content in soil was determined by the wet digestion method [14] and then converted to organic matter according to Jackson (1958) [15].

After determination of pH and organic matter content, soil samples with the given values of pH and OM were analyzed for heavy metals. These samples were digested in aqua regia (1:3 $HNO_3$: HCl) and heated under reflux. After filtration, solutions were diluted with 2M $HNO_3$. The heavy metal in resulting solutions was determined using Atomic absorption spectrometer (AAS model Shimadzu AA-360). Concentrations of several cations including K, Mg and Ca were determined using Flame Atomic Absorption Spectrometer (FAAS). In the elemental analysis by AAS, quality control was monitored using 10% sample blanks and 10% sample replicates in each set of sample analysis. A coefficient of variation for replicates was less than 2% for all elements. Standard reference material (SRM 2710) was used to have a check on the accuracy of the results. Normally the corresponding results matched within ±1.0% to ±1.5%.

### Statistical analysis

**Discriminant analysis:** To investigate whether there are differences in the heavy metal concentrations between the two sites, discriminate analysis was used. The results of this analysis were assessed by examining the canonical correlation statistics, the Wilk's lambda, the significance level and the percentage of original group cases correctly classified.

**Analysis of variance (ANOVA):** To assess the relationship between heavy metal concentrations and three factors (pH, OM content and Site), two-way ANOVA test was conducted. The results of this analysis will reveal the most significant factor in terms of heavy metal accumulation in soils.

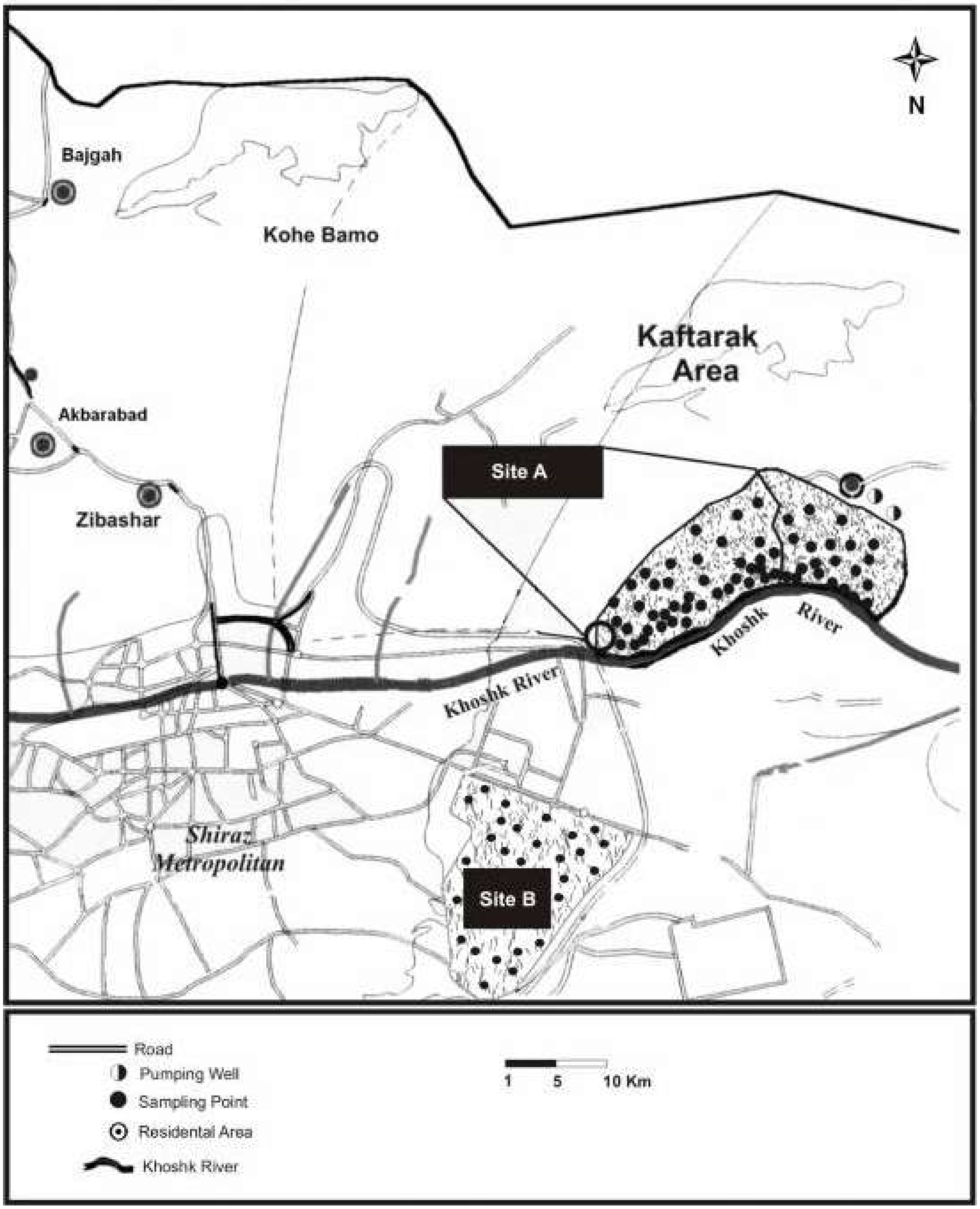


Fig. 1: Map of study sites in suburban Shiraz

**Correlation analysis:** In order to quantitively analyze and confirm the relationship among soil properties (pH and OM) and heavy metal content, a Pearson's correlation analysis was applied to dataset.

**Principal component analysis:** PCA was adopted to assist the interpretation of elemental data. This powerful method allows identifying the different groups of metals that correlate and thus can be considered as having a similar behavior and common origin [16]. The theoretical aspects of these statistical methods have been described in advanced statistical literatures [17].

It should be noted that parametric statistical tests require the data to be normally distributed. Therefore, it was checked if the data came from a population with normal distribution by applying Shapiro-Wilk's test (significance level, $\alpha = 0.05$). The non-normal data were transferred logarithmically to ensure normal distribution. All the statistical analysis were performed using SPSS for Windows (release Ver.11, Inc, Chicago, IL)

## RESULTS AND DISCUSSION

The soil samples from both areas under investigation reveal varying concentrations of all six analyzed heavy metals (Cd, Cr, Pb, Ni, Zn and Cu) (Table 1). There are also noticeable differences in the concentration of metals in each of samples depending on pH values and organic matter content. Using the neutral soils as reference, it was found that soil samples with alkaline pH and high OM content accumulated significantly higher concentrations of heavy metals compared with other soil samples. The soil samples also varied widely in terms of pH and OM content at two sites.

**Discriminant analysis:** We employed the discriminant analysis to determine whether two investigated sites differed significantly in terms of heavy metal concentration. For this purpose, we first entered the two sites (A and B) as grouping variables. The six heavy metal concentrations were also entered as the independent variables. The obtained results presented in Table 2 clearly indicate that site A and site B exhibit different concentrations heavy metals. It is evident that for each metal under investigation, a high degree of between site variations exist (canonical correlation have values between 0.698 to 0.848), whereas there is a few lower degree of within-group site variations (Wilk's lambda statistic range from 0.282 to 0.420). (Generally, the larger

Table 1: Total concentration of heavy metals and selected properties of soil samples collected from the study area

| Sample | Variables | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| No | Pb | Ni | Zn | Cd | Cr | Cu | pH | OM(%) |
| SOR-1 | 93.8 | 68.9 | 175.2 | N.D | 12.6 | 150.2 | 8.26 | 1.5 |
| SOR-2 | 110.1 | 75.6 | 35.6 | 1.2 | 18.5 | 100.2 | 7.11 | 3.5 |
| SOR-3 | 100.5 | 72.6 | 27.4 | 1.1 | 17.8 | 25.3 | 7.13 | 3.4 |
| SOR-4 | 112.2 | 77.6 | 156.2 | 1.5 | 20.5 | 140.2 | 4.23 | 5.2 |
| SOR-5 | 117.1 | 87.6 | 142.5 | 1.5 | 20.3 | 156.3 | 7.01 | 3.7 |
| SOR-6 | 200.3 | 150.6 | 147.6 | 2.5 | 100.5 | 78.5 | 8 | 10.3 |
| SOR-7 | 255.9 | 180.3 | 53.6 | 3.2 | 152.6 | 163.2 | 8.45 | 14.5 |
| SOR-8 | 140.3 | 120.6 | 85.6 | 1.8 | 27.9 | 27.8 | 4.15 | 5. 2 |
| SOR-9 | 300.2 | 198.5 | 38.7 | 1.2 | 170.2 | 85.9 | 8.5 | 15.2 |
| SOR-10 | 319.7 | 247.5 | 170.1 | 4.5 | 180.5 | 101.6 | 8.45 | 17.5 |
| SOR-11 | 198.5 | 146.3 | 52.6 | 2.1 | 56.4 | 52.6 | 6.19 | 10.2 |
| SOR-12 | 172.4 | 129.5 | 120.5 | 2 | 29.3 | 26.3 | 6.19 | 10 |
| SOR-13 | 209.8 | 152.6 | 127.9 | 2.9 | 125.3 | 145.6 | 4.25 | 11.5 |
| SOR-14 | 157.1 | 127.1 | 45.9 | 2 | 28.6 | 154.3 | 5.62 | 6.3 |
| SOR-15 | 212.9 | 158.6 | 122.6 | 1.5 | 145.9 | 190.3 | 5.6 | 12.9 |
| SOR-16 | 400.2 | 265.3 | 140.9 | 4.7 | 185.3 | 142.3 | 7.95 | 18.6 |
| SOR-17 | 219.1 | 103.2 | 32.5 | 3.1 | 148.3 | 34.6 | 7.41 | 14.2 |
| SOR-18 | 215.1 | 140.3 | 110.8 | 3. 4 | 147.6 | 100.6 | 7 | 14.2 |
| SOR-19 | 227.3 | 188.2 | 152.3 | 3.2 | 152.6 | 115.6 | 8.01 | 14.5 |
| SOR-20 | 402.3 | 240.3 | 146.3 | 5 | 185.6 | 36.2 | 4.22 | 18.9 |
| SOR-21 | 257.4 | 170.2 | 35.4 | 3.2 | 157.6 | 187.9 | 8.22 | 15.2 |
| SOR-22 | 223.9 | 184.2 | 117.9 | 3.2 | 150.6 | 29.6 | 7.81 | 14.2 |
| SOR-23 | 125.5 | 60.5 | 90.2 | 1.5 | 25.8 | 45.6 | 4.22 | 7.3 |
| SOR-24 | 300.9 | 201.6 | 155.6 | 4.2 | 177.2 | 24.8 | 4.51 | 16.3 |
| SOR-25 | 200.2 | 120.9 | 85.2 | 2.3 | 90.5 | 29.6 | 8.52 | 10.2 |
| SOR-26 | 300.7 | 200.6 | 45.6 | 3.6 | 174.6 | 45.1 | 5.21 | 15.2 |
| SOR-27 | 317.7 | 127.1 | 160.5 | 4.5 | 178.9 | 188.2 | 7.52 | 17.5 |
| SOR-28 | 305.7 | 205.6 | 164.2 | 4.3 | 178.5 | 29.5 | 6.69 | 17.2 |
| SOR-29 | 378.2 | 257.2 | 152 | 4.6 | 184.9 | 187.6 | 7.69 | 17.8 |
| SOR-30 | 407.2 | 250.4 | 166.9 | 5.2 | 188.4 | 25.6 | 7.85 | 19.3 |
| SOR-31 | 258.6 | 183.4 | 28.9 | 3.3 | 160.2 | 120.6 | 7.41 | 15.2 |
| SOR-32 | 405.5 | 277.5 | 165.3 | 5.1 | 187.9 | 42.6 | 4.28 | 19.3 |
| SOR-33 | 422.3 | 297.2 | 120.6 | 5.5 | 189.6 | 28.6 | 6.15 | 20.3 |
| SOR-34 | 419.7 | 275.4 | 157.8 | 5.2 | 189.3 | 180.5 | 6.39 | 20.1 |
| SOR-35 | 90.9 | 55.4 | 170.1 | ND | 10.3 | 125.3 | 8.71 | 1.1 |
| SOR-36 | 440.6 | 205.4 | 168.5 | 5.6 | 190.3 | 45.5 | 7.42 | 20.2 |
| SOR-37 | 327.6 | 254.9 | 168.3 | 4.5 | 184.2 | 154.2 | 8.2 | 17.5 |
| SOR-38 | 416.2 | 290.4 | 153.3 | 5.2 | 189.2 | 165.3 | 6.01 | 21.3 |
| SOR-39 | 327.6 | 254.9 | 168.3 | 4.5 | 184.2 | 154.2 | 8.21 | 17.1 |
| SOR-40 | 95.1 | 55.8 | 123.4 | 1 | 15.5 | 95.3 | 8.23 | 3.2 |
| Mean | 254.6 | 171.4 | 117 | 5.2 | 124.5 | 96.9 | 6.75 | 10.2 |
| SD | 110.2 | 72.8 | 50.8 | 1.49 | 68.9 | 60.3 | 1.49 | 6.21 |
| Median | 241.6 | 175.2 | 134.4 | 3.2 | 152.6 | 100.4 | 7.27 | 14.5 |
| Mode | 327.6 | 127.1 | 170.1 | 3.2 | 152.6 | 29.6 | 8.45 | 15.2 |

Heavy metal concentrations in mg/kg

SD: Standard Deviation

ND: Not Detected

Table 2: Discriminant analyses results for the two investigated sites

| Variable | Canonical correlation | Wilk's Lambda statistic | Chi-squares | D.F. | Sign. | Percentage of grouped cases correctly classified |
|---|---|---|---|---|---|---|
| Zn | 0.762 | 0.420 | 405.224 | 8 | 0 | 91.8 |
| Cu | 0.848 | 0.282 | 114.016 | 32 | 0 | 95.5 |
| Cr | 0.698 | 0.513 | 60.781 | 32 | 0.002 | 70.2 |
| Pb | 0.800 | 0.360 | 477.581 | 8 | 0 | 82.4 |
| Cd | 0.791 | 0.374 | 89.594 | 32 | 0 | 100.0 |
| Ni | 0.786 | 0.382 | 449.526 | 8 | 0 | 91.7 |

the canonical correlation statistic, the greater between groups variation as a proportion of the total variation and the larger the Wilk's lambda statistic, the greater is the within-group variation as a proportion of the total variation.). The statistically significant results also demonstrate that the originally grouped cases have very high percentage (70.2% to 100.0%). The histogram plots (Fig. 2) illustrate the significant differences between the two areas in terms of the frequency concentrations of the various heavy metals according to soil organic matter content.

**ANOVA analysis:** Although discriminant analysis proved to be useful in establishing the fact that there are variations in heavy metal concentrations from the two sites, it does not provide information as to why there are differences in heavy metal concentrations between two sites. With the knowledge that the heavy metal can be associated with high soil pH and OM content, a two-way analysis of variance was performed to determine which variable being the most important factor in controlling spatial differences in heavy metal concentration. In this model, we first entered Site-OM and then Site-pH as grouping variables.

The two-way ANOVA results presented in Table 3a-b indicate that the concentrations of each of the heavy metals under investigation are significantly

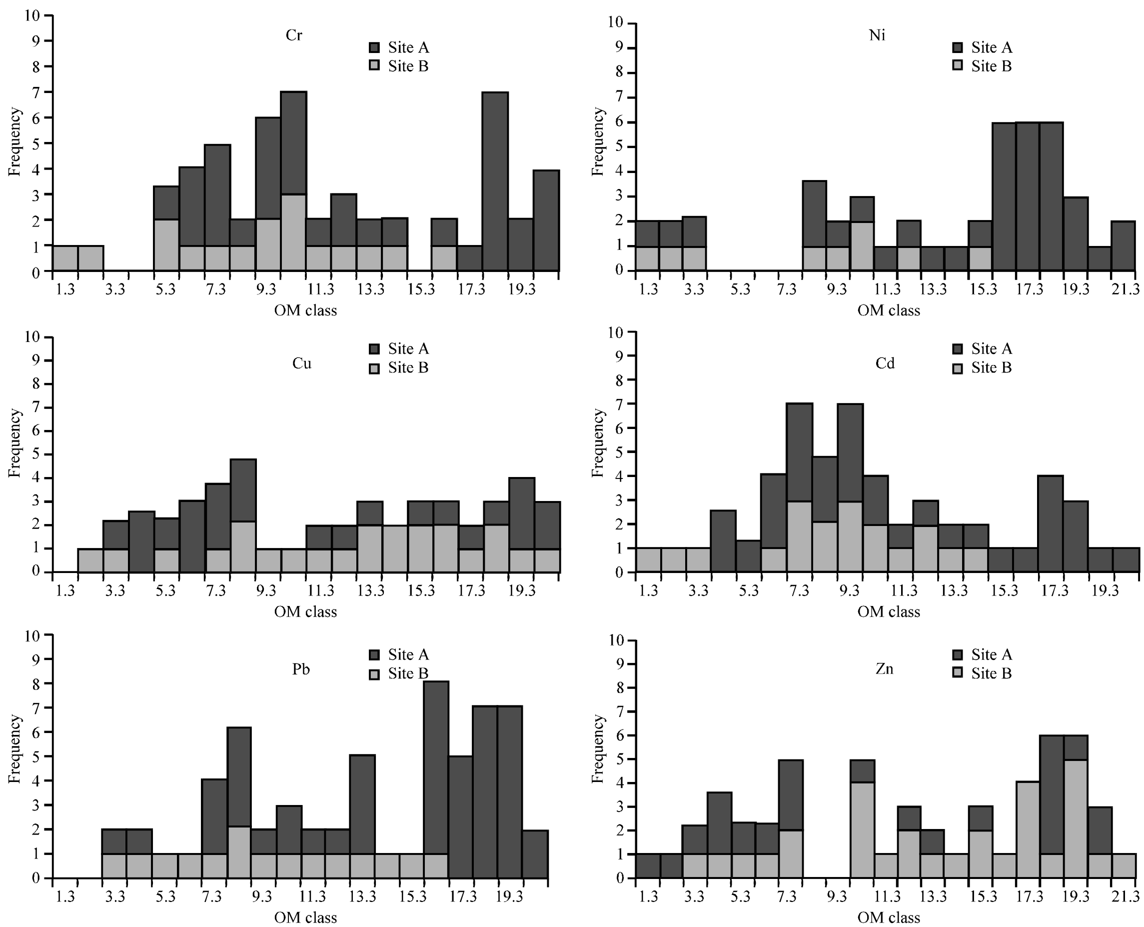


Fig. 2: Histogram plots showing the significant diffrences between the two sites in terms of the concentration of heavy metal and Organic Matter (OM)

Table 3a: Two-way ANOVA results (test of between subjects) for Site and OM as grouping variables (Dependent variables were subjected to log-normal transformation)

| Source of Variation | Dependent Variables | SS | D.F | MS | F | Sign. |
|---|---|---|---|---|---|---|
| Site | Pb | 0.113 | 1 | 0.113 | 0.43 | 0.836 |
| | Zn | 9.98 | 1 | 9.98 | 6.942 | 0.009 |
| | Ni | 6.688 | 1 | 6.688 | 0.024 | 0.877 |
| | Cr | 0.0567 | 1 | 0.0567 | 0 | 0.983 |
| | Cu | 43.467 | 1 | 43.467 | 4.573 | 0.033 |
| | Cd | 0.429 | 1 | 0.429 | 0.036 | 0.849 |
| OM | Pb | 8.954 | 1 | 8.954 | 6.229 | 0.013 |
| | Zn | 1.583 | 1 | 1.583 | 0.133 | 0.715 |
| | Ni | 15.317 | 1 | 15.317 | 5.797 | 0.016 |
| | Cr | 7.975 | 1 | 7.975 | 5.882 | 0.016 |
| | Cu | 0.58 | 1 | 0.58 | 0.049 | 0.825 |
| | Cd | 75.281 | 1 | 75.281 | 7.921 | 0.005 |
| Site*OM | Pb | 0.444 | 1 | 0.444 | 0.057 | 0.812 |
| | Zn | 5.491 | 1 | 5.491 | 7.155 | 0.008 |
| | Ni | 5.857 | 1 | 5.857 | 0.21 | 0.885 |
| | Cr | 16.353 | 1 | 16.353 | 1.374 | 0.242 |
| | Cu | 7.921 | 1 | 7.921 | 6.337 | 0.012 |
| | Cd | 3.153 | 1 | 3.153 | 2.194 | 0.139 |
| Corrected Model | Pb | 38.791 | 3 | 12.93 | 1.65 | 0.000 |
| | Zn | 16.934 | 3 | 5.646 | 2.136 | 0.094 |
| | Ni | 4651.474 | 3 | 1550.491 | 5.577 | 0.001 |
| | Cr | 106.527 | 3 | 35.509 | 3.736 | 0.011 |
| | Cu | 16.707 | 3 | 5.569 | 3.874 | 0.009 |
| | Cd | 14.725 | 3 | 4.908 | 3.62 | 0.013 |

SS: Type III sum squares
MS: Mean Square

Table 3b: Two-way ANOVA results (test of between subjects) for Site and pH as grouping variables (Dependent variables were subjected to log-normal transformation)

| Source of variation | Dependent variables | SS | D.F | MS | F | Sign. |
|---|---|---|---|---|---|---|
| Site | Pb | 0.391 | 1 | 0.391 | 1.57 | 0.212 |
| | Zn | 1.863 | 1 | 1.863 | 3.047 | 0.83 |
| | Ni | 0.607 | 1 | 0.607 | 0.92 | 0.762 |
| | Cr | 1.528 | 1 | 1.528 | 0.543 | 0.462 |
| | Cu | 63.991 | 1 | 63.991 | 0.314 | 0.576 |
| | Cd | 13.653 | 1 | 13.653 | 0.768 | 0.382 |
| pH | Pb | 1.606 | 1 | 1.606 | 0.244 | 0.622 |
| | Zn | 0.174 | 1 | 0.174 | 0.062 | 0.804 |
| | Ni | 1.101 | 1 | 1.101 | 0.117 | 0.733 |
| | Cr | 2.522 | 1 | 2.522 | 0.379 | 0.539 |
| | Cu | 32.685 | 1 | 32.685 | 3.021 | 0.084 |
| | Cd | 4.065 | 1 | 4.065 | 0.488 | 0.486 |
| Site*pH | Pb | 0.588 | 1 | 0.588 | 0.588 | 0.126 |
| | Zn | 0.253 | 1 | 0.253 | 0.977 | 0.324 |
| | Ni | 0.375 | 1 | 0.375 | 0.57 | 0.812 |
| | Cr | 2.394 | 1 | 2.394 | 0.85 | 0.358 |
| | Cu | 116.296 | 1 | 116.296 | 0.57 | 0.451 |
| | Cd | 1.283 | 1 | 1.283 | 0.119 | 0.731 |
| Corrected Model | Pb | 0.664 | 3 | 0.221 | 0.889 | 0.448 |
| | Zn | 3.893 | 3 | 1.298 | 2.045 | 0.109 |
| | Ni | 2.191 | 3 | 0.73 | 0.111 | 0.954 |
| | Cr | 2.852 | 3 | 0.951 | 0.338 | 0.798 |
| | Cu | 7.979 | 3 | 2.66 | 0.319 | 0.811 |
| | Cd | 2.182 | 3 | 0.727 | 0.077 | 0.972 |

SS: Type III sum squares
MS: Mean square

different between the two sites. The results are in agreement with those obtained from the execution of the discriminant analysis and highlight which of the independent variable and or interactions between them can explain the variations in the concentrations of heavy metals. It is evident from the results of the tests of between-subject effects for Site-OM variables (Table 3a) that OM content accounts for significant variations between the group means of Pb, Ni, Cd and Cr. It is also observed that variable Site show no significant variation between the group means of the heavy metals except for Zn and Cu. The effects of the interactions between two independent variables Site and OM highlight the significant variations in the concentrations of only two latter heavy metals (Zn and Cu). This is probably due to the different sources of these heavy metals at investigated sites.

From Table 3b, it can be observed that neither Site nor pH variables show significant variations between the group means of the heavy metals. The interactions between these independent variables are not significant for all heavy metals. It can be concluded that, from the variables entered into the model, OM content explains the majority of the variations in the concentration of heavy metals from the two sites.

**Correlation analysis:** The significant relationships between concentration of heavy metals and OM content were further substantiated by performing correlation analysis (Table 4). It is clear that almost all heavy metals, especially Pb, Ni and Cr are significantly correlated with OM content. The results indicate that between 61 and 99% of the variations in the concentrations of heavy metals can be attributed to the variation in the OM content of soils.

The observation that soil organic matter is a dominant variable affecting the spatial distribution of heavy metals is consistent with well-investigated findings [18-23]. Organic matter content is one of the most important factors that control the accumulation, mobility and bioavailability of heavy metals in soils. Increase in SOM content can lead to elevate the soil adsorption capacity by which accumulation of heavy metals will be enhanced. Gao *et al*. (1997) suggested that metal adsorption at low metal loadings is related to soil organic matter content [24]. Hence, soil samples with high organic matter content from the site A are characterized by high level of heavy metals as in soils which have received organic matter from unnatural sources, OM acts both as a source of several organic and inorganic

Table 4: Pearson correlation among selected physicochemical properties and elements in soils of the study area

| | | Pb | Ni | Zn | Cd | Cr | Cu | pH | OM |
|---|---|---|---|---|---|---|---|---|---|
| Pb | *Pearson Correlation* | 1 | 0.788** | 0.327* | -0.007 | 0.805** | -0.021 | -0.008 | 0.952** |
| | *Sig. (2-tailed)* | . | 0 | 0.039 | 0.841 | 0 | 0.897 | 0.959 | 0 |
| | *N* | 40 | 40 | 40 | 40 | 40 | 40 | 40 | 40 |
| Ni | *Pearson Correlation* | 0.788** | 1 | 0.318* | 0.12 | 0.720** | 0.016 | 0.004 | 0.970** |
| | *Sig. (2-tailed)* | 0 | . | 0.046 | 0.011 | 0 | 0.924 | 0.978 | 0 |
| | *N* | 40 | 40 | 40 | 40 | 40 | 40 | 40 | 40 |
| Zn | *Pearson Correlation* | 0.327* | 0.318* | 1 | 0.31 | 0.237 | 0.762** | -0.056 | 0.25 |
| | *Sig. (2-tailed)* | 0.039 | 0.046 | . | 0.051 | 0.141 | 0 | 0.732 | 0.12 |
| | *N* | 40 | 40 | 40 | 40 | 40 | 40 | 40 | 40 |
| Cd | *Pearson Correlation* | -0.007 | 0.12 | 0.31 | 1 | -0.047 | -0.034 | -0.062 | 0.177 |
| | *Sig. (2-tailed)* | 0.841 | 0.011 | 0.051 | . | 0.524 | 0.833 | 0.702 | 0.414 |
| | *N* | 40 | 40 | 40 | 40 | 40 | 40 | 40 | 40 |
| Cr | *Pearson Correlation* | 0.805** | 0.720** | 0.237 | -0.047 | 1 | 0.051 | 0.073 | 0.870** |
| | *Sig. (2-tailed)* | 0 | 0 | 0.141 | 0.524 | . | 0.753 | 0.655 | 0 |
| | *N* | 40 | 40 | 40 | 40 | 40 | 40 | 40 | 40 |
| Cu | *Pearson Correlation* | -0.021 | 0.016 | 0.762** | -0.034 | 0.051 | 1 | 0.166 | -0.013 |
| | *Sig. (2-tailed)* | 0.897 | 0.924 | 0 | 0.833 | 0.753 | . | 0.307 | 0.938 |
| | *N* | 40 | 40 | 40 | 40 | 40 | 40 | 40 | 40 |
| pH | *Pearson Correlation* | -0.008 | 0.004 | -0.056 | -0.062 | 0.073 | 0.166 | 1 | 0.611* |
| | *Sig. (2-tailed)* | 0.959 | 0.978 | 0.732 | 0.702 | 0.655 | 0.307 | . | 0.048 |
| | *N* | 40 | 40 | 40 | 40 | 40 | 40 | 40 | 40 |
| OM | *Pearson Correlation* | 0.952** | 0.970** | 0.25 | 0.177 | 0.870** | -0.013 | 0.611* | 1 |
| | *Sig. (2-tailed)* | 0 | 0 | 0.12 | 0.414 | 0 | 0.938 | 0.048 | . |
| | *N* | 40 | 40 | 40 | 40 | 40 | 40 | 40 | 40 |

**Correlation is significant at the 0.01 level (2-tailed)

* Correlation is significant at the 0.05 level (2-tailed)

pollutants and also as the major adsorbent for them. Although both sites are receiving large amount of OM from the anthropogenic sources, there are site-specific differences in OM content and associated metal concentration. Also, it must be stressed that although heavy metal loading is presently low at the investigated sites, high addition of OM from anthropogenic sources will gradually increase the accumulation of heavy metals in the soil samples leading to the future soil contamination,especially at site A.

The findings from this study indicate that determination of soil organic matter content and predication of its relationship with heavy metals concentration in soil by means of statistical methods can be a strong tool for monitoring of metal contamination in the agricultural soils. In this study, we focused on OM content of soil and pH, it should, however, be emphasized that other physicochemical properties of soil such as salinity, clay content, temperature, depth and geochemical and mineralogical composition can influence the spatial distribution of heavy metal. Further studies are needed to these variables and their interrelationships.

Principal Component Analysis (PCA): This analysis, applied to the autoscaled data matrix, shows a differentiation between the heavy metals at the two investigated sites. The variables are correlated with three principal components in which 88.41% of the total variance in the data is found. The number of significant principal components is selected on the basis of the Kaiser criterion with eigenvalue higher than 1 [25]. According to this criterion, only the first three principal components are retained because subsequent eigenvalues are all less than one. Hence, reduced dimensionality of the descriptor space is three.

After varimax orthogonal rotation, three components (factors) are extracted. These components are related to the sources of elements in the studied samples (Table 5). The first component with 53.23% of variance comprises Pb, Cr, Ni and OM (bold figures) with high loadings. This association strongly suggests that these variables have a similar source. It seems that use of untreated wastewater recently reported at site A [26] is the main reason for this association. The physicochemical meaning of PC1 also agrees with the correlation coefficient between these

Table 5: Principal component loadings (Varimax-normilzed) for experimented variables in the soil samples (n = 40)

| Element | PC1 | PC2 | PC3 |
|---|---|---|---|
| Ca | 0.032 | 0.316 | 0.027 |
| K | 0.131 | 0.711 | 0.11 |
| Mg | 0.143 | 0.672 | 0.054 |
| Ni | 0.808 | 0.019 | 0.019 |
| Pb | 0.72 | 0.054 | 0.026 |
| Zn | 0.061 | 0.658 | 0.161 |
| Cr | 0.514 | 0.027 | 0.117 |
| Cu | 0.026 | 0.918 | 0.011 |
| Cd | 0.239 | 0.001 | 0.227 |
| OM | 0.667 | 0.063 | 0.043 |
| pH | -0.204 | 0.103 | 0.21 |
| Eigen values | 7.588 | 1.632 | 1.39 |
| % Total variance | 53.232 | 23.6 | 11.585 |
| Cumul. % | 53.232 | 76.832 | 88.417 |

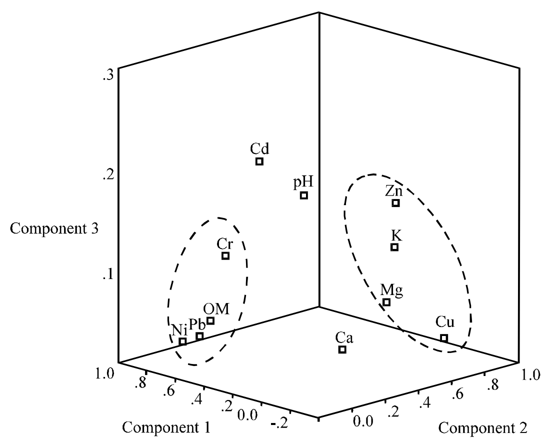


Fig. 3: Principal component analysis loading plot for the two rotated components

variables. Extensive application of wastewater has also resulted in deterioration of the soil quality through increase in SOM content facilitating the accumulation of heavy metals in the surface soils.

The second component (PC2) contributes Zn and Cu (as heavy metals) and K and Mg (as alkaline metals) at 23.60% total variance. This component seems to be arisen from a different source such as agrochemical products (organic fertilizes) or solid manure. Figure 3 shows PCA plots for these rotated components. The third component (PC3) alone explains 11.58% of the variance of our results. This component can be pooled variable. It is more difficult to ascertain the physicochemical meaning of this pooled variable.

The obtained results demonstrate that statistical procedures towards classifying the metals as groups in terms of relationship with soil properties and identifying their probable origin in soil.

## CONCLUSIONS

In this study, we used several statistical methods (Discriminant analysis, ANOVA, correlation analysis, PCA) for determining the environmental quality of two sites in terms of heavy metal accumulation and soil properties. Using discriminant analysis, it was found that the metal concentrations are fairly well discriminated and correctly classified. From the ANOVA, it was discovered that the SOM content have a pronounced effect on the distribution of heavy metals. Correlation analysis confirms the ANOVA results on the effects of OM content on heavy metal accumulation.

Principal component analysis summarizes (reduces) the dataset into two major components representing the different sources of the elements. Irrigation with untreated wastewater may be responsible for the observed association of Pb, Ni, Cr and OM in PC1 at site A. PC2 with high loadings of Cu, Zn and alkaline metals (K and Mg) is attributed to other sources such as excess use of organic fertilizers and/or solid manure at site B. Although metal loading from these sources are presently low, build-up of heavy metals associated with changes in soil properties should be considered as an environmental concern in the study area.

This study generally concludes that the statistical methods can be a strong tool for monitoring of current environmental quality of agricultural soils in terms of heavy metal accumulation and for predicating the future soil contamination.

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