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Comparative statistical analysis of chrome and vegetable tanning effluents and their effects on related soil

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ABSTRACT

Two tanning units of Pakistan, namely, Kasur and Mian Channun were investigated with respect to the tanning processes (chrome and vegetable, respectively) and the effects of the tanning agents on the quality of soil in vicinity of tanneries were evaluated. The effluent and soil samples from 16 tanneries each of Kasur and Mian Channun were collected. The levels of selected metals (Na, K, Ca, Mg, Fe, Cr, Mn, Co, Cd, Ni, Pb and Zn) were determined by using flame atomic absorption spectrophotometer under optimum analytical conditions. The data thus obtained were subjected to univariate and multivariate statistical analyses. Most of the metals exhibited considerably higher concentrations in the effluents and soils of Kasur compared with those of Mian Channun. It was observed that the soil of Kasur was highly contaminated by Na, K, Ca and Mg emanating from various processes of leather manufacture. Furthermore, the levels of Cr were also present at much enhanced levels than its background concentration due to the adoption of chrome tanning. The levels of Cr determined in soil samples collected from the vicinity of Mian Channun tanneries were almost comparable to the background levels. The soil of this city was found to have contaminated only by the metals originating from pre-tanning processes. The apportionment of selected metals in the effluent and soil samples was determined by a multivariate cluster analysis, which revealed significant differences in chrome and vegetable tanning processes.

1. Introduction

The leather and leather product sector represents one of the most labor intensive industrial commodities. It is estimated that this sector directly employs more than 200,000 workers and it is believed that over one million people depend for their livelihood on this sector, in Pakistan. More than 600 tanneries have been found to be housed in clusters either in residential/industrial areas or in close vicinity of agricultural lands. Tannery operations in such areas have high environmental implications and impacts on the land and human health [1]. The uncontrolled and haphazard mushrooming growth of this industry has posed a serious threat to the urban life and sustainability. This industry uses a wider range of chemicals during various tannery processes and significant quantities of the chemicals are not fixed in the collagen, and thus either remain in the spent float, or squeezed off during the various operations or washed out by the wet finishing float.

A large number of small scale tanneries located within the country have no access to the common treatment plants and discharge their waste into open fields or ditches. Toxic chemicals present in these effluents take diverse rout to reach food chain, i.e. by passing from soil to plants, and then via herbivorous animals to meat or milk. The use of sludge as a chief manure in agricultural practices is also common. These indiscrete methods of waste disposal contaminate the groundwater and soil in vicinity of tanneries. The landscape of some areas housing these tanneries has been devastated by chromium and other chemicals used in the tannery process. The environmental concerns arising from the global industrial activities demand integrated cleaner leather processing towards a greener environment for sustainable leather industry [2,3].

Chrome chemicals and vegetable extracts are the two substances currently used in tanning of animal hides and skins. Vegetable tanning, an older and more traditional tanning method, utilizes tannin derived from bark of chestnut, oak, gallnuts, or wattle trees. At present, this method is generally used for the manufacture of heavy leather. In conventional chrome tanning processes, chromium salts are used in an amount of 1.5–2.5% by weight of Cr (III) oxide, based on pelt weight, to obtain leather which resists the boiling test. A considerable portion of the offered Cr is neither bound nor incorporated in the hide tissue and as a result passes into the wastewater. Chrome tanning is currently the preferred technique being more rapid process for leather production. It is also more versatile and imparts a better combination of chemical and physical properties to leather than vegetable tanning [4], thereby producing a softer and

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Table 1
Basic statistics for the distribution of selected metals (mg/L) in tannery effluent samples from Kasur and Mian Channun ($n = 34$).

	Kasur							Mian Channun						
	Min.	Max.	Mean	Median	S.D.	S.E.	Skew	Min.	Max.	Mean	Median	S.D.	S.E.	Skew
Na	244.7	53,673	15,186	7983	16,856	2890	0.987	167.2	527.0	275.0	235.3	118.7	20.36	1.568
Ca	1.500	695.9	214.0	157.3	181.6	31.15	0.689	62.00	97.70	79.82	80.20	11.14	1.911	0.105
K	3.500	1240	72.95	15.67	215.6	36.98	5.136	6.500	114.8	35.89	21.30	35.04	6.009	1.650
Mg	0.068	730.0	178.9	79.75	193.6	33.21	0.954	27.38	138.5	51.35	33.20	40.38	6.925	1.761
Fe	0.009	13.92	2.948	1.110	3.731	0.640	1.589	0.006	0.105	0.059	0.060	0.034	0.006	−0.020
Mn	0.003	0.816	0.256	0.160	0.246	0.042	0.888	0.002	0.023	0.013	0.013	0.006	0.001	0.059
Cr	0.393	3956	505.6	28.55	853.9	146.4	2.497	0.013	0.172	0.037	0.023	0.043	0.007	2.861
Co	0.019	3.216	0.867	0.636	1.010	0.173	1.225	0.220	0.725	0.491	0.568	0.199	0.034	−0.311
Cd	0.001	0.160	0.052	0.033	0.049	0.008	0.765	0.003	0.038	0.020	0.024	0.009	0.001	−0.014
Ni	0.004	0.372	0.140	0.087	0.119	0.020	0.499	0.009	0.311	0.116	0.088	0.096	0.016	1.365
Pb	0.010	2.910	0.742	0.485	0.751	0.129	0.940	0.015	0.397	0.196	0.205	0.121	0.021	0.267
Zn	0.004	1.649	0.520	0.461	0.509	0.087	0.670	0.001	0.069	0.042	0.048	0.021	0.004	−0.747

better quality cowhides with uniform texture. Cr (VI) was formerly used by chrome tanners, but it is no longer employed nowadays due its toxicity and lower chemical costs associated with the use of Cr (III) [5,6].

In order to evaluate the pollution status arising due to the two tanning methodologies, the tanneries of two cities of Pakistan, namely, Kasur and Mian Channun were selected as case studies. The main objectives of the present study were to assess the trace metal burden in the tannery effluents and then to evaluate their effects on related soil. The study was also aimed to explore the inter-relationships of the trace metals in effluents and related soils by using multivariate statistical methods. Moreover, the metal pollution index of the soil would be examined in comparison with the background levels. It is anticipated that the present study would provide a baseline data for the development of an eco-friendly tanning agent based on either the chrome or vegetable tanning.

2. Materials and methods

2.1. The study area

Kasur an industrial city in central Punjab, Pakistan, spans over a vast area, most of which consists of plain fields irrigated by water from the Indus River and groundwater by tube-wells. Wheat, rice, sugarcane and cotton are rich cash crops of the area feeding more than five million people of the region. The city with long standing tradition of tanning, houses about 50% tanneries in Pakistan and about 90% of tanning is carried out by chrome tanning. The entire wastewater from these industries is being discharged untreated through a natural drain, 'Rohi Nullah' to the virgin land, thereby rendering a big stretch of fertile lands into lakes of stagnant wastewater. Due to high porosity of soil, the groundwater is rapidly contaminated by the hazardous chemicals emanating from the tannery effluents. As many as 10,000 people are getting drinking water from hand pumps or electric motor pumps sunken in this polluted aquifer, so they are victim of diseases like skin irritations, kidney failures and gastrointestinal problems [7,8]. Other industries in the city include textile, sugar, glazed pottery, embroidery and wood-works.

Mian Channun the main city of district Khanewal, Pakistan, is well known for food, cottage, handicrafts and textiles in addition to tanneries. It has irrigated plains and wheat, rice, sugarcane, cotton are grown as the main cash crops. These plains with the water table existing at 30–45 m not only feed a population of 70,000, but also supply these crops to other parts of the country. Mian Channun employs vegetable tanning as the major tanning methodology. Most of the tanneries located here are small units which use barks for various trees as the tanning agents.

2.2. Sampling

For the present investigation, as many 16 tanneries of Mian Channun and Kasur were investigated. A total of thirty four effluent samples and as many soil samples were collected from the adjoining areas of the Kasur and Mian Channun tanneries during the peak running period of these industries. The soil samples consisting of 1–5 cm deep top layer were collected from a distance of 100 m from the effluent discharge point. Following the standard sampling guidelines [9], 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. For background analysis, the soil samples were obtained from remotely located site. Prior to sampling, all soil samples were cleaned manually for any foreign matter. All sample containers were duly labeled and coded at the time of sampling.

Table 2
Correlation coefficient matrix[a] for selected metals in tannery effluent samples from Kasur (above the diagonal) and Mian Channun (below the diagonal) ($n = 34$).

	Na	Ca	K	Mg	Fe	Mn	Cr	Co	Cd	Ni	Pb	Zn
Na	1	0.388	0.364	0.526	0.282	0.715	0.444	0.734	0.605	0.667	0.581	0.766
Ca	0.489	1	0.143	0.127	0.249	0.428	0.321	0.265	0.406	0.432	0.407	0.347
K	0.114	−0.224	1	−0.079	0.384	0.049	0.249	0.386	0.036	−0.032	−0.004	0.059
Mg	0.431	0.797	−0.376	1	0.355	0.717	0.136	0.757	0.613	0.526	0.641	0.577
Fe	0.256	0.019	0.744	−0.176	1	0.395	0.470	0.383	0.528	0.182	0.571	0.336
Mn	0.547	0.922	−0.275	0.823	0.001	1	0.296	0.775	0.648	0.704	0.720	0.660
Cr	0.413	0.761	0.047	0.689	0.009	0.788	1	0.066	0.364	0.403	0.326	0.249
Co	0.544	0.741	0.096	0.642	0.113	0.766	0.934	1	0.471	0.504	0.583	0.611
Cd	0.677	0.505	0.090	0.517	0.363	0.514	0.235	0.345	1	0.601	0.868	0.724
Ni	0.110	0.561	0.213	0.515	0.053	0.549	0.884	0.827	−0.043	1	0.591	0.565
Pb	0.757	0.626	−0.361	0.622	−0.142	0.695	0.575	0.707	0.466	0.301	1	0.769
Zn	0.354	0.547	−0.304	0.579	−0.096	0.532	0.388	0.469	0.386	0.192	0.432	1

[a] r values >0.397 or <−0.397 are significant at $p \leq 0.01$.

2.3. Extraction procedure and analysis

A 25.0 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 Atomic Absorption Spectrophotometer (AA-670, Japan) for the estimation of the solubilized selected metals [10–12]. The filtered soil solutions were diluted, where necessary, with doubly 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, Cd, Ni, Pb and Zn. STATISTICA software was used to compute the relevant statistical analysis of the data [13].

All chemicals and reagents used in the preset investigation were of spectroscopic grade with a certified purity of 99.99%, procured either from E-Merck, Germany or BDH, England. Standard optimum analytical conditions were maintained and periodically checked on AAS system for each metal. Inter-laboratory comparison of the furnished data was conducted at National Institute of Health, Islamabad. Standard reference material (OL-96) was used to have a check on the accuracy of the results and the precision of the instrument. Normally the corresponding results matched within ±1.5%.

3. Results and discussion

The data showing the distribution of selected metals in terms of the concentrations along with some related statistical parameters for various tannery effluents of Kasur and Mian Channun 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. The data on metal distribution in effluent samples from Kasur tanneries (Table 1) showed that five of the selected metals (Na, Ca, K, Mg and Cr) exhibited dominant concentration levels. Highest concentration was shown by Na with a mean level of 15.186 g/L, most likely derived from preservation and stage of hides/skins [14]. Chromium, most extensively used tanning reagent, showed a mean concentration of 505.6 mg/L. The present study evidenced much higher levels of Cr in tannery effluents than reported previously [15,16]. The mean concentrations of Ca, Mg and K were 214.0, 178.9 and 72.95 mg/L, respectively. The standard deviation, standard error and skewness values reflected an overall non-normal/asymmetric distribution of the selected metal levels in the tannery effluent samples from Kasur. This evidenced randomized flushing of effluents from the tanneries outlets at times and occasions not well defined. Among other metals, Fe, Co, Pb and Zn also showed relatively higher levels in effluent samples and some of them are occasionally used in chemicals used in dyeing of leather.

The data presented in Table 1 for Mian Channun tanneries revealed major contributions of Na, Ca, Mg and K in effluent samples. The highest mean concentration was noted for Na at 275.0 mg/L, followed by Ca at 79.82 mg/L, Mg at 51.35 mg/L and K at 35.89 mg/L. The mean concentration of Cr was recorded at 0.037 mg/L, with a range of 0.013–0.172 mg/L. The highest Cr level in Mian Channun tannery effluents was too meek compared with the highest (3956 mg/L) or average (505.6 mg/L) level of the metal found in tannery effluents from Kasur. Other metals in the effluents, such as Co, Pb, Ni and Zn, were found at sub-ppm levels. The randomness and asymmetry in the selected metals levels were found to have relatively lower in these effluent samples compared with the Kasur tanneries. At Mian Channun tanneries vegetable tanning process is in vogue involving the use of mimosa and walnut tree barks for routinely tanning. It is known that although the vegetable tanning process is slow, it is useful to avoid Cr pollution [17,18].

Table 2 contains the metal-to-metal correlation data in terms of linear correlation coefficient (r) values (r values >0.397 or <−0.397 are significant at $p < 0.01$) for Kasur and Mian Channun tannery effluents. The listed r values reveal a large number of strong positive correlations ($r > 0.500$) between various pairs of the selected metals in Kasur tanneries, except Cr, Ca and K which are only weakly correlated with few other metals. The possible reason for this observation could be traced in the elevated amounts of these metal compounds used in various tanning processes, against other metals that are used at relatively lower concentrations. Obviously, any strong correlation under the circumstances was highly untenable [19]. In the effluent samples, therefore, selected metals other than Cr, Ca and K are mutually correlated. The highest correlation coefficient value is noted for Pb–Cd ($r = 0.868$), followed by Mn–Co, Pb–Zn, Na–Zn, Na–Co, Zn–Cd, Mn–Pb, Co–Mg, Mg–Mn, Na–Mn and Ni–Mn, thus evidencing their common sources in the tannery effluents.

For Mian Channun tanneries the correlation data (Table 1, below the diagonal) indicated numerous significantly strong correlations between the metal pairs. Both Ca and Mg exhibited strong correlations with most of the other metals, including Mn, Cr, Co, Cd, Ni, Pb and Zn. In addition, Cr was found to have strong positive correlation with Co, Ni and Pb. This could be considered to arise because of the simultaneous presence of these metals in effluents from a common source, together with a reduced use of Cr compounds. The strongest correlations observed are between Cr–Co ($r = 0.934$) and Ca–Mn ($r = 0.922$), followed by those between Ni–Cr ($r = 0.884$), Ni–Co ($r = 0.827$), Mg–Mn ($r = 0.823$) and Ca–Mg ($r = 0.797$), thereby indicating their common sources in the effluents. At Mian Channun tanneries, Mg compounds are used in the basification process, and Ca in the form of lime to control the pH of hide baths. The correlation data thus evidenced the simultaneous use of the multiple chemicals in various tanning operations.

Source identification/apportionment was one of the major concerns of the present study, for which Cluster Analysis (CA) was used following the standard procedure reported in the literature [11,12,20]. As shown in Fig. 1(a), the dendrogram of selected metals pertaining to Kasue tannery effluents reveals two major clusters. The strongest clustering is observed for Pb–Cd, which showed close association with other groups comprising of Na–Zn–Ni and Co–Mn–Mg. These metals emanate from chemicals used in pre-tanning procedures or flushed out from other industrial units situated beside the tanneries. Other significant cluster is observed among Cr–Fe–K–Ca, and these metals are strongly believed to originate from tanning processes. The CA of selected metals from Mian Channun tannery effluents shows distinctly different clustering compared with the former case. A large communal cluster for Ca–Mg–Mn–Co–Pb–Zn–Cd is obtained as shown in Fig. 1(b). The source of these metals could be traced in liming and deliming stages of leather manufacture. Strongest cluster is observed among Na–Cr–Ni, which came from chemicals, used abundantly in the preservation, tanning, retanning and dyeing of leather. Another cluster comprising of Fe–K is also observed which could be traced in chemicals used in other adjoining industries, which occasionally share a common influx of effluents in the drain line of these tanneries.

According to the strategy conceived for the present investigation, soil was considered the most endangered compartment of the environment in proximity of tanneries in Pakistan. Most of the pollutants from effluents get accumulated onto soil. Over time the buffering capacity of the soil is exhausted and detrimental effects on the quality of groundwater start setting in. These considerations formed the basis of soil metal analysis in the present study towards assessing the pollution status, and detecting the potential sources. In view of the multivariate nature of the problem, any study such as the present one, based on the estimation of the metal concentrations going to the soil from effluents cannot be simply worked

Table 3
Basic statistical parameters for the distribution of selected metals (mg/kg) in soil samples from Kasur and Mian Channun ($n = 34$).

	Kasur							Mian Channun						
	Min.	Max.	Mean	Median	S.D.	S.E.	Skew	Min.	Max.	Mean	Median	S.D.	S.E.	Skew
Na	998.0	98,745	18,765	90,303	228,081	39,116	1.957	102	2548	1192	1319	757.8	91.89	0.052
Ca	85.00	3015	1335	1446	711.0	121.9	0.178	279	1618	800.0	673.5	405.9	49.23	0.744
K	98.00	1853	610.4	548.0	412.3	70.71	1.600	280	4040	1840	1589	1270	154.0	0.550
Mg	14.50	955.0	137.2	97.80	175.2	30.05	3.750	15.96	194.2	57.90	41.00	47.39	5.747	1.975
Fe	0.320	56.28	14.24	11.95	10.24	1.756	2.217	0.850	24.46	5.944	3.975	6.824	0.828	2.012
Mn	0.200	1.910	0.743	0.655	0.411	0.071	1.134	0.020	0.523	0.177	0.137	0.128	0.016	0.842
Cr	2.000	26.00	10.58	8.580	6.799	1.166	1.242	0.150	1.990	0.990	1.110	0.519	0.063	−0.106
Co	0.100	15.60	2.794	0.665	4.415	0.757	1.839	0.390	5.380	2.841	2.725	1.597	0.194	−0.073
Cd	0.010	0.350	0.099	0.070	0.085	0.015	1.473	0.050	0.580	0.309	0.335	0.150	0.018	−0.118
Ni	0.040	1.200	0.556	0.475	0.293	0.050	0.503	1.070	3.420	1.975	1.690	0.669	0.081	0.586
Pb	0.000	4.270	1.090	0.855	0.751	0.129	2.817	0.160	6.600	2.057	0.715	2.253	0.273	1.114
Zn	0.100	1.572	0.582	0.610	0.290	0.050	0.975	0.050	0.670	0.325	0.330	0.149	0.018	0.215

Table 4
Correlation coefficient matrix[a] for selected metals in soil samples from Kasur (above the diagonal) and Mian Channun (below the diagonal) ($n = 34$).

	Na	Ca	K	Mg	Fe	Mn	Cr	Co	Cd	Ni	Pb	Zn
Na	1	−0.087	−0.154	−0.112	0.037	0.295	−0.071	0.408	0.058	0.465	0.262	−0.023
Ca	0.275	1	0.693	0.389	−0.078	−0.072	0.121	−0.130	0.206	0.156	0.362	0.174
K	0.715	−0.096	1	0.389	−0.041	−0.317	0.118	−0.303	0.184	−0.015	0.213	0.002
Mg	0.203	0.127	0.511	1	0.090	0.137	−0.101	0.107	0.591	0.307	0.463	−0.242
Fe	−0.639	−0.104	−0.449	−0.183	1	0.352	0.095	−0.051	0.132	−0.074	0.060	−0.440
Mn	−0.382	0.312	−0.409	−0.189	0.771	1	−0.066	0.520	0.526	0.413	0.421	−0.337
Cr	0.290	0.142	0.368	0.084	−0.112	−0.041	1	−0.017	0.123	−0.058	0.012	−0.014
Co	0.294	0.433	0.137	−0.126	0.051	0.325	0.005	1	0.567	0.649	0.306	−0.359
Cd	−0.012	−0.233	0.282	0.223	0.194	0.072	0.118	−0.046	1	0.536	0.678	−0.414
Ni	−0.118	−0.309	0.312	0.342	0.165	−0.122	0.393	−0.498	0.582	1	0.465	−0.218
Pb	−0.082	−0.157	0.285	0.497	−0.212	−0.480	0.236	−0.510	0.323	0.766	1	−0.168
Zn	0.063	−0.211	0.421	0.232	0.099	0.023	0.397	−0.031	0.733	0.710	0.346	1

[a] r values >0.397 or <−0.397 are significant at $p \leq 0.01$.

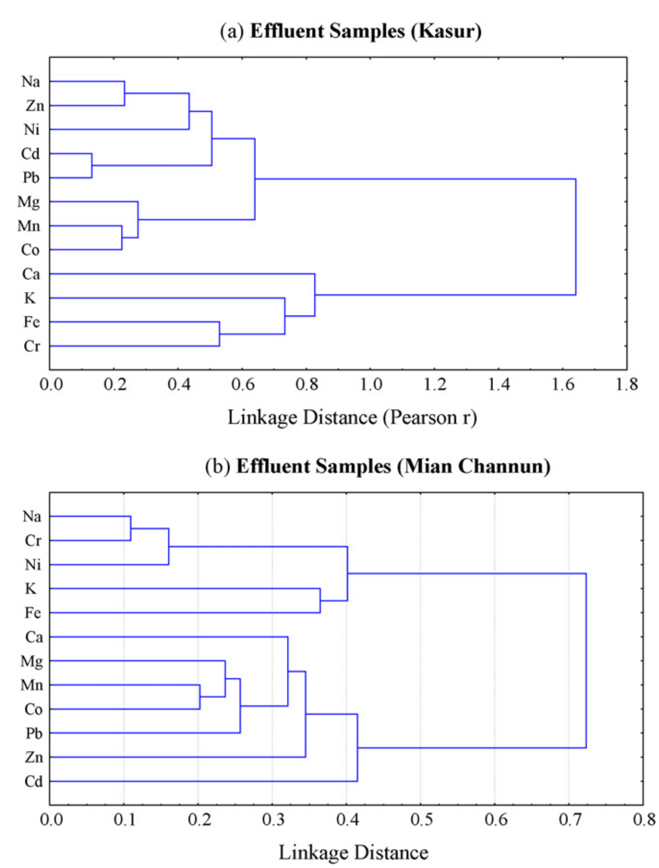

Fig. 1. Dendrogram of cluster analysis for selected metals in effluent samples from (a) Kasur and (b) Mian Channun.

out. It was, therefore, considered adequate to investigate and analyze the water extract of the soil samples for the selected metals. This was a more realistic approach since the effluents first enrich the soil with metals/pollutants and then this leached phase finally transfers the metals/pollutants into the groundwater [21].

The data in Table 3 provide the summary of metal distribution in the water extracted soil samples from proximity of tanneries. In the soil from Kasur, the observed order of mean concentration of selected metals is Na > Ca > K > Mg > Fe > Cr > Co > Pb > Mn > Zn > Ni > Cd. The major contributions are observed for Na, Ca, K and Mg with respective mean values of 18,765, 1335, 610.4 and 137.2 mg/kg. The observed levels of the Cr varied between 2.0 and 26.0 mg/kg. This indicated that the effluent metal content could badly affect the quality of the soil system through high metal accumulation. The overall distribution of the metals was random, evidenced by substantial differences between the mean and the median levels, on one hand, and large magnitudes of the S.D., S.E. and skewness, on the other. This amply signified random intrusion of high levels of metal contaminants from effluents into the soil resulting in the observed enhanced metal levels in the relevant soil.

The data for soil samples from Mian Channun (Table 3) evidenced the highest mean level for K at 1840 mg/kg, followed by Na at 1192 mg/kg, Ca at 800 mg/kg and Mg at 57.9 mg/kg. It indicated that the soil was enriched with K when in contact with effluents. Of the heavy metals, Fe showed a mean concentration of 5.944 mg/kg, while Pb, Co and Cr remained respectively at 2.057, 2.841 and 0.990 mg/kg mean levels; rest of the metals were only at sub-ppm mean concentration levels. Overall, the distribution of all the metals remained non-normal and thus random intrusion could be held responsible for it. These enhanced inputs of heavy metals from effluents to soil could generate adverse impact on soil fertility and to ultimately affect the humans through food chain [22].

Table 4 brings forth the correlation matrix showing linear relationships between pairs of metals in the soil samples adjacent to tanneries. For the soil from Kasur, the data revealed that most of the selected metals are significantly correlated with other metals. Once again Cr is an isolated case and does not show significant relationship with any other metal. The correlation coefficients for K–Ca, Cd–Mg, Mn–Cd, Cd–Co, Mn–Co, Ni–Co, Ni–Cd and Pb–Cd evidence a strong mutual dependence between the pairs of metals. In case of the soil from Mian Channun, Na established strong correlation with K ($r = 0.715$) and inverse relationship with Fe ($r = -0.639$). The strongest correlation was for Fe–Mn ($r = 0.771$), followed by Ni–Pb ($r = 0.766$), Cd–Zn ($r = 0.733$) and Ni–Zn ($r = 0.710$). The correlation results thus provided evidence of enrichment of soil by the selected metals, which emanate from effluents mixing with the soils in adjoining areas of the tanneries. A cumulative and prolonged process of this kind could result in still more severe metal contamination of soil and the situation may be aggravated by the synergistic effects of various metals.

The method of multivariate cluster analysis [11,12,23] was used to identify the source relationships between various metals present in the soil, as shown in the form of dendrogram in Fig. 2. Significant cluster observed in the soils of Kasur are Na–Mn–Co–Ni, Mg–Cd–Pb, Ca–K–Zn and Fe–Cr. In comparison, the soils from Mian Channun reveal strong clusters among Na–K–Cr, Mg–Ni–Pb–Cd–Zn, Ca–Co, Fe–Mn, which are considerably different than those of Kasur. The sources of the selected metals could be attributed to various processes in industries, along with the soil-based origin. It is evident from this data that the soil in proximity of Mian Channun tanneries was not highly contaminated with the Cr due to adoption of vegetable tanning.

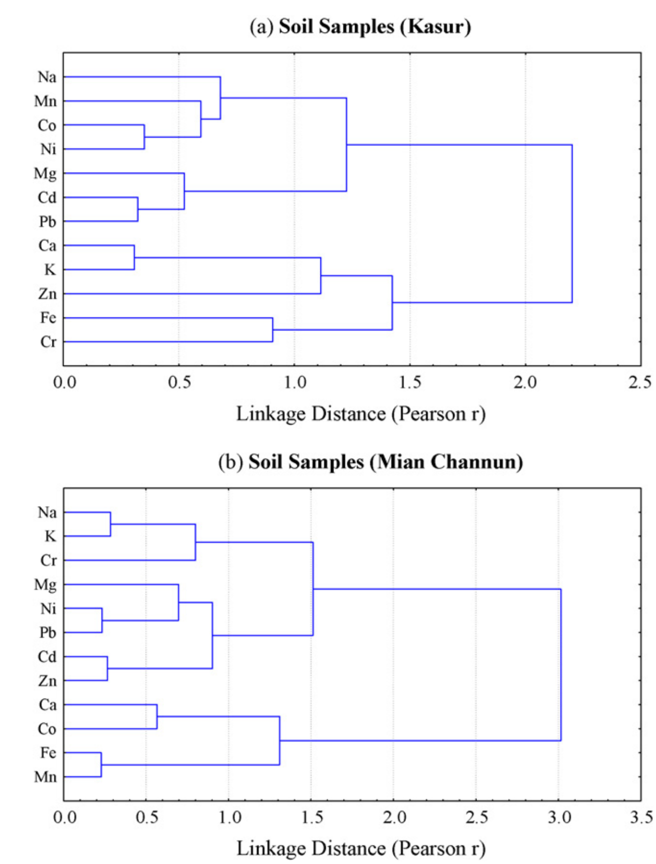

Fig. 2. Dendrogram of cluster analysis for selected metals in soil samples from (a) Kasur and (b) Mian Channun.

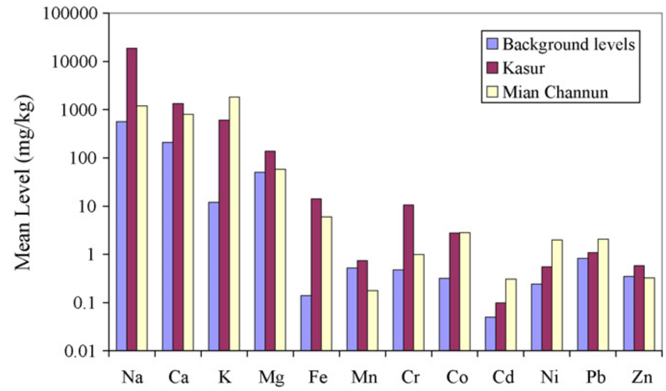

Fig. 3. Mean metal levels in soil samples of Kasur and Mian Channun as compared to background levels.

A comparison of the mean metal levels in soils of Kasur and Mian Channun with that of background levels is furnished in Fig. 3. Most of the metals were found at much higher concentrations than the background levels in the soil of Kasur, with the exception of Mn, Pb and Zn. The most important case was that of Cr which was present at a magnitude of many orders higher than background level. Kasur has the long standing tradition of tanning and chrome tanning is the most prevalent mode exercised in Kasur. Thus voluminous amounts of Cr bearing effluents are discharged onto the soils adjacent to tanneries. As far as Mian Channun tanneries are concerned, although some metals (Na, Ca, K, Fe, Co, Cd and Ni) were found at levels higher than background levels, but the degree of contamination was much lower than Kasur tanneries with the exception of K, Ni and Pb.

4. Conclusions

In conclusion, the present investigation on the selected metal contamination of soils in proximity of tanneries evidences enhanced levels of Cr and other metals in the soils of Kasur due to the chrome tanning, whereas the extent of metal contamination of soils in vicinity of Mian Channun tanneries was quite low due to the vegetable tanning. The correlation study revealed significantly different mutual variations of the trace metals in effluents and soils of the two locations. The apportionment of the selected metals was also considerably different at the two sites. In view of these findings, it is high time to redress the problem of environmental pollution caused by the tanneries. Efforts should be directed towards finding a tanning agent which produces the leather with better qualities and at the same time should be environmental friendly. Although some new tanning agents [18,24,25] have been developed but their practical applications are limited.

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