

# SURFACE AND GROUNDWATER POLLUTION: THE INVISIBLE, CREEPING THREAT TO HUMAN HEALTH

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## Abstract

This study reports pollution source apportionment of surface waters and human health risk assessment based on 18 physicochemical and traces elements from 24 water quality monitoring sites for surface and groundwater around the two trans-boundary rivers of Pakistan: The Ravi and Sutlej. The principal component analysis identified 6 principal components (76.98 % cumulative variance) which are mainly caused by untreated industrial effluents, intense agricultural activities, and irrigation tailwater discharges. For all dissolved trace elements in surface waters, health hazard indices (HI) and hazard quotients (HQ) through ingestion and dermal contact are  $< 1$  except As and Cr through ingestion only (for both adults and children). For adults and children, the HQ<sub>ingestion</sub> and HI values for As, Mn, Cu (for children only) and As, Fe, Mn (for children only) are  $> 1$ , indicating that As, Mn, Fe, and Cu are the most important pollutants causing chronic risks among the selected trace elements in both shallow and deep groundwater respectively. HQ<sub>ingestion</sub>, HQ<sub>dermal</sub>, and HI values are higher for children than that of adults which shows the high susceptibility of children to these dissolved trace elements. The carcinogenic indices for the entire surface water elements exceed  $10^{-6}$  through dermal and ingestion pathways suggesting carcinogenic health risk to the surrounding community. Hence, to protect human health, wastewater treatment plants and best management practices should be practiced to control point source and nonpoint source pollution respectively in the understudied area.

## Keywords:

Hazard index (HI);  
Hazard quotient (HQ);  
Human health;  
Risk assessment;  
Surface and groundwater.

## 1 Introduction

Urban sprawl, industrial growth, and intense agricultural activities have grievously deteriorated surface water quality at global scale particularly trace elements concentration in surface waters [1]. Anthropogenic activities, like coal combustion, mining, metallurgy and metal smelting, and natural processes like volcanism and bedrock weathering allow trace elements concentration in the fluvial marine system [2] Exceeding the concentration of noxious metals in surface water makes it unsuitable for different agricultural and industrial activities[3]. Dermal and oral ingestion of toxic water causes severe health risks [4]. The life-threatening cancers and aquatic diseases are reported due to considerable metal intake [1]. Aquatic ecosystems and human health have severe potential threats from dissolved trace elements pollution [5]. Hence the trace elements concentration, distribution and pollution sources, and its hazardous effects on human health are extremely important to examine [6]. Surface water carries significant pollutants load in particulate as well as dissolved phases from both anthropogenic and natural sources. At any point, by water quality, several major influences are reflected, including basin lithology, atmospheric inputs, anthropogenic inputs and climatic conditions [7]. Rivers play a vital role to assimilate and transport industrial and municipal wastewater in addition to agricultural tailwater discharge. Municipal and industrial wastewaters transport constant pollutants load which are temporally influenced by river flow [8]. The discharge and pollutant concentration in the

river waters are greatly affected by the seasonal variations in the precipitation and surface runoff [9]. Investigating Physico-chemical and trace elements concentration in the surface water is important for surface water protection and long-term policy formulation [10]. Multivariate statistical approaches, like correlation analysis, cluster analysis (CA), and principal component/factor analysis (FA/PCA) are the powerful tools used for environmental studies. These techniques give better idea about possible pollution sources with minor loss of information [8]. Little information on the Physico-chemical and trace elements pollution, source apportionment, health risk and water quality assessment in the Ravi and Sutlej rivers are available, although for management of water such information is important. Ravi and Sutlej rivers are two of the major five rivers in Pakistan. Low or no water is available during most parts of the year. Regular water quality monitoring is essential for rivers' health assessment and mitigating water pollution control plans. Data of 6 strategic locations along the 2 rivers, 9 surface drains and 9 groundwater is collected only monthly basis from August 2015 to July 2016 with the aim of 1) physicochemical and trace element source apportionment using multivariate statistical techniques; 2) spatial homogeneity of physicochemical and dissolved trace elements; and 3) water quality hazardous impacts on human health posed by trace elements using Hazard Quotient/Index (HQ/HI). To improve surface water quality, the results can be implemented which will help in water resources protection and to thwart harmful trace element pollution to the public via water sources.

## 2 Materials and methods

### 2.1 Study area

The study area included 6 sampling points located along the Ravi (Ravi 1(R1), Ravi 2(R2) and Ravi 3(R3)) and Sutlej (Sutlej 1(S1), Sutlej 2(S2) and Sutlej 3(S3)) rivers, seven drains (Shahdara Drain(SD), Babu Sabu Drain(BSD), Hadiara Drain 1(HD1), Hadiara Drain 2(HD2), Madvana Drain(MD), Sukhrawa Drain(SW), Upper Chenab Canal(UCCD)) entering into Ravi river and two drains entering into Sutlej river (Rangewala/Pandoki Drain(RD), Chishtian Drain(CD)), and 7 groundwater sampling points along the Ravi River while 2 groundwater sampling points along the Sutlej River as shown in Fig. 1. In the Indus System in Punjab region, Pakistan, Ravi River is among the six rivers. Ravi River crosses northern India and eastern Pakistan and drains into the Indus River. The Ravi confluence with the Indus River that ultimately falls into the Arabian Sea. The total length of the Ravi River is 720 km that drain 14,442 square kilometers of the total catchment area in India. Ravi River originates from Himachal Pradesh. Among five rivers of Punjab, Ravi is the smallest one that rises from glacier fields at an elevation of 4.267 km on the southern side of the Mid Himalayas. It passes through districts of Bara Bansu, Barabhangal, and Chamba. In the initial reaches, the velocity currents in the river are fast enough which scatter the bed boulders. The Ravi river has a slope of 34.7 m/km flowing in a gorge and is mostly fed by snowmelt, as this region lies in a rain shadow. This trans-boundary river passes through the urban areas of Lahore. Reportedly the river has a very high level of pollution due to disposal of agricultural and industrial wastewater without any appropriate wastewater treatment. Sutlej River passes through China, India, and Pakistan. It is 1500 km long and drains 395,000 km<sup>2</sup> catchment area. The source of Sutlej river is Langqên Zangbo which is located in Tibet China and crosses Himachal Pradesh, Haryana, Rajasthan, and Punjab at the Indian side, enters Pakistan about 15 km east of Bhedian Kalan, Kasur District Punjab province, continuing southwest Bahawalpur princely state.

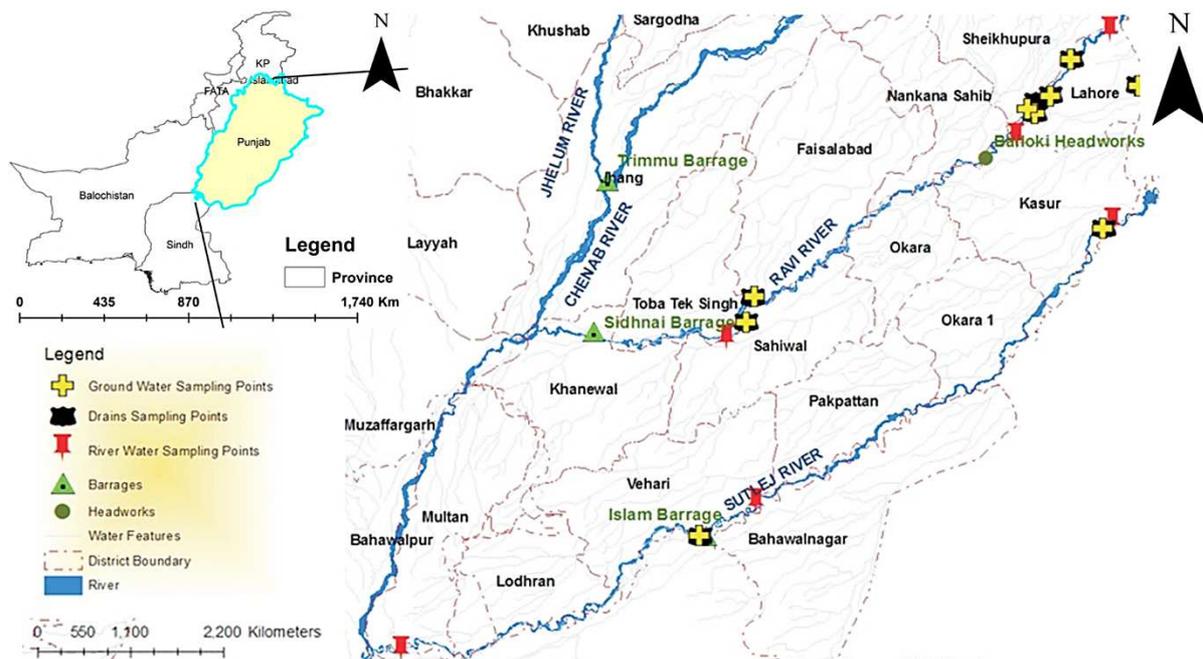


Fig. 1: Study area map showing water sampling points.

## 2.2 Data collection

Water quality data were collected from the Pakistan Council of Research in Water Resources (PCRWR)[11]. This study is based on 18 physicochemical and trace elements (Power of hydrogen (pH), Turbidity, Electrical conductivity (EC), Nitrates ( $\text{NO}_3^-$ ), Total dissolved solids (TDS), Chemical oxygen demand (COD), Biochemical oxygen demand (BOD), Dissolved oxygen (DO), Hardness, Total Nitrogen, Phosphorus ( $\text{PO}_4^{3-}$ ), copper (Cu), lead (Pb), Arsenic (As), Chromium (Cr), Manganese (Mn), Zinc (Zn), and Cadmium (Cd) from 24 water quality monitoring stations: 6 monitoring sites located along the Ravi and Sutlej rivers, 7 groundwater and 7 drains monitoring stations along the Ravi river as well as 2 groundwater and 2 drains monitoring sites along the Sutlej river. Water quality samples were regularly collected and tested in the PCRWR laboratory on a monthly basis from August 2015 to July 2016.

## 2.3 Statistical analysis

Correlation analysis, cluster analysis (CA), principal component analysis (PCA) and Box plot were used to assess relationship among water quality parameters, spatial homogeneity among water quality monitoring sites, data distribution patterns and water pollution source apportionment via dimension reduction respectively [12].

## 3 Health risk assessment

### 3.1 Non-carcinogenic risk assessment

It is well-founded knowledge that trace elements have adverse effects on human health [13]. Trace elements toxicity assessment is a prerequisite for determining appropriate management actions. U.S. Environmental Protection Agency (EPA) has suggested the application of hazard quotient (HQ) and hazard index (HI) for the aquatic risk evaluation [14]. For human beings, dermal absorption and direct ingestion (except inhalation via nose and mouth) are the two dominant exposure pathways of trace elements in water systems [15]. HI (summation of HQs of individual trace element) gauges the total possible non-carcinogenic risk on a human being health. HQ is the proportion of human exposure to trace element and reference dose (RfD). When the  $\text{HQ}/\text{HI} < 1$ , then no harmful risk exist; however, if  $\text{HQ}/\text{HI} \geq 1$ , then it causes non-carcinogenic risk/ adverse impacts on human health [16]. HI, and HQ is calculated by using Eqs. 1 to 5.

$$\text{ADD}_{\text{ingestion}} = (\text{C}_w \times \text{IR} \times \text{EF} \times \text{ED}) / (\text{BW} \times \text{AT}), \quad (1)$$

$$ADD_{\text{dermal}} = (C_W \times SA \times K_p \times ET \times EF \times ED \times 10^{-3}) / (BW \times AT), \quad (2)$$

$$HQ = ADD / RfD, \quad (3)$$

$$HQ = RfD \times ABS_{\text{GI}}, \quad (4)$$

$$HI = \sum HQ_s, \quad (5)$$

where:  $ADD_{\text{dermal}}$  and  $ADD_{\text{ingestion}}$  are dermal absorptions and average daily dose, respectively, shown as  $\mu\text{g}\cdot\text{kg}^{-1}\cdot\text{day}^{-1}$ ;  $C_W$  is an average trace elements concentration in the water sample ( $\mu\text{g}\cdot\text{L}^{-1}$ ); IR is ingestion rate (0.64 and 2  $\text{L}\cdot\text{day}^{-1}$  for children and adults, respectively); ED is the duration of exposure (6 and 30 years for children and adults, respectively); exposure frequency (EF) is (350 days/year); AT represents the average time ( $ED \times 365$  days/year); SA represents the time of exposed (6600 and 18,000  $\text{cm}^2$  square for children and adults, respectively); ET is the exposure time (1 and 0.58  $\text{h}\cdot\text{day}^{-1}$  for children and adults, respectively); RfD show the corresponding reference dose ( $\mu\text{g}\cdot\text{kg}^{-1}\cdot\text{day}^{-1}$ );  $K_p$  ( $\text{cm}\cdot\text{h}^{-1}$ ) is dermal permeability coefficient in the water; BW denotes the body weight (average) (70 kg for children and 15 kg for adults); and  $ABS_{\text{GI}}$  is gastrointestinal absorption factor (dimensionless) [17].

### 3.2 Carcinogenic risk assessment

Carcinogenic risk can be assessed using the below-mentioned equation. Detail computation procedure is illustrated in [17] was followed using Eq. 6.

$$\text{Carcinogenic risks} = \text{CSF} \times \text{ADD}, \quad (6)$$

where CSF = cancer slope factor. Carcinogenicity of chemicals in the grouping system of International Agency for Research on Cancer (IARC) and World Health Organization (WHO), the carcinogenic CSF value is 1500  $/(\mu\text{g}\cdot\text{kg}^{-1}\cdot\text{day}^{-1})$  [30]. According to U.S. EPA, the acceptable or acceptable limit of carcinogenic risks was  $10^{-6}$  to  $10^{-4}$ , [19] while in some European Union countries the control standards are  $1 \times 10^{-6}$  [18]. But the acceptable range of carcinogenic risks is different for different countries. The water samples were collected and analyzed using the American Public Health Association (APHA, 2012) standard methods.

## 4 Results and discussion

### 4.1 Statistical assessment

#### 4.1.1 Water quality data patterns

Spatial patterns were evaluated in surface water quality via box plot analysis as shown in Fig. 2 & Fig. 3. The concentration of pH, turbidity, TDS, and EC are high at R3 sampling site which is due to Sukhrawa drain carrying waste of Sahiwal, Okara entered at Kanyianlal point into Ravi. The concentration of COD and BOD is high as compared to the other water quality parameters at SD, BSD, HD1 and HD2 water sampling points which is due to sewage and industrial effluents. The concentration of DO is higher at R1 and S1 monitoring sites because both rivers make entry into Pakistan without having significant pollution load from Pakistan. The concentration of hardness,  $\text{NO}_3^-$ , total nitrogen and phosphorus are high at MD, RD, MD, and R3 sampling sites respectively which are primarily caused by municipal and industrial wastes, and agricultural fertilizers. The concentration of Cu, Pb, and Zn is high at station SD which is linked with industrial effluents of the plastic industry, leather industry and PVC, etc. The concentration of As and Cd is high at station RD which is attributed to industrial effluents of Kasur district. The elevated concentration of Cr at CD sampling point is attributed to the waste of district Bahawalpur. Mn concentration is higher in drains as compared to rivers.

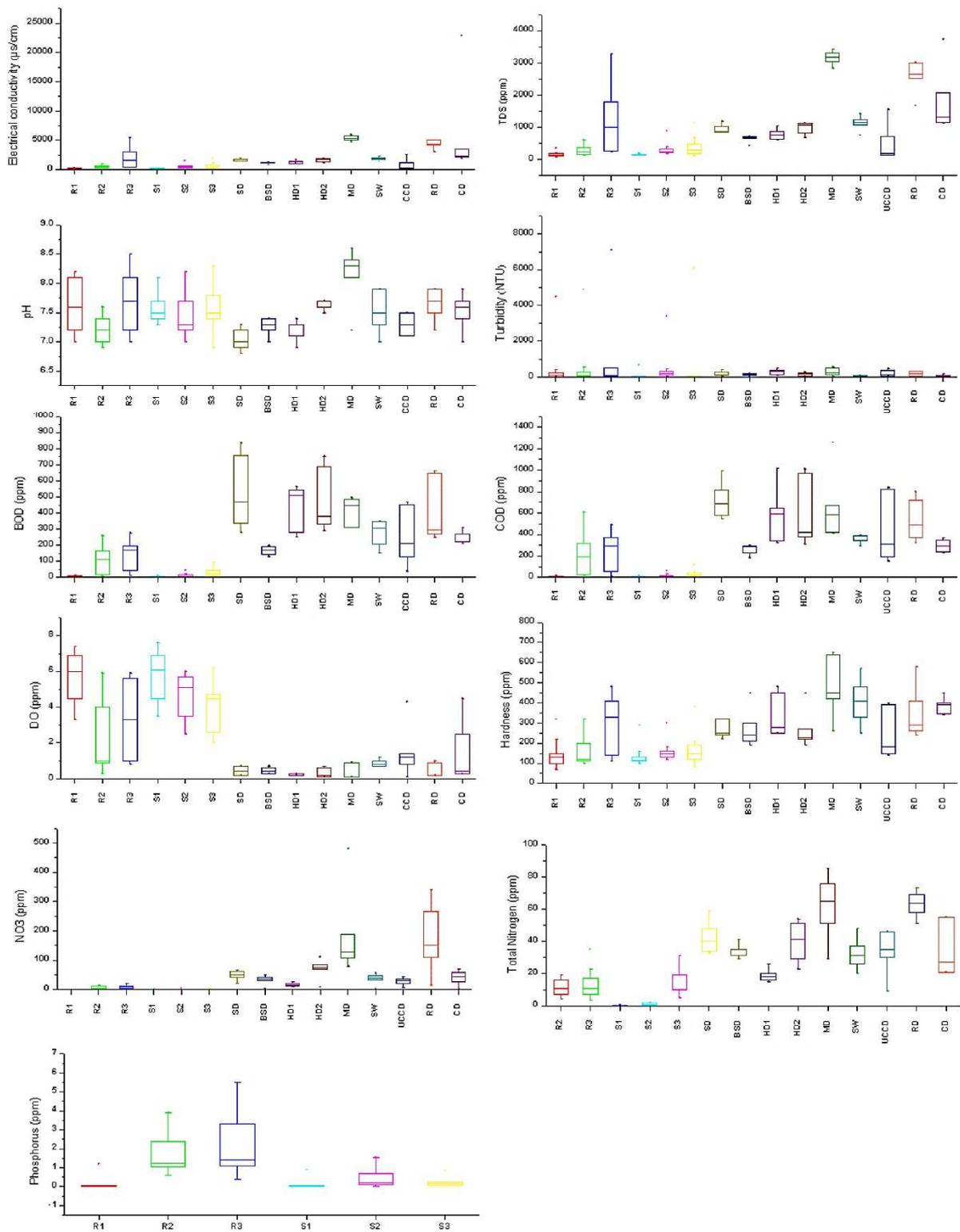


Fig. 2: Physicochemical observed values of each sampling sites.

#### 4.2 Generic relationships between water quality parameters

A correlation matrix is a suitable tool for the examination of associations between the water quality variables [19]. To expose the linkage between the 18 physicochemical parameters and trace elements, the correlation matrix was used, as demonstrated by Fig. 4. A strong positive correlation ( $p < 0.01$ ) having correlation coefficients range from 0.5-0.997 were noted between each pair of physicochemical parameters and trace elements, TDS, EC, NO<sub>3</sub><sup>-</sup>, hardness, BOD, COD, nitrogen,

PO<sub>4</sub><sup>3-</sup>, As, Cu, Cr, P b, Ni, and TSS. High correlations between EC and TDS (0.997), and between TDS and Hardness (0.865) were also obtained. It emphasized that trace elements and physicochemical parameters with strong relationships (high correlation) in the rivers and its tributaries could have alike hydrochemical features in the understudied area [19].

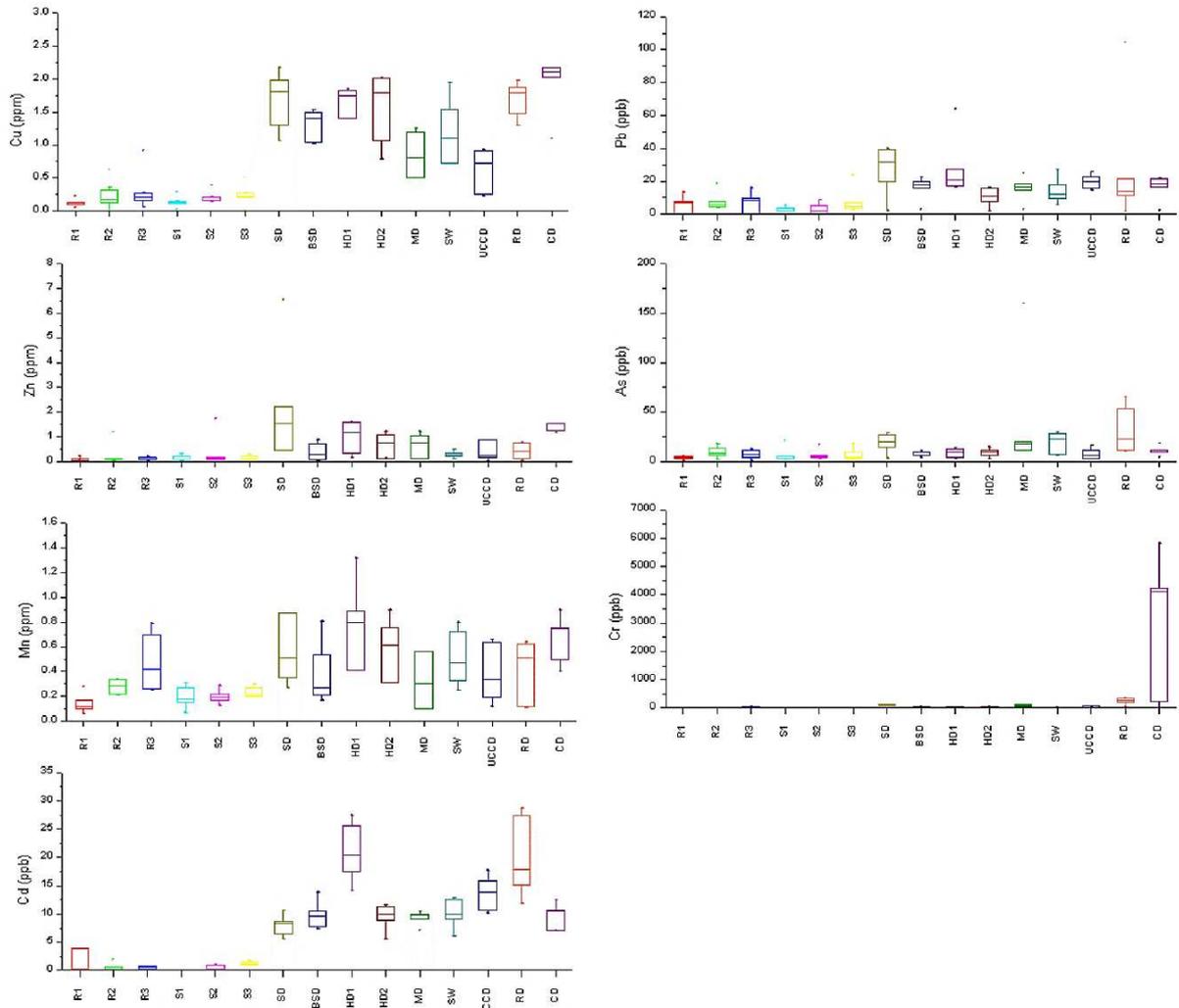


Fig. 3: Dissolved trace elements observed values of each sampling sites.



Fig. 4: Correlation matrix of trace elements and physicochemical parameters in surface waters.

### 4.3 Source apportionment

PCA was used for pollution source apportionment of both trace elements and physicochemical parameters by minimizing the data matrix to a few major components [13]. By applying factor analysis (FA) with varimax rotation method, the variables or factors with a minor contribution (lowest significance) attained by the PCA were reduced further. The Bartlett's sphericity test and Kaiser-Meyer-Olkin (KMO) was used to check the appropriateness of data for FA [1]. The significance of Bartlett's sphericity test and KMO is less than 0.001 [19]. The FA/PCA results, comprising the variance, commonalities, and eigenvalues are tabulated in Table 1. Eigenvalue presents the degree of the significance of factor; factor having the highest eigenvalues is most significant. A factor having an eigenvalue  $\geq 1$  is considered significant [21] as shown in Fig 5. In the current study, 6 independent principal components were extracted (eigenvalues  $> 1$ ) which accounts for 76.98 % cumulative variance. The factor loadings were divided into 3 classes based on absolute loading values; strong (greater than 0.75); moderate (0.75 to 0.50); and weak (0.50 to 0.30) [22]. The first principle component explains 24.4 % of the total variance, have strong positive loading of As (0.78), and Hardness (0.779); moderate positive loading of pH (0.73), TDS (0.523), and Nitrogen (0.554); and weak loading of  $\text{PO}_4^{3-}$  (0.493). The strong, moderate and weak positive loading of principal component 1 is attributed to intense anthropogenic activities i.e. industrial effluents (leather industry, plastic industry, and PVC, etc.) and, organic pollution from domestic and municipal waste [23]. The second principal component, responsible for 16.304 % of the total variance, also have the strong positive loading of  $\text{NO}_3^-$  (0.805); moderate loading of Nitrogen (0.718), Mn (-0.719), and B (-0.58); and weak loading of TDS (0.487),  $\text{PO}_4^{3-}$  (0.35), Pb (0.38), and TSS (0.326). Considering the strong, moderate and weak positive loading of principal component 2 probably suggests intense agricultural activities. Irrigation tailwater discharge fuels soil erosion and drains fertilizer to nearby water bodies [24]. High nitrogen and phosphorus concentration can cause eutrophication [25]. The third principal component which is responsible for 14.897 % of the total variance, have strong positive loading of Cr (0.897), and EC (0.846); moderate loading of TDS (0.622); and weak loading of Cu (0.447), B (0.464) and TSS (0.476). The strong positive loading of Cr is correlated with industrial waste [5]. Moderate positive loading of Cu and B is linked with coal combustion and industrial waste, respectively [26]. The fourth principal component which elucidates 9.57 % of the total variance, shows high loading of Cu (0.766); moderate loading of COD (0.607), BOD (0.682), Zn (0.661), and Ni (0.649); and weak loading of TSS (0.462). The presence of BOD, COD and trace elements indicate the concentration of untreated industrial effluents [49]. The fifth principal component, responsible for the total variance of 6.619 %, have high loading of Turbidity (0.809), and DO (-0.798); moderate loading of COD (0.503), and BOD (0.502); and weak loading  $\text{PO}_4^{3-}$  (0.311), Zn(0.463) and B(-0.491), showing the presence of trace elements from the coal combustion and industrial waste [26]. The presence of BOD, COD and trace elements indicate the concentration of untreated industrial effluents [27]. The moderate negative value of DO in this factor also described that utilization of large amounts of oxygen is due to the high concentration of dissolved organic matter, which experiences the anaerobic fermentation process that leads to the creation of ammonia and organic acids [15]. The sixth factor, accounting for the total variance 5.186 %, have a high loading of Cd (0.817); moderate loading of Pb (0.685), and Ni (0.526); and weak loading of TSS (-0.402). Cd contaminated water is attributed to anthropogenic activities i.e. untreated industrial effluents [28].

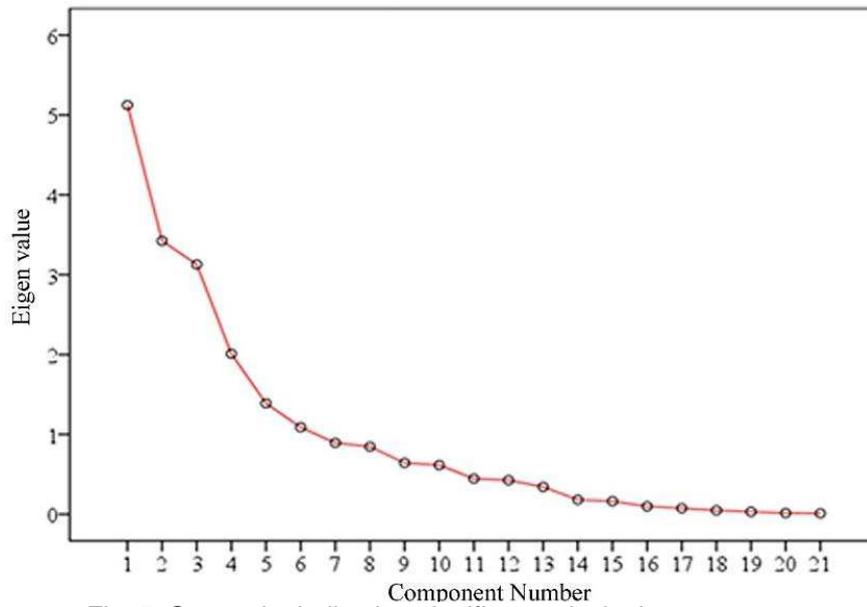


Fig. 5: Scree plot indicating significant principal components.

Table 1: Varimax rotated component matrix for physicochemical and trace elements of surface waters (the significance of Kaiser-Meyer-Olkin (KMO) and Bartlett's sphericity test is <0.001).

Eigen values	5.124	3.424	3.128	2.010	1.390	1.089	Communalities
Variance (%)	24.400	16.304	14.897	9.571	6.619	5.186	
Cumulative (%)	24.400	40.704	55.601	65.171	71.790	76.976	
Variable	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5	Factor 6	
pH	.730	.382	.156	-.039	-.009	-.230	.757
EC	.146	.163	.846	.042	.073	-.009	.772
TDS	.523	.487	.622	.097	.051	.111	.922
NO <sub>3</sub> <sup>-</sup>	.289	.805	.135	.003	.186	.171	.814
Turbidity	.135	.089	-.009	.233	.809	.021	.736
Hardness	.779	-.181	.225	.042	.104	.097	.712
COD	.201	-.006	-.217	.607	.503	.202	.749
BOD	.237	-.078	-.194	.682	.502	.236	.873
DO	-.114	-.005	-.113	-.062	-.798	-.260	.734
Nitrogen	.554	.718	-.122	.150	-.039	.035	.863
PO <sub>4</sub> <sup>3-</sup>	.493	.350	-.294	-.213	.311	-.142	.614
As	.781	.030	-.031	.078	.155	-.031	.643
Cu	-.052	-.093	.347	.766	-.004	-.021	.718
Zn	-.102	-.204	.290	.661	.463	-.144	.808
Mn	.219	-.719	-.032	.239	.147	.034	.645
Cr	-.063	-.224	.897	.059	-.075	-.037	.870
Cd	.088	-.122	.000	-.012	.297	.817	.779
Pb	-.274	.380	.048	.224	.035	.685	.741
Ni	-.047	.247	-.176	.649	.010	.526	.792
B	.036	-.580	.464	-.107	-.491	.028	.806
TSS	.284	.326	.476	.462	.171	-.402	.818

Extraction method: Principal component analysis; Rotation method: Varimax with Kaiser normalization

#### 4.4 Spatial pattern of water quality

The water samples groups can be differentiated by Hierarchical cluster analysis (CA) based on spatial variations in their chemical composition [15]. In this study, 15 monitoring sites were categorized into the 3 statistically significant clusters ( $(D_{link}/D_{max}) \times 100 < 25$ ); the cluster-1 (R1, R2, R3, S2 and S3); cluster-2 (BSD, HD1, SD, HD2, SW, UCCD, and S1); cluster-3 (MD and RD); and stand-alone (CD) as shown in Fig 6. Cluster-1 is mainly composed of water quality monitoring sites located on Ravi and Sutlej rivers except for S1. The remaining 2 clusters are composed of water sampling sites located on drains. Several reasons may be beyond this grouping pattern; the difference in point source pollution; the difference in nonpoint source pollution; the difference in discharge and difference in culture [29]. Tributary drains are highly polluted as compared to main rivers i.e. carry municipal and industrial wastes from various parts of Punjab province. Besides, discharge is lower in tributary drains as compared to the main rivers which cause lower dilution effects [29].

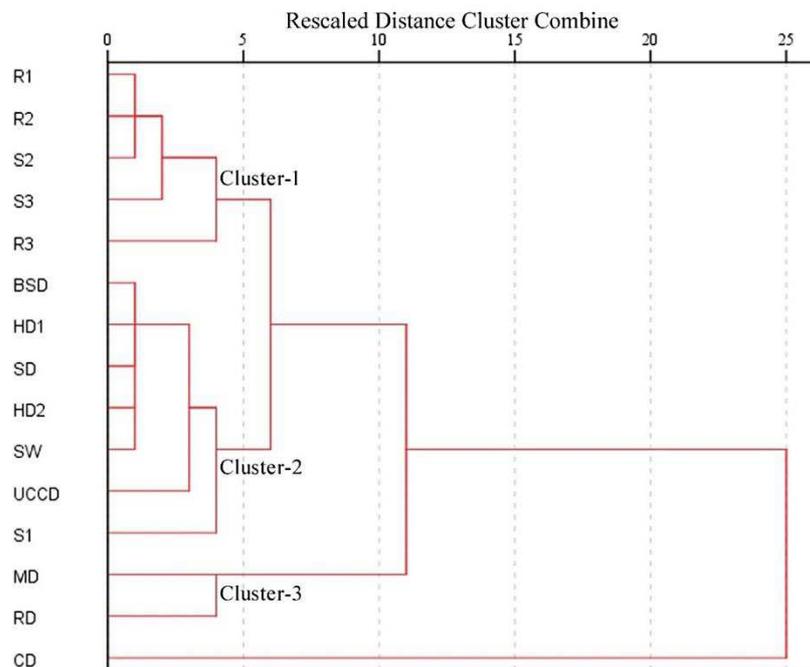


Fig. 6: Dendrogram showing homogeneity of monitoring points.

### 5 Risk assessment

#### 5.1 Human health risk assessment from surface water

Table 2 demonstrates the values of HQ and HI of trace elements for both adults and children by ingestion and dermal pathways. For both children and adults, the values of  $HQ_{ingestion}$  for Pb, Zn, and Cd were  $< 1$ , while for Cr and As, the values of  $HQ_{ingestion}$  are  $> 1$  which indicates possible non-carcinogenic apprehension by everyday oral consumption and unfavorable health impacts on the human body. For children & adults, the  $HQ_{dermal}$  values were  $< 1$ , shows that these elements, through dermal absorption, have no hazard. Comparatively, both  $Q_{ingestion}$  and  $Q_{dermal}$  values are higher for children than that of adults proposing that when expose to trace elements in water, children are more susceptible. The HI's for As and Cr for the adults and children were  $> 1$ . Hence, we presume that the major donors to chronic risks amongst the particular elements are As and Cr in these Rivers and drains. The assessment of carcinogenic risk (CR) of trace elements via ingestion and dermal interaction for the surface water is given in Table 3. The carcinogenic indices for the entire elements were exceeding the limit  $10^{-6}$  for both children and adults through both dermal and ingestion pathways. These illustrate that dermal and ingestion of surface water pose a carcinogenic risk for entire elements. But the children are more vulnerable as compared to adults in surface water.

Table 2: Dermal permeability coefficient, reference dose and hazard quotient for dissolved surface water trace metals.

Elements	Kp	RfD <sub>ingestion</sub>	RfD <sub>dermal</sub>	HQ <sub>ingestion</sub>		HQ <sub>dermal</sub>		HI	
				( $\mu\text{g/L}$ )	cm/hr	Adults	Children	Adults	Children
Pb	0.001	1.4	0.42	0.265	0.395	0.00000461	0.0000136	0.265	0.395
As	0.001	0.3	0.8	1.03	1.53	0.00000201	0.00000593	1.03	1.53
Cr	0.001	3	0.075	1.74	2.60	0.000363	0.00107	1.74	2.60
Zn	0.0006	300	60	0.0438	0.0655	0.000000686	0.00000203	0.0438	0.0655
Cd	0.001	0.5	0.025	0.474	0.708	0.0000495	0.000146	0.474	0.708

Table 3: The Carcinogenic risks of trace elements in surface waters.

Elements	Kp	CSF	ADD <sub>ingestion</sub>		ADD <sub>dermal</sub>		Carcinogenic Risk (Through ingestion)		Carcinogenic Risk (Through Dermal Absorption)	
			cm/hr	( $\mu\text{g/kg/day}$ )	Adults	Children	Adults	Children	Adults	Children
Pb	0.001	1500	0.371	0.554	0.00000193	0.00000571	556	830	0.00290	0.00856
As	0.001	1500	0.308	0.460	0.00000161	0.00000475	462	690	0.00241	0.00712
Cr	0.001	1500	5.22	7.79	0.0000272	0.0000804	7830	11700	0.0409	0.121
Zn	0.0006	1500	13.2	19.6	0.0000412	0.000122	19700	29500	0.0618	0.182
Cd	0.001	1500	0.237	0.354	0.00000124	0.00000365	355	531	0.00186	0.00547

## 5.2 Risk assessment of human health from ground waters

### 5.2.1 Non-carcinogenic risk

The HQ and HI values of trace elements through dermal and ingestion pathways for adults and children are presented in Table 4 & Table 5 both for the deep and shallow groundwater respectively. The HQ value  $> 1$ , non-carcinogenic effects might concern. For both children and adults, the HQ<sub>ingestion</sub> value for As, Mn, and Cu (for children only) was  $> 1$  in shallow groundwater and As, Fe and Mn (for children only) values in deep groundwater, which causes ill influence on human body and possible non-carcinogenic concern by everyday oral consumption, whereas values of HQ<sub>dermal</sub> for entire components both for children and adults in both sources of water are less than 1, representing that these components have no threat via dermal absorption in shallow and deep groundwater. Comparatively, both Q<sub>ingestion</sub> and Q<sub>dermal</sub> values are higher for children than that of adults proposing that children are susceptible more to exposure to trace elements in the water. Hazard index (HI) was established to assess the total carcinogenic and non-carcinogenic risks. The HI  $> 1$  indicates potential hazardous impacts on the health of human beings or the need for future research work [28]. From Table 4 the HI values of As, Mn (only for children) and Fe are  $> 1$  both for adults and children, whereas from Table 5 the HI values for As, Mn, and Cu (only for children) are  $> 1$ . Therefore, we conclude from the non-carcinogenic risk assessment that As, Mn, Fe, and Cu were the most important pollutant to chronic risks amongst the certain elements both in deep groundwater and shallow water.

Table 4: Dermal permeability coefficient, reference dose and hazard quotient for dissolved deep groundwater trace metals.

Elements	Kp	RfD <sub>ingestion</sub>	RfD <sub>dermal</sub>	HQ <sub>ingestion</sub>		HQ <sub>dermal</sub>		HI	
				( $\mu\text{g/L}$ )	cm/hr	( $\mu\text{g/kg/day}$ )	( $\mu\text{g/kg/day}$ )	Adults	Children
Cu	0.001	40	8	0.151	0.225	0.00000393	0.0000116	0.151	0.225
Pb	0.001	1.4	0.42	0.0994	0.148	0.00000173	0.00000510	0.0994	0.148
As	0.001	0.3	0.8	5.42	8.09	0.0000106	0.0000313	5.42	8.09
Mn	0.001	24	0.96	0.753	1.13	0.0000983	0.000290	0.754	1.13
Zn	0.006	300	60	0.0247	0.0368	0.000000386	0.00000114	0.0247	0.0368
Cd	0.001	0.5	0.025	0.0104	0.0155	0.00000109	0.00000321	0.0104	0.0156
Ni	0.0002	20	0.8	0.00673	0.01	0.000000351	0.000000518	0.00673	0.01
Fe	0.001	700	140	121	181	0.00210	0.00621	121	181

Table 5: Dermal permeability coefficient, reference dose and hazard quotient for dissolved shallow groundwater trace metals.

Elements	Kp	RfDingestion	RfDdermal	HQingestion		HQdermal		HI	
				( $\mu\text{g/L}$ )	cm/hr	( $\mu\text{g/kg/day}$ )	( $\mu\text{g/kg/day}$ )	Adults	Children
Cu	0.001	40	8	0.781	1.17	0.0000204	0.0000116	0.781	1.17
Pb	0.001	1.4	0.42	0.320	0.477	0.00000556	0.0000164	0.320	0.477
As	0.001	0.3	0.8	2.42	3.61	0.00000474	0.0000140	2.42	3.61
Mn	0.001	24	0.96	1.04	1.55	0.000136	0.0004	1.04	1.55
Zn	0.0006	300	60	0.0922	0.138	0.00000144	0.00000426	0.09.22	0.138
Cd	0.001	0.5	0.025	0.0433	0.0646	0.00000452	0.0000133	0.0433	0.0647
Ni	0.0002	20	0.8	0.00806	0.0120	0.0000000421	0.000000621	0.008.06	0.0120
Fe	0.001	700	140	0.00	0.00	0.00	0.00	0.00	0.00

## 6 Management and policy implications

The present study demonstrated that water pollution threatened human health. Water pollution is mainly caused by untreated industrial effluents, intense agricultural activities, and irrigation tailwater discharges. By controlling the aforementioned pollution sources stream health can be improved in the understudied area. Different activities alter water quality differently and the residents should concentrate on reducing pollutants caused by the aforementioned point and nonpoint pollution sources. Various preventive measures i.e. wastewater treatment plants and best management practices should be introduced to control pollution and protect human health. This study will be helpful in preparing a water pollution control plan in the study area.

## 7 Conclusion

The current study was carried out to apportion pollution sources and their impacts on human health. Cluster analysis distinguished 3 main classes where cluster-1 is mainly composed of monitoring sites located on Ravi and Sutlej rivers while the rest 2 clusters are composed of sampling sites located on tributary drains. A total of 6 important factors were identified by FA/PCA that accounted for 76.97 % of the total variance which is linked with multiple pollution emission sources i.e. municipal, industrial, agricultural and domestic. For all dissolved trace elements in surface waters, hazard quotients and health hazard indices by ingestion and dermal contact are  $< 1$  except As and Cr for both adults and children. For adults and children, the HQingestion and HI values for As, Mn, Cu (for children only) and As, Fe, Mn (for children only) are  $> 1$ , indicating that As, Mn, Fe, and Cu are the most important pollutant, among selected elements, to chronic risks in both shallow and deep groundwater respectively. The carcinogenic indices for the entire surface water elements exceed  $10^{-6}$  for both children and adults through both dermal and ingestion pathway suggesting carcinogenic health risk to the surrounding community. Hence, to protect human health, wastewater treatment plants and best management practices should be practiced to control point source and nonpoint source pollution respectively in the understudied area.

## References

- [1] ISLAM, M. S. - AHMED, M. K. - RAKNUZZAMAN, M. - HABIBULLAH-AL-MAMUN, M. - ISLAM, M. K.: Heavy metal pollution in surface water and sediment: a preliminary assessment of an urban river in a developing country. *Ecol. Indic.*, 48, 2015, pp. 282-291.
- [2] [https://www.researchgate.net/publication/265385526\\_Heavy\\_metal\\_pollution\\_in\\_surface\\_water\\_and\\_sediment\\_A\\_preliminary\\_assessment\\_of\\_an\\_urban\\_river\\_in\\_a\\_developing\\_country](https://www.researchgate.net/publication/265385526_Heavy_metal_pollution_in_surface_water_and_sediment_A_preliminary_assessment_of_an_urban_river_in_a_developing_country).
- [3] KUMAR, M. - RAMANATHAN, A. - TRIPATHI, R. - FARSWAN, S. - KUMAR, D. - BHATTACHARYA, P.: A study of trace element contamination using multivariate statistical techniques and health risk assessment in groundwater of Chhaprola Industrial Area, Gautam Buddha Nagar, Uttar Pradesh, India. *Chemosphere*, 166, 2017, pp. 135-145. <https://www.ncbi.nlm.nih.gov/pubmed/27693874>.
- [4] NAZEER, S. - HASHMI, M. Z. - MALIK, R. N.: Heavy metals distribution, risk assessment and water quality characterization by water quality index of the River Soan, Pakistan. *Ecol. Indic.*, 43, 2014, pp. 262-270. <http://agris.fao.org/agris-search/search.do?recordID=US201700161554>.
- [5] PEKEY, H. - KARAKAŞ, D. - BAKOGLU, M.: Source apportionment of trace metals in surface

- waters of a polluted stream using multivariate statistical analyses. *Mar. Pollut. Bull.*, 49(9-10), 2004, pp. 809-818. <http://europepmc.org/abstract/med/15530525>.
- [6] FARAHAT, E. - LINDERHOLM, H. W.: The effect of long-term wastewater irrigation on accumulation and transfer of heavy metals in *Cupressus sempervirens* leaves and adjacent soils. *Sci. Total Environ.*, 512, 2015, pp. 1-7. <https://www.ncbi.nlm.nih.gov/pubmed/25613764>.
- [7] XIAO, J. - JIN, Z. - WANG, J.: Geochemistry of trace elements and water quality assessment of natural water within the Tarim River Basin in the extreme arid region, NW China. *J. Geochem. Explor.*, 136, 2014, pp. 118-126. [https://www.researchgate.net/publication/259127824\\_eochemistry\\_of\\_trace\\_elements\\_and\\_water\\_quality\\_assessment\\_of\\_natural\\_water\\_within\\_the\\_Tarim\\_River\\_Basin\\_in\\_the\\_extreme\\_arid\\_region\\_NW\\_China](https://www.researchgate.net/publication/259127824_eochemistry_of_trace_elements_and_water_quality_assessment_of_natural_water_within_the_Tarim_River_Basin_in_the_extreme_arid_region_NW_China).
- [8] BRICKER, O. P. - JONES, B. F.: Main factors affecting the composition of natural waters. Trace elements in Natural Waters; Eds Salbu B.; Steinnes E, 1995, pp. 1-20. <https://www.crcpress.com/Trace-Elements-in-Natural-Waters/Salbu-Steinnes/p/book/9780849363047>.
- [9] Afed, U. K. - Jiang, J. - Wang, P.: Land use impacts on surface water quality by statistical approaches. *GJESM.*, 4(2), 2018, pp. 231-250. [https://www.gjesm.net/article\\_29934\\_308ed81e6c066f5e80a10020aa0b8012.pdf](https://www.gjesm.net/article_29934_308ed81e6c066f5e80a10020aa0b8012.pdf).
- [10] VEGA, M. - PARDO, R. - BARRADO, E. - DEBÁN, L.: Assessment of seasonal and polluting effects on the quality of river water by exploratory data analysis. *Water Res.*, 32(12), 1998, pp. 3581-3592. <https://www.sciencedirect.com/science/article/pii/S0043135498001389>.
- [11] DIXON, W. - CHISWELL, B.: Review of aquatic monitoring program design. *Water Res.*, 30(9), 1996, pp. 1935-1948. [http://www.scirp.org/\(S\(czeh2tfqyw2orz553k1w0r45\)\)/reference/ReferenesPapers.aspx?ReferenceID=1425391](http://www.scirp.org/(S(czeh2tfqyw2orz553k1w0r45))/reference/ReferenesPapers.aspx?ReferenceID=1425391).
- [12] IMRAN, S. - BUKHARI, L. N. - ASHRAF, M.: Spatial and Temporal Trends in River Water Quality of Pakistan (Sutlej and Ravi 2018). *PCRWR*, 83 p. [http://www.pcrwr.gov.pk/Publications/Water%20Quality%20Reports/CISRO%20Report\\_Final.pdf](http://www.pcrwr.gov.pk/Publications/Water%20Quality%20Reports/CISRO%20Report_Final.pdf).
- [13] KHOOND, N. J. - BHATTACHARYYA, K. G.: Multivariate statistical evaluation of heavy metals in the surface water sources of Jia Bharali river basin, North Brahmaputra plain, India. *Appl. Water Sci.*, 7(5), 2017, pp. 2577-2586. <https://link.springer.com/article/10.1007/s13201-016-0453-9>.
- [14] JUNG, K. Y. - LEE, K. L. - IM, T. H. - LEE, I. J. - KIM, S. - HAN, K. Y. - AHN, J. M.: Evaluation of water quality for the Nakdong River watershed using multivariate analysis. *Environ. Technol. Innovation*, 5, 2016, pp. 67-82. <https://www.ncbi.nlm.nih.gov/pmc/articles/PMC6209875/>.
- [15] WU, B. - ZHAO, D. - JIA, H. - ZHANG, Y. - ZHANG, X. - CHENG, S.: Preliminary risk assessment of trace metal pollution in surface water from Yangtze River in Nanjing Section, China. *Bull. Environ. Contam. Toxicol.*, 82(4), 2009, pp. 405-409. <https://link.springer.com/article/10.1007/s00128-009-9673-0>.
- [16] LEMLY, A. D.: Evaluation of the hazard quotient method for risk assessment of selenium. *Ecot. Environ. Saf.*, 35(2), 1996, pp. 156-162. <https://www.sciencedirect.com/science/article/pii/S0147651396900950>.
- [17] LI, S. - ZHANG, Q.: Risk assessment and seasonal variations of dissolved trace elements and heavy metals in the Upper Han River, China. *J. Hazard. Mater.*, 181(1-3), 2010, pp. 1051-1058. (18 pages). <https://www.ncbi.nlm.nih.gov/pubmed/20638969>.
- [18] TRIPATHEE, L. - KANG, S. - SHARMA, C. M. - RUPAKHETI, D. - PAUDYAL, R. - HUANG, J. - SILLANPÄÄ, M.: Preliminary health risk assessment of potentially toxic metals in surface water of the Himalayan Rivers, Nepal. *Bull. Environ. Contam. Toxicol.*, 97(6), 2016, pp. 855-862. [https://www.researchgate.net/publication/309032878\\_Preliminary\\_Health\\_Risk\\_Assessment\\_of\\_Potentially\\_Toxic\\_Metals\\_in\\_Surface\\_Water\\_of\\_the\\_Himalayan\\_Rivers\\_Nepal](https://www.researchgate.net/publication/309032878_Preliminary_Health_Risk_Assessment_of_Potentially_Toxic_Metals_in_Surface_Water_of_the_Himalayan_Rivers_Nepal).
- [19] DE MIGUEL, E. - IRIBARREN, I. - CHACON, E. - ORDONEZ, A. - CHARLESWORTH, S.: Risk-based evaluation of the exposure of children to trace elements in playgrounds in Madrid (Spain). *Chemosphere*, 66(3), 2007, pp. 505-513. <https://www.ncbi.nlm.nih.gov/pubmed/16844191>.
- [20] TIAN, Y. - YU, C. - ZHA, X. - WU, J. - GAO, X. - FENG, C. - LUO, K.: Distribution and potential health risks of arsenic, selenium, and fluorine in natural waters in Tibet, China. *Water*, 8(12), 568, 2016, pp. 1-16. <https://www.mdpi.com/2073-4441/8/12/568/htm>.
- [21] CHEN, K. - JIAO, J. J. - HUANG, J. - HUANG, R.: Multivariate statistical evaluation of trace elements in groundwater in a coastal area in Shenzhen, China. *Environ. Pollut.*, 147(3), 2007, pp. 771-780. <https://www.ncbi.nlm.nih.gov/pubmed/17134805>.
- [22] WANG, J. - LIU, G. - LIU, H. - LAM, P. K.: Multivariate statistical evaluation of dissolved trace elements and a water quality assessment in the middle reaches of Huaihe River, Anhui, China. *Sci. Total Environ.*, 583, 2017, pp. 421-431. <https://www.ncbi.nlm.nih.gov/pubmed/28126280>.
- [23] KIM, J.O. - MULLER, C.: Introduction to Factor Analysis: What It Is and How To Do It, Series:

- Quantitative Applications in the Social Sciences. Beverly Hills, CA, Sage, 1978, 80 p. <https://www.amazon.com/Introduction-Factor-Analysis-Quantitative-Applications/dp/0803911653>.
- [24] GAO, L. - WANG, Z. - SHAN, J. - CHEN, J. - TANG, C. - YI, M. - ZHAO, X.: Distribution characteristics and sources of trace metals in sediment cores from a trans-boundary watercourse: An example from the Shima River, Pearl River Delta. *Ecotox Environ Safe*, 134, 2016, pp. 186-195. <https://www.ncbi.nlm.nih.gov/pubmed/27622601>.
- [25] SHRESTHA, S. - KAZAMA, F.: Assessment of surface water quality using multivariate statistical techniques: A case study of the Fuji river basin, Japan. *Environ. Model. & Soft.*, 22(4), 2007, pp. 464-475. [https://www.researchgate.net/publication/222422396\\_Assessment\\_of\\_Surface\\_Water\\_Quality\\_Using\\_Multivariate\\_Statistical\\_Techniques\\_A\\_Case\\_Study\\_of\\_the\\_Fuji\\_River\\_Basin\\_Japan](https://www.researchgate.net/publication/222422396_Assessment_of_Surface_Water_Quality_Using_Multivariate_Statistical_Techniques_A_Case_Study_of_the_Fuji_River_Basin_Japan).
- [26] KHAN, A. U. - JIANG, J. - WANG, P. - ZHENG, Y.: Influence of watershed topographic and socio-economic attributes on the climate sensitivity of global river water quality. *Environ. Res. Lett.*, 12(10), 104012, 2017, 10 p. [https://www.researchgate.net/publication/319492310\\_Influences\\_of\\_topographic\\_and\\_socio-economic\\_attributes\\_on\\_the\\_climate\\_sensitivity\\_of\\_global\\_river\\_water\\_quality](https://www.researchgate.net/publication/319492310_Influences_of_topographic_and_socio-economic_attributes_on_the_climate_sensitivity_of_global_river_water_quality).
- [27] ASHRAF, M. - KHAN, M.: Sustainable environment management: impact of agriculture. *Sci. Tech. and Devel.*, 19(4), 2000, pp. 51-57. <http://www.uaf.edu.pk/EmployeeDetail.aspx?userid=607>.
- [28] TANG, Q. - LIU, G. - ZHOU, C. - SUN, R.: Distribution of trace elements in feed coal and combustion residues from two coal-fired power plants at Huainan, Anhui, China. *Fuel*, 107, 2013, pp. 315-322. [https://www.researchgate.net/publication/235935238\\_Distribution\\_of\\_trace\\_elements\\_in\\_feed\\_coal\\_and\\_combustion\\_residues\\_from\\_two\\_coal-fired\\_power\\_plants\\_at\\_Huainan\\_Anhui\\_China](https://www.researchgate.net/publication/235935238_Distribution_of_trace_elements_in_feed_coal_and_combustion_residues_from_two_coal-fired_power_plants_at_Huainan_Anhui_China).
- [29] AFZAL, S. - AHMAD, I. - YOUNAS, M. - ZAHID, M. D. - KHAN, M. A. - IJAZ, A. - ALI, K.: Study of water quality of Hudaira drain, India-Pakistan. *Environ. Int.*, 26(1-2), 2000, pp. 87-96. <https://www.ncbi.nlm.nih.gov/pubmed/11345744>.
- [30] OBIRI, S.: Determination of heavy metals in water from boreholes in Dumasi in the Wassa West District of western region of Republic of Ghana. *Environ. Monit. Assess.*, 130(1-3), 2007, pp. 455-463. <https://link.springer.com/article/10.1007/s10661-006-9435-y>.
- [31] ASARE-DONKOR, N. K. - KWAANSA-ANSAH, E. E. - OPOKU, F. - ADIMADO, A. A.: Concentrations, hydrochemistry and risk evaluation of selected heavy metals along the Jimi River and its tributaries at Obuasi a mining enclave in Ghana. *Environ. Syst. Res.*, 4(1), 2015, pp. 1-9. <https://link.springer.com/article/10.1186/s40068-015-0037-y>.