# Hydrochemical Characteristics of Groundwater for Drinking Purpose and Health Risk Assessment

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# Abstract

21 Urbanization and industrialization in many parts of the world contaminate ground and surface 22 water resources. The present study is designed to investigate the hydrochemical characteristics, spatial distribution of major cations/anions, heavy metal pollution and associated health risk 23 assessment of groundwater. In total 30 groundwater samples were taken from different urban 24 localities of Multan, suggesting an elevated level of EC and TDS. Major cations and anions 25 except SO<sub>4</sub><sup>2-</sup> and HCO<sub>3</sub><sup>-</sup> in one area were below World Health Organization (WHO) guidelines 26 for drinking purpose. Hydrochemical results also indicates groundwater pollution is attributed to 27 28 rock-water interaction. Medium to low microbial concentration was also noted in groundwater by seepage of sewage water. Elevated heavy metal concentration (As, Cd, Cr & Fe) was recorded 29 30 in most of the sampled groundwater. Piper plot indicates mixed water type with  $Na^+/K^+$  and Na<sup>+</sup>/HCO<sub>3</sub><sup>-</sup> type. Water Quality Index (WQI) and Heavy metal Pollution Index (HPI) ranked 31

groundwater of Multan from very poor to hazardous posing health hazards. Total hazard quotient 32 value by ingesting groundwater exceeds non-carcinogenic threshold HO = 1.0 in half of 33 groundwater samples. Potential cancer risk was obtained for children in selected areas. 34 Therefore, an effective management and monitoring system is applied in study area to safeguard 35 the local community from potential illness. Major response action require to restore groundwater 36 quality is to cut off contamination sources such as industrial effluents, fertilizers and pesticides 37 application. Installing water treatment plants in study area to reduce cancer risk for local 38 community is an effective and tangible solution. 39

40 Key words: Hydrochemical, Water quality, Heavy metals, Non-carcinogenic, Cancer risk

#### 41 Introduction

Water is fundamental compound essential to living organisms (Al-Rashed, 2024, 2025). Only 42 3% fresh water is available of which 67% is stored in glaciers, 30% in ground and 3% on surface 43 44 (Ofosu et al. 2021; Hosseininia and Hassanzadeh, 2023). Groundwater is an important resource as one third population around the globe rely on it for drinking, domestic and irrigation purposes 45 (Piyathilake et al., 2022). Only in South Asia around one billion people rely on groundwater to 46 fulfill basic necessities (Adimalla et al. 2018). For decades, demand of fresh water resource is 47 increasing for drinking purpose which otherwise polluted due to industrial effluents and sewage 48 water. Therefore, groundwater quality is of great importance as is easy to pull up and access 49 contamination (Adimalla et al. 2018a). Various researchers extensively investigated the 50 groundwater quality for human consumption, domestic and irrigation purposes. Adimalla, (2019) 51 did an extensive study in groundwater of South India with arid to semi-arid conditions and 52 reported the potential health concern related to drinking poor quality of groundwater. Similarly, 53 Ayadi et al. (2018) investigate the groundwater of Tunisia and found that weathering of rocks 54 influence groundwater quality. 55

Presence of heavy metals in groundwater poses significant environmental concern. Toxic nature of heavy metal, persistence in the environment made them suitable candidate to persist in living organisms for years which poses health risk including skeletal, cardiovascular and infertility (Ali et al. 2023). Limited movement of water within the ground aquifer made the situation even worse and groundwater become contaminated over the period of time. Nitrate, fluoride, chloride and iron are also widely accepted ions which contaminate the groundwater with potential to risk
public health in Southern Punjab (Iqbal et al. 2023).

Public health standard for a community largely relies on availability of pure drinking water. Potable groundwater is safe to drink without any health related concerns (Hossain et al. 2024). Safe groundwater for drinking purpose is scarce in developing countries like Pakistan which might be responsible for lot of diseases. Drinking contaminate water in developing countries is accountable for more than 80% of water borne diseases which ultimately leads to death (Xiao et al. 2022). Quality of groundwater is important for public health as ingesting tainted water could causes serious illness due to transmission of diseases throughout the world.

Groundwater contamination poses various health related challenges in various areas of Punjab, 70 Pakistan. Toxic metals persistence in poorly urbanize and industrial cities of Punjab is of serious 71 72 health concern according to the surveys and findings of Pakistan Council for Research in Water Resources (PCRWR). Previous research also provides preliminary estimates of groundwater 73 quality in different areas of Punjab however water characterization associated with different 74 factors to influence water quality has not been fully investigated. Under such prevailing 75 conditions this study is designed with an aim to evaluate groundwater quality of Multan city for 76 drinking purpose with predication of water quality index (WQI) and health risk assessment. 77 Results from this study give essential insights for quality of groundwater quality with special 78 reference to health risk in study area. 79

# 80 Material and method

## 81 Study area

Multan city (30.1864° N 71.4886° E) with an area of 3721 km<sup>2</sup>, home to 2.2 million people is the 82 6<sup>th</sup> largest city of Pakistan. It is an ancient city along Chenab river in Southern Punjab with arid 83 to semi-arid climatic conditions. Groundwater aquifer of Multan is not recharge for years as 84 85 water is not flown except for the monsoon season where river flow is considerably high. Mean annual rainfall is between 175 and 86 mm is less enough to recharge groundwater aquifers 86 87 therefore groundwater aquifers are present at the depth 25 and 40 meters. Although soil is sandy loam in nature but less rainfall doesn't recharge groundwater aquifers. Sediments of salt 88 89 containing rocks were deposited in the alluvial plans of Multan by Chenab river for thousands of

years ago therefore groundwater hydrological characteristics were largely depends upon 90 geological changes. Mean annual temperature is 25.6 °C. Therefore groundwater quality is poor 91 for safe water consumption. Since Multan city is an urban area surrounded by industries 92 therefore it is important to assess the health risk in terms of carcinogenic and cancer risk which 93 haven't been done in recent past. Current work is novel in its type that it comprises water quality 94 indices along with health risk assessment whereas pervious researcher only focuses on the 95 groundwater quality with special reference to calculate salts, cations and anions as limiting 96 factor. Moreover previous research were designed to only assess arsenic which is in abundant in 97 the area with limited scope i.e., in city center or in a school while current work established a way 98 by assessing other heavy metals including cadmium, chromium and iron not in city but also in 99 city suburban's (Gul et al. 2020; Mahar et al. 2024). 100

#### 101 Groundwater sampling

Thirty groundwater samples were collected from six different locations (Five samples from each 102 area) on the basis of population density and water consumption of Multan city. Water sample 103 was taken in a pattern that each sampling point is in the range of 500 meters in specific 104 coordinates. Borehole electric pump with the depth between 25 and 40 meters was running for 5 105 minutes prior to sampling for homogeneity. Groundwater temperature, pH and electrical 106 conductivity were recorded at the time of sampling. 1 liter groundwater sample was stored in 107 108 pre-sterilized polythene container to assess the physicochemical properties, heavy metal and pathogenic microbial concentration. Coordinates of the water sampling site was also recorded at 109 the time of sampling by using Global Positioning System (GPS) is shown in figure 1. 110

# 111 Groundwater quality assessment

Groundwater samples collected from different locations of Multan were analyzed for temperature from mercury thermometer, pH is noted by dipping glass electrode pH meter in water sample (Model: Mi-1700), Electrical conductivity of water sample was noted by dipping pre-calibrated EC meter (3100C) with KCL solution. Total dissolved solids (TDS) in the solution was determined by using following equation

(1)

117  $TDS = EC dS cm^{-1} \times 650$ 

Groundwater hardness was determined in terms of calcium carbonates by forming complexes 118 with calcium and magnesium ions through EDTA titration method. Calcium and magnesium was 119 120 determined by treated with buffer solution and erichorme black until color changes from red to blue end point. Sodium and potassium was noted by flame photometer (Model: BWB 121 technologies) by adapting standard protocol used for waste water evaluation (Rice et al. 2012). 122 HCO<sub>3</sub> was determined by titrimetric method by adding few drops of methyl orange indicator and 123 titrated against 0.1 N H<sub>2</sub>SO<sub>4</sub> while chloride ion concentration is noted by adding potassium 124 chromate solution into water sample and titrated against 0.05 N AgNO<sub>3</sub> solution. NO<sub>3</sub><sup>-</sup> is noted 125 by cadmium reduction method and running the sample on UV-vis spectrophotometer at 540 nm. 126 Similarly, F<sup>-</sup> is also noted by colorimetric method by mixing SPADNS regent with water sample 127 and subsequently run it on spectrophotometer (Model: CE7400S) at 570 nm. All physic-128 chemical parameters were done according to the protocol by American Public Health 129 Association (APHA) (Greenberg et al. 2005). Microbial concentration in water sample was 130 determined by filtering 100 ml of water through membrane having mesh size of 0.45 µm and 131 subsequently incubate on selective media for 48 hrs at 37° C. Pathogenic bacterial colonies were 132 counted by colony counter and expressed as colony per 100 ml of water (Forbes et al. 2007). 133 Water quality index from the selected site was determined by computing parameters into 134 135 equation;

136 
$$WOI = \sum_{i=1}^{n} Oi$$
 (2)

Where; n is the number of samples, i is parameter range and Qi is relative measure of waterspecific to each parameter.

All groundwater samples were analyzed for heavy metals. Among all arsenic was determined by 139 molybdenum blue method as As (V) which reacts with ammonium molybdate under acidic 140 141 condition to form arsenomolybdic acid. Thereafter, this complex was turned into molybdenum blue complex which then run into UV-vis spectrophotometer at 870 nm. Cd, Cr & Fe were 142 143 detected in groundwater samples after digesting it in HNO<sub>3</sub> in digestion tubes until the sample become colorless and run it in Atomic Absorption Spectrophotometer (ASS) (Model: Shimadzu 144 145 7000F) at wavelength of 228 nm, 357 nm and 248 nm, respectively. Heavy metal pollution index 146 (HPI) was calculated by using following formula;

147 
$$HPI = \frac{\sum_{i=1}^{n} WiQi}{\sum_{i=1}^{n} Wi}$$
(3)

Where; n is the number of samples to be analyzed, Qi is sub-index of ith parameter and Wi is ithunit parameter weight. Qi for HPI was calculated by using following equation;

150 
$$Qi = \sum_{i=1}^{n} \frac{Mi - li}{Si - li} \times 100$$
 (4)

Where; Mi is the concentration of ith metal, li is the ideal value and Si is the maximum value of ith metal.

#### 153 Health risk assessment

Drinking poor/contaminated water for long time significantly affect human health by causing different diseases. Non-carcinogenic risk from ingesting contaminated drinking water is calculated by following formula;

157 Intake<sub>Oral</sub> = 
$$\frac{C \times IR \times EF \times ED}{BW \times AT}$$
 (5)

(6)

158 
$$HQ_{Oral} = \frac{Intake_{Oral}}{RfD_{Oral}}$$

159 Inputs are;

- 160 Intake <sub>Oral</sub> is daily intake of contaminant (mg/kg/day<sup>-1</sup>)
- 161 C is pollutant concentration (mg/L)
- 162 IR is daily ingestion rate of water (1.5 L/day for adult and 0.52 L/day for child)
- 163 EF is exposure frequency (365 day/year)
- 164 ED is exposure duration (year); in current study 60 years for adult and 6 years for child
- according to USEPA (1989, Washington, USA)
- 166 BW is average weight (60 kg for an adult and 15 kg for child)
- 167 AT is average exposure time (ED $\times$ 365)

168 HQ is Hazard Quotient, RfD <sub>Oral</sub> is reference dose of contaminant (mg/kg/day<sup>-1</sup>). RfD <sub>Oral</sub> for As,

(7)

- 169 Cd and Cr are 0.0003, 0.0005 and 0.003 mg kg<sup>-1</sup> day<sup>-1</sup>.
- 170 Life time cancer risk (CR) assessment was calculated according to the equation;
- 171 Cancer risk<sub>Oral</sub> = Intake<sub>Oral</sub>  $\times$  SF
- 172 SF is cancer slope factor for As is 1.5 and for Cr is 0.5 according to USEPA (1989).

## 173 Results

# 174 Physiochemical properties of groundwater samples

Table 1 exhibit physiochemical properties of groundwater samples collected from different 175 locations of Multan city. pH, electrical conductivity and total dissolved solids are the basic 176 parameters to identify the groundwater property and their concentration for drinking purpose 177 strictly within the limits set by World Health Organization (WHO). pH in drinking water must be 178 6.5-8.5, EC <400  $\mu$ S cm<sup>-1</sup> and TDS <1000 mg L<sup>-1</sup>. pH form selected sites were within limits with 179 highest value of 7.76. EC ranges between 1493-2558 µS cm<sup>-1</sup> and TDS is 1206 mg L<sup>-1</sup> to 2501 180 mg L<sup>-1</sup>. 33% sample were above 2000  $\mu$ S cm<sup>-1</sup> while remaining sample were within the range of 181 1493 µS cm<sup>-1</sup> and 2000 µS cm<sup>-1</sup>. Similar trend was noted for TDS where also 33% samples 182 exceed 2000 mg L<sup>-1</sup> limit while other exhibit moderate to high TDS concentration. However, 183 water from all sampling sites is unfit for drinking purpose according to WHO limits. Hardness of 184 water samples were also within in the range of 306-543 mg L<sup>-1</sup> having water samples only from 185 one site exceeds WHO limits (500 mg L). 186

Major cations (Na<sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup> & K<sup>+</sup>) and anions (HCO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup> & F<sup>-</sup>) were also calculated given in table 2. All parameters in sampled water were under recommended range as per WHO except  $HCO_3^{-}$ , which concentration in one sample exceeds which suggest its unsuitability for drinking purpose. Mixed concentration of cations and anions were widely distributed in selected area and is not coupled to any single pollution causing source.

192 Total coliform and E. coli in groundwater sample was recorded from lower to medium range 193 usually brought about by seepage of sewage water into ground aquifers. Increased Colony Forming Unit (CFU) might cause disease however according to WHO zero CFU was present inwater used for drinking purpose.

As, Cd, Cr and Fe are heavy metal found in groundwater sample indicating its origin from industries. Since heavy metal in groundwater is in large concentration therefore its consumption for long time is lethal to public health. Arsenic usually derived into water through increased Al and Mo after increased pH therefore its anthropogenic origin in groundwater is not neglected.

#### 200 Major water type in groundwater aquifers of Multan

Major water type in sampling site is sodium/potassium and sodium/bicarbonate type as given in piper plot (Figure 2). Among cations dominant one is Na<sup>+</sup> while other were in the sequence of K<sup>+</sup>  $> Ca^{2+} > Mg^{2+}$ . Among anions dominant is  $HCO_3^-$  with sequence of remaining anion is  $Cl^- >$  $SO_4^{2-} > CO_3^-$ . Samples in diamond and lower triangle exhibit mixed water type originate from single aquifer. All cations and anions were evenly distributed with no dominant water type.

## 206 Water Quality Index (WQI)

Water quality index is complete set of water quality indices to estimate for drinking suitability by using physiochemical and heavy metal. Water quality index is scaled from 0-100 where 0-25 is good groundwater quality, 26-50 is good, 51-75 is poor, 76 to and 100 is hazardous. Results suggest that all samples exceed hazardous limit (100%) making water harmful to consume (Figure 3).

# 212 Heavy Metal Pollution Index (HPI)

Similar to WQI, heavy metal pollution index describe the groundwater contamination due to overall concentration of metal (As, Cd, Cr & Fe) (Figure 4). HPI is also divided in different categories < 25 excellent, 26-50 good, 51-75 poor, 76-100 very poor and >100 is hazardous. Case study explains that HPI of all water samples were hazardous which upon drinking causes serious health hazards. Almost 50% groundwater samples exhibit increasing trend in heavy metal which mentions its anthropogenic origin from industries.

# 219 Principle Component Analysis (PCA)

A score plot was generated by using Principle Component Analysis (PCA) between two factors 220 (PC1: 29.92%) and (PC2: 24.84%) as depicted in figure 5. PC1 & PC2 together exhibit variance of 221 222 54.76% having significant portion of variability. Shershah town and Shraif Pura in upper quadrant have highest EC, TDS, nitrates and hardness suggested that groundwater is mineralized 223 by high level of pollutants. Suraj Miani and Tariq Abad in lower quadrant exhibit increase 224 bicarbonate, Chromium, Arsenic and sulphate which suggests its less association with variables 225 of PC1 and PC2. Liaqat Abad and Basti Baghbanpura are clustered in the center of score plot 226 indicating average value of measured parameters. Na, Cd, F and coliform is associated to middle 227 of score plot indicating its influence to middle centered clusters. PCA score plot also indicate 228 that Shershah town and Suraj Miani is less prevalent to overall distributed parameters. 229

## 230 Person correlation matrix for groundwater samples

A person correlation matrix for physicochemical, microbial and heavy metals characteristics of 231 collected groundwater from Multan is given in table 2. Positive correlation is determined 232 between number of parameters in water samples like pH and  $Mg^{2+}$  (r = 0.81), EC and TDS (r = 233 0.86), EC and hardness (r = 0.74), TDS and hardness (r = 0.80), hardness and NO<sub>3<sup>-</sup></sub> (r = 0.61), 234  $HCO_3^-$  and  $Mg^{2+}/As$  (r = 0.66), Cl<sup>-</sup> and  $NO_3^-$  (r = 0.69), Na<sup>+</sup> and Cd (r = 0.68), As and Fe (r = 235 0.91). Matrix indicates type of correlation among water parameters and potential contaminants. 236 Person correlation is important in sampling, analyzing and ranking groundwater quality to carry 237 238 out sustainable management measures.

# 239 Human health risk assessment

## 240 Non-carcinogenic risk

Tables 3 (CDI) and 4 (HQ) encompasses the non-carcinogenic risk of heavy metal through oral exposure of two population groups i.e., adult and children. Calculated CDI for ingestion in adult and children is in the following order Cd > Cr > Fe > As. Hazard Quotient was noted by calculating exposure risk to reference dose. HQ <1 is regarded as non-carcinogenic while >1 is carcinogenic in terms of environmental and toxicological risk analysis. Mean HQ for adult and children is found in following order As > Cd > Cr > Fe. HQ suggests that all heavy metals are potential risk to health in study area especially for children.

#### 248 Cancer risk

Cancer risk for arsenic and chromium through ingestion is given in table 5. WHO recommends safe limit of cancer risk is 1 in 1,000,000 lifetimes. Across all sites, Sharif Pura exhibit highest arsenic/chromium level making it most at risk location in terms of potential cancer development by ingesting groundwater. Both age groups have potential cancer risk but children with higher ingestion intake to body ratio made it vulnerable to toxins during body development.

## 254 Discussion

Poor groundwater quality significantly hinders the economic growth and development of an area 255 since both are interconnected (Wang et al. 2025). This led to the development of innovative 256 enterprises for construction technologies that minimize water use or use of gray water for 257 building purpose (Shen et al. 2025). Sustainable water management therefore, for agriculture and 258 human health is important in water scarcity and contamination (Raveena and Surendran, 2024; 259 Surendran and Krishnan, 2024). Environmental assessment is important for quality living 260 standard for wellbeing of local community and sustainable economy (Wen et al. 2025). 261 Assessment of groundwater quality is important for drinking and domestic purposes. 262 Groundwater is important source easily accessible to inhabitants in arid areas. Groundwater 263 analysis revealed that pH of groundwater is natural to slightly alkaline. Presence of  $HCO_3^{-1}$  is the 264 265 single possible reason of alkaline nature of water samples due to weathering of carbonaceous rocks. Elevated electrical conductivity of water samples indicates presence of dissolved solids 266 267 which exceeds the maximum permissible range of WHO (2011) guidelines. It was noted that TDS is evenly distributed in overall study area attributed to ion exchange between soil minerals 268 269 and soil water giving increased TDS and EC (Kurakalva et al. 2021). Water hardness is due to calcium carbonate rocks covering groundwater aquifers which upon weathering add into water. 270 271 In most cases water hardness is due to dissolved form of calcium and carbonate containing ions as described by Mohsin et al. (2013). 272

Among tested cations and anions only  $HCO_3^-$  gives increased value in one study area attributed to the increased fertilizer and household waste input. Weathering of carbonaceous rock is another possible reason behind elevated  $HCO_3^-$  level in water (Li et al. 2019). Among other anions  $SO_4^{2^-}$ ,  $Cl^-$ ,  $F^-$  and  $NO_3^-$  was also detected in groundwater samples.  $NO_3^-$  detected in water samples due

to intensive agricultural activates by which synthetic fertilizers seeps through soil profile.  $NO_3^{-1}$  is 277 also added to groundwater through sewage water, feces and dead decaying plants. FAO (2004) 278 279 reported that use of fertilizers has been increases in Pakistan, Punjab is the major agricultural province thus increasing trend in NO<sub>3</sub><sup>-</sup> is common scenario (Akhtar et al. 2021). Moderate level 280 of SO42-, Cl- and F- is also present indicating anthropogenic input through sewage and bio 281 wastes. Moreover study area is present in arid to semi-arid thus water naturally flows from North 282 to South West helps increase in SO<sub>4</sub><sup>2-</sup> and Cl<sup>-</sup> concentration. It is important to note that increased 283 SO<sub>4</sub><sup>2-</sup> concentration gives bitter taste to water (Arshad and Umar, 2022). Cation occurrence in 284 groundwater is similar to that of anions where  $Ca^{2+}$  and  $Na^+$  was added to soil through infiltration 285 of soluble salts from irrigation water. K<sup>+</sup> is mostly fixed with clay minerals and released with 286 slow process. Mg<sup>2+</sup> also increases in groundwater through industrial effluents and leachate from 287 landfills (Jehan et al. 2023). 288

Moderate level of Total coliform and E. coli was also noted. Enrichment of T. coliform does indicate presence of pathogenic microbes while E. coli present in large intestine of human body excrete out by feces. Consuming such water may cause fatal illness. Microbial concentration was found in heavily populated areas (Vendrell and Atiles, 2013).

Piper plot describes mixed water type largely influenced by water/rock interaction with low 293 rainfall and increased evaporation in arid areas. This is largely due to associated carbonate rocks 294 precipitation and dissolution with groundwater (Pei-Yue et al. 2010). Water Quality Index (WQI) 295 was executed to check overall water quality indicating hazardous nature of sampled water. The 296 water samples collected from all sites were affected by domestic and industrial waste. Previous 297 water quality reports from PCRWR also indicate the similar issue. Addition of agricultural waste 298 299 is also reported which contain pesticides also pollute groundwater quality. According to Venkatraman et al. (2024) groundwater quality was predicated by a novel technique by using 300 optimization driven deep differential recur flow net which indicates water quality assessment up 301 to 98%. Similarly in another work by Maruthi et al. (2025) a real time quality data prediction is 302 303 made based on Internet of Things (IoT) sensors which helps in protecting water bodies from pollution. Similar to it score plot for Principle Component Analysis (PCA) indicates least 304 305 hydrochemical concentration in Tariq Abad and Shershah Town giving relatively good water quality than others (Su et al. 2020). 306

Spatial distribution of trace metals (As, Cd, Cr & Fe) with varying concentration in study area 307 was done to assess its enrichment. Arsenic enrichment in groundwater is attributed to the nearby 308 309 presence of iron, aluminum and manganese which also increase pH (Sharma et al. 2022). 310 Cadmium, chromium and iron in water sample is due to geogenic processes which was enhanced by anthropogenic activities mainly due to industrial effluents, fertilizers application and 311 312 transportation of weathered material (Wang et al. 2020). High concentration of heavy metal is summarized by the Heavy metal Pollution Index (HPI) indicates hazardous nature of all selected 313 samples. It was concluded that the presence of iron and manganese rocks near groundwater 314 systems gives enhanced Cd, Cr and Fe concentration after weathering. Use of agrochemicals, 315 pesticides and tanneries increase trace metals in soil as well as in water. It was determined that 316 increasing use of agrochemicals in Punjab province increases the amount of heavy metals in 317 318 groundwater used for drinking purpose (NFDC, 2016).

Public health of the community lies in successfully conducting environmental assessment vital 319 for living standards and welfare of the community, while encouraging growth of sustainable 320 321 businesses in the region (Shen et al. 2025). Non-carcinogenic risk associated with the studied metal exhibits an increasing HQ trend in all water samples for both age groups i.e., adult and 322 children. HQ > 1 is carcinogenic while HQ < 1 is non-carcinogenic for human health. Our results 323 revels HO > 1 for arsenic in most water samples, which are consistent with the work of Alves et 324 325 al. (2014), which suggests anthropogenic activities and use of herbicides is the main problems. On the other hand, cadmium, chromium, and iron are non-carcinogenic for adults, while 326 potentially carcinogenic for children. Only reason behind exceeding the potential risk is 327 increased water intake as the study area lies in an arid climatic condition with relatively high 328 humidity thus the daily average intake also increased. Prolonged exposure to low concentrations 329 of heavy metals could potentially increase risk of cancer. Our results regarding health risk are 330 also supported by Wongsasuluk et al. (2014), which suggests a high consumption ratio of 331 groundwater to body weight poses cancer risk after prolonged time. Our results followed the 332 work of Cao et al. (2014) where high cancer risk is detrimental to human health. 333

#### 334 Conclusion

335 Study was conducted to determine physiochemical characteristics and health risk exposure to 336 heavy metal in groundwater of Multan, Punjab, Pakistan. Hydrochemical study exhibit that

major cations and anions in study area influenced by rock-water interaction. Piper plot exhibit 337 mixed water type of Na<sup>+</sup>/K<sup>+</sup> and Na<sup>+</sup>/HCO<sub>3</sub><sup>-</sup>. Water Quality Index (WOI) and Heavy metal 338 339 Pollution Index (HPI) exceeds hazardous limit poses danger to health if consumed for long time. Heavy metal distribution in the study area is in the order As > Fe > Cr > Cd. Person correlation 340 matrix and Principal Component Analysis (PCA) were performed to check the geochemical 341 342 nature of groundwater. Potential risk assessment in the study area is computed by carcinogenic and non-carcinogenic risk of groundwater ingestion. Mean Hazard Quotient (HQ) indicates that 343 most of the samples exceed the potential non-carcinogenic threshold for both age groups, i.e., 344 adults and children. Among all studied heavy metals, arsenic has the highest risk of cancer. The 345 present study provides an insight into groundwater quality deteriorating through anthropogenic 346 inputs and geochemical weathering, which have a potentially harmful effect on human health. 347 Health risk assessment also clarifies that consuming groundwater for a long time may affect the 348 health and daily lifestyle of a person. Therefore, protective measures should be adapted, 349 including the prohibition of discharge of effluents from industries, protected discharge of 350 domestic waste, lining of landfills, surface runoff from agricultural areas, along with the 351 installation of water filtration plants to reduce heavy metal input into groundwater resources, 352 especially in urban areas. All this was adapted by strict monitoring of water quality as per WHO 353 354 standards.

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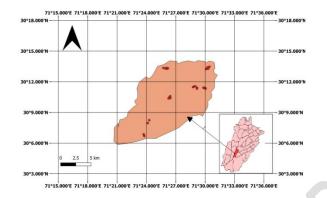


Figure 1. Map indicating water sampling sites from Multan city, Punjab, Pakistan

Sampling Sites	Ph	EC (µS	TDS (mg/	Hardn ess	SO4 <sup>2-</sup> (mg/	F⁻ (mg	HCO <sub>3</sub> <sup>-</sup> (mg/L	Cl <sup>-</sup> (mg	NO <sub>3</sub> <sup>-</sup> (mg/	Mg <sup>2</sup>	Na <sup>+</sup> (mg/	K <sup>+</sup> (mg	Ca <sup>2</sup> +	Total Colifor	E. coli (CFU	As (µg/	Cd (µg/L	Cr (µg/	Fe (µg/
		cm <sup>-1</sup> )	L)	(mg/L)	L)	/L)	)	/L)	L)	(mg /L)	L)	/L)	(mg /L)	m (CFU)	)	L)	)	L)	L)
Shershah Town	7.35	2369	2071	371	70	1.36	206	107	0.67	35.2	163. 2	5.36	35. 2	24	15	8.67	3.69	3.58	2.26
Suraj Miani	7.33	1547	1773	379	164	0.29	175	84	0.68	35	149. 9	6.12	38. 6	19	16	11.94	4.81	4.74	3.14
Liaqat Abad	7.76	1873	1889	360	169	0.66	312	122	0.86	51.4	159. 6	5.61	49. 8	17	16	12.65	3.82	3.07	2.48
Tariq Abad	7.41	1493	1206	306	123	0.75	550	96	0.47	47	119. 8	6.74	43. 2	20	16	15.95	2.28	4.49	5.11
Sharif Pura	7.34	2558	2501	543	85	0.56	320	125	0.89	39.8	127. 1	8.26	54. 8	19	17	16.44	3.01	3.65	5.07
Basti Baghbanpura	7.54	1898	1525	408	86	1.03	339	115	1.02	42	91.6	9.39	38. 2	18	18	11.39	2.82	4.15	3.22
Maximum	7.76	2558	2501	543	169	1.36	550	125	1.02	51.4	163. 2	9.39	54. 8	24	18	16.44	4.81	4.74	5.11
Minimum	7.33	1493	1206	306	70	0.29	175	84	0.47	35	91.6	5.36	35. 2	17	15	8.67	2.28	3.07	2.26
Mean	7.45	1956 .57	1827. 90	394.77	116.8 0	0.77	317.52	108. 69	0.76	41.7	135. 2	6.91	43. 3	19.5	16.33	12.84	3.41	3.95	3.55
Standard Deviation	0.17	430. 09	446.7 6	80.09	42.70	0.37	132.01	15.7 3	0.20	6.53	27.5 7	1.59	7.6	2.43	1.03	2.93	0.89	0.63	1.25
Coefficient of Variation	2.28	21.9 8	24.44	20.29	36.56	48.3	41.58	14.4	25.8	15.6	20.3 9	23.0 7	17. 55	12.46	6.32	22.83	26.25	15.8 5	35.1 9
Median	7.38	1885	1831	375.4	105.3	0.70	316.5	111	0.77	40.9	138. 5	6.43	40. 9	19.0	16.0	12.29	3.35	3.90	3.19
Kurtosis	1.81	-1.45	0.20	3.12	-2.21	0.03	1.80	-0.9	-0.47	-1	-0.56	-0.8	-1.0	2.88	0.58	-0.85	0	-1.2	-1.8

Table 1. Physiochemical properties of groundwater samples from Multan city, Punjab, Pakistan

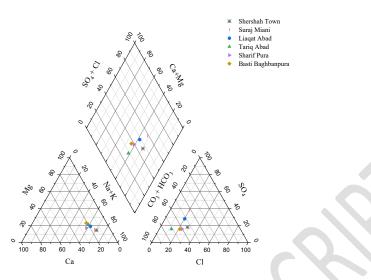


Figure 2. Piper plot representing groundwater type in Multan city, Punjab, Pakistan

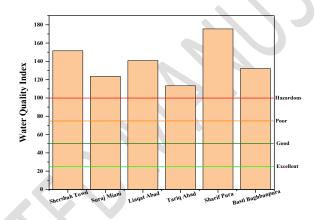


Figure 3. Groundwater quality index of Multan city, Punjab, Pakistan

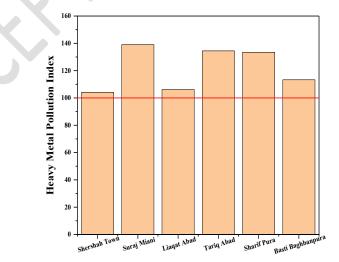
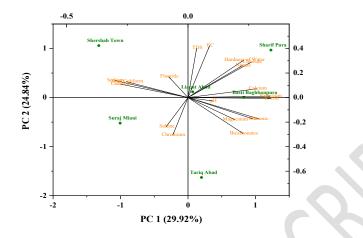


Figure 4. Heavy metal pollution index (HPI) of groundwater from Multan city, Punjab, Pakistan



**Figure 5.** Principle component analysis (PCA) for groundwater samples collected from various locations of Multan city, Punjab, Pakistan

	рН	EC	TDS	Hardness	F-	HCO3 <sup>-</sup>	Cl-	NO <sub>3</sub> -	SO₄⁻	Na <sup>+</sup>	$\mathbf{K}^{+}$	Ca <sup>2+</sup>	Mg <sup>2+</sup>	Total coliform	E. coli	As	Cd	Fe	Cr
рН	1.00																		
EC	-0.19	1.00																	
TDS	-0.2	0.86	1.00										$\sim$						
Hardness	-0.27	0.74	0.80	1.00							. C								
F-	0.03	0.38	-0.05	-0.19	1.00														
HCO3 <sup>-</sup>	0.17	-0.33	-0.57	-0.28	0.00	1.00													
Cŀ	0.49	0.69	0.53	0.55	0.26	0.06	1.00												
NO3 <sup>-</sup>	0.41	0.43	0.40	0.61	0.05	-0.31	0.69	1.00											
SO4 <sup>-</sup>	0.43	-0.69	-0.28	-0.4	-0.71	-0.03	-0.35	-0.20	1.00										
Na <sup>+</sup>	0.02	0.14	0.40	-0.19	-0.05	-0.54	-0.11	-0.34	0.36	1.00									
$\mathbf{K}^{+}$	-0.05	0.15	-0.04	0.53	-0.00	0.29	0.33	0.60	-0.44	-0.92	1.00								
Ca <sup>2+</sup>	0.26	0.32	0.47	0.55	-0.49	0.28	0.61	0.26	0.17	-0.00	0.17	1.00							
Mg <sup>2+</sup> T.	0.81	-0.31	-0.36	-0.31	-0.11	0.66	0.39	0.05	0.41	-0.13	-0.00	0.49	1.00						
1. coliform	-0.61	0.34	0.14	-0.15	0.62	-0.20	-0.26	-0.50	-0.57	0.35	-0.40	-0.52	-0.59	1.00					
E. coli	0.18	0.03	-0.07	0.48	-0.14	0.23	0.37	0.72	-0.20	-0.86	-0.95	0.23	0.15	-0.63	1.00				
As	-0.07	-0.08	-0.00	0.30	-0.58	0.66	0.14	-0.12	0.14	-0.36	0.34	0.76	0.42	-0.44	0.32	1.00			
Cd	-0.04	-0.09	0.31	-0.02	-0.35	-0.86	-0.34	0.02	0.51	0.68	-0.54	-0.22	-0.43	0.00	-0.40	-0.50	1.00		
Fe	-0.38	-0.02	-0.07	0.31	-0.38	0.68	-0.00	-0.23	-0.16	-0.52	0.47	0.51	0.14	-0.15	0.33	0.91	-0.63	1.00	
Cr	-0.56	-0.63	-0.56	-0.25	-0.33	0.15	-0.84	-0.41	0.12	-0.40	0.21	-0.46	-0.38	0.03	0.14	0.14	0.01	0.35	1.00

Table 2. Person correlation among different measured parameters of groundwater from Multan city, Punjab, Pakistan

Sampling	1	As	0	Cd	С	r	F	e
Sites								
	Adult	Children	Adult	Children	Adult	Children	Adult	Children
Shershah Town	0.00021	0.030	0.000092	0.012	7.67143E-	0.012	4.84286E-	0.0078
					05		05	
Suraj Miani	0.00029	0.041	0.00012	0.016	0.00010	0.016	0.000078	1.08
Liaqat Abad	0.00031	0.043	0.000095	0.013	0.000076	0.010	0.000062	0.0085
Tariq Abad	0.00039	0.055	0.000057	0.0079	0.00011	0.015	0.00012	0.017
Sharif Pura	0.00041	0.056	0.000075	0.010	0.000091	0.012	0.00012	0.017
Basti Baghbanpura	0.00028	0.039	0.000070	0.0097	0.00010	0.014	0.000080	0.011

**Table 3.** Chronic daily intake of heavy metal (CDI) from drinking groundwater of Multan city,Punjab, Pakistan

 Table 4. Non-carcinogenic human health risk Hazard Quotient (HQ) by heavy metal in the groundwater of Multan city, Punjab, Pakistan

AdultChildrenAdultChildrenAdultChildrenShershah Town0.72100.180.1825.580.024.13Suraj Miani0.99137.970.2433.340.035.47Liaqat Abad1.05146.170.1926.480.023.54Tariq Abad1.32184.310.1115.800.035.18	Adult	~	
Suraj Miani0.99137.970.2433.340.035.47Liaqat Abad1.05146.170.1926.480.023.54		Children	
Liaqat Abad 1.05 146.17 0.19 26.48 0.02 3.54	0.01	2.61	
	0.02	2.84	
<b>Tariq Abad</b> 1.32 184.31 0.11 15.80 0.03 5.18	0.02	2.86	
	0.04	5.90	
Sharif Pura         1.37         189.97         0.15         20.86         0.03         4.21	0.04	5.85	
Basti         0.94         131.61         0.14         19.55         0.03         4.79           Baghbanpura	0.02	3.72	
Permissible limit 1.0 1.0 1.0	1.0		

Sampling Sites	As	5	C	r
	Adult	Children	Adult	Children
Shershah Town	0.00014	0.020	0.00015	0.024
Suraj Miani	0.00019	0.027	0.00020	0.032
Liaqat Abad	0.00021	0.029	0.00015	0.021
Tariq Abad	0.00026	0.036	0.00022	0.031
Sharif Pura	0.00027	0.037	0.00018	0.025
Basti Baghbanpura	0.00018	0.026	0.00020	0.028

**Table 5.** Life time cancer risk (LCR) of human health exposed to drinking water in Multan city,Punjab, Pakistan