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Multivariate statistical analysis of heavy metals pollution in industrial area and its comparison with relatively less polluted area: A case study from the City of Peshawar and district Dir Lower

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ABSTRACT

Multivariate and univariate statistical techniques i.e., cluster analysis PCA, regression and correlation analysis, one way ANOVA, were applied to the metal data of effluents soil and ground water to point out the contribution of different industries towards the metals pollution, their source identification and distribution. The samples were collected from different industries and different downstream points of the main effluents stream and from the relatively less polluted area considered as control area. The samples were analyzed for metal concentration levels by flame atomic absorption spectrophotometer. The metal concentration data in the three media of the polluted area were compared with background data and control data as well as with the WHO safe limits. The results showed that soil has high metals concentration compared to effluents and water. The data also showed elevated levels of Mn and Pb in water that are 8.268 and 2.971 mg/L, respectively. Principal component analysis along with regression analysis showed that the elevated levels of metals in the effluents contaminate adjacent soil and ultimately the ground water. The other elements Co, Cd, Ni and Cu were also found to have correlation in the three media.
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1. Introduction

Humans depend on their surrounding physical environment for the resources they need for their survival. However human exploitation of these resources causes environmental degradation [1]. Due to increased industrialization, the problem of environmental pollution has been increasing for several decades. These problems are caused by the disposal of industrial wastes whether solids, liquids or gases, which have potential of ultimately polluting soil and water they come in contact with. Several studies have shown that the area in close proximity with industrial activity is marked by contamination of soil, water and agriculture fields [2–5]. Water demand for agricultural, industrial, commercial and domestic uses is steadily increasing. This increase in demand is due to the increase of world population characterized by an accelerated growth of urban population with almost half of the total population living in the cities. The growing urbanization increases the domestic water use while supplying waste water that can be used for non-potable purpose such as agricultural irrigation [6]. Along with the other toxic substances in the industrial wastes, heavy metals are considered to be one of the main pollutants in the environment, since they have a significant effect on its ecological quality. Human activities lead to increasing level of heavy metals contamination in the environment. Heavy metals owing to atmospheric and industrial pollution accumulate in the soil and influence the ecosystem nearby. Lead, cadmium, copper, manganese, etc. were chosen as representative trace metals whose levels in the environment represent a reliable index of environmental pollution. Metals like copper, zinc and manganese are essential metals since they play an important role in the biological system, whereas lead and cadmium are non-essential metals as they are toxic even in traces. The essential metals can also produce toxic effects when the metal intake is excessively elevated [6–10]. Industrial pollution is also on its peak in the most congested city of Peshawar the capital of NWFP, North West Frontier Province. due to the increasing growth of industries and unplanned urbanization. The effluents from different industries are discharged indiscriminately into natural water bodies or on open land resulting in the contamination of the surface and ground water. These toxic effluents flow into river Kabul directly or indirectly thus rendering its water unfit for irrigation. The removal of toxic trace metals like Cd, Pb and Cr from the receiving water bodies and soil has been a subject of serious concern worldwide. In Pakistan too there is a dire need to examine and redress the present pollution status of toxic trace metals in industrial effluents

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and affected soil and water system [11–15]. The aim of the present study was to asses the level of different heavy metals in the industrial effluents, their downstream dilution in relation to the soil, their effects on the ground water quality and also to compare the status of industrial water pollution in Peshawar with the relatively less polluted area, district Dir which is a hilly area nearly free of heavy traffic density and industrial pollution. The results obtained have to be evaluated statistically so different researchers have applied multivariate and univariate analysis, i.e. principal component analysis (PCA), cluster analysis (CA) and multiple regression analysis and correlation techniques to the situation like this to evaluate the relationship between the levels of metals in these media and then to identify their mutual concentration dependence to their source /origin [16]. PCA provides a base for interpreting different cluster of metals based on their co-variation while cluster analysis provides a mean for source identification for a given metal distribution pattern in the effluents or any other medium [17].

Though a number of studies [18,19,20] have been undertaken from time to time on metals pollution of different industries in the study area, as well as on the industries located in the city of Peshawar away from industrial zone but they have only analyzed the effluents of those particular industries, i.e. textile, tannery and leather industries and studied their effect on the surrounding soil and ground water only in the vicinity of the installation. No study is available for the information of the public to show the contamination of the soil and ground water where the stream passes. The present study is the first of its nature in the area designed with the aim to know about the contribution of different industries towards the metal contents of the main effluents stream and then to point out the combined effects of these effluents on the contamination of the surrounding soil and ground water of the stream catchment's localities. This study will provide sufficient informations about the control of metal pollution by proper recycling process. In the future this will ensure the reclamation of lost ground water quality.

2. Materials and methods

2.1. Sampling areas

2.1.1. Peshawar

Peshawar is the capital of North West Frontier Province that occupies an area of 77 km^2 with a population of more than one million. It is a water rich valley through which flows River Kabul. The surrounding areas of Peshawar consist of irrigated plains as a part of the huge basin drained and irrigated by River Kabul. Industrial zone in Peshawar is Hayatabad where all the major industries, i.e. pharmaceutical, glass rubber, plastic, textile, ghee, woolen mills and marbles mills, etc. are housed. The effluents from these industries are directly discharged into two streams which join together shortly after passing through the industrial zone that flow all along the way passing through different localities of Peshawar from southwest to northeast. It joins Shalam River a part of canal from the River Kabul and again flows into River Kabul in the East. River Kabul is the main irrigation source in district Peshawar and surrounding areas [21].

2.1.2. Dir

Topographically Dir has been dominated by mountains and hills which are parts of ranges /branches of Hindukush and Hindu Raj. The mountain ranges run from north to south and from northeast to southwest along the northern borders with Chitral district. The important river is Panjkora which enters the district from northeast and flows southwest along boundary with the Bajour Agency up to its co-fluence with Swat River. Panjkora River is made up of several streams in the lower Dir and a main stream form Upper Dir called Dir River. Though individual streams in the catchment areas are used as a source of irrigation, River Panjkora is the main irrigation source in the downstream plain areas of Lower Dir. The sources of drinking water in district Dir are pipelines, hand pumps, wells and springs. Dir is a hilly area and the mineral contents of water may be enhanced when it passes through the hills [22,23]. Fig. 1 shows the sites where the samples were collected in the study areas.

2.2. Sampling plan

In sampling plan for the metal characterization in effluents, soil and ground water samples, factors which are of significant importance in the chemistry of soil and water were included to ensure accuracy and precision. Replicate samples were drawn from each sampling point. A similar procedure was followed for soil and ground water samples. The samples were collected both from industrial area background remote area and relatively less polluted area the district lower Dir (Fig. 1).

2.3. Samples collection and pretreatment

Samples from effluents of different industries were collected from their drainage outlets. Effluent and soil samples were also collected from and in the surrounding of the two main streams that join together shortly after their exit from the industrial zone. Other effluents soil and water samples were collected at a distances of about 2 km from the main effluents stream till it joins the River Kabul. Samples of water and soil were also collected from and in surroundings of River Kabul where canals have been drawn to be used as a source of irrigation. Ground water samples were collected from the outlets of tube wells or machine driven hand pumps. A similar plan for sample collection from background area and control area that is district Dir was adopted, where water and soil samples were collected from and in surrounding individual streams up to River Panjkora. A sample of soil and water was also collected from and in surroundings of River Panjkora. Ground water samples were collected from the springs, pipelines, hand pumps and wells in different areas where these streams pass through both the polluted area and the control area. Collection of water and soil samples was conducted during October 2008 to December 2009 when the industries were running at their peak capacity. Water samples were kept in 2 L polyethylene plastic bottles cleaned with metal free soap rinsed many times with distilled water, soaked in 10% HNO_3 for 24 h and finally rinsed with ultra pure water. All samples were stored in the insulated cooler containing ice and delivered on the same day to the laboratory and all the samples were kept a 4 °C until processing and analysis [24]. Soil samples were dried at 110 °C and ground to pass through 200 mesh sieve and transferred to polyethylene bottles until analysis.

2.4. Chemical reagents

Ultra pure water was used throughout the analysis. All the chemicals were of analytical grade with high spectroscopic purity of 99.9% (Merck Darmstadt, Germany) and were checked for possible trace metal contamination. Standard solutions of all eight elements were prepared by dilution of 1000 ppm certified standards solutions (Fluka Kamica Busch Switzerland) of corresponding metal ions.

2.5. Acid digestion of the mud sample

0.5 g of dried soil sample were digested with 15 mL of HNO_3, H_2SO_4 and $HClO_4$ in the ratio of 5:1:1 at 80 °C until a transparent solution was obtained. The solution was filtered through Watt

Fig. 1. Location map of the samples collection points in the polluted area and control area.

man No. 42 filter paper and the solution was diluted to 50 mL with distilled water [25].

2.6. Analytical procedure

All the effluents, soil and water samples were analyzed for eight heavy metals, Pb, Ni, Cr, Cu, Co, Mn, Cd and Zn by using flame atomic absorption spectrophotometer PerkinElmer AAS 700 [26]. The instrumental parameters for each element are listed in the given Table 1. The instrument was calibrated for the determination of each element by analyzing the standard solution (concentration usually in ppm) of each element provided by the company. Hollow cathode lamps were used as a source of light for each element.

2.7. Statistical analysis

Univariate analysis was applied to process the analytical data in terms of its distribution and correlation between pairs of metals. The multivariate analysis involving PCA and CA were used to determine the point sources of elements in effluents soil and water samples. The PCA was also supported by univariate analysis and linear regression analysis. SPSS software version 16 for windows was used to process the data.

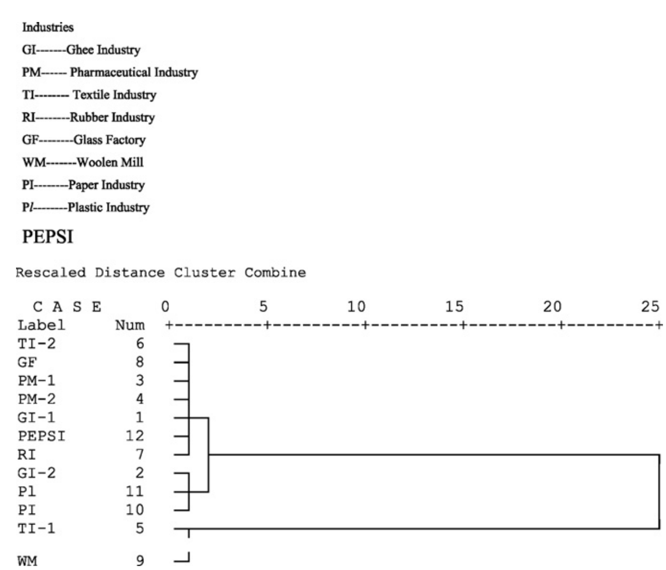

Fig. 2. Dendogram of selected metals in different industrial effluents using complete linkage method.

Table 1
Instrumental analytical conditions for analysis of selected heavy metals.

Element	Acetylene (L/min)	Air (L/min)	Wavelength (nm)	Slit width (nm)	Lamp current (Ma)	Limit of detection (mg/L)
Pb	2.0	17.0	283.3	0.7	30	0.015
Ni	2.0	17.0	232.0	0.2	25	0.006
Cr	2.5	17.0	357.9	0.7	25	0.003
Cu	2.0	17.0	324.8	0.7	15	0.0015
Co	2.0	17.0	240.7	0.2	30	0.009
Mn	2.0	17.0	279.5	0.2	20	0.0015
Cd	2.0	17.0	228.8	0.7	4	0.0008
Zn	2.0	17.0	213.9	0.7	15	0.0015

Table 2
Statistical summary of selected metals concentrations in different industrial effluents ($n = 36$).

Metals	Industries			
	Minimum	Maximum	Mean	Standard deviation
Cr (mg/L)	0.003	1.125	0.1007	0.322
Mn (mg/L)	0.028	31.450	6.849	10.578
Zn (mg/L)	0.016	0.277	0.073	0.068
Cd (mg/L)	0.011	2.048	0.1912	0.585
Pb (mg/L)	0.663	4.095	2.440	1.102
Ni (mg/L)	0.111	0.701	0.479	0.221
Cu (mg/L)	0.014	0.313	0.160	0.083
Co (mg/L)	0.009	0.516	0.106	0.179

3. Results

The statistical summary of selected metal concentration in different industrial effluents has been presented in Table 2. These data represent a total of 36 samples that correspond to 12 industries. From the data on metal distribution in industrial effluents, it is clear that Cd, Pb and Ni are the dominant metals with high mean concentration of Mn 6.849 mg/L followed by Pb 2.440 mg/L, Ni 0.479 mg/L, Cd 0.192 mg/L and then Cr 0.100 mg/L, respectively. The order of distribution is Mn > Pb > Ni > Cd. The statistical summary of metal concentration in the three media (effluents from different down stream points, soil and water) from the polluted area is given in Table 3. From the data it is clear that with downstream points the metal distribution follows the same order as in case of the different industrial effluents. The highest mean concentration was of Mn 11.810 mg/L followed by Pb 3.748 mg/L and Ni 0.542 mg/L respectively while Co mean concentration exceeded the Cu and Cd concentration that is 0.734 mg/L. The order of distribution is Mn > Pb > Ni > Co > Cu > Cd. Chromium mean concentration in case of effluents from different industries as well as different down stream points was found low that was 0.100 and 0.015 mg/L, respectively. In soil samples from polluted area along downstream points at increasing distances from the point sources, Mn mean concentration was found that is 130.452 mg/L followed by Pb 5.680 mg/L, Co 1.286 mg/L, Zn 0.685 mg/L, Cu 0.507 mg/L, Cd 0.157 mg/L and Ni 0.152 mg/L, respectively. The order of distribution is Mn > Pb > Co > Zn > Cu > Cd > Ni. The ground water owing to high mean concentration of Mn in the effluent has high Mn contents of 8.268 mg/L followed by Pb 2.974 mg/L, Cd 1.954 mg/L, Ni 0.371 mg/L, Co 0.306 mg/L Cu 0.217 mg/L and Zn 0.204 mg/L, respectively. The order of distribution is Mn > Pb > Cd > Ni > Co > Cu > Zn. The oblivious sources of dominant metals Mn, Pb, Ni, Co in these effluents are their respective compounds which are used in the industries for various purposes, i.e. as catalysts, modifiers and dyers, etc. The downstream dilution was also noticed from our results in case of effluents and soil samples at increasing distances from the point sources. The statistical summary of mean metals concentration in different streams water, soil and ground water samples from the control area have been given in Table 4. The overall mean metal concentration in the three media

Table 3
Statistical summary of selected metals concentrations in the effluents, soil, and drinking water samples from polluted ($n = 30$ each).

Element	Effluents				Soil				Drinking water			
	Minimum	Maximum	Mean	Standard deviation	Minimum	Maximum	Mean	Standard deviation	Minimum	Maximum	Mean	Standard deviation
Cr (mg/L)	0.003	0.043	0.015	0.012	0.040	0.068	0.053	0.009	0.003	0.046	0.011	0.010886
Mn (mg/L)	0.020	84.810	11.810	25.999	84.743	159.710	130.452	23.858	0.172	79.850	8.268	21.61151
Zn (mg/L)	0.025	0.123	0.051	0.028	0.281	2.937	0.685	0.803	0.034	0.926	0.204	0.25039
Cd (mg/L)	0.012	0.052	0.032	0.012	0.032	0.591	0.157	0.227	0.009	25.000	1.954	6.924504
Pb (mg/L)	1.213	4.662	3.748	1.016	4.321	6.304	5.68	0.608	0.080	5.497	2.974	1.674047
Ni (mg/L)	0.029	1.953	0.542	0.572	0.007	0.388	0.152	0.1286	0.001	0.740	0.371	0.290853
Cu (mg/L)	0.026	2.183	0.440	0.632	0.341	0.640	0.507	0.097	0.080	0.758	0.217	0.176431
Co (mg/L)	0.014	3.038	0.734	0.894	1.057	1.534	1.286	0.148	0.013	1.144	0.306	0.431395

Table 4
Statistical summary of selected metals concentrations in the stream water, soil and drinking water samples from control area ($n = 30$ each).

Element	Stream water				Soil				Drinking water			
	Minimum	Maximum	Mean	Standard deviation	Minimum	Maximum	Mean	Standard deviation	Minimum	Maximum	Mean	Std. Deviation
Cr (mg/L)	0.018	0.306	0.144	0.112	0.043	0.773	0.256	0.234	0.018	0.306	0.167	0.113
Mn (mg/L)	0.024	0.108	0.060	0.0299	0.861	7.384	3.148	2.009	0.024	0.108	0.061	0.028
Zn (mg/L)	0.000	0.007	0.002	0.003	0.334	1.811	0.672	0.474	0.000	0.007	0.070	0.140
Cd (mg/L)	0.020	0.092	0.058	0.023	0.083	0.148	0.111	0.0216	0.020	0.092	0.061	0.035
Pb (mg/L)	0.358	1.118	0.747	0.243	1.677	2.560	2.006	0.312	0.358	1.118	0.731	0.288
Ni (mg/L)	0.010	0.098	0.047	0.032	0.254	0.582	0.359	0.123	0.010	0.098	0.051	0.039
Cu (mg/L)	0.006	0.015	0.012	0.003	0.014	0.025	0.018	0.004	0.006	0.015	0.009	0.004
Co (mg/L)	0.058	0.158	0.098	0.039	0.239	0.378	0.27	0.043	0.058	0.158	0.095	0.045

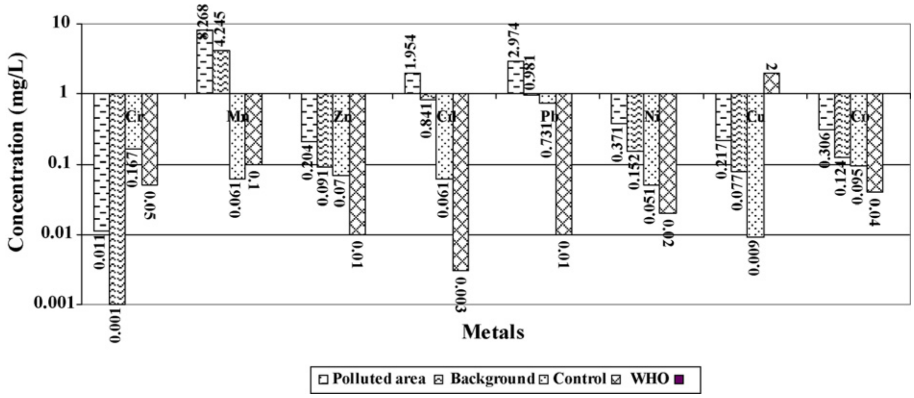

Fig. 3. Comparison average metal level in ground water based on present study vs Background level, control and WHO safe limits.

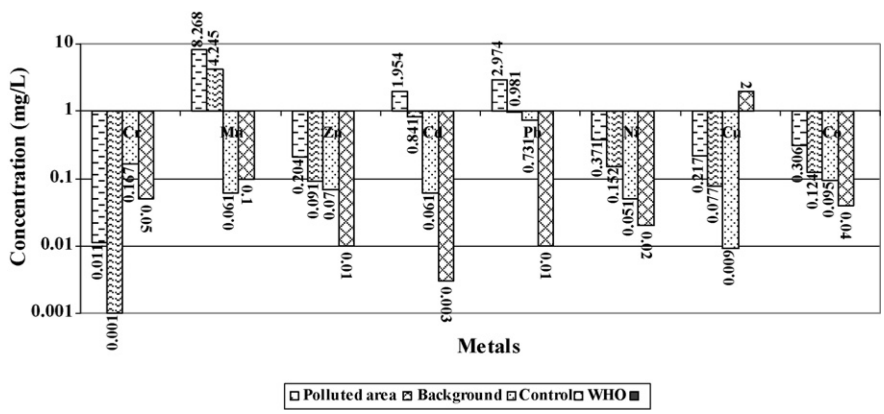

Fig. 4. Comparison average metal level in ground water based on present study vs background level, control and WHO safe limits.

is quite low compared to the polluted area. Highest Pb mean concentration was found in case of stream water 0.747 mg/L which can be attributed to the discharge of effluents from service stations in the area, followed by Cr which can be attributed to the natural enrichment due to weathering. The other mean metals concentration in these cases was found low. Soil samples showed reasonably high mean metal concentration compared to stream water, which clearly indicate the retention of metals by the adjacent soil matrix. Mn mean concentration in soil was 3.148 mg/L followed by Pb 2.006 mg/L, Zn 0.672 mg/L, Ni 0.359 mg/L and Cr 0.256 mg/L, respectively. In ground water samples the mean metals concentration compared to stream water and corresponding soil was found low with the exception of Pb 0.731 mg/L which can be attributed to the service stations, natural enrichment process, wood and low grade coal combustion in homes. Comparison was also done between mean metal concentration in the ground water sample from the polluted area and the corresponding metal levels in the samples from the background area control area as well as with the WHO safe limits. From Figs. 3 and 4 it is clear that some metals like Cr are higher in mean concentration in ground water sample from control area than the polluted area as well as WHO safe limits while Zn and Pb were found higher than the WHO safe limits but lower than the corresponding metals levels in the polluted area. This can be attributed to the metal enrichment depending on individual metal soil chemistry.

The mean values of various physicochemical parameters of effluents of different industries, downstream points, stream water and ground water from both polluted and relatively non-polluted area have been given in Table 5. The data indicate that the electrical conductance of effluents and ground water is much high (WHO limit is 0.40 mS/cm) compared to the stream water and ground water from relatively non-polluted area which indicate the ground water in the surrounding locality unfit for drinking. The high electrical conductance indicates the presence of high concentration of mineral ions present in effluents. This also clearly indicates the effect of these effluents on the ground water quality. The pH is also quite low indicating the acidic nature of the effluents. The low pH increases the toxicity and mobility of several metal ions. The pH of stream water and ground water of polluted area and relatively non-polluted area was within the range of WHO guidelines (6.5–9.2). The other parameters like dissolved oxygen and total dissolved solids were found not within WHO limits while in case of stream water and ground water these were found with in the range. The statistical comparison of the pollution of differ-

Table 5
Mean values of different physicochemical parameters of effluents and ground water collected from polluted and relatively non-polluted area.

Sites	Hardness (mg/L)	Specific conductance (mS/cm)	Dissolved oxygen (mg/L)	pH	Total dissolved solids (g/L)
Industrial effluents	340.382	0.813	1.709	4.45	0.475
Downstream points	352.610	0.789	3.881	5.32	0.510
Drinking water from polluted area	267.983	0.729	7.851	7.163	0.400
Stream water from non-polluted area	134.572	0.336	7.618	7.900	0.240
Drinking water from non-polluted area	127.346	0.480	7.18	7.660	0.287

Table 6
ANOVA table for comparison of Industries with regards to selected metals pollution.

Source of variation	Sum of squares	df	Mean square	F	p-Value
Between industries	154.312	11	14.028	0.781	0.658
Within industries	1508.282	84	17.956		
Total	1662.594	95			

ent industrial effluents using one way ANOVA (Table 6) showed no statistical difference ($p = 0.658$) which indicates that all these industries contribute equally to the mean metals concentrations in the main effluents stream. Cluster analysis using complete linkage method classified various industries into two broad groups (Fig. 2) and a minor group. The first broad group comprised of industries (TI-2, GF, PM-1, PM-2, GI-1, PEPSI and RI) the second group of industries (GI-2, PI, and P*l*) and the third minor group comprised of (TI-1 and WM). The statistical correlation study pertaining to metal-to-metal relationship in the three media was conducted on mutual inclusive basis. It should be kept in mind that each downstream collection point was considered as separate pollution source of soil and ground water of the nearest location. In order to know about the effect of these effluents on the surrounding soil and ground water correlation study between metals was undertaken which was further supported by principal components analysis. In case of effluents samples from different downstream points, the correlation coefficient evaluation yielded r value ≥ 0.492 or $= -0.492$ as significant at $p < 0.001$ revealing that there was a significant correlation between Pb and Cr ($r = 0.597$) and Pb and Cd ($r = 0.685$) in the effluents from different downstream points as shown in Table 7. For soil matrix the correlation study showed positive relationship between pairs of metals (Table 8) like Cd and Mn ($r = 0.553$) Ni and Mn ($r = 0.629$) Cu and Mn ($r = 0.580$) Cu and Cd ($r = 0.706$) Co and Cr ($r = 0.617$) Co and Zn ($r = 0.656$) and Co and Cu ($r = 0.658$) Cd concentration related to Cr in the effluent samples and to Cu in the soil samples indicates high dependent concentration levels of metals in the two media. Third correlation aspect of metals pair was found in ground water (Table 9) showing that there is significant correlation between Pb and Mn ($r = 0.492$) Ni and Pb ($r = 0.596$). A cross correlation study between effluents and soil multiple correlation showed that in effluent soil system Cr and Zn ($r = 0.650$) Cd and Cr ($r = 0.669$, Cd and Mn ($r = 0.763$) Cd and Ni ($r = 0.664$) Cu and Cr ($r = 0717$) Cu and Zn ($r = 0.691$) and Co and Ni ($r = 0.680$) are strongly correlated. In case of effluent and water system the correlation between Zn and Pb ($r = 0.771$) Cu and Zn ($r = 0.640$) and Cu and Ni ($r = 0.639$) were found to be positive. Correlation study conducted for soil water system showed a strong positive correlation between various pairs of metals including Cu, Mn, Cd, Zn, Ni, Cr, and Co. The study based on metal-to-metal correlation was further sustained by linear regression data in Table 10, which list significant linear regression equations in terms of pairs of metals for three media. For finding the source identification of metals concentration in the three media and interpretation of correlation study principal components analysis using varimax normalized rotation for the three media was conducted which is given in Tables 11–13. It should be noted that significant correlation means the existence of a strong relationship between two metals while in case of regression significant results indicates the high dependence of one metal over the other. PCA was applied to extract factor loading in each media. In case of effluents PCA extracted two factors together, embodying 96% of total variance. The contribution by the two factors is 72.506% and 23.238%, respectively. Principal

Table 7
Linear correlation coefficient matrix for selected metals in the effluents samples form different downstream points ($n = 30$).

	Cr	Mn	Zn	Cd	Pb	Ni	Cu	Co
Cr								
Mn	0.873							
Zn	0.953	0.913						
Cd	-0.033	-0.459	-0.213					
Pb	0.597	0.245	0.410	0.685				
Ni	0.844	0.897	0.938	−0.388	0.125			
Cu	0.869	0.985	0.916	−0.435	0.266	0.901		
Co	0.942	0.906	0.956	−0.123	0.486	0.901	0.934	

r-Values ≥ 0.492 or $= -0.492$ are significant at $p < 0.05$.

Table 8
Linear correlation coefficient matrix for selected metals in the soil samples form different downstream points ($n = 30$).

	Cr	Mn	Zn	Cd	Pb	Ni	Cu	Co
Cr								
Mn	0.720							
Zn	0.074	0.534						
Cd	0.852	0.553	−0.038					
Pb	0.074	0.112	−0.172	0.126				
Ni	0.534	0.629	0.383	0.242	0.296			
Cu	0.924	0.580	0.132	0.706	−0.052	0.535		
Co	0.617	745	0.656	0.391	−0.263	0.417	0.658	

r-Values ≥ 0.492 or $= -0.492$ are significant at $p < 0.05$.

Table 9
Linear correlation coefficient matrix for selected metals in the drinking water samples form different localities in polluted area ($n = 30$).

	Cr	Mn	Zn	Cd	Pb	Ni	Cu	Co
Cr								
Mn	0.973							
Zn	−0.171	−0.113						
Cd	−0.053	−0.106	−0.164					
Pb	−.0391	−0.492	0.206	−0.036				
Ni	−0.430	−0.344	0.036	0.173	−0.596			
Cu	−0.168	−0.200	0.742	−0.034	0.742	−0.435		
Co	−0.092	−0.124	0.362	−0.202	0.842	−0.738	0.781	

r-Values ≥ 0.492 or $= -0.492$ are significant at $p < 0.05$.

Table 10
Significant correlation and linear regression analysis for effluents, soil and water samples from polluted area ($n = 99$).

Matrix	Regression equation	Correlations (r)
Effluents	[Pb] = 51.025[Cr] + 2.978	0.597
	[Pb] = 58.649[Cr] + 1.898	0.685
Soil	[Co] = 10.739[Cr] + 0.718	0.517
	[Cu] = 0.0023{Mn]0.200	0.580
	[Co] = 0.121[Zn] + 1.204	0.656
	[Cu] = 0.301[Cd] + 0.460	0.706
	[Co] = 1.007[Cu] + 0.776	0.658
Water	[Pb] = 0.038[Mn] + 3.289	0.492
	[Ni] = −0.104[Pb] + 0.679	0.596

Table 11
Principal Component loadings (varimax normalization) for metals in the effluents samples form different downstream points ($n = 30$).

	Factor 1	Factor 2
Cr	0.941	0.294
Mn	0.971	−0.138
Zn	0.978	0.093
Cd	−0.316	0.924
Pb	0.350	0.910
Ni	0.945	−0.158
Cu	0.976	−0.114
Co	0.969	0.177
Eigen values	5.80	1.859
%Total variance	72.506	23.238
Cumul.%	72.506	95.743

Table 12
Principal component loadings (varimax normalization) for metals in the drinking water samples form different localities ($n = 30$).

	Factor 1	Factor 2	Factor 3
Cr	0.021	0.412	0.034
Mn	−0.034	0.414	0.116
Zn	−0.151	−0.027	0.686
Cd	0.065	−.0111	−0.336
Pb	0.345	−0.139	−0.170
Ni	−0.368	−0.218	0.197
Cu	0.146	−0.036	0.318
Co	0.311	0.018	0.022
Eigen values	3.407	2.300	1.158
%Total variance	42.586	28.755	14.480
Cumul.%	42.586	71.341	85.821

Table 13
Principal component loadings (varimax normalization) for metals in the soil samples form different downstream points ($n = 30$).

	Factor 1	Factor 2	Factor 3
Cr	0.328	−0.087	−0.002
Mn	0.063	0.248	0.127
Zn	−0.231	0.515	−0.042
Cd	0.363	−0.208	−0.029
Pb	−0.061	−0.041	0.736
Ni	−0.040	0.258	0.410
Cu	0.305	−0.053	−0.092
Co	0.067	0.285	−0.228
Eigen values	4.235	1.560	1.189
%Total variance	52.941	19.498	14.866
Cumul.%	52.941	72.440	87.306

component loading for soil sample extracted three factors. The percentage of total variance being 86% the contribution of each factor being 42.586% and 28.755% and 14.460% towards the total variance, respectively. Principal component loading for ground water extracted three components with percentage of total variance of 87% with the contribution of each factor being 52.941%, 19.498% and 14.866%, respectively.

4. Discussion

In order to find out the contribution of different industries towards metals pollution in the main effluent stream, statistical comparison which compared different industries in terms of metals as variables yielded no significant difference between different industries with the $p = 0.658$. This indicates that these industries contribute equally in terms of selected metals pollution. The cluster analysis using complete linkage method was followed in order to put industries of equal metals pollution efficiencies in groups, this grouped industries into two broad groups and a minor group. From the data, it is clear that Mn, Pb, Cd, Co are the dominant elements in the effluents soil and ground water; their concentration is higher in case of soil samples compared to water samples as indicated in the previous studies [27,28].

This study also reveals moderately high concentration in effluents and low concentration in water samples. The order of metals distribution in the three media is Soil > effluents > water.

The effluents stream accumulate a large influx of metals in the surrounding soil in the vicinity through which it passes by, which causes the contamination of the ground water of the area nearby. Our observation is also supported by the mean metals concentration of the ground water in polluted area and metal concentration in water from background area and control area as indicated in Fig. 1. The order of distribution of mean metals concentration in the effluents samples is Mn > Pb > Ni > Co > Cu > Cd while small variation was observed in case of soil samples where the distribution order was Mn > Pb > Co > Zn > Cu > Cd > Ni. Ni and Zn, Co and Cu and Cu and Cd have changed their ranking positions this could be explained on the basis of possible chemical exchange process among atoms under given prevailing conditions of pH and temperature [29].

This high concentration level of metals in soil samples in the polluted area was compared with the soil samples from the background and control area. This clearly supported our view that soil sample in the vicinity of the polluted stream accumulates high concentration metals like Mn, Pb, Ni, Cd, Co and Zn than the WHO limits. In case of control soil, samples only Mn and Pb were found to have high mean concentration which can be attributed to the weathering of rocks natural enrichment or other physical and chemical processes. The metal-to-metal correlation study in the effluent data showed that the mean concentration of Pb, Cr and Cd mutually depends on each other. In case of soil, strong correlation was observed among Cd, Mn, Ni, Cu, Zn, Co. It indicates that their compounds are used in various industries for various purposes. Cd showed a strong correlation to Cu, Mn in the soil media while to Cr and Pb in the effluent media. In ground water strong correlation was noticed in Pb and Mn ($r = 0.492$) Ni and Pb ($r = 0.596$). This indicates that the ground water system is influenced by relation between these metals pairs. A cross correlation study between effluents and soil multiple correlation showed that in effluent soil system Cr and Zn ($r = 0.650$) Cd and Cr ($r = 0.669$, Cd and Mn ($r = 0.763$) Cd and Ni ($r = 0.664$) Cu and Cr ($r = 0717$) Cu and Zn ($r = 0.691$) and Co and Ni ($r = 0.680$) are strongly correlated. In case of effluent water system the correlation between Zn and Pb ($r = 0.771$) Cu and Zn ($r = 0.640$) and Cu Ni ($r = 0.639$) were found to be positive. Correlation study conducted for soil water system showed a strong positive correlation between various pairs of metals including Cu, Mn, Cd, Zn, Ni, Cr, and Co. It can be pointed out from the results that the soil system rich in these metals can substantially affect the quality of ground water. Our metal-to-metal correlation was further supported by linear regression analysis in terms of linear regression equations (Table 10) which supports the correlation coefficient analysis earlier described in terms of correlation dependence of various metals pairs like Pb–Cr, Pb–Cd, Cd–Mn, Ni–Mn, Cu–Cd, Co–Cr, Co–Zn, Pb–Mn, and Ni–Pb, etc. The PCA reduces a large number of variables into a new set of variables based on their mutual dependence. PCA, using varimax normalized rotation, was used for factor loading in the three media. In case of effluents the factor analysis extracted two factors embodying together 96% of total variance. The contribution of the first factor was 72.506% which shows high loading for Zn, Cu, Mn, Co, Ni, Cr, with significant loading for Pb which indicates the use of these chemicals in the various industries under study. Factor 2 contributed for 23.238% of total variance showed maximum loading for Cd, Pb, Cr and significant loadings for Co, Mn, Ni, Cu manifesting common source of these chemicals in various industries. In case of soil samples (Table 12) three factors were extracted with a total variance of 86% with the contribution of the first factor 42.586% of the total variance showed maximum loadings for Ni, Pb, Co and significant loadings for the Cu and Zn probably originating in the soil from the effluents along with other factors such as soil texture, natural enrichment process, etc. Factor 2 contributed 28.755% of the total variance with maximum loadings for Mn, Cr, Ni and significant loadings for Cd and Pb which can be attributed to the effluents. Factor 3 contributed 14.480% of the total variance with the loadings for Zn Cd, Cu and significant loadings for Ni, Mn and Pb originating from the industrial effluents which contaminate the adjacent soil. The PCA factor loading for ground water (Table 13) also extracted three factors with a total variance of 87% the contribution of the first factor 52.941% to the total variance with maximum loadings for Cd, Cu, Cr and significant loadings for the Zn showing water soluble metals from the soil and effluents. Factor 2 contributed 19.498% to the total variance showed maximum loading for Zn, Co, Ni, which mainly originate from industrial effluents. Factor 3 contributed 19.866% of the total variance with maximum loading for Pb, Ni and significant for Co and Mn is assumed to originate from the soil contaminated by effluents. The correlation and principal component analysis study of the results indicates that the soil and the ground water in the surrounding of effluent stream are contaminated by the effluents. Our study is in good agreement with the earlier studies [18,19,20,31].

5. Conclusion

It can be concluded from the present study that multivariate and univariate statistical analyses hold good in point source identification, classification of various sources, the correlation between different metal pairs in effluents, soil and ground water. Principal components analysis reduced a large number of variables to a new set of variables based on mutual dependence. In short, multivariate statistical analysis aids a lot in the interpretation of the complex data. In order to compare the contribution of various industries towards metal pollution in the main effluent stream, one way ANOVA was applied which resulted in a $p = 0.658$ showing that there is no significant difference between different industries in terms of contribution to the metals pollution. Cluster analysis using complete linkage method classified different industries into two broad groups and a minor group. From the data it is clear that Mn, Pb, Cd, Ni, and Cu were found to be the most abundant elements in the three media. The principal component analysis revealed that these effluents are causing the contamination of the adjacent soil and corresponding water. By comparison between the metal levels with the background area and the control area it is evident that the effluents cause a potential health risk to the inhabitants in the surrounding area. This study provides a substantial information to the government agencies to implement strict regulatory procedures for the safer discharge of effluents from these industries and devise procedure for the safe recycling of effluent to ensure reclamation and the lost quality of ground water. The environmental contamination of the adjoining areas by the effluents stream must be constantly monitored according to the WHO guidelines [30].

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