ORIGINAL PAPER

# Enrichment, risk assessment, and statistical apportionment of heavy metals in tannery-affected areas

Z. Ali · R. N. Malik · Z. K. Shinwari ·
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**Abstract** Tannery-affected surface soils from 72 sampling sites from industrial area of Sialkot district, Pakistan, were collected and analyzed for nine physicochemical parameters, nine heavy metals, and four macro-nutrients. Most of the soils were poor in organic matter (0.11–2.98 %), basic in nature with pH (7.1–10.6) and electrical conductivity (1.2–17.9 mS/cm). Mean concentration of total dissolved solids, $Cl^{1-}$, alkalinity, $NO_3^1$-N, salinity, and $PO_4^{3-}$ was 3,093 mg/L, 6,587, 3,929, 301.3, 10.3, and 1.7 mg/kg. The results showed that concentration of macro-nutrients was in the order: Na>Mg>K>Ca whereas heavy metals followed the order: Cr>Fe>Ni>Mn>Cu>Zn>Co>Pb>Cd. Factor analysis based on principal component analysis, cluster analysis, and correlation analysis identified contribution of metals from tannery effluents, agrochemicals, automobiles exhaust, and natural weathering processes. Tannery-affected soils were enriched with Cd followed by Cr, Pb, Ni, Cu, Co, Zn, and Mn. Geo-accumulation index ($I_{geo}$) classified the soil samples in unpolluted to moderately polluted categories. Metal pollution index provided better estimation of heavy metal pollution as compared to pollution load index. Ecological risk index showed high potential ecological risk associated with Cd and Cr with mean concentrations above respective average shale/background values. The results are useful for heavy metals source identification, enrichment, risk assessment, and management of tannery-affected soils and can contribute to monitoring programs at regional levels.

**Keywords** Cluster analysis · Ecological risk index · Enrichment indices · Factor analysis · Geo-accumulation

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## Introduction

Leather industry plays a major role in economic uplift of many developing countries including Pakistan. It is associated with the generation of huge amount of liquid and solid wastes. Improper disposal of hazardous/toxic waste coupled with inadequate management has resulted in serious environmental problems in recent years. Leather-manufacturing processes such as soaking, liming/deliming, bathing, pickling, skin degreasing, tanning, and post-tanning of raw hides/skins involve chemicals such as sodium hydroxide, sodium hypochlorite, enzymes, lime, chlorides, sulfuric acid, formic acid, ammonium salts, and kerosene, etc. (Tariq et al. 2006). Among these processes, liming and tanning are the most polluting steps. Liming involves excessive use of sulfite ions while tanning entails either usage of Cr salts or plant tannins (Tariq et al. 2009).

In Pakistan, >600 tannery units have been reported. They are mostly centered in formally designated industrial zones of big cities such as Karachi, Kasur, Sialkot, and Peshawar (Qadir et al. 2008), and produce approximately

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36.2 million skins and 7.4 million hides with mean annual growth of 1.47 and 2.9 %, respectively. Unfortunately, disposal strategies for tannery solid waste and effluents are inadequate. Waste is usually dumped in dug wells, released to the water channels or open lands without prior treatment. Usually, 30–35 L of effluents is generated during chemical processing of 1 kg raw material and 600 kg solid waste for every 200 kg of finished leather (Qadir et al. 2008). Tannery effluents containing heavy metals have raised serious environmental concerns in recent years regarding potential risk to human health, bioaccumulation through food chain, and their impacts on ecological system.

Sialkot district is known worldwide for its leather industry, furniture, cutlery, musical, and surgical instruments. It is the third most important economic hub and second largest source of foreign exchange earner of Pakistan. There are 3,229 industrial units, including 264 tannery units which produce approximately 547–814 m$^3$ of tannery effluents/day (Qadir et al. 2008). Over the last decades, soil contamination problems related to discharge of untreated industrial/urban effluents and wastes, indiscriminate use of chemical fertilizers/pesticides in surface soils and sewage irrigation have emerged as major environmental problems. There are serious concerns about the quality of surface soils in urban and peri-urban areas, considering the potential negative environmental influences from the tanning industry (Malik et al. 2010).

In Pakistan, few studies have been conducted so far to determine the level of heavy metals in the soils around the cities (Tariq et al. 2006; Malik et al. 2010). Different pollution indices that may help in quantification, monitoring studies, and regional management plans are also less often applied. Studies on the characteristics, spatial trends, and sources of heavy metals in soils receiving tannery effluents in particular are still needed. No study as yet has been reported from Sialkot district determining the impact of tannery effluents on the surrounding soils. There is dire need for better knowledge of heavy metal contamination in soils adjacent to tannery industries. Present study, therefore, aims at (1) determining the concentration of heavy metals, (2) ecological risk assessment, (3) correlation between metals and soil properties, (4) enrichment, and (5) source apportionment in soils of Sialkot district through pollution indices and multivariate techniques.

Pollution indices vis. enrichment factor (EF) by Dantu (2009); EF (%) by Zonta et al. (1994) and geo-accumulation index ($I_{geo}$) by Muller (1979); metal pollution index (MPI) by Usero et al. (2000); and ecological risk index (RI) by Hakanson (1980) and pollution load index (PLI) by Tomlinson et al. (1980) were used to compare these indices as a contribution toward building consensus on methodologies applicable to study surface soils impacted by tannery effluents. Besides, RI ecological risk was evaluated by soil quality guidelines (SQGs). Multivariate techniques, i.e., FA/PCA, cluster analysis, and correlation matrix, were applied to determine the association of selected metals with other physicochemical properties and source identification. This study not only provides information on trends, distributional pattern, fate, and apportionment of heavy metals, but also indicates the current quality of surface soils of Sialkot district. Present research was carried out between October 2009 and January 2010 at Environmental Biology Laboratory, Department of Plant Sciences, Faculty of Biological Sciences, Quaid-i-Azam University, Islamabad, Pakistan.

## Materials and methods

### Soil sampling and laboratory analysis

Sialkot district lies at latitude of 32°20′–32°35′N and longitude of 74°10′–74°30′E in northeast of the Punjab province, and covers an area of 3,016 km$^2$ with population density of 903 persons/km$^2$. Sialkot soils belonged to four great groups, i.e., Haplustalf's (order; Alfisols), Ustochrepts (order; inceptisol), Ustofluvents (order; entisols), and Natrustalf's (order; Alfisols). Sialkot series (50 %; non-calcareous silt loam) was dominant with Gujranwala (20 %; non-calcareous silty clay loam) and Sialkot shallow phase (20 %; non-calcareous) being minor constituents. Remaining 10 % include Pasrur series (non-calcareous silty clay), Shahdra (calcareous, stratified silt/sand loam), and Argan series (calcareous silt loam).

Preliminary survey was conducted to identify tannery units located in peri-urban areas of Sialkot city discharging effluents into the adjacent lands which are used for agricultural activities. Seventy-two tannery units were identified (Fig. 1), and soil samples were collected between October 5 and 21, 2009 from their periphery which received effluents actively throughout the year. From each site, triplicate surface soil samples were collected from depth of 3–10 cm within distance of 50 m from the point of discharge, including points where effluents appeared to have affected the relevant soils. Triplicate samples were composited and kept in labeled zip precleaned polythene bags. Each sample was air-dried, crushed, passed through 2-mm mesh sieve, and kept in prewashed metal-free glass containers at room temperature. Soil pH, electrical conductivity (EC), TDS, and salinity were determined using 1:10 suspension of soil (w/v) in deionized water. Soil pH was determined by pH meter (Thermo Orien 240A); EC, TDS, and salinity were determined using combine meter (HI 8033). Alkalinity, chlorides, phosphates, and nitrate nitrogen were determined using standard procedures (APHA 1998). Organic matter (OM) was determined using Tyurin's method (Nikolskii 1963).
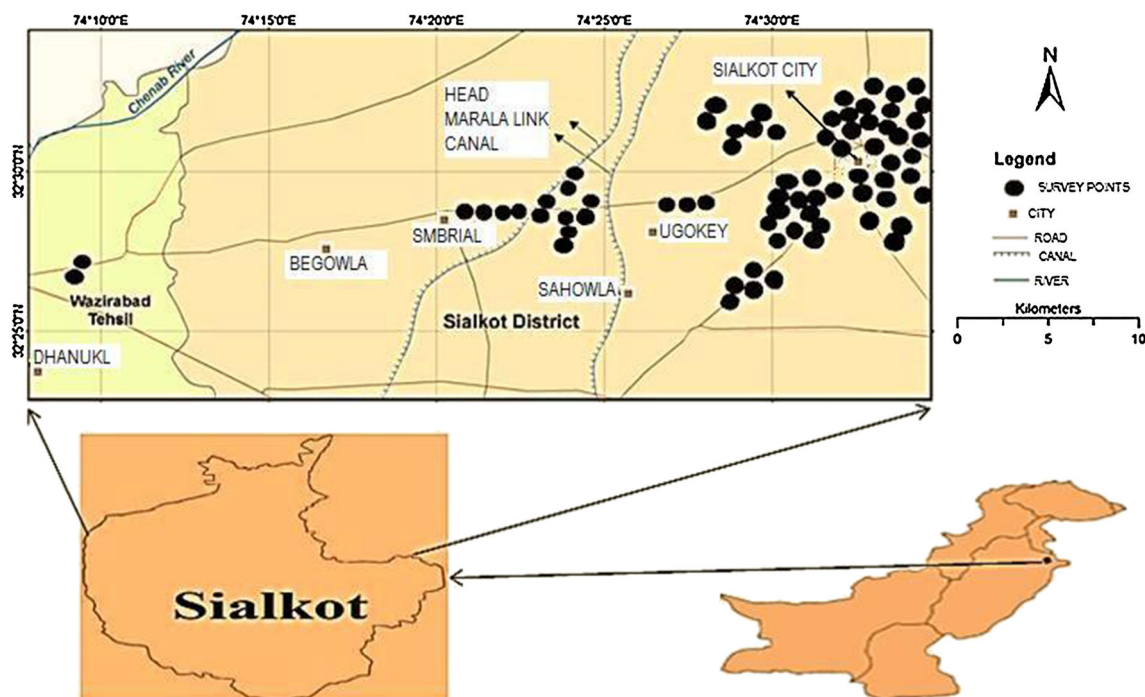
**Fig. 1** Map of study area showing location of Tannery units (soil sampling points) in Sialkot district ($n = 72$)

### Heavy metal analysis and quality control/quality assurance (QC/QA)

For measurement of total metal concentrations, acid digests of each soil sample were prepared using USEPA method 3051A. Each soil sample measuring 0.5 g was placed in prewashed Teflon vessel and digested in microwave-accelerated reaction system (MARS, CEM) at 220 °C for 15 min in the presence of 9 mL conc. $HNO_3$ supplemented with 3 mL of conc. HCl. Microwave unit was calibrated by ramping temperature to $220 \pm 5$ °C and 1,200 W of power. Digested samples were filtered and diluted, and metal concentrations were determined in triplicate in air/acetylene flame using Fast Sequential Atomic Absorption Spectrophotometer (Model: AA240 FS by Varian, USA). The results of triplicate analyses were averaged and reanalyzed when relative standard deviation exceeded 5 %. Analytical blanks and standard reference material were prepared and run in the same way as soil samples, and heavy metal concentrations were determined using standard solutions prepared in the same acid matrix. Certified reference material CRM 320 ($N = 3$) of the Community Bureau of Reference (Belgium) was used to ensure the validation of data and accuracy/precision of analytical method. The recoveries were 84–101 % for all metals. Metal concentrations were expressed in mg/kg dry soil. Chemicals/reagents used were of analytical grade. All glassware and plasticware used were soaked in 30 % $HNO_3$ overnight, rinsed with deionized water before analysis.

### Statistical analysis

Multivariate techniques such as factor analysis based on principal components (FA/PCA) were used to infer sources of metals either from natural or anthropogenic input. Varimax rotation was used to normalize principal component axes. Correlation matrix (CM) using Pearson coefficient was employed for relationship between heavy metals and other soil physiochemical parameters. Another multivariate technique Canonical correlation analysis (CCA) was used to analyze relationship between soil properties and metal concentrations. To account for changes in soil physicochemical properties in response to fluctuating total metal content, linear regression analysis was performed between soil parameters and total metal content expressed as MPI at each site. Cluster analysis was used to identify metal groups. *Unweighted Pair-Group Average (median)* was used as a linkage method and *Pearson-r* as a distance matrix. The statistical software package Statistica version 7.0 (Stat Soft Inc. USA) and Microsoft Excel, 2007 (Microsoft 2007) were used for all the statistical computations.

### Quantification of metal pollution

Enrichment factor (EF) was calculated to determine anthropogenic input of metals in soils following Dantu (2009) using Eq. 1. Iron (Fe) was used for geochemical normalization and shale reference values were taken after Turekian and Wedepohl (1961).

$$EF = \frac{(C_i/C_{Fe})_S}{(C_i/C_{Fe})_r} \quad (1)$$

where EF is enrichment factor of an element, $(C_i/C_{Fe})_S$ is the ratio of the concentration of an element with that of iron at each sampling point, and $(C_i/C_{Fe})_r$ is same ratio of the concentration with respect to reference soil. Soils were categorized into seven classes based on the value of EF: If EF <1 no enrichment, <3 minor enrichment, 3–5 moderate enrichment, 5–10 moderate-to-severe enrichment, 10–25 severe enrichment, 26–50 very severe enrichment, >50 extremely severe enrichment.

Enrichment factor percentage (EF %) was calculated after Zonta et al. (1994) using Eq. 2:

$$EF(\%) = \frac{C - C_{min}}{C_{max} - C_{min}} \times 100 \quad (2)$$

where $C$ = mean concentration of element in the soil, $C_{max}$ = maximum concentration, while $C_{min}$ = minimum concentrations measured in current study.

Geo-accumulation index ($I_{geo}$) was calculated after Muller (1979) using Eq. 3:

$$I_{geo} = \log 2 \times \frac{C_n}{1.5B_n} \quad (3)$$

where $C_n$ = concentration of metal determined in the soil sample, $B_n$ = same metal's background concentration in the earth's crust adopted from Turekian and Wedepohl (1961), whereas 1.5 acts as a constant factor to neutralize variations due to lithogenic actions. Geo-accumulation index was described similar to that in the reference (Forstner et al. 1990).

In this study, EF, EF (%), and $I_{geo}$ were calculated for heavy metals excluding macro-nutrients.

Metal pollution index (MPI) was calculated to estimate total metal load at individual sites, following Usero et al. (2000) using Eq. 4:

$$MPI = (Cf1 \times Cf2 \times Cf3 \ldots Cfn)^{1/n} \quad (4)$$

where Cf = concentration of metal in the sample.

Ecological risk assessment was performed using two risk indices viz. potential ecological risk index (RI) and pollution load index (PLI). Potential ecological risk index was developed after Hakanson (1980) for five toxic metals using Eqs. 5, 6, and 7:

$$RI = \sum_{i=1}^{m} E_r^i \quad (5)$$

$$E_r^i = T_r^i \times C_f^i \quad (6)$$

$$C_f^i = C_s^i / C_n^i \quad (7)$$

where $C_f^i$ = contamination factor for ith metal; $C_s^i$ = ith metal concentration in the soil sample; $C_n^i$ = background concentration of ith metal taken from the uncontaminated soils due to the absence of background metal levels in the soils investigated (CEPA and CGSEM 1990); $T_r^i$ = toxic response factor suggested by Hakanson (1980) for five metals Cd (30), Cr (2), Cu (5), Pb (5), Zn (1); $E_r^i$ = potential ecological risk factor of individual metals; RI = potential ecological risk factor of multiple metals; $r$ = response factor in $T_r^i$ and risk factor in $E_r^i$; $n$ = pristine or uncontaminated soils; $s$ = soil sample investigated; $i$ = any one of the above five metals. Modified standards for $C_f^i$, $E_r^i$, and RI classification criteria were adopted after Cao et al. (2007).

Pollution load index (PLI) was developed after Tomlinson et al. (1980) using Eq. 8 for comparison of pollution on different sites or at same site on temporal scale. Determination of PLI involves the calculation regarding concentration factor obtained by dividing the measured concentration of an element with the background concentration of the same element in shale (Turekian and Wedepohl 1961).

$$PLI = n\sqrt{CF1 \times CF2 \times CF3 \times \cdots CFn} \quad (8)$$

$$CF_{metal} = \frac{C_{metal}}{C_{background}} \quad (9)$$

where CF = contamination factor; $n$ = number of metals; $C_{metal}$ and $C_{background}$ are the metal concentrations in the soil and background value of same element in the shale (Turekian and Wedepohl 1961).

## Results and discussion

### Macro-nutrients (Na, K, Ca, and Mg)

Basic statistical summary of studied metals is given in Table 1. Macro-nutrients were in the order: Na>Mg>K>Ca with mean concentrations of 4,738, 2,925, 2,622, and 1,902 mg/kg, respectively. Macro-nutrients are essential for plant metabolism and generally not classified as dangerous elements. These nutrients constitute primary elements in parent rock material and are present in higher concentrations in upper horizons of earth core in associations with other metals. Their preferential accumulations in mobile forms (top 10 cm fraction) revealed that these can be readily transformed, liberating cations with slight change in pH. Among the studied nutrients, none exceeded average shale values and remained at relatively lower concentrations. Elevated Na concentration can damage soil structure in certain soil types by limiting water movement and replacing Ca/Mg ions affecting plant growth. Na levels (1,782 mg/kg) in our earlier study on urban soils of Sialkot were quite lower than present study due to substantial tanneries input (Malik et al. 2010). Mg becomes available

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**Table 1** Basic statistical summary for the distribution of selected parameters in soil samples from Sialkot ($n = 72$)

| S. no. | Parameters | Mean ± SD | Min–max | ASV[a] | BV[b] | TEL/PEL[c] | ERL/ERM[d] |
|---|---|---|---|---|---|---|---|
| 1 | pH | 8.2 ± 1.2 | 7.1–10.6 | – | – | – | – |
| 2 | EC (mS/cm) | 4.6 ± 5.3 | 1.3–17.9 | – | – | – | – |
| 3 | TDS (mg/L) | 3,093 ± 3,518 | 800–11,700 | – | – | – | – |
| 4 | Salinity (mg/kg) | 10.3 ± 15.6 | 1.8–49 | – | – | – | – |
| 5 | Alkalinity (mg/kg) | 39,294 ± 506 | 600–18,990 | – | – | – | – |
| 6 | $Cl^{1-}$ (mg/kg) | 6,587 ± 8,471 | 282–24,088 | – | – | – | – |
| 7 | $PO_4^{3-}$ (mg/kg) | 1.7 ± 1.3 | 0.3–5.20 | – | – | – | – |
| 8 | $NO_3^{1-}$-N (mg/kg) | 301.3 ± 743 | 0.4–2,640 | – | – | – | – |
| 9 | OM (%) | 1.3 ± 0.8 | 0.1–3 | – | – | – | – |
| 10 | Cr (mg/kg) | 206 ± 193 | 21–675 | 90 | 49.3 | 37.3/90 | 80/145 |
| 11 | Ni (mg/kg) | 6.4 ± 4.4 | 0.1–18 | 68 | – | 18/36 | 30/50 |
| 12 | Mn (mg/kg) | 5.8 ± 3.6 | 0.1–11.7 | 850 | – | – | – |
| 13 | Na (mg/kg) | 4,738 ± 8,313 | 307–29,626 | 9,600 | – | – | – |
| 14 | K (mg/kg) | 2,622 ± 1,187 | 765–4,789 | 26,600 | – | – | – |
| 15 | Fe (mg/kg) | 44.4 ± 29.2 | 2.5–97 | 47,200 | – | – | – |
| 16 | Co (mg/kg) | 4 ± 2.7 | 0.01–5.3 | 19 | – | – | – |
| 17 | Cu (mg/kg) | 4.2 ± 3.3 | 0.1–11.6 | 45 | 26.7 | 35.7/197 | 70/390 |
| 18 | Ca (mg/kg) | 1,902 ± 1,167 | 305–4,986 | 22,100 | – | – | – |
| 19 | Mg (mg/kg) | 2,925 ± 2,117 | 456–5,071 | 15,000 | – | – | – |
| 20 | Zn (mg/kg) | 4.2 ± 2.4 | 0.5–8.7 | 95 | 68.8 | 123/315 | 120/270 |
| 21 | Cd (mg/kg) | 0.7 ± 0.6 | 0.02–1.8 | 0.3 | 0.12 | 0.60/3.53 | 5/9 |
| 22 | Pb (mg/kg) | 3.4 ± 1.5 | 0.2–5.3 | 20 | 19.4 | 35/91.3 | 35/110 |

[a] Average shale values taken from Turekian and Wedepohl (1961)

[b] Background values taken from CEPA and CGSEM (1990)

[c] TEL/PEL values taken from Smith et al. (1996)

[d] ERL/ERM values taken form Long and Morgan (1991)

to plants at higher pH. Mean pH (8.2) coupled with elevated Mg levels can harm plant metabolic functions. Soil cation exchange capacity, and strong competitors like K can impair Mg availability to plants (Bermudez et al. 2010). No phytotoxicity is associated with Ca which acts as guard against Cd, Zn, Pb, Ni, and Cu pollution in surface soils. Ca increases solubility of Na, K, $NH_4^{1+}$, $Fe^{2+}$, $Al^{3+}$, and Mg as it competes for adsorption sites. Higher concentration of macro-nutrients in soil speeds up plant growth on uptake and favors heavy metal accumulation. In natural soils, these are mostly derived from geogenic sources; however, anthropogenic feedbacks from agrochemicals, organic fertilizers, solid manures, industrial effluents, and municipal wastes also contribute considerably. Soils being sink route metals to ground water, plants, and animals also referred as soil–water–plant–animal systems adversely affecting soil fertility, soil organisms, and humans through the food chain (McLaughlin et al. 2006).

Measured concentrations of Ca and K were higher than those reported in tannery-affected soils from Pakistan (Tariq et al. 2005, 2006, 2009) and India (Chandra et al. 2009). However, mean Na concentration was lower compared to those of tannery-affected soils from Peshawar (12,912 mg/kg) and Kasur (18,765 mg/kg) cities, Pakistan (Tariq et al. 2006, 2009). The results also indicated that measured Mg contents were the second highest from Pakistan after Peshawar (3,018 mg/kg; Tariq et al. 2006).

**Heavy metals**

Distribution of heavy metals in tannery-affected soils was in the order: Cr>Fe>Ni>Mn>Cu>Zn>Co>Pb>Cd. Mean concentration of Cr (205.9 mg/kg), Ni (6.4 mg/kg), Mn (5.8 mg/kg), Fe (44.4 mg/kg), Cu (4.2 mg/kg), Zn (4.2 mg/kg), and Cd (0.7 mg/kg) was higher to those found in tannery-affected soils from other parts of Pakistan (Tariq et al. 2005, 2006, 2009). However, measured concentrations of Cr, Mn, Fe, Cu, Zn, Cd, Ni, and Pb were far lower to those reported in tannery-affected soils from the Uttar Pradesh, India (Chandra et al. 2009). Mean concentrations of Ni, Mn, Pb, Cu, Zn, Co, and Fe were well below to average shale values given in Turekian and Wedepohl

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(1961), whereas Cu, Zn, and Pb mean levels were less than background levels (Table 1). Similarly, mean concentration of Ni, Cu, Zn, and Pb was well below to low range values, i.e., TEL's/ERL's, after Long and Morgan (1991) and Smith et al. (1996).

Mean Cr concentration (206 mg/kg) exceeded its average shale value (90 mg/kg), background value (49.3 mg/kg), and maximum level (100 mg/kg) that may be present in soil (Chaney and Ryan 1993). Chromium is a less mobile element at neutral pH, and its salts are used in un-hairing of hides in Pakistan (Qadir et al. 2008). $Cr^{6+}$ adsorption decreases with increasing pH, whereas, $Cr^{3+}$ adsorption increases with increasing pH (Gowd et al. 2010). Owing to low solubility and mobility of Cr, only small amount of Cr is bioavailable; therefore, in agricultural, soils treated with Cr bearing effluents/sludge, phytotoxicity is hardly observed (Alloway 1990). However, Cr is potentially toxic for agronomic plants at 0.5–5 mg/L in nutrient solution and 5–100 mg/kg in soils; therefore, its bioaccumulation can be fatally toxic to higher trophic levels. Chromium generates reactive oxygen species (ROS) in higher concentrations, which strongly interfere with biochemical processes. Mean Cr concentration exceeded TEL–PEL (threshold effect level–probable effect level) and ERL–ERM (effect range low–effect range median) values (Long and Morgan 1991; Smith et al. 1996).

Iron being an essential element is generally not considered hazardous metal pollutant, and its concentration ranged from 2.5–97 mg/kg. At neutral to alkaline pH, Fe is not known to cause toxicity. Measured Cu concentrations (4.2 mg/kg) were lower than soil environmental quality standards (35 mg/kg). It accumulates in surface soils from different anthropogenic sources (Kabata-Pendias 2004). In current study, its concentration in soils was mainly due to industrial and urban effluents. However, applications of agrochemicals can also be considered its possible source (Gowd et al. 2010). Hooda et al. (1997) determined heavy metals, i.e., Ni, Cu, Zn, Pb, and Cd toxicities from biosolid-amended soils and suggested that Cd, Ni, and Zn can pose greater hazard than Cu/Pb on account of their bioaccumulation efficiency. Anthropogenic inputs of cobalt in agricultural soils include industrial effluents, traffic activities, and application of sewage sludge (Wei et al. 2010). Approximately, 33–44 % of Co occurs as stable organic complexes and is unavailable to aquatic or soil-dwelling organisms. Its bioavailability is essential for normal functioning of leguminous plants. In present investigation, mean Co levels (4 mg/kg) were far less than prescribed SQGs and possibly pose no threat to soil ecosystem.

Lead concentration ranged from 0.2–5.3 mg/kg and was within allowable levels, i.e., 15 mg/kg in soil (Chaney and Ryan 1993). Among trace metals, Cd is of particular interest as its concentration (0.02–1.8 mg/kg) in 40 % soils was above permissible level in natural soils (0.01–0.7 mg/kg). In such soils, acute Cd toxicity is expected which can harm production quality due to higher accumulation in edible portion of crops (McLaughlin et al. 2006). Industrial effluents especially tannery, motor vehicle exhaust, storage batteries, and agrochemicals can contribute to increased Cd levels in soils. Mean Cd concentration (0.7 mg/kg) exceeded its average concentration present in shale (0.3 mg/kg), background levels (0.12 mg/kg), and TEL (0.6 mg/kg); however, measured concentrations were lower to those of PEL (3.5 mg/kg) and ERL (5)/ERM (9) values (Long and Morgan 1991; Smith et al. 1996).

Relationship between metals and other soil properties

Most of the studied soils were basic in nature with pH ranging 7.1–10.6 and lower in OM that varied between 0.1 and 3 %. Soil pH positively correlated with alkalinity ($r = 0.8$), $PO_4^{3-}$ ($r = 0.6$), and Mn ($r = 0.7$) (Table 2). Soil pH indirectly/directly affects solubility, adsorption, retention, movement, and distribution of metals in surface soils (Equeenuddin et al. 2013). Manganese is a redox-sensitive element, which showed positive correlation with pH. It is mobile particularly at lower pH, while at basic pH, it forms $Mn(OH)_4$ that instantaneously traps substantial amounts of Cd, Co, Pb, Ni, and Zn by adsorption and coprecipitation (Braungardt et al. 2003). Mean concentration of $PO_4^{3-}$, alkalinity, $Cl^{-1}$, and $NO_3^{1-}$-N was 1.7, 3,929, 6,587, and 301 mg/kg. TDS, salinity, OM, Cr, and Na showed significantly positive correlation ($r \geq 0.7$) with EC and can be supported by the observation that tannery effluents generally increase soil salinity and sodicity decreasing crop production. Mean EC level (4.6 mS/cm) exceeds the salinity limit of 3 mS/cm, rendering soils potentially unfit for salt-sensitive crops. Salinity also disturbs plant physiology by affecting plant–water status, nitrogen fixation, and ionic equilibrium. Significant correlation between OM and EC indicates strong affinities for cations/anions (Bermudez et al. 2010). Soil $Cl^{-1}$ contents were positively correlated with metals, i.e., Cr ($r = 0.7$), Pb ($r = 0.7$), and Na ($r = 0.6$) highlighting the use of their salts in leather-manufacturing process.

Measured OM contents were far lower than 5.8 and 7.8 % reported from industrially affected soils (Bermudez et al. 2010). Accumulation of contaminants, salinization, and reduced OM levels may indicate chemical deterioration of soil ecosystems. Heavy metals accumulation affects soil characteristics, i.e., grain size, type and quantity of OM, CEC, soil biota, and mineral composition. Heavy metals in soils may inhibit activity of soil biota reducing the amount of OM incorporated into the soil system. Relatively lower mean OM (1.3 %) in studied soils can be

**Table 2** Correlation coefficient matrix for soil parameters (significant correlations at $p < 0.05$)

| | pH | EC | TDS | Sal | Alk | Cl$^{1-}$ | PO$_4^{3-}$ | NO$_3^{1-}$-N | OM (%) | Cr | Ni | Mn | Na | K | Fe | Co | Cu | Ca | Mg | Zn | Cd | Pb |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| pH | 1 | | | | | | | | | | | | | | | | | | | | | |
| EC | 0.4 | 1 | | | | | | | | | | | | | | | | | | | | |
| TDS | 0.4 | 0.9 | 1 | | | | | | | | | | | | | | | | | | | |
| Sal | 0.4 | 0.9 | 0.9 | 1 | | | | | | | | | | | | | | | | | | |
| Alk | 0.8 | 0.5 | 0.5 | 0.5 | 1 | | | | | | | | | | | | | | | | | |
| Cl$^{1-}$ | 0.5 | 0.6 | 0.6 | 0.5 | 0.3 | 1 | | | | | | | | | | | | | | | | |
| PO$_4^{3-}$ | 0.6 | 0.3 | 0.3 | 0.3 | 0.3 | 0.4 | 1 | | | | | | | | | | | | | | | |
| NO$_3^{1-}$-N | 0.2 | 0.1 | 0.1 | 0.1 | 0.2 | 0.2 | 0.1 | 1 | | | | | | | | | | | | | | |
| OM (%) | 0.01 | 0.7 | 0.7 | 0.7 | 0.1 | 0.2 | 0.3 | 0.2 | 1 | | | | | | | | | | | | | |
| Cr | 0.5 | 0.9 | 0.9 | 0.9 | 0.4 | 0.7 | 0.02 | 0.04 | 0.7 | 1 | | | | | | | | | | | | |
| Ni | 0.4 | 0.1 | 0.1 | 0.1 | 0.2 | 0.02 | 0.4 | 0.2 | 0.03 | 0.1 | 1 | | | | | | | | | | | |
| Mn | 0.7 | 0.3 | 0.3 | 0.3 | 0.6 | 0.2 | 0.4 | 0.4 | 0.2 | 0.4 | 0.1 | 1 | | | | | | | | | | |
| Na | 0.2 | 0.9 | 0.9 | 0.9 | 0.1 | 0.6 | 0.3 | 0.1 | 0.5 | 0.8 | 0.1 | 0.1 | 1 | | | | | | | | | |
| K | 0.2 | 0.3 | 0.3 | 0.3 | 0.3 | 0.2 | 0.4 | 0.3 | 0.01 | 0.3 | 0.01 | 0.2 | 0.3 | 1 | | | | | | | | |
| Fe | 0.2 | 0.2 | 0.2 | 0.2 | 0.1 | 0.1 | 0.5 | 0.4 | 0.1 | 0.07 | 0.4 | 0.1 | 0.2 | 0.8 | 1 | | | | | | | |
| Co | 0.1 | 0.1 | 0.1 | 0.1 | 0.04 | 0.2 | 0.2 | 0.3 | 0.2 | 0.05 | 0.6 | 0.03 | 0.1 | 0.7 | 0.7 | 1 | | | | | | |
| Cu | 0.01 | 0.2 | 0.2 | 0.2 | 0.3 | 0.01 | 0.02 | 0.3 | 0.3 | 0.03 | 0.2 | 0.4 | 0.1 | 0.2 | 0.01 | 0.1 | 1 | | | | | |
| Ca | 0.2 | 0.2 | 0.2 | 0.2 | 0.1 | 0.3 | 0.1 | 0.2 | 0.5 | 0.01 | 0.1 | 0.2 | 0.1 | 0.03 | 0.1 | 0.3 | 0.1 | 1 | | | | |
| Mg | 0.2 | 0.4 | 0.4 | 0.4 | 0.4 | 0.01 | 0.1 | 0.4 | 0.3 | 0.3 | 0.5 | 0.2 | 0.2 | 0.2 | 0.5 | 0.7 | 0.2 | 0.2 | 1 | | | |
| Zn | 0.04 | 0.3 | 0.3 | 0.3 | 0.3 | 0.02 | 0.4 | 0.1 | 0.1 | 0.1 | 0.7 | 0.1 | 0.1 | 0.2 | 0.4 | 0.4 | 0.2 | 0.2 | 0.03 | 1 | | |
| Cd | 0.1 | 0.2 | 0.2 | 0.2 | 0.32 | 0.02 | 0.12 | 0.2 | 0.5 | 0.2 | 0.4 | 0.4 | 0.3 | 0.1 | 0.2 | 0.02 | 0.2 | 0.2 | 0.2 | 0.5 | 1 | |
| Pb | 0.2 | 0.02 | 0.02 | 0.04 | 0.03 | 0.7 | 0.4 | 0.3 | 0.1 | 0.2 | 0.3 | 0.3 | 0.1 | 0.4 | 0.1 | 0.04 | 0.1 | 0.2 | 0.3 | 0 | 0 | 1 |

**Table 3** Linear regression analysis of soil physicochemical parameters versus total metal content, i.e., MPI ($n = 72$); $R^2$ is a regression coefficient

| Regression equation | $R^2$ |
|---|---|
| EC = −5.091 + 0.26 MPI | 48.6 |
| TDS = −3,242 + 170.1 MPI | 47.6 |
| Salinity = −17.94 + 0.76 MPI | 48.0 |
| OM (%) = −0.20 + 0.042 MPI | 49.3 |

attributed to high metal concentrations which may possibly be reduced/depleted soil fauna. As OM recycles nutrients, maintains water content, and helps in aeration, comparatively lower levels measured may alter soil processes and can damage soil ecosystem. According to Beyer (2001), if OM below 2.5-cm soil layer is reduced significantly, then soil ecosystem may be considered as damaged; however, there exist few constraints regarding this approach. Standard soils generally contain 10 % organic matter, and lowering of OM content can release OM-bound metal fractions increasing metal toxicity and bioavailability in soil. Greater level of salinity in studied soils can also limit OM's role as metal complex agent. This was obvious by positive correlation ($r = 0.7$) of OM with salinity, EC, TDS; and metals such as Cr ($r = 0.7$), Na ($r = 0.5$), and Ca ($r = 0.5$). Metals generally show affinities with organic matter (Bermudez et al. 2010). Chromium showed stronger affinities with OM with higher level of enrichment and accumulation and is highly toxic to biological organisms (Kabata-Pendias 2004). Relation of Na and Ca with OM % was also described by Malik et al. (2010) in urban soils of Sialkot district with low OM contents which ranged from 0.04–0.7 %. Linear regression analysis revealed that soil properties viz. EC, TDS, salinity, and OM was considerably affected by soil metal content ($R^2 \geq 48$) (Table 3). This relationship reflected significant changes in important soil physicochemical characteristics due to the accumulation of relatively higher metal content by various tanning related processes.

Canonical correlation analysis (CCA) predicted important correlations of soil physicochemical properties and metal concentrations. Soil physicochemical properties were represented by arrows and their respective length indicated importance of these variables in CCA (Fig. 2). First canonical axis was positively correlated with EC ($r = 0.92$), TDS ($r = 0.92$), salinity ($r = 0.92$), and OM % ($r = 0.55$) explaining 66.18 % of variance (Table 4). The plane of the first canonical axis indicated Na and Cr being the dominant metals substantially impacting soil characteristics, i.e., EC, TDS, salinity, and OM % in the investigated soils. Both metals originated in large quantities from salting and tanning of animal skins. Second

canonical axis correlated positively with nitrates ($r = 0.56$) and was relatively less impacted by the metals, i.e., Ca and K. Variance explained by second canonical axis was 11.66 %. Eigen values of the first two canonical axes were 0.34 and 0.06, respectively. Overall CCA results supported correlation and regression analysis results and showed changes in important soil properties due to higher metal built up in tannery adjacent soils.

### Enrichment (EF/EF %), geo-accumulation ($I_{geo}$), and MPI results for heavy metals

Mean EF of heavy metals was in the order: Cd (8,598)>Cr (5,704)>Pb (652)>Ni (522.1)>Cu (283)>Co (245)>Zn (92)>Mn (25). Except for Mn which was severely enriched, all other metals showed extremely severe enrichment (Table 5). All soils with Cr and >90 % soils with Cd were extremely enriched (EF values > 50). EF (%) pointed substantial loading for Cd (37) contamination and comparatively lower for Cr (33) in studied soils. Lead showed extremely severe enrichment in >84 % of soils. About 77.8 % of soils showed extremely severe enrichment with Ni. However, mean Ni concentration (6.4 mg/kg) was well below to sediment quality guidelines (mg/kg), e.g., TEL/PEL (18/36), ERL/ERM (30/50), and average Ni shale value, i.e., 68. Cobalt and Cu also showed extremely severe enrichment in >70 % of soils samples. In contrast, Zn showed extremely severe enrichment in 47 % of soils. Manganese showed variations in enrichment patterns as compared to other metals. In contrast, >69 % of soils showed moderate to extremely severe enrichment for Mn. Mean Mn concentration (5.8 mg/kg) was far lower than its concentration in shale (850 mg/kg). EF values discriminated between the metals originating from anthropogenic activities and those from natural origin or mixed sources of heavy metals.

Geo-accumulation index calculated background metal enrichment by comparing recent and preindustrial concentrations, though it was not easy to reach preindustrial soil/sediment layers. $I_{geo}$ classified all soils in unpolluted to moderately polluted ($I_{geo}$ value = 0–1) class with Pb and Zn (Table 5). Mean $I_{geo}$ values followed the order: Cr (0.5)>Cd (0.5)>Co (0.04)>Pb (0.03)>Ni, Cu (0.02)>Zn (0.01)>Mn (0.001). Mn and Zn also indicated similar pattern of accumulation using mean $I_{geo}$ and mean EF values. Nearly, 24 % soil with Mn and soil with Co showed $I_{geo} < 0$ and grouped in unpolluted category, whereas the remaining soils for both metals qualified for unpolluted to moderately polluted group. For Cd and Cr, >19 % of soils were classified as moderately polluted conflicting with EF results (EF > 50) which categorized nearly all soils extremely severe enriched with these metals. Geo-accumulation index classified all soils as unpolluted to

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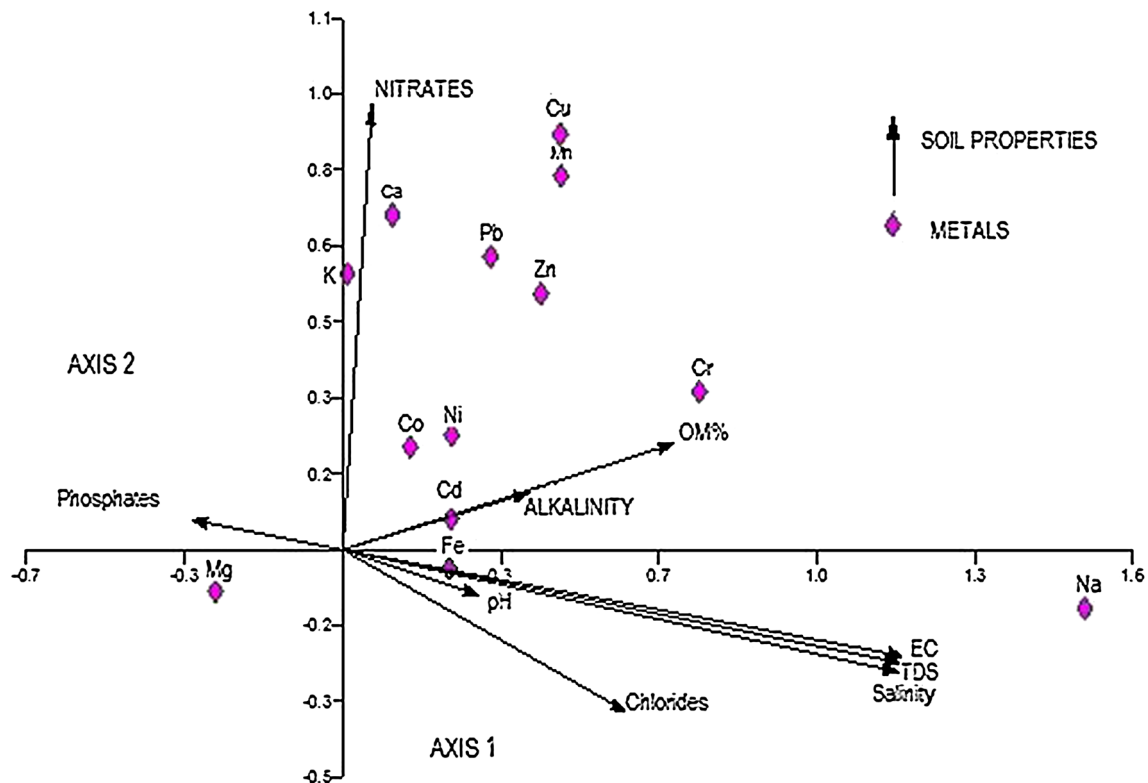


**Fig. 2** Canonical correlation analysis (CCA) showing association between soil properties and metal concentrations

**Table 4** Summary statistics of CCA

| Parameters | Canonical axis 1 | Canonical axis 2 | Canonical axis 3 |
|---|---|---|---|
| Eigenvalues | 0.34 | 0.06 | 0.01 |
| Variance explained (%) | 66.18 | 11.66 | 2.04 |
| Cumulative (%) | 66.18 | 77.84 | 79.88 |
| pH | 0.22 | −0.06 | 0.01 |
| EC | *0.92* | −0.14 | −0.06 |
| TDS | *0.92* | −0.13 | −0.06 |
| Salinity | *0.92* | −0.15 | −0.03 |
| Alkalinity | 0.31 | 0.07 | 0.12 |
| Chlorides | 0.47 | −0.20 | −0.23 |
| Phosphates | −0.25 | 0.04 | −0.15 |
| Nitrates | 0.05 | *0.56* | −0.09 |
| OM (%) | *0.55* | 0.13 | 0.21 |

Significant correlation values are highlighted in italics with underlined at $p < 0.05$

moderately polluted class ($I_{geo}$ value = 0–1) with Cu. $I_{geo}$ result for Cu differed significantly from EF results which showed its extremely severe enrichment in 67 % soils. In contrary based on $I_{geo}$, soils were classified in unpolluted to moderately polluted category with Ni, and based on EF, 18 % soils showed very severe and 76 % as extremely severe enrichment. Metal pollution index (MPI) values

ranged from 18.7–67.9, indicating relatively higher contamination levels. Soils with MPI ≤1 were classified as unpolluted, but in general, its class definition is biased, and there exists no threshold classification from unpolluted to highly polluted categories. Mean MPI value (36) suggested moderately high metal burden in investigated soils and 72 % soils had MPI value >30.

Heavy metal risk assessment and impacts on adjacent ecological compartments

Table 5 represents ecological risk factor for individual metals ($E_r^i$). The results showed that Cd (167) poses greater potential ecological risk followed by Cr (10), Pb (0.8), Cu (0.8), and Zn (0.1) reflected by their $E_r^i$ values. Cadmium has no biological function and is highly toxic to living organism (Alloway 1990). Toxic response factor ($T_r^i$) for Cd was high (30) as compared to $T_r^i$ of Cr, Cu, Zn, and Pb which along with relatively low background value (0.12) is responsible for high Cd $E_r^i$ (Wei et al. 2010; CEPA and CGSEM 1990). Potential ecological risk factor for multi-metal (RI) represents the sensitivity of various biological communities to toxic heavy metals. RI classified examined soils in four risk categories, i.e., 54 % soil were considered at low risk, 14 % at moderate, 8 % at high risk, and 25 % soils at significantly high-risk categories.

**Table 5** Heavy metals enrichment, geo-accumulation, and risk assessment results in tannery-affected soils

|  | Cr | Cu | Zn | Cd | Pb | Ni | Mn | Co |
|---|---|---|---|---|---|---|---|---|
| EF min | 186 | 1.3 | 10.2 | 34.1 | 15.3 | 1.1 | 0.5 | 3.6 |
| EF max | 20,643 | 1,374 | 358 | 66,521 | 5,041 | 4,998 | 160 | 985 |
| EF mean | 5,704 | 283 | 92 | 8,598 | 652 | 522 | 25 | 245 |
| EF (%) | 33 | 35 | 45 | 37 | 57 | 36 | 49 | 45 |
| $I_{geo}$ min | 0.05 | 0.001 | 0.001 | 0.01 | 0.01 | 0.01 | 0 | 0 |
| $I_{geo}$ max | 1.5 | 0.05 | 0.02 | 1.2 | 0.05 | 0.1 | 0.003 | 0.09 |
| $I_{geo}$ mean | 0.5 | 0.02 | 0.01 | 0.5 | 0.03 | 0.02 | 0.0013 | 0.04 |
| $C_f^i$ Min | 0.4 | 0 | 0.01 | 0.2 | 0.02 | – | – | – |
| $C_f^i$ max | 13 | 0.4 | 0.13 | 14.2 | 0.3 | – | – | – |
| $C_f^i$ mean | 4.9 | 0.2 | 0.1 | 5.6 | 0.2 | – | – | – |
| $E_r^i$ min | 0.8 | 0.01 | 0.02 | 5.3 | 0.1 | – | – | – |
| $E_r^i$ max | 26 | 2.2 | 0.13 | 425 | 1.4 | – | – | – |
| $E_r^i$ mean | 9.7 | 0.8 | 0.1 | 167 | 0.8 | – | – | – |

Pollution load index (PLI) also categorized ecological risk and its values ranged from 0.1 to 0.2. Mean PLI value (0.1) recorded in this study was far lower than the threshold (<1), indicating the absence of baseline pollutants or loads near to background levels (Tomlinson et al. 1980). Such low PLI values predicted that no drastic rectification measures are needed in the soils adjacent to tanneries; however, continued discharge of effluents can increase these values if waste and effluents coming from tanning industry are discharged without prior treatment. The results highlighted that ecological risk assessment approaches (e.g., $E_r^i$, RI, and PLI) can be used as a decision-support tools or instruments for prioritizing soil conservation and integrity assessment studies.

Heavy metals laden tannery effluents have not only impacted surface soils but also threatened underground aquifer, water channels, and aquatic diversity therein (Malik et al. 2010). Ground water is the sole irrigation and drinking source in Sialkot and facing considerable deterioration due to untreated disposal of tannery effluents. This scenario is particularly worse in and around the tannery hubs. Water channels, i.e., Nullah Palkhu and Nullah Aik (feeding tributaries of River Chenab), passing through the Sialkot district receive untreated tannery effluents in voluminous amounts which not only put local population at risk but also disturb the ecological integrity of these fresh waters (Qadir et al. 2008). In a study on eight edible species of fish found in these two streams described potential health risk for humans as their tissues metal contents were beyond permissible limits (Qadir and Malik 2011). Heavy metal inputs from tannery industries have a major proportion in contamination of these aquatic environments. In addition, waste water of Nullah Palkhu and Nullah Aik is used in vegetable and crops production in nearby areas, using electric pumps which pose potential exposure risk to soil-dwelling organisms, phytotoxicity, vulnerability of agricultural products through bioaccumulation, and human health hazards. Besides impacts on the environmental compartments, tannery workers are also at risk due to elevated metal concentrations used in tanning operations. This overall metal contamination intensity requires priority concerns for management of safe tannery effluents disposal strategies.

Index comparison

Two enrichment indices, i.e., EF, EF (%), and accumulation index ($I_{geo}$) were applied to evaluate metal status and their trends in surface soils. Among these, relative efficiency of EF and EF (%) was better which presented fairly accurate and authentic picture of soils metal contents. $I_{geo}$ (background enrichment index) on the other hand did not predict actual metal accumulation levels and showed relatively very low level of metal accumulation contradicting EF and EF (%) results. With few exceptions, $I_{geo}$ classified all soils as unpolluted to moderately polluted with heavy metals. For this reason, some authors (Abrahim and Parker 2008) criticized $I_{geo}$ application to determine pollution status of soils and proposed normalized values instead. According to Abrahim and Parker (2008), $I_{geo}$ factors are not freely comparable to other metal enrichment indices due to its calculation procedures. It involves background multiplication of 1.5 and a log function. The results obtained from $I_{geo}$ were therefore distinctly variable from enrichment indices (EF and EF %). The latter methods are, however, mostly related to tannery-affected soils. Equations used to determine geo-accumulation index (Eq. 3) and EF (Eq. 1) showed that final values are affected by the geochemical background levels (Dantu 2009). Differences produced in (enrichment and geo-accumulation) can also

**Table 6** Rotated factor loadings (varimax normalized) of all parameters in soil samples ($n = 72$) with marked loadings highlighted in italic and bold $p > 0.7$ factor loadings of $PO_4^{3-}$, $NO_3^{1-}$-N, Cu, Ca, Mg, and Cd were <0.7 and not shown

| Parameters | VF 1 | VF 2 | VF 3 | VF 4 | VF 5 |
|---|---|---|---|---|---|
| pH | 0.24 | 0.01 | *0.87* | 0.32 | 0.2 |
| EC | *0.97* | 0.03 | 0.19 | 0.09 | 0.07 |
| TDS | *0.97* | 0.03 | 0.21 | 0.08 | 0.09 |
| Salinity | *0.97* | 0.08 | 0.2 | 0.05 | 0.02 |
| Alkalinity | 0.29 | 0.1 | *0.85* | 0.05 | 0.13 |
| $Cl^{1-}$ | 0.5 | 0.13 | 0.19 | *0.78* | 0.02 |
| OM (%) | *0.76* | 0.2 | 0.15 | 0.31 | 0.07 |
| Cr | *0.89* | 0.02 | 0.28 | 0.19 | 0.03 |
| Ni | 0.09 | 0.29 | 0.34 | 0.12 | *−0.78* |
| Mn | 0.15 | 0.13 | *0.84* | 0.21 | 0.21 |
| Na | *0.9* | 0.09 | 0.08 | 0.16 | 0.1 |
| K | 0.24 | *−0.83* | 0.24 | 0.33 | 0.12 |
| Fe | 0.13 | *0.92* | 0.03 | 0.03 | 0.21 |
| Co | 0.11 | *0.84* | 0.09 | 0.1 | 0.22 |
| Zn | 0.21 | 0.34 | 0.04 | 0.03 | *0.75* |
| Pb | 0.01 | 0.14 | 0.14 | *−0.8* | 0.14 |
| Eigenvalue | 6.51 | 3.83 | 2.91 | 2.53 | 2.15 |
| Total variance explained (%) | 29.6 | 17.41 | 13.23 | 11.49 | 9.77 |

be attributed to the nature of their respective algorithms used since identical background values were applied in both type of indices. Enrichment and geo-accumulation indices results differed for most metals and, however, predicted similar enrichment patterns for Cr and Cd. Highest EF (EF Cd = 8,598, EF Cr = 5,704) and similarly highest $I_{geo}$ values ($I_{geo}$ Cd = 0.5, $I_{geo}$ Cr = 0.5) were scored by these two metals.

Metal pollution index and PLI classified soils in terms of total metal content present irrespective of toxicities of individual metals. For MPI, the greater the metal concentrations in individual soils the greater the MPI values, urging strong need for rectification measures. MPI did not compare total metal content with any value; therefore, it showed low performance score owing to comparability and sensitivity criteria. Moreover, this index is based on geometric averages and can be advantageous if compared with other aggregation techniques. The results of PLI were not promising, and PLI values for all soils remained very low (<1) reflecting no need for soil remedial measures. However, soils were contaminated to varying degrees with heavy metals, and significant risk was associated with them. Hence, PLI did not prove useful and effective enough to extract meaningful information regarding metal pollution. Potential ecological risk index identified high risk ($E_r^i$) associated with Cd (167) and Cr (10). Ecological

risks posed by Cd and Cr in the soils of study area were also well accounted with enrichment and geo-accumulation indices along with two SQG's followed.

### Source identification

FA/PCA for the soil parameters resulted in five variofactors (VFs) with eigenvalues >2 (Table 6; Fig. 3a, b). VF 1, 2, 3, 4, and 5 accounted 29.6, 17.4, 13.2, 11.5, and 9.8 % of total variance. Varimax factor 1 revealed significant loading for EC, TDS, salinity, OM %, Cr, and Na indicating input from tannery effluents. Correlation coefficient matrix also highlighted strong positive relationships. Chromium pollution is attributed to chrome plating, paint/pigments manufacturing, and leather tanning (Qadir et al. 2008). Tannery industry is the chief culprit for high Cr levels in surface soils of current study. VF2 loaded for Co, Fe, and K and their sources mainly related to parent rock material. However, these metals are also used in liming processes and may contribute toward soils contamination (Wei et al. 2010). VF3 showed highest loading for pH ($r = 0.87$), indicating pH as one of the controlling factor for Mn availability. Solubility of Mn decreases at neutral to alkaline pH, and it becomes unavailable to plants for normal growth and metabolism (Braungardt et al. 2003). Manganese is used in the form salts [$MnCO_3$ and $Mn(SO_4)_2$] in tannery industry (Tariq et al. 2006). This may be a possible reason for Mn and alkalinity relation; another explanation can be presence of rhodocrosite ($MnCO_3$) in soils, a natural mineral of Mn.

VF4 highlighted sources of Pb and $Cl^{1-}$ from tannery effluents. Major sources of Pb in present soils include tannery effluents, automobiles exhaust fumes, paint/pigments manufacture, and less likely from atmospheric deposition. Its solubility in soil is principally controlled by its respective carbonates. Chloride's loading ($r = 0.78$) was second to Pb ($r = −0.8$), and its presence can be due to use of NaCl in tanning process. VF5 showed significant loadings for Ni ($r = −0.78$) and Zn ($r = 0.75$), highlighting sources related to anthropogenic activities in particular to tannery effluents. Zinc is an essential trace element in living organisms whose higher concentrations are potentially toxic, but very insoluble and very rare in its nature (Alloway 1990). Mean Zn concentration found in this study was 4.15 mg/kg, which is fairly low-to-normal threshold value set in agricultural soils, i.e., 200 mg/kg. Relatively low levels of Zn in soil may be attributed to tannery effluents and usage of agrochemicals; however, to some extent, it can be lithogenic. Permissible range for Ni in natural soils in mg/kg is 4.3–7 compared to mean Ni concentration 6.4. Measured concentrations are within the safer limits; however, continuous discharge of untreated effluents may lead to higher concentrations in

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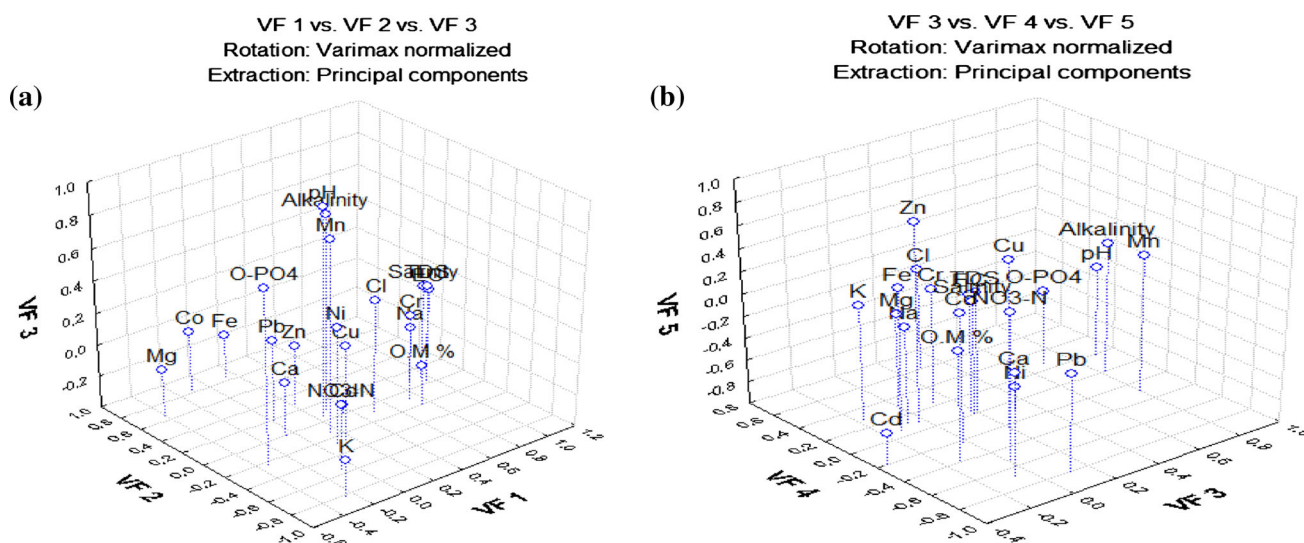


**Fig. 3** **a** FA/PCA 3D scatterplot of first three variofactor loadings, **b** 3D scatterplot of VF 3 versus VF 4 versus VF 5

**Fig. 4** Dendrogram of soil metals using UPGMA (*Pearson-r*)
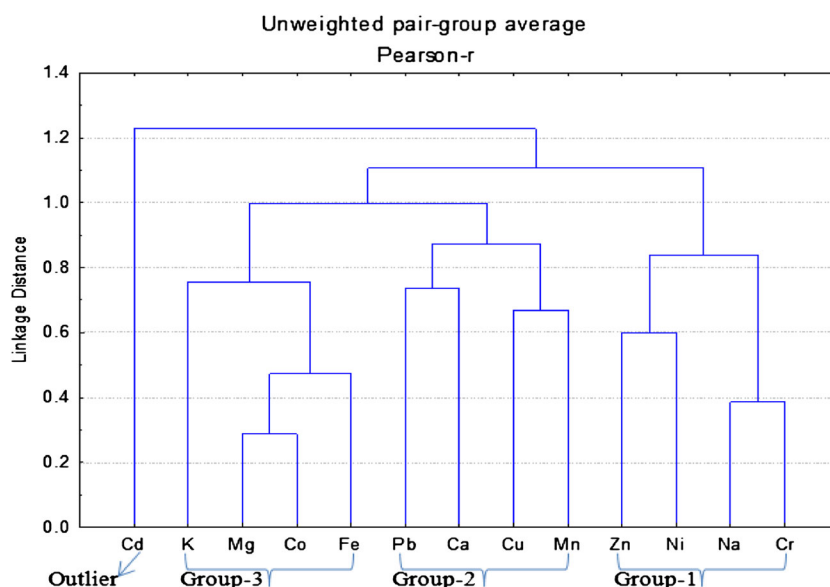


future. Presence of Ni can either be related to industrial effluents or with various metallurgical operations, burning of fossil fuels, and atmospheric deposition. Similarly, heavy metals such as Cu, Pb, Zn, and Ni have also been linked to their use in various industrial processes in an earlier study by Qadir et al. (2008). Metal smelting, refining, agricultural and urban activities, and waste incineration are common in study area and can effectively contribute toward atmospheric input of heavy metals to the surface soils.

Cluster analysis identified three main groups of metals strengthening metals interrelationship as identified by FA/PCA and correlation analysis (Fig. 4). Identified metal groups were used in similar tanning batch processes and

provided a mean for source apportionment in the soil media. The resultant metal groups/clusters showed high intra-cluster homogeneity with origin in similar tannery operations. First group included metals, i.e., Cr, Na, Ni, and Zn which were extensively employed in preservation, disinfection, and un-hairing processes of hides. Second group consisted of Pb, Mn, Cu, and Ca used in retaining processes (post-tanning operations). Third group comprised of Fe, Co, Mg, and K, Cd being the outlier. These metals were employed in skin/hide treatment and liming/de-liming processes. Other than tannery input, 3rd group sources were also related to parent rock material. Soil metal clustering and their origin in related tanning operations evidenced soil contamination via tannery effluents.

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## Conclusion

The impact of tannery industries on adjacent surface soils in terms of heavy metal enrichment, source apportionment, and associated risk was determined. Measured concentrations of macro-nutrients, i.e., Ca, K, and heavy metals, i.e., Cr, Ni, Mn, Fe, Cu, Zn, and Cd were higher in comparison with earlier studies conducted on tannery-affected soils from other parts of Pakistan. Soils were extremely enriched with Cd, Cr, Pb, Ni, Cu, Co, and Zn. The results obtained from geo-accumulation index ($I_{geo}$) were distinctly variable from EF and EF (%). Only Cd and Cr (>19 % soils) showed moderate pollution ($I_{geo}$ value = 1–2), and other heavy metals showed uncontaminated to moderately polluted soils ($I_{geo}$ value = 0–1) contradicting the results of EF/EF (%). EF and EF (%) are more relevant for the evaluation of metal pollution related with tannery adjacent surface soils as compared to $I_{geo}$. Among pollution load (ecological risk index) and metal pollution index (contamination index), former index results were not satisfactory in interpreting risk associated with total metal content at individual sites, whereas later provided important information that can be used to plan remedial measures. PLI values for surface soils were low (<1), suggesting the soils were unpolluted; however, MPI values ranged from 19–68 above threshold ≤1 depicting metal contamination from low-to-high degree. Potential ecological risk index determined high risk associated with Cd and Cr. SQG's also highlighted Cd and Cr risk in tannery adjacent soils. Applied indices offered valuable information as long as their limitations are recognized. Multivariate analysis identified metals, i.e., Cr, Co, Zn, Pb, Na, Cd, Fe, Mn, and Ni originating from tannery input to surrounding soils. Source apportioning of metals in surface soils can help decision-makers to initiate management plans to reduce soil contamination. Substantial information extracted on elevated metal levels in tannery adjacent surface soils of Sialkot urges regulatory procedures for soil reclamation by available techniques.

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