# Multivariate analysis of selected metals in tannery effluents and related soil

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## Abstract

Effluent and relevant soil samples from 38 tanning units housed in Kasur, Pakistan, were obtained for metal analysis by flame atomic absorption spectrophotometric method. The levels of 12 metals, Na, Ca, K, Mg, Fe, Mn, Cr, Co, Cd, Ni, Pb and Zn were determined in the two media. The data were evaluated towards metal distribution and metal-to-metal correlations. The study evidenced enhanced levels of Cr (391, 16.7 mg/L) and Na (25,519, 9369 mg/L) in tannery effluents and relevant soil samples, respectively. The effluent versus soil trace metal content relationship confirmed that the effluent Cr was strongly correlated with soil Cr. For metal source identification the techniques of principal component analysis, and cluster analysis were applied. The principal component analysis yielded two factors for effluents: factor 1 (49.6% variance) showed significant loading for Ca, Fe, Mn, Cr, Cd, Ni, Pb and Zn, referring to a tanning related source for these metals, and factor 2 (12.6% variance) with higher loadings of Na, K, Mg and Co, was associated with the processes during the skin/hide treatment. Similarly, two factors with a cumulative variance of 34.8% were obtained for soil samples: factor 1 manifested the contribution from Mg, Mn, Co, Cd, Ni and Pb, which though soil-based is basically effluent-derived, while factor 2 was found associated with Na, K, Ca, Cr and Zn which referred to a tannery-based source. The dendograms obtained from cluster analysis, also support the observed results. The study exhibits a gross pollution of soils with Cr at levels far exceeding the stipulated safe limit laid down for tannery effluents.
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## 1. Introduction

Tanning industry is recognized as a serious environmental threat all over the world. A variety of chemicals is used in the tanning process along with large quantities of water which are discharged as effluents, containing a huge bulk of liquid and solid wastes, and substantial quantities of Cr and other heavy toxic trace metals, organic matter, lime and sulfide. For an average tannery, it is estimated that 40,000 t of basic chemicals and 15,000 t of chromium as chromium sulfate are used annually, only to be discharged as waste surplus in effluents which may be advantageously recovered [1]. In developing countries, as a matter of common practice, the effluents discharged from the leather processing units are stored in large lagoons or dumped into open lands, without exercising any proper methods of waste disposal and recovery [2,3]. From these, the dissolved chemicals infiltrate into the surrounding soil, rendering it unfit for cultivation [4–6]. In addition, the ground water is also affected by the continued seepage of effluents, resulting in soil and water pollution [7,8]. This is a usual phenomenon wherever a cluster of tanneries operate in close proximity to each other, as is the case in several big cities of Pakistan.

In Pakistan, during the last decade the percentage share of leather export has increased by an average of over 8%. However, this economic growth has not gone in hand with environmental safety. There are 600 tanneries in the formal sector of the country and 50% of these are located in Kasur, a district of Punjab province, with a long standing tradition of leather tanning [9]. It is estimated that about 9000 cm$^3$ of heavily polluted effluents from the Kasur tannery network

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are discharged per day, without any attention being paid to the occupational health standards, protection from exposure to harmful chemicals and safety at the work place. Improper and unguarded use of chemicals has exposed the workers and residents of the adjoining areas to health hazards of varied types. Respiratory disorders, lung infection related diseases, diarrhea/dysentery and typhoid are common among the community population [10]. Currently 50,000–60,000 local inhabitants are exposed to the adverse health conditions arising from a rapid environmental degradation being caused by this industry [11–13].

There is thus a dire need to examine and redress the present status of toxic trace metal distribution in the tannery effluents and affected soil so that evaluation could be made of the relationship between the levels of the metals in the two media in terms of their origin and mutual dependence. In a situation like this, the multivariate techniques such as principal component analysis (PCA), and cluster analysis (CA) have been applied successfully in some earlier studies [14,15]. Accordingly, the metals may be arranged into different groups/factors on the basis of contribution from a probable source. The PCA would then provide the useful information on these groups based on their co-variation. Together with CA, this method would help evolve a given complex effluent soil system. Such estimates would be more useful towards futuristic metal estimates in the two media [16,17].

The objective of the present study stems from the considerations given above. The data on levels of selected trace metals (Na, Ca, K, Mg, Fe, Mn, Cr, Co, Cd, Ni, Pb, Zn) in tannery effluents and relevant soils determined by the atomic absorption method are intended for statistical evaluation of simple and multiple correlations, together with apportionment properties. It is envisaged that the approach would provide the correlation patterns of the metals in effluents and soil and this would in turn help evolve an effluent management strategy towards control over enhanced metal levels through the use of recycling of effluents for toxic metal separation, to thus avert the current gross environmental pollution in the Kasur tannery area. The proposed study, the first of its kind in the area, would also evolve a workable source appointment process for affected soils leading to the reclamation of lost fertility towards crop-raising.

## 2. Materials and methods

Thirty-eight tanneries of Kasur were included in the present study. A total of 68 effluent samples and as many soil samples from the adjoining areas of the industries were collected from May 2003 to September 2003 when the industries were running at peak capacity. The surface soil samples consisting of 1–5 cm deep top layer were collected manually with a plastic scoop from a distance of 100 m where the effluent had mixed and spread out homogenously onto the soil. The selection of soil sampling site located at 100 m was made

on the basis of visual inspection of the place up to which the effluents appeared to have affected the relevant soil. Following the standard sampling guidelines [18], the effluent samples were collected in 500 mL strong plastic bottles, whereas zip-mouthed high-density polythene bags of appropriate size were used to collect about 500 g soil sample. Prior to sampling, all soil samples were cleaned manually for any foreign matter (e.g. rock pieces, leaves, organic debris, etc.).

A 25 g portion of soil sample, added to 250 mL of distilled water, was stirred for 5 min on an auto-shaker and allowed to settle for 30 min. The solution was then filtered for direct aspiration onto a Shimadzu AA Spectrophotometer, AA-670 for the estimation of the solubilized selected metals [19–21]. The filtered soil solutions were diluted, where necessary, with distilled water prepared in all-glass apparatus. The effluent samples were directly aspirated, without adding any stabilizer for pH adjustment. The following metals were estimated in the effluent and soil samples: Na, Ca, K, Mg, Fe, Mn, Cr, Co, Ni, Pb and Zn. STATISTICA software was used to compute the relevant statistical analysis of the data [22].

All chemicals and reagents used in the study were of spectroscopic grade with a certified purity of 99.9%, procured either from E-Merk, Germany or BDH, England. Pyrex glassware was used for the processing and preparation of samples. Standard optimum analytical conditions were maintained and periodically checked on AAS system for each metal as per manufacturer's instructions. Inter-laboratory comparison of the furnished data was conducted at National Institute of Health, Islamabad. Standard reference material (SR-96 OL) was used to have a check on the accuracy of the results and the precision of the instrument. Normally the corresponding results matched within ±1.0 to ±1.5%.

## 3. Results and discussion

The data on the levels of selected metal concentrations, together with related statistical parameters reflecting the metal distribution pattern in various tannery effluents are presented in Table 1, followed by the metal-to-metal correlation matrix given in Table 2. The counterpart data for the soil samples are summarized in Tables 3 and 4.

An examination of Table 1 shows that out of macro-constituents (Na, Ca, K and Mg), in effluent samples the highest mean concentration is exhibited by Na (25,519 mg/L), while the mean levels of Ca, K, and Mg remain comparatively very low: at 255, 183 and 268 mg/L, respectively. This reflects the use of large amounts of sodium salts (NaCl and Na$_2$S) during the preparatory stages of the tanning process. Of the trace metals, Cr is found to be at an alarmingly high concentration of 391 mg/L, followed by a meager concentration of Fe at 4.4 mg/L. With the exception of Co (1.55 mg/L) all other trace metals remain at sub-mg/L levels; Pb and Zn being at comparable mean levels. The data thus reflect a great dispersion in the metal contents of the effluent samples, evidenced by high standard deviation (S.D.) values (Table 1).

Table 1
Basic statistical parameters (mg/L, where applicable) for the distribution of selected metals in tannery effluent samples from Kasur ($n = 68$)

|          | Na    | Ca     | K    | Mg    | Fe    | Mn     | Cr    | Co     | Cd     | Ni     | Pb    | Zn     |
|----------|-------|--------|------|-------|-------|--------|-------|--------|--------|--------|-------|--------|
| Minimum  | 245   | 1.5    | 1.1  | 0.068 | 0.009 | 0.003  | 0.151 | 0.019  | 0.001  | 0.004  | 0.010 | 0.004  |
| Maximum  | 79565 | 696    | 1295 | 1185  | 15    | 0.990  | 3956  | 5.64   | 0.160  | 0.550  | 4.362 | 1.906  |
| Mean     | 25519 | 255    | 183  | 268   | 4.4   | 0.396  | 391   | 1.55   | 0.056  | 0.179  | 0.872 | 0.684  |
| Median   | 14493 | 305    | 20.6 | 265   | 3.85  | 0.309  | 26.3  | 0.991  | 0.054  | 0.140  | 0.823 | 0.608  |
| S.D.     | 24502 | 163    | 282  | 250   | 4.02  | 0.31   | 710   | 1.36   | 0.042  | 0.135  | 0.764 | 0.530  |
| S.E.     | 2971  | 19.83  | 34.2 | 30.3  | 0.488 | 0.038  | 86    | 0.165  | 0.005  | 0.016  | 0.093 | 0.064  |
| Kurtosis | −1.1  | −0.838 | 5.47 | 2.33  | 0.150 | −1.343 | 9.144 | −0.509 | −0.699 | −0.908 | 5.408 | −0.705 |
| Skewness | 0.6   | 0.003  | 2.24 | 1.32  | 0.911 | 0.369  | 2.71  | 0.653  | 0.479  | 0.438  | 1.658 | 0.456  |

Table 2
Correlation coefficient matrix[a] for selected metals in tannery effluent samples from Kasur ($n = 68$)

|    | Na        | Ca        | K         | Mg        | Fe        | Mn        | Cr    | Co        | Cd        | Ni        | Pb        |
|----|-----------|-----------|-----------|-----------|-----------|-----------|-------|-----------|-----------|-----------|-----------|
| Ca | **0.402** |           |           |           |           |           |       |           |           |           |           |
| K  | **0.440** | 0.264     |           |           |           |           |       |           |           |           |           |
| Mg | **0.389** | 0.230     | **0.507** |           |           |           |       |           |           |           |           |
| Fe | 0.363     | 0.320     | 0.167     | 0.134     |           |           |       |           |           |           |           |
| Mn | **0.553** | **0.617** | 0.341     | **0.494** | **0.418** |           |       |           |           |           |           |
| Cr | 0.094     | 0.267     | 0.013     | −0.058    | 0.249     | 0.222     |       |           |           |           |           |
| Co | **0.540** | **0.495** | **0.527** | **0.689** | **0.378** | **0.827** | 0.063 |           |           |           |           |
| Cd | **0.390** | **0.540** | 0.180     | **0.461** | **0.390** | **0.637** | 0.309 | **0.547** |           |           |           |
| Ni | **0.469** | **0.583** | 0.272     | **0.397** | 0.367     | **0.710** | 0.315 | **0.630** | **0.641** |           |           |
| Pb | 0.262     | **0.446** | 0.103     | **0.407** | **0.391** | **0.675** | 0.223 | **0.587** | **0.781** | **0.471** |           |
| Zn | **0.482** | **0.490** | 0.246     | **0.383** | **0.384** | **0.688** | 0.251 | **0.638** | **0.716** | **0.711** | **0.686** |

[a] Bold values are significant at $p < 0.001$.

Table 3
Basic statistical parameters (mg/L, where applicable) for the distribution of selected metals in soil samples from Kasur ($n = 68$)

|          | Na    | Ca    | K    | Mg   | Fe    | Mn    | Cr     | Co    | Cd     | Ni     | Pb    | Zn     |
|----------|-------|-------|------|------|-------|-------|--------|-------|--------|--------|-------|--------|
| Minimum  | 100   | 85    | 78   | 5    | 0.320 | 0.020 | BDL    | 0.010 | 0.010  | 0.010  | BDL   | 0.030  |
| Maximum  | 98746 | 3794  | 4234 | 2000 | 91    | 2.2   | 50     | 15.6  | 0.700  | 1.500  | 5.16  | 1.57   |
| Mean     | 9369  | 1448  | 765  | 200  | 14.8  | 0.647 | 16.7   | 2.33  | 0.191  | 0.535  | 0.958 | 0.396  |
| Median   | 4231  | 1513  | 621  | 116  | 9.47  | 0.510 | 13     | 0.565 | 0.110  | 0.455  | 0.690 | 0.325  |
| S.D.     | 16535 | 678   | 611  | 287  | 14.4  | 0.535 | 13     | 4.028 | 0.191  | 0.334  | 1.017 | 0.255  |
| S.E.     | 1157  | 47.5  | 42.8 | 20.1 | 1.01  | 0.037 | 0.911  | 0.282 | 0.013  | 0.023  | 0.071 | 0.018  |
| Kurtosis | 1.05  | 0.901 | 10.2 | 19.6 | 8.4   | 0.307 | −0.240 | 3.2   | 0.061  | −0.196 | 6.105 | 3.599  |
| Skewness | 0.313 | 0.320 | 2.5  | 4.15 | 2.52  | 1.01  | 0.858  | 2.11  | 1.120  | 0.643  | 2.468 | 1.49   |

BDL: below detection limit.

Also, large skewness and kurtosis values evidence that the trace metals in effluents are not normally distributed. This situation thus unveils a random distribution of the metals in the effluents, in agreement with the sequence of chemical operations conducted in different batches during the hide/skin processing in a given tannery. The study evidences an enhanced level of Cr than the levels determined and reported previously by other workers (200–2400 mg/L) [23–25]. Also,

Table 4
Correlation coefficient matrix[a] for selected metals in soil samples from Kasur ($n = 68$)

|    | Na        | Ca     | K      | Mg        | Fe     | Mn        | Cr     | Co        | Cd        | Ni        | Pb     |
|----|-----------|--------|--------|-----------|--------|-----------|--------|-----------|-----------|-----------|--------|
| Ca | −0.170    |        |        |           |        |           |        |           |           |           |        |
| K  | −0.143    | 0.238  |        |           |        |           |        |           |           |           |        |
| Mg | −0.053    | 0.291  | 0.035  |           |        |           |        |           |           |           |        |
| Fe | 0.007     | −0.002 | 0.027  | 0.178     |        |           |        |           |           |           |        |
| Mn | **0.382** | 0.093  | −0.071 | 0.233     | 0.217  |           |        |           |           |           |        |
| Cr | −0.100    | 0.279  | 0.094  | 0.084     | −0.115 | 0.066     |        |           |           |           |        |
| Co | **0.484** | 0.006  | −0.107 | 0.311     | 0.073  | **0.546** | −0.033 |           |           |           |        |
| Cd | −0.026    | 0.293  | 0.082  | 0.252     | 0.060  | **0.449** | 0.228  | **0.385** |           |           |        |
| Ni | 0.325     | 0.221  | 0.044  | 0.319     | −0.081 | **0.491** | 0.131  | **0.497** | **0.484** |           |        |
| Pb | 0.357     | 0.128  | −0.017 | **0.412** | 0.147  | **0.505** | −0.077 | **0.698** | 0.307     | **0.476** |        |
| Zn | 0.203     | −0.081 | −0.046 | −0.044    | −0.175 | 0.026     | −0.060 | −0.068    | −0.262    | 0.035     | −0.009 |

[a] Bold values are significant at $p < 0.001$.

Table 5
Correlation coefficient matrix[a] for selected metals in tannery effluent vs. soil samples from Kasur ($n = 68$)

|  | Na(e) | Ca(e) | K(e) | Mg(e) | Fe(e) | Mn(e) | Cr(e) | Co(e) | Cd(e) | Ni(e) | Pb(e) | Zn(e) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Na(s) | 0.256 | 0.202 | 0.204 | 0.011 | 0.160 | 0.236 | −0.023 | 0.150 | 0.032 | 0.128 | −0.029 | 0.085 |
| Ca(s) | −0.119 | −0.088 | 0.001 | −0.065 | 0.129 | −0.008 | −0.165 | −0.035 | 0.003 | 0.019 | 0.002 | −0.106 |
| K(s) | −0.023 | −0.058 | −0.030 | −0.197 | −0.010 | 0.000 | −0.010 | −0.120 | −0.104 | −0.045 | −0.056 | −0.032 |
| Mg(s) | 0.043 | −0.025 | −0.057 | 0.051 | −0.014 | 0.061 | −0.092 | 0.060 | −0.013 | −0.028 | 0.069 | 0.030 |
| Fe(s) | 0.055 | **0.393** | 0.028 | −0.011 | 0.121 | 0.088 | **0.472** | −0.014 | 0.093 | 0.159 | 0.097 | −0.033 |
| Mn(s) | 0.162 | 0.196 | 0.043 | 0.217 | 0.175 | 0.290 | 0.040 | 0.271 | 0.097 | 0.144 | 0.222 | 0.145 |
| Cr(s) | −0.253 | −0.215 | −0.212 | −0.175 | −0.171 | −0.202 | **0.605** | −0.206 | −0.075 | −0.197 | −0.089 | −0.093 |
| Co(s) | 0.238 | 0.095 | 0.177 | 0.057 | 0.143 | 0.255 | −0.121 | 0.181 | 0.016 | 0.106 | 0.102 | 0.138 |
| Cd(s) | **0.366** | 0.313 | 0.334 | **0.417** | 0.356 | **0.508** | −0.187 | **0.621** | 0.117 | 0.307 | 0.212 | 0.365 |
| Ni(s) | 0.163 | −0.039 | 0.186 | 0.287 | 0.190 | 0.181 | −0.194 | 0.303 | 0.081 | 0.107 | 0.084 | 0.119 |
| Pb(s) | 0.060 | −0.036 | 0.073 | 0.095 | −0.007 | 0.070 | −0.158 | −0.008 | −0.014 | −0.064 | 0.020 | 0.009 |
| Zn(s) | 0.163 | 0.119 | 0.064 | 0.036 | 0.043 | 0.026 | −0.083 | 0.122 | −0.084 | 0.007 | 0.014 | 0.065 |

[a] Bold values are significant at $p < 0.001$.

these levels are much higher than the international standard for Cr bearing discharges [26,27]. Actually only 50–70% of chrome is taken up by the skin collagen during tanning, while the rest is discharged in effluents [28,29].

Table 2 contains the metal-to-metal correlation data in terms of linear correlation coefficient ($r$) values that are significant at $r > 0.369$, $p < 0.001$. The listed $r$-values reveal a number of significantly positive correlations between various pairs of metals, except Cr which is not significantly correlated with any other metal. This observation could be supported by the fact that chromium is used in independent batch operations, and in high concentrations, irrespective of the concentration of other metals. In the effluent samples, therefore, metals other than Cr could be correlated mutually, but they bear no apparent correlation with Cr.

Table 3 provides data on distribution of metals in various soil samples collected from close proximity of effluent drainage points. In water-extracted soil samples, sodium is found at the highest concentration of 9369 mg/L, followed by Ca, K, and Mg at lower concentrations of 1448, 765, and 200 mg/L, respectively. This elevated level of sodium may be traced in huge amounts of sodium salts (notably, NaCl and $Na_2S$) used in the tanning process which ultimately accumulate in the soil in contact with the effluents. Amongst metals, the soil is found to have enhanced levels of Cr (16.7 mg/L) and Fe (14.8 mg/L), followed by Co with a concentration of 2.33 mg/L, the remaining metals being at sub-mg/L levels. As in case of effluents, the metal distribution in the soil samples was also found not to follow normal distribution since the data have high degree of skewness and kurtosis. The metal-to-metal correlation matrix (Table 4) brings out numerous significant positive correlations ($r > 0.369$, $p < 0.001$); Cr once again being an almost isolated case.

The effluent (e) versus soil (s) trace metal content relationship is also investigated. Table 5 brings out this relationship for the two media ($r > 0.369$, $p < 0.001$). The data confirm the significant role of Cr once again; the effluent Cr is strongly correlated with soil Cr ($r = 0.605$), clearly signifying that Cr in soil samples taken from 100 m away from the effluent drains are mutually related together. Effluent Cr also exhibits signif-

icant positive correlation with soil Fe at $r = 0.472$. The other metal pairs showing this kind of behavior are Mn(e)–Cd(s) ($r = 0.508$), Mg(e)–Cd(s) ($r = 0.417$), Na(e)–Cd(s) ($r = 0.366$) and Co(e)–Cd(s) ($r = 0.621$). The data evidence no significant correlation between the Pb, Ni, Zn and K in the two media.

Source identification was one of the major concerns of the present study, for which a combination of two multivariate techniques, namely, principal component analysis (PCA) and cluster analysis (CA), was used following the standard procedure reported in literature [30,31]. The principal component loadings using Varimax Normalized rotation for both effluent and soil samples are shown in Table 6. Two factors are obtained for effluent samples with eigenvalues >1, cumulatively explaining more than 62% of variance. Factor 1 which accounts for 49.6% of total variance has significant loading for Ca, Fe, Mn, Cr, Cd, Ni, Pb and Zn, which emanate from chemicals used in tanning process. Factor 2 with high loading for Na, K, Mg, and Co, and with 12.6% of total variance, is associated with processes involving skin/hide treatment.

Table 6
Rotated factor loadings (varimax normalized) of selected metals in tannery effluent samples ($n = 68$) and soil samples ($n = 68$)

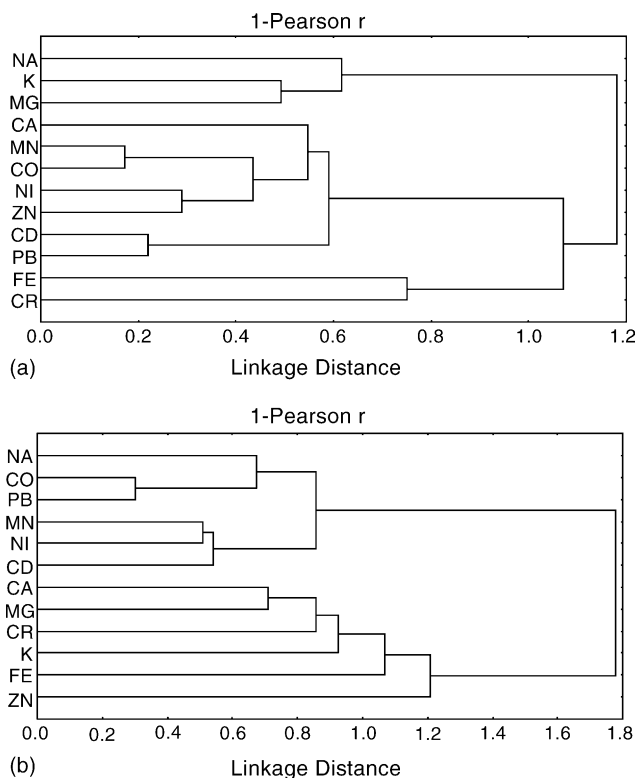| Components | Effluent samples | | Soil samples | |
|---|---|---|---|---|
|  | Factor 1 | Factor 2 | Factor 1 | Factor 2 |
| Na | 0.366 | **0.598** | −0.482 | **0.503** |
| Ca | **0.661** | 0.255 | 0.159 | **0.570** |
| K | 0.008 | **0.784** | −0.048 | **0.295** |
| Mg | 0.192 | **0.795** | **0.401** | 0.291 |
| Fe | **0.568** | 0.110 | 0.127 | 0.028 |
| Mn | **0.722** | 0.523 | **0.709** | −0.003 |
| Cr | **0.592** | −0.318 | 0.042 | **0.369** |
| Co | 0.515 | **0.754** | **0.831** | −0.156 |
| Cd | **0.815** | 0.256 | **0.521** | 0.473 |
| Ni | **0.735** | 0.361 | **0.675** | 0.162 |
| Pb | **0.770** | 0.218 | **0.764** | −0.045 |
| Zn | **0.774** | 0.343 | 0.024 | **0.262** |
| Eigenvalue | 5.95 | 1.51 | 2.96 | 1.22 |
| Total variance (%) | 49.6 | 12.6 | 24.7 | 10.1 |
| Cumulative eigenvalue | 5.95 | 7.45 | 2.96 | 4.18 |
| Cumulative percentage | 49.6 | 62 | 24.7 | 34.8 |

Fig. 1. Dendrogram of selected metal data using Ward's method: (a) effluent samples and (b) soil samples.

The corresponding CA in the form of dendogram is shown in Fig. 1a which supports the above observation.

The principal factor loading for soil metal data using varimax normalized rotation is also shown in Table 6. Again, two factors are obtained with eigenvalues >1, cumulatively contributing 34.8% of variance. The first factor with a total variance of 24.7% manifests the contributions from Mg, Mn, Co, Cd, Ni and Pb in the soil samples which though soil-based, are actually effluent-derived. The second factor with significant loadings for Na, K, Ca, Cr, and Zn contributes to 10.1% of total variance, and is considered to originate from tannery effluents, which contaminate the adjoining soils. The dendrogram for the soil samples is shown in Fig. 1b, which supports the findings of PCA, correlation and regression analysis.

## 4. Conclusions

The present investigation on the current status of trace metal distribution in tannery effluents from Kasur evidences enhanced levels of Cr in the effluents as well as in soils in close proximity to the tanneries. Maximum concentration of Cr (3956 mg/L) was found in the effluent samples, which together with that of Na (79,569 mg/L) are high enough to pose serious pollution stress to the environment in the proximity of the tanneries. The high Cr levels are hazardous for human

health, especially of Cr(VI). The elevated Na could turn the groundwater into saline water, thus affecting the proper utilization of this kind of water for irrigation and human ingestion purposes. This is high time to look into the seriousness of this gross contamination problem and to redress the elevated metal levels by proper industrial waste management policy. For this purpose, due legislative measures must be made legally binding on the individual industries, towards controlling the discharge of unguarded effluents. The present work demonstrates the usefulness of the statistical multivariate methods towards classifying the metals as groups in terms of their independent behavior and identifying their probable origin in effluents. The cluster analysis evidences the contamination of the soils in the vicinity of the tanneries by the emanating effluents. It is anticipated that any feasible futuristic solution to the industrial pollution problem should be based on the recovery and recycling of chemicals used in the tanning process.

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