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Spatial distribution and pollution source (s) apportionment in adjacent tributaries of River Panjkora

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Abstract

Water quality degradation in river systems has caused great concerns all over the world. Identifying the spatial distribution and sources of water pollutants is the very first step for efficient water quality management. A set of water samples collected bimonthly at 6 monitoring sites during 2013. The samples were analyzed to determine the spatial distribution of critical parameters with the objective to apportion the sources of pollutants in tributaries of Panjkora River of summer season in the North East Pakistan. For this 6 monitoring sites were divided into three administrative zones of rural, suburban, and urban zones. Multivariate statistical methods [Kruskal-Wallis (H test), principal component analysis (PCA), and absolute principal component score-multiple linear regression (APCS-MLR) methods] were used to investigate the spatial distribution of water quality and to apportion the pollution sources. Results showed that most water quality parameters had shown significant difference among different zones. The urban and suburban zones, showed worse water quality than the rural zone. Based on PCA and APCS-MLR analysis, natural pollution source and geogenic pollution with rural domestic sewage, soil weathering and subsequent run-off pollution with domestic sewage, and commercial service, were identified to as main pollution sources. Understanding the water pollution characteristics of different administrative zones could put insights into effective water management policy making especially in the area across various administrative zones.

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Introduction

Water quality problems have posed serious threat to human health, ecology and environment all over the world especially in developing countries (Saksena *et al.* 2008; Liu *et al.* 2011; Brown and Froemke 2012). With the growing population and fast developing economy, pollution problems become highlighted; especially when fundamental facilities (e.g., sewage networks and sewage treatment plants) cannot keep up the pace of economy development, water quality problems are getting increasingly serious anthropogenic contamination caused by city expanding and extensive population growth has long been criticized for their adverse effects on water quality (Xu *et al.* 2009; Mei *et al.* 2011; Su *et al.* 2013). But few researches investigating water quality on different administrative divisions (rural, suburban, and urban zones), especially in Pakistan where owing to different functions and water management policies among various administrative zones, the water quality and pollution source could be different. Moreover, for a river the area is usually across several administrative zones and this would bring difficulty for water quality management and protection.

To ensure that any investment in remedial works reaps maximum improvements in most heavily polluted area at watershed scale, it is imperative that the pollution critical zones are pointed out. In other words, spatial distribution of pollutants are characterized, besides the primary sources of each pollutant are identified both in terms of profile and contribution. Source identification and source apportionment of polluted water systems can provide basis for better water management practices to improve the quality of the waters and thus they deserve more attention (Howarth *et al.* 2002; Singh *et al.* 2005; Ma *et al.* 2009).

To quantify the contributions of all sources to each measured pollutant, the receptor model absolute principal component score-multiple linear regression (APCS-MLR) method was used. It was firstly used for pollution source (s) identification and apportionment in atmospheric environment due to its little relies on the number of sources or their compositions (Miller *et al.* 2002; Guo *et al.* 2004; Singh *et al.* 2008). APCS-MLR is based on the assumption that all pollutants in the receptors were the linear combination of several pollution sources; thus, it can calculate the contribution of each source. In recent years, there have been many researchers who used this model to apportion the pollution sources in aquatic systems (Zhou *et al.* 2007b; Wu *et al.* 2009; Su *et al.* 2011).

Tributaries of Panjkora River flowing through upper and lower Dir districts and then goes straight into the Panjkora River. It flows through a densely populated area of districts Dir and highly developed area of lower Dir Timergara city, which is situated in north part of Khyber Pakhtunkhwa (KP) province, Pakistan and finally merges into Swat River. These tributaries provide most water supply to municipal use and supporting daily life activities. But due to the severe pollution load, the tributaries are now under multiple water quality impairments and losing its water supplying functions.

As the knowledge of spatial distribution and pollution source apportionment for water quality in each administrative zone is very important for providing scientific information on policy-making decision for local government, the objectives of this study are (1) to understand the status of the water quality in various tributaries of Panjkora River in different administrative zones (2) to find out the spatial distribution of critical water quality parameters using multivariate analysis methods in various tributaries and (3) to identify the pollution sources and apportion their contributions for each pollutant in the three administrative zones.

Material and methods

Study area

The tributaries of Panjkora River (Fig. 1) is located in Dir valley consist on two districts upper Dir and Lower Dir. Due to the rapid urbanization and significant population expansion, the water quality of the tributaries are deteriorated which is a growing threat for the local people.

River administrative zoning

The concept of river administrative zone was employed into this study. To investigate the spatial distribution of water quality in tributaries of Panjkora River, the study area was divided on their differences in population density, land use and land cover into three administrative zones i.e. rural, suburban, and urban,. Among them the urban zone is densely populated with commercial and services activities. Water quality of rural zone is expected to be better than water quality of suburban and urban zones. Rural zone are sparsely populated with low agricultural practices. The suburban zone is moderately populated as compared to urban zone.

In the study area no sewage effluent network has been constructed in these zones and all sewage is discharged directly into the river without any treatment.

This study was conducted in the three administrative zones to investigate the spatial distribution of water quality in tributaries of Panjkora River. For this purpose, six tributaries (monitoring sites) in the whole watershed area were selected. Out of which two lies in the rural zone (site 1 Gualdai and Site 2 Dobando), two were in suburban zone (site 3 Barawal and site 4 Usherai) and the other two are located in urban zone (site 5 Kunai Khwar and site 6 Roud Khwar). Understanding the relationship between water quality and administrative zones will greatly help implementing water quality improvement plans.

Sampling and chemical analysis

During study period eighteen composite samples were collected from pre-specified points, each month across the tributaries width at all the six sites with a view to monitor changes caused by the seasonal and hydrological cycle. Sampling, preservation and transportation to the Laboratory were as per standard methods (Federation 2008). The samples were analyzed for 21 parameters namely temperature (T), pH, turbidity, electrical conductivity (EC), total alkalinity, total hardness, total dissolved solids (TDS), total suspended solids (TSS), dissolved oxygen (DO), 5-days biochemical oxygen demand (BOD_5) and chlorides (Cl) were determined through titration methods while sodium (Na), potassium (K) zinc (Zn), cadmium (Cd), chromium (Cr), iron (Fe), manganese (Mn), copper (Cu), lead (Pb) and cobalt (Co) concentration were determined using graphite furnace (GF) as suggested by Arnold *et al.*, (1992). The analytical data quality was ensured through careful standardization, procedural blank measurements, spiked and duplicate samples. Statistics of the summer season data set on tributaries of Panjkora River water quality is summarized in Table. 1.

Result and discussion

Basic statistic of water quality of sampling sites

Original data descriptive statistics summary of the 21 water quality parameters of the tributaries is presented in Table. 1 and compared surface water quality standards of WHO (2008), Pak-EPA (2008) US-EPA (2012). All the parameters were under the permissible limits except turbidity and Cd which exceeds the permissible limits. In rural zone mean water T was 16 °C, 16.5 °C in suburban zone and was 19.6 °C in urban zone. T increase from rural to urban zone was recorded. Such increase in T is due to change in metrological characteristic of the zones. pH of water was neutral to alkaline in the whole administrative zone. Its mean value was 7.6 in rural zone, 7.5 in suburban zone and it was slightly decreased to 7.3 in urban zone. Decrease in pH was due to sewage and domestic wastes influx into the tributaries. As high levels of these organic matter consume excess amounts of oxygen, which undergoes anaerobic fermentation processes leading to formation of ammonia and organic acids. Hydrolysis of these acidic materials causes a decrease of water pH values in urban zone (Singh *et al.*, 2005).

Alkalinity (as $CaCO_3$) mean value was 121 mg/l in rural zone, 132 mg/l in suburban zone and 157 mg/l in urban zone. Alkalinity in different administrative zones cushions against rapid change in pH, harmful to aquatic life, counter result is obtained in our study which is comparable to the study of Zeeshan on Himalayan River India (Zeeshan *et al.* 2016).

The mean values of hardness (as $CaCO_3$) of rural, suburban and urban zones was 60mg/l, 75mg/l, 66mg/l respectively. Values of hardness in different administrative zone fall in category of soft water as per Sawyer and McCartly (1967). TDS mean value in rural zone was 210 mg/l while its mean value in suburban zone was 235 mg/l and 291 mg/l in urban zone. Similarly the value of EC were 328µs/cm, 339µs/cm and 405µs/cm in rural, Sub-urban and urban zones respectively. EC reflecting the amount of inorganic chemicals in the water (Bhardwaj and Singh 2011; Kumar *et al.* 2014).

The values of TDS and EC were increased from rural zone to urban zone is possibly due to proportionately higher sewage entry into urban zone. Higher value of TDS and EC in urban zone could also be attributed to release of dissolved solids from agricultural land run off (Ravindra and Garg 2007). Similar results for TDS and EC were reported from River Jhelum's tributaries (Mir and Jeelani 2015). The mean value of turbidity in rural zone was 68 NTU while its mean value in suburban zone was 55 NTU in urban zone its mean value was 45 NTU. Similarly the value of TSS in rural zone was 1.9 mg/l in rural, 0.5 mg/l in sub-urban and 0.49 mg/l in urban. The turbidity of water in three different administrative zone was higher than permissible limits. High level of turbidity and TSS in rural and suburban zone is possibly due to faster water flow, as the rural and suburban zones lies in the area of steep slope. Rural zone is a mountainous region, followed by suburban zone, and many locations are prone to landslide and soil erosion, which also cause the water to be turbid. Counter result is obtained in our study which is comparable to the study of Zeeshan on Himalayan River India (Zeeshan *et al.* 2016). The mean value DO was 13 mg/l, 11 mg/l and 9 mg/l in rural, sub-urban and rural zone respectively. The value decreases from rural to urban zone. BOD_5 mean value was 3.2 mg/l in rural, 3.4 mg/l in sub-urban and 4.1 mg/l in urban zone. Contrary to DO results, the value of BOD_5 decreased form rural zone to urban zone. Low level of DO in urban zone is associated with higher surface water T which leads to decrease the solubility of O_2 in water (Hanson *et al.*, 2006; Yang *et al.*, 2015). On the other hand agriculture activities, such as crop planting, fertilizer application, crop harvesting and discharge of domestic waste increases in urban zone. Municipal effluents and surface runoff always loaded with biodegradable organic pollutants.

These biodegradable substances consumes more oxygen by oxidation through microbes which decrease the level of DO in suburban and urban zones. High BOD_5 indicate high scale contamination of organic matter in the urban zone. Though high BOD_5 is always accompanied by low DO level in suburban and urban zone. Counter result is obtained in our study which is comparable to the study of Anhwange on River Benue, Nigeria and the study of Qadir on Nullah Aik-tributary of the River Chenab (Anhwange *et al.* 2012; Qadir *et al.*, 2008). Chloride mean concentration in the water of rural zone was 112 mg/l, 121 mg/l in suburban zone and 126 mg/l in urban zone. Increase in Cl concentration towards urban zone could be attributed to the inflow of domestic waste. Its concentration in water bodies indicates organic pollutant. The possible sources of Cl are surface runoff, discharge of industrial effluents and domestic sewages (Trivedi, *et al.*, 2010). Na essential for regulating fluid level and neural conduction in animals. Its mean value was 10 mg/l in rural zone, 11 mg/l in suburban zone and 12 mg/l in urban zone. Similarly concentration of K in rural zone was 8 mg/l, 9mg/l and 10 mg/l in rural, sub urabn and urban zones. The concentration of Na and K was in the order urban zone > suburban zone > rural zone in the three administrative zones. Concentration of heavy metals (HMs) in the administrative zones was in order urban zone > suburban zone > rural zone. Among HMs the concentration of Cd exceed the permissible limits. The main sources of HMs in different administrative zones were atmospheric deposition, use of fertilizers, surface runoff and solid waste disposal (Abouhend *et al.*, 2015; Vaishnavi *et al.*, 2015). As the concentration of HMs increase from rural zone to urban zone is mainly due to increase in agriculture activities, solid waste disposal and domestic waste water in suburban and urban zone tributaries, which might leads to increase its concentrations (Table 1 and Fig. 1).

Table 1. Summary of water quality parameters in three administrative zones of the study area (n=126).

Rural zone						Sub-urban zone				Urban zone			Quality standards		
	T1		T2		T3		T4		T5		T6		WHO	Pak-EPA	US-EPA
Parameter	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	2008	2008	2012
T (°C)	17	1	16	1	17	1.15	16	0.57	19	1	20.33	2.08	NA	NA	NA
pH	7.07	0.45	7.03	0.49	7.7	0.46	7.57	0.45	7.53	0.32	7.13	0.65	6.5-8.5	6.5-8.5	6.5-8.5
EC(μs/cm)	286.33	146.83	370	183.3	370.33	71.7	308.33	146.83	470	199.75	340	213.78	1400	NA	NA
TDS (mg/l)	163.67	93.59	256.67	122.2	259.33	54.6	211.67	93.59	345.67	158.23	236.33	143.07	<1000	<1000	500
Turbidity (mg/l)	62.67	93.88	73.67	90.39	36	22.72	74.67	93.88	24.33	15.7	65.33	83.77	>5	>5	>5
DO (mg/l)	13.55	10.14	13.33	6.11	11	8.69	15.55	10.14	10.21	2.76	13.72	11.09	5	NA	NA
TSS (mg/l)	0.84	1.46	3.02	5.18	0.16	0.21	0.92	1.46	0.09	0.09	0.9	1.48	NA	NA	NA
Alkalinity (mg/l)	98.67	64.39	143.33	98.43	205.67	43.06	108.67	64.39	253	125.65	210.33	151.76	NA	NA	NA
Hardness (mg/l)	35.67	16.17	84.33	35.44	110	52.42	40.67	16.17	91.67	46.42	41.8	13.19	NA	NA	NA
BOD mg/l)	5.6	3.81	2.7	1.3	0.77	0.59	6.2	3.81	2.17	0.75	4.3	3.46	NA	NA	NA
Na (mg/l)	11	2	10.33	2.08	11.67	2.52	10	2	13.33	2.52	10.33	3.06	200	NA	20
K (mg/l)	8.15	1.53	8.67	2.08	9.67	2.52	8.67	1.53	10	3	9	3	250	NA	NA
Cl (mg/l)	114.33	7.51	129	17.78	125.67	10.69	126.33	7.51	108	15.13	115.67	10.02	250	NA	NA
Zn (ug/l)	56.3	2.89	69.28	3.91	73.76	5.43	85.03	3.67	82.77	6.2	90.85	2.34	3000	5000	5000
Cu (ug/l)	4.62	0.56	6.4	0.38	6.56	0.51	10.67	0.4	7.55	3.61	11.32	1.15	2000	2000	1300
Fe (ug/l)	3.26	0.32	4.69	0.22	6.47	0.25	12.6	0.37	8.7	1.62	12.01	3.21	300	NA	300
Cd (ug/l)	9.68	0.33	12.83	0.58	16.63	0.33	17.74	0.65	18.16	4	22.52	2.8	3	10	5
Mn (ug/l)	96.79	3.1	108.28	5.3	108.94	4.51	119.04	4.66	110.88	6.86	123.06	2.54	500	500	50
Pb (ug/l)	2.66	0.31	2.71	0.24	3.14	0.32	3.83	0.17	2.23	0.35	3.12	1.24	10	50	15
Co (ug/l)	0.28	0.07	0.5	0.15	0.57	0.18	0.79	0.14	0.77	0.15	0.77	0.3	5000	NA	NA
Cr (ug/l)	3.66	0.2	3.54	0.31	3.86	0.14	4.49	0.33	17.5	22.03	4.16	1.35	50	50	100

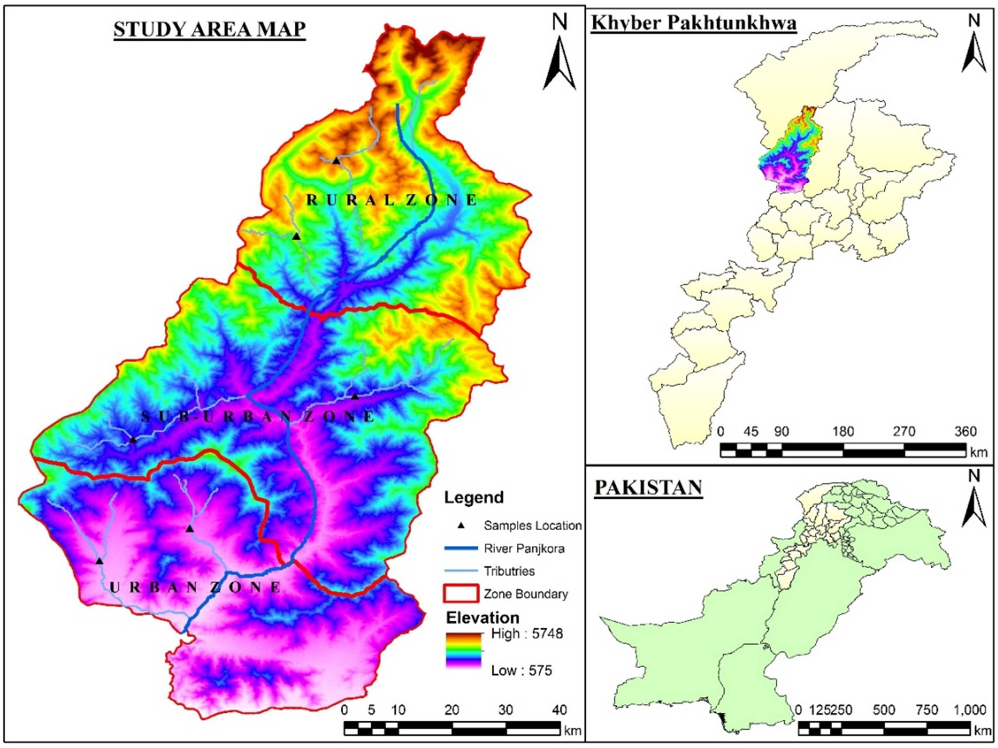


Fig. 1. Administrative zones and sampling point's location map of district Dir.

Descriptive and multivariate statistical analysis

Spatial variation

In order to expose the spatial distribution pattern of the degraded water quality parameters in different administrative zones, Kruskal-Wallis ($p < 0.01$) test was used (Table. 3). It is a non-parametric method for testing whether the sample originates from the same distribution or not. This H-test is generally used for the comparison of two or more independent samples of equal or different size equivalent to one way ANOVA on ranks (McDonald *et al.*, 1996). Correlation structure between the variables was studied using the

Spearman R coefficient as a non-parametric measure of the correlation between the variables (Wunderlin *et al.* 2011). In this study, the data set of the tributaries water quality parameters (Table. 2) were evaluated through spatial-parameter correlation matrix using the Spearman non-parametric correlation coefficient (Spearman R). The Water quality parameters were grouped in three different administrative zones and each assigned a numerical value in the data file, which as a variable corresponding to the different administrative zones was correlated (pair by pair) with all the measured parameters. In the water samples correlation matrices show positive correlation in various parameters like TDS-EC (r=0.988), DO-turbidity (r=0.902), alkalinity-EC (r=0.941), alkalinity-TDS (r=0.851), BOD-DO (r=0.884), Na-hardness (r=0.634), K-pH (r=0.728), K-EC (r=0.809), K-TDS (r=0.859), K-alkalinity (r=0.813), K-hardness (r=0.826), K-Na (r=0.630), Cl-Na (r=0.973), Cu-Zn (r=0.921), Fe-Zn (r=0.933), Fe-Cu (r=0.622), Cd-Temp (r=0.622), Cd-alkalinity (r=0.620), Cd-Zn (r=0.961), Cd-Cu (r=0.877), Cd-Fe (r=0.855), Mn-Zn (r=0.960), Cd-Cu (r=0.952), Cd-Fe (r=0.936), Pb-turbidity (r=0.762), Pb-DO (r=0.866), Pb-BOD (r=0.612), Pb-Cl (r=0.681), Co-TDS (r=0.662), Co-K (r=0.759), Co-Zn (r=0.784), Co-Fe (r=0.612) Cr-EC (r=0.855) and Cr-TDS (r=0.813) as shown in Table. 2.

Table 2. Correlation matrix of water quality parameters in three administrative zones.

	T	pH	EC	TDS	Turbidity	DO	TSS	Alkalinity	Hardness	BOD	Na	K	Cl	Zn	Cu	Fe	Cd	Mn	Pb	Co	Cr
T	1																				
pH	-.111	1																			
EC	.396	.430	1																		
TDS	.391	.483	.988	1																	
Turbidity	-.429	-.578	-.765	-.715	1																
DO	-.333	-.333	-.848	-.785	.902	1															
TSS	-.444	-.667	-.283	-.275	.759	.417	1														
Alkalinity	*.733*	.341	*.841*	.851	-.785	-.787	-.509	1													
Hardness	-.067	.467	.733	.723	-.523	.756	-.196	.605	1												
BOD	-.236	-.354	-.776	-.773	.724	.884	.265	-.797	-.944	1											
Na	.289	.577	.715	.643	-.971	-.866	-.722	.637	*.634*	-.612	1										
K	.243	*.728*	*.809*	.859	-.743	-.728	-.485	*.813*	*.826*	-.857	*.630*	1									
Cl	-.736	.022	-.356	-.275	.523	.350	.525	-.433	.182	-.039	.973	.005	1								
Zn	.536	.374	.341	.464	-.107	.036	-.273	.550	-.010	-.170	-.062	.516	-.084	1							
Cu	.385	.289	-.029	.103	.176	.397	-.217	.214	-.342	.191	-.313	.210	0.000	.921	1						
Fe	.365	.365	.070	.199	.118	.342	-.228	.243	-.295	.169	-.237	.266	-.042	.933	.988	1					
Cd	*.662*	.284	.281	.393	-.167	-.020	-.365	*.620*	-.001	-.236	-.035	.501	-.130	.961	*.877*	*.855*	1				
Mn	.407	.220	.113	.253	.153	.260	-.080	.351	-.146	-.028	-.329	.344	.118	.960	.952	.936	*.926*	1			
Pb	-.577	0.000	-.794	-.701	*.762*	.866	.289	-.733	-.509	*.612*	-.750	-.420	*.681*	.050	.375	.316	0.000	.277	1		
Co	.149	.447	.541	*.662*	-.158	-.224	0.000	.560	.487	-.553	0.000	*.759*	.342	*.784*	.581	*.612*	.707	*.760*	0.000	1	
Cr	.447	.447	*.855*	*.813*	-.745	-.671	-.447	.655	.379	-.395	.775	.542	-.694	.257	.000	.122	.163	-.009	-.775	.200	1

Bold correlation is significant is the 0.01 level (2-tailed).

Bold and Italic correlation is significant is the 0.05 level (2-tailed).

Principal component analysis and receptor modeling

To identify the source (s) as well as to apportion the contributions of each pollution source (s), principal component analysis (PCA) and receptor modeling (APCS-MLR) were conducted on the datasets of the different administrative zones. PCA is often used to simplify the numeric matrix of dataset by reducing their dimensionality and to concentrate most information of the original dataset into several new principal components through varimax rotation with Kaiser normalization.

These newly generated principal components were orthogonal and each component explain part of the variance of the whole dataset. Thus principal components were considered as pollution sources (Zhou *et al.* 2007a).

APCS-MLR was then applied to estimate the pollutant contribution of each pollution source by combining multiple linear regression with the denormalized principal component score values generated from varimax rotated PCA and the measured concentrations of a particular pollutant; it was described elsewhere in detail (Zhou *et al.* 2007b; Su *et al.* 2011).

After confirming the number and identity of the possible sources influencing the river water quality in the three administrative zones through PCA, source contributions were computed using APCS-MLR technique. All statistical data analyses were determined using the IBM SPSS 20 version for Windows Table. 4.

Table 4. Varimax rotated loadings of water quality parameters in the rural, suburban and urban zones.

Parameter	Rural zone				Sub-urban zone				Urban zone		
	F1	F2	F3	F4	F1	F2	F3	F4	F1	F2	F3
T	0.339	0.168	0.149	0.909	-0.439	0.392	0.761	-0.274	0.831	0.287	0.465
pH	-0.303	-0.439	-0.208	0.21	0.056	-0.872	-0.225	-0.432	-0.055	0.283	-0.935
EC	0.294	0.106	0.945	-0.043	0.154	0.195	0.958	0.144	0.955	-0.241	-0.104
TDS	0.31	0.103	0.936	-0.043	0.11	0.122	0.974	0.157	0.928	-0.325	-0.156
Turbidity	-0.058	0.941	0.082	-0.244	0.012	0.329	0.26	0.908	0.829	0.512	-0.214
DO	-0.153	0.822	0.39	-0.375	0.029	0.825	0.066	-0.561	-0.164	0.061	0.98
TSS	0.215	0.933	-0.129	0.196	0.1	0.353	0.137	0.92	0.01	0.306	0.879
Alkalinity	0.348	-0.487	0.753	0.243	-0.287	0.417	0.464	-0.727	0.979	0.157	-0.112
Hardness	0.674	0.694	0.035	0.251	-0.561	0.746	0.14	-0.33	0.933	0.263	-0.239
BOD_5	-0.542	0.106	0.235	-0.798	0.425	0.141	-0.111	0.887	-0.399	0.545	0.716
Na	0.118	0.485	0.83	-0.097	-0.491	0.666	0.559	0.042	0.887	0.386	0.252
K	0.012	0.945	0.309	0.067	-0.428	0.737	0.52	-0.058	0.995	-0.08	0.015
Cl	0.069	0.957	0.154	0.222	-0.14	0.959	0.003	0.244	0.944	0.305	-0.123
Zn	0.927	-0.023	0.308	0.153	0.964	-0.172	0.036	0.199	0.24	0.938	-0.11
Cu	0.932	-0.139	0.249	0.219	0.839	-0.188	-0.324	0.395	-0.301	0.933	0.151
Fe	0.972	-0.003	0.03	0.205	0.799	-0.106	-0.426	0.411	0.439	0.811	0.341
Cd	0.945	0.195	0.161	0.109	0.963	-0.019	0.267	-0.033	0.633	0.756	0.16
Mn	0.854	0.047	0.446	0.215	0.971	-0.084	0.184	0.128	0.154	0.985	-0.072
Pb	0.612	0.357	0.469	-0.349	0.908	-0.408	0.035	0.086	0.928	-0.135	-0.062
Co	0.616	0.302	0.351	0.472	0.653	-0.236	0.709	-0.128	0.787	0.602	0.019
Cr	0.074	0.55	0.816	0.111	0.991	-0.058	-0.106	0.063	-0.098	0.965	0.17
Eigen values	9.877	5.525	5.525	1.441	9.77	6.044	3.853	1.332	11.02	6.248	3.196
Total Variance %	47.035	26.31	14.973	6.86	46.526	28.782	18.348	6.344	52.477	29.751	15.22
Cumulative Variance %	47.035	73.345	88.318	95.178	46.526	75.308	93.656	100	52.477	82.229	97.449

Extraction Method: Principal Component Analysis.

Rotation Method: Varimax with Kaiser ormalization.

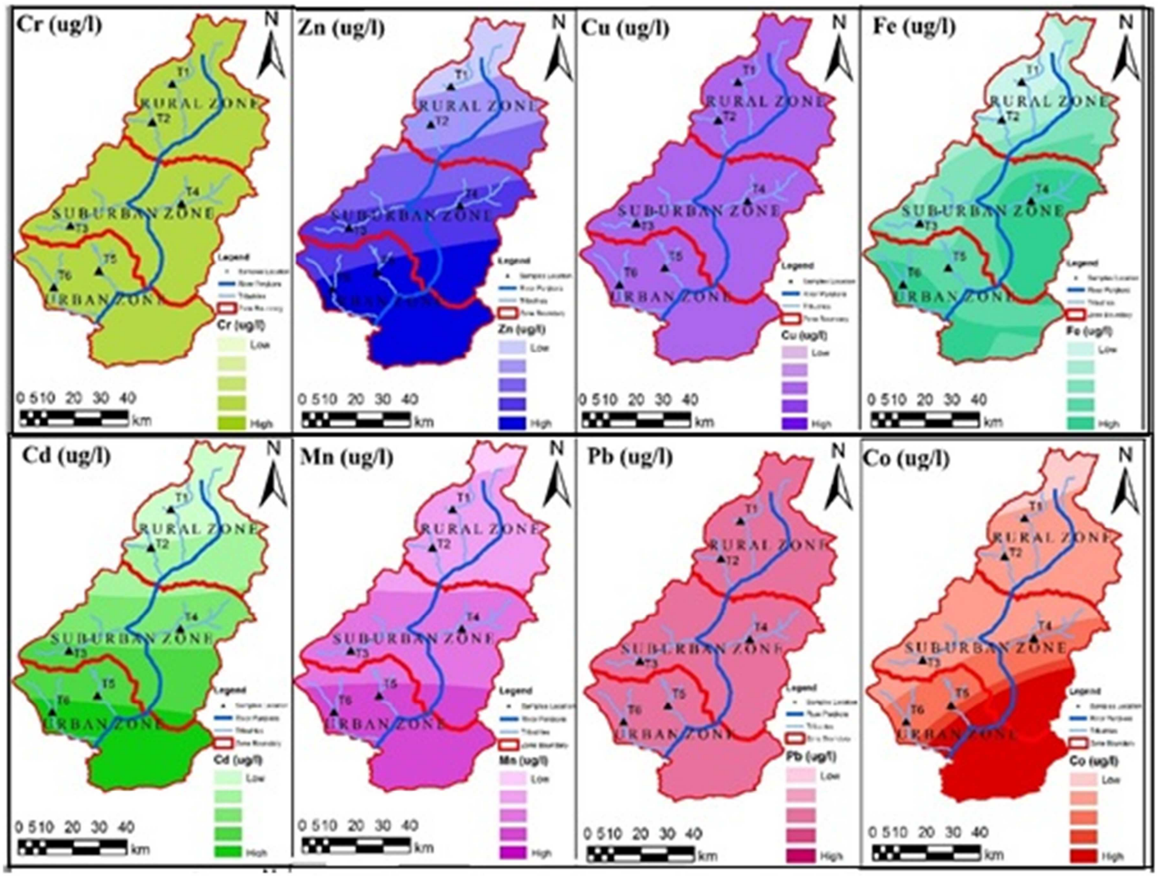


Fig. 2. Heavy metals concentration in rural, sub-urban and urban zone.

Spatial similarities and sites grouping

Cluster analysis (CA) was applied to detect spatial similarity for grouping of sites under the monitoring network. It rendered a dendrogram (Fig. 3), grouping all the Six sampling sites in to three statistically significant clusters at (Dlink/Dmax) ×100 < 70. The clustering procedure generated three groups of sites in a very convincing way, as the sites in these groups have similar characteristic features and natural background source types. Cluster 1 (Rural 1 and Rural 2), cluster 2 (Suburban 1 and Suburban 2) and cluster 3 (Urban 1 and Urban 2) correspond to a relatively low pollution, high pollution and moderate pollution regions respectively. It implies that for rapid assessment of water quality. Only one site in each cluster may serve as good in spatial assessment of the water quality as the whole network. It is evident that the CA technique is useful in offering reliable classification of surface waters in the whole region and will make possible to design a future spatial sampling strategy in an optimal manner. Thus the number of sampling sites in the monitoring network will be reduced, hence cost without losing any significance of the outcome. There are other reports where similar approach has successfully been applied in water quality programs (Ying *et al.*, 2013; Zeeshan *et al.* 2016).

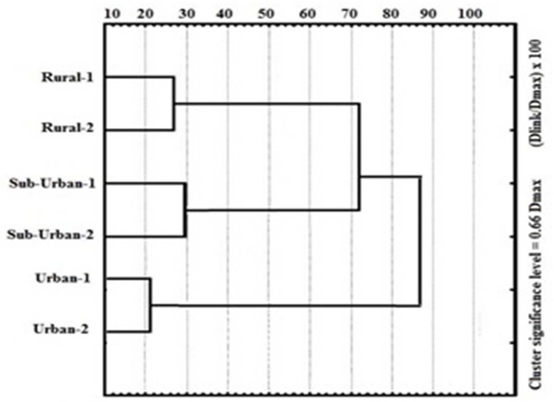


Fig. 3. Dendrogram of physico-chemical parameters (within group linkage).

Spatial distributions of water quality parameters in the three administrative zones

To study the spatial distribution pattern of water quality parameters in the different tributaries, the novel concept of assessing water quality based on administrative zones was implemented in this study.

The comparisons of means of all parameters in the three administrative zones are shown in Table. 3. Most of the water quality parameters except for T, pH, EC, TDS, Hardness, BOD_5, Cl and Turbidity showed significant difference ($p<0.001$) in all three of the three administrative zones. The trend of spatial variation of the parameters among different administrative zones was DO (1.79E-40), TTS (590E-35), Alkalinity (5.73E-21), Na (4.61E-10), K (1.29E-18), Zn (9.60E-24), Cu (8.49E-15), Fe (4.99E-33), Cd (1.30E-16), Mn (9.35E-35), Pb (2.83E-24), Co (1.94E-23) and Cr (1.34E-20) respectively. DO concentration values were higher among the parameters in three zones. It's concentration in the rural zone was higher than that of the suburban zone and the urban zone, indicating that water quality was the best in the rural zone followed by the suburban zone and the urban zone was badly affected by organic pollution. The concentration of HMs in the urban zone was significantly higher than the other two zones which indicated anthropogenic source (s) pollution in the urban zone. T, pH, EC, TDS, Hardness, BOD, Cl and Turbidity did not show any significant differences among the three zones. In general, we can conclude that most of the parameters, were under the permissible limits in different administrative zones. As the urban zone received less attention on its pollution problems, this finding just give us an alarm that the urban zone should be paid concentration. Three water quality parameters were identified to be critical to sustain water quality either for their serious deterioration or for the large difference among the three administrative zones. For evaluating the most seriously deteriorated parameters, Cd (more deteriorated than other HMs) and turbidity were chosen for pollution in each administrative zone. Additionally, DO was selected for their largest difference of means among the three administrative zones.

Pollution source (s) identification in the three administrative zones

Source identification of different pollutants was performed with PCA, carried out on the basis of different activities in the watershed area or in light of previous literature. A receptor model, APCS-MLR was then used in pollution source apportionment.

A total of 21 parameters were employed to assist the source identification. Kaiser-Meyer-Olkin (KMO) and Bartlett test of sphericity were used to examine whether PCA was an effective method to assess the measured water quality parameters in the three administrative zones that indicating PCA could be a helpful method for analyzing these three datasets. Under the guidance of eigenvalue >1 (Pekey *et al.* 2004), four principal components were extracted from the rural zone, four from the suburban zone and three from the urban zone, respectively (Table. 4). According to Su *et al.* (2011), and Ying *et al.* (2013) the terms of “strong,” “moderate,” and “weak” loadings are used for describing factor loadings with absolute factor loading values >0.75, 0.75– 0.5 and 0.5–0.3 respectively.

For the rural zone, four components were extracted. Component 1 explained 47% of total variance and it had strong positive loading on Zn, Cu, Fe, Cd and Mn, moderate positive loading on Pb, Co and Hardness. Previous work signified that high loading could be due geogenic sources e.g. Erosion from surface of rocks and surface run-off as stated by (Gozzard *et al.*, 2011; Shah *et al.*, 2012). Thus this component is mainly due to geogenic pollution. Component 2 explained 26.3% of total variance and it had strong positive loading on turbidity, DO, TSS, K, and Cl, moderate positive loading on Hardness. This component represents natural sources of these parameters in catchments from soil weathering and subsequent run-off. Component 3 explained 14.9% of total variance and it had strong positive loading on EC, TDS, Alkalinity and Na. This component has both anthropogenic and geogenic sources.

The high loading of physico-chemical parameters (EC, TDS and alkalinity) and Na is due to anthropogenic source (agricultural runoff, sewage, domestic wastewater and manure application) as stated by Khan *et al.* (2013) and geogenic source (erosion of schistose rocks) as stated by Shah *et al.* (2012). Thus this component is mainly due to mixed pollution. Component 4 explained 6.8% of total variance and it has strong positive loading on T, strong negative loading on BOD_5. High loading of water T leads to decrease the solubility of O_2 in water and decreases BOD_5 in rural zone. Thus this component is mainly due to natural sources.

For the suburban zone, four components were extracted. Component 1 explained 46.5 % of the total variance and had strong positive loadings on Zn, Cu, Fe, Cd, Mn, and Cr while moderates positive loading on Co. Previous work signified that Zn, Cu, Fe, Cd, Mn, and Cr could come from geogenic sources e.g. Erosion from surface of rocks as stated by (Shah *et al.*, 2012). Gozzard *et al.* (2011) found that HMs in surface water come from surface runoff during higher flows when the river level was elevated thus this component might be pollution from natural sources. Component 2 explained 28.7 % of the total variance.

It had high positive loadings on Hardness, Cl, Na and DO, moderate positive loading on K while high negative loading on pH. This component represents natural sources of these parameters in catchments from soil weathering and subsequent run-off. Component 3 explained 18.3 % of the total variance, it had strong positive loading on T, EC, TDS, moderates positive loading on Na, K. This component loaded with solids indicates towards their origin in run-off from the fields with high load of solids and waste disposal activities. Thus, this component is mainly attributed to be pollution from natural and anthropogenic sources (mixed pollution).

Component 4 explained lower variance 6.3 % of the total variance, and it had strong positive loadings on turbidity, TSS and BOD_5, moderate negative loading on DO. This component represent an oxide-related process associated with negative DO and positive BOD_5. When organic matter in the surface water was oxidized at the expense of dissolved oxygen, the BOD_5 concentrations increased with decreasing DO (Chen *et al.*, 2015). Thus, this component is mainly attributed to be pollution from agricultural nonpoint source pollution and suburban domestic sewage pollution.

For the urban zone, component 1 showed strong positive loadings on T, EC, TDS, Turbidity, T, Hardness, Na, K, Cl, Mn and Co, moderate positive loadings on Cd and weak negative loadings on BOD5. This component explained 52.4 % of the total variance, implying that this is typical mixed-type pollution. High loading T, EC, TDS, Turbidity, Alkalinity, Hardness, Na, K, Cl, Mn, Co, has both anthropogenic and natural impacts. The high loading of physico-chemical parameters (EC, and TDS) and light metals (Na and K) is due to strong anthropogenic impacts such as (agricultural runoff, urban domestic sewage, domestic and manure application) as stated by (Zhou *et al.* 2007; Khan *et al.*, 2013). Based on the above analysis, component 1 represented natural pollution and anthropogenic pollution from urban domestic sewage and commercial or service pollution. Component 2 explained 29.7 % of the total variance and had strong positive loadings on Zn, Cu, Fe, Cd, Mn and Cr while moderates positive loading on Co, BOD5 and Turbidity. According to World Health Organization, HMs is founded widely in Earth's crust and with levels in natural waters generally range between 1 and 2 µg/l, which is in accord with our concentration status. Thus it was attributed to HMs derived from geologic materials through natural weathering processes (Barringer *et al.* 2007; WHO 2011). Component 3 explained 15.2 % of the total variance and it showed strong positive loadings on TSS and BOD$_5$, strong negative loading on DO and pH. It is thus a group of purely organic pollution indicator parameters. This component represents anthropogenic pollution sources and can be explained that high levels of dissolved organic matter consume large amounts of oxygen, which undergoes anaerobic fermentation processes leading to formation of ammonia and organic acids. Hydrolysis of these acidic materials causes a decrease of water pH values (Singh *et al.*, 2005).

Pollution source (s) apportionment in the three administrative zones

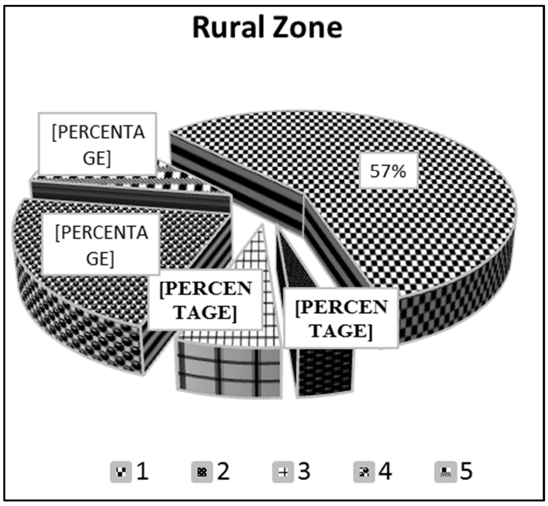
The main source (s) of pollution in the urban, suburban and rural zones are natural and anthropogenic sources such as domestic and commercial sewage and agricultural runoff.

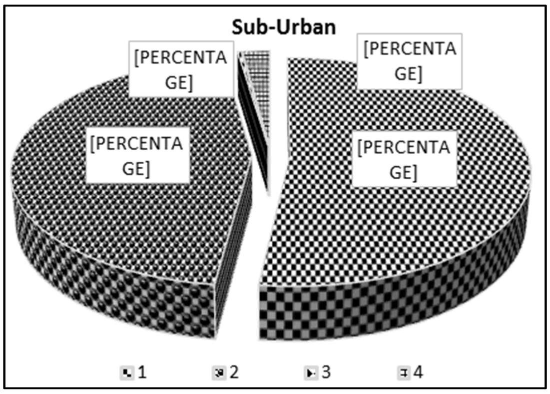
From the above analysis, we can conclude that different administrative zones were influenced by different pollution source (s) as shown in Fig 4. Besides the pollution types, main source (s) contribution percentage were also determined using the APCS-MLR method (Zhou *et al.*, 2007b; Su *et al.*, 2011).

In the rural zone, most of the sites were influenced by natural pollution source and geogenic pollution (57%), soil weathering and subsequent run-off (22%), natural pollution sources (11%) and mixed pollution sources (10%).

In the suburban zone, most sites were influenced by natural source pollution and surface run-off pollution (52%), soil weathering and subsequent run-off (46%) and mixed pollution sources (2%).

In the urban zone, the major pollutants were mainly related to urban domestic sewage pollution and commercial or service pollution (47%), natural weathering processes pollution (30%) and anthropogenic pollution (23%).





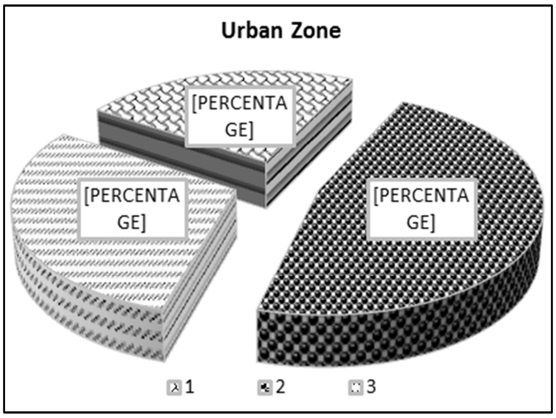


Fig. 4. Pollution source (s) apportionment in Rural, Sub-urban and Urban zone.

Conclusion

This study analyzed spatial distribution and source apportionment of water pollution in six seriously polluted tributaries of Panjkora River, Pakistan through the analysis of major pollutants (Physico-chemical parameters and HMs concentration) in different administrative zones (rural, suburban and urban zones). The main findings are as follows:

(a) Tributaries of Panjkora River were seriously polluted by natural and anthropogenic pollutants, among them turbidity and Cd are the most deteriorated. All the samples exceeded the water quality standards and the highest concentration of Cd was 8 times higher than the permissible limits.

(b) The spatial distribution of most water quality parameters varied among the three administrative zones evaluated through Kruskal-Wallis H test. The pollution of most deteriorated water quality parameters (turbidity and Cd) in the urban zone and suburban zone were severer than in the rural zone.

(c) Source identification using PCA revealed that domestic sewage, soil weathering and subsequent run-off pollution were most responsible for the water pollution in rural, suburban and urban zones respectively.

(d) Source apportionment through APCS-MLR indicated that some variables received the contribution from the unidentified pollution sources. Thus, further investigation of the unknown pollution sources is needed. The local government should strengthen the water quality monitoring and management under fast economic development, control point source pollution, accelerate infrastructure construction in suburban and rural zones, pay more attention to water quality in the urban zone and advocate rational fertilization in the rural and suburban zones to protect water quality.

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Conflict of interests

All the authors declare no conflict of interest.

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