

1 **Groundwater quality assessment for drinking and irrigation purposes in arid**
2 **to semiarid region of Indus Basin of South Punjab, Pakistan**

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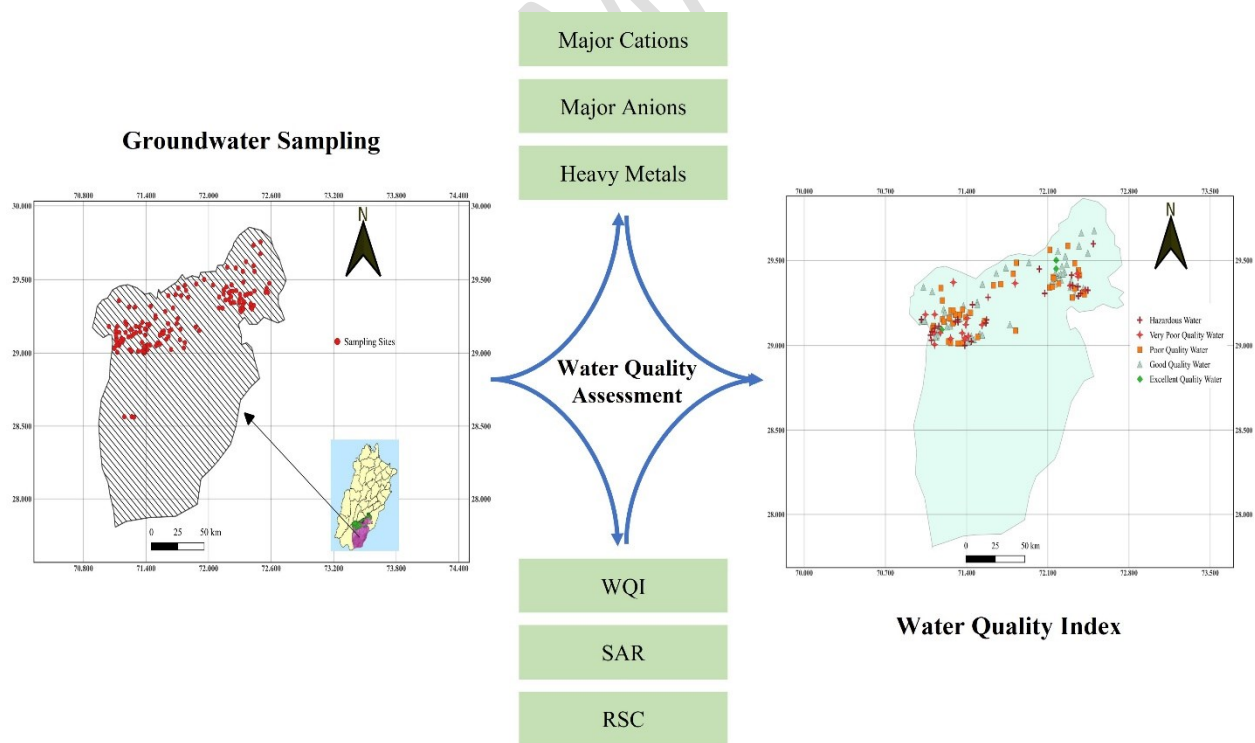
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16 **GRAPHICAL ABSTRACT**



17

18

19 Abstract

20 As the groundwater pollution is increasing, it is crucial to assess groundwater quality and
21 characterize hydrogeochemistry accurately for long term water supply. In this study groundwater
22 samples were collected from 120 locations from Bahawalpur district and analyzed for electrical
23 conductivity (EC), pH, total dissolved solids (TDS), sodium (Na^+), potassium (K^+), calcium
24 (Ca^{2+}), magnesium (Mg^{2+}), carbonate (CO_3^{2-}), bicarbonate (HCO_3^-), sulfate (SO_4^{2-}), chloride (Cl^-),
25 nitrate (NO_3^-), fluoride (F^-) and heavy metals. The results obtained from the analysis of samples
26 showed that the SAR of nearly 65% of samples collected from Bahawalpur district were in
27 acceptable limit ($<6 \text{ meq L}^{-1}$), while 12% found to be unfit for irrigation ($>10 \text{ meq L}^{-1}$).
28 Similarly, the RSC values depicted that 8% samples were unfit while 64% samples were falling
29 in the category of fit irrigation water. Most of the water samples were predominantly Ca^{2+} - HCO_3^-
30 and Na^+ - HCO_3^- type, that were controlled by various processes of cation exchange, water-rock
31 interaction, dissolution and evaporation. Some samples fall in the middle of diamond and lower
32 triangles of Piper diagram are showing no dominant type of water (mixed water type) due to the
33 complex influence of rock-water interactions as well as anthropogenic activities. The Water
34 Quality Index (WQI) showed that out of total 120 sampling sites in Bahawalpur the number of
35 excellent water samples were only 2% while 18% water samples were characterized as
36 hazardous. Moreover, the number of samples falling in the categories of good, poor and very
37 poor quality water were 36%, 29% and 13% respectively.

38 **Keywords:** Bahawalpur, groundwater quality, heavy metals, hydrogeochemistry, water quality
39 index

40 1. Introduction

41 Water is the most valuable and crucial resource for all life on earth especially for human
42 development (Loganathan and Ahamed 2017). Aquifers which are exploited on every part of
43 earth and serve as the prime source of drinking water for >1.5 billion people globally contain
44 over 97% of liquid fresh water and 30% of all fresh water (Oskin 2018). As one of the most
45 fundamental humanitarian objectives dependable access to inexpensive, clean water is still a
46 significant global concern in the 21st century. The current worldwide water problem is largely
47 caused by industrial water use, as a result of a significance rise in both industry and population
48 (Santos *et al.* 2014). Presently, above 2 billion people live in areas facing high water stress and

49 their number would remain to rise (He *et al.* 2021). The problems related to water are likely to
50 grow worse in the coming decades with water stress occurring worldwide even in the regions
51 currently considered water rich (Malato *et al.* 2022).

52 The quality of water represents a vital role for its use in domestic, industrial as well as
53 agricultural purposes. With respect to chemical contaminants the water quality is considered with
54 respect to soluble ions, heavy metals, hardness and nitrate in rural as well as urban areas of the
55 world (Amarasooriya and Kawakami 2019, Ahamad *et al.* 2020). Many countries in Asia are
56 facing increased level of water pollution due to the addition of untreated waste water containing
57 organic and inorganic pollutants into water resources (Uddin and Jeong 2021). Since the middle
58 of the 20th century, groundwater resources have considerably decreased in both quantity and
59 quality because of anthropogenic constraints, population growth, expanding urbanization,
60 pollutant runoff, poor sanitation and industrial and agricultural development (Ray *et al.* 2017).

61 There is growing evidence that irrigation water may need to be filtered sooner rather than later
62 due to the occurrence of heavy metals in food. The world's freshwater supply is under pressure
63 from growing irrigation but there are additional factors contributing to the freshwater access
64 (Mishra 2023). Freshwater bodies are being redistributed to a once-balanced hydrosphere as a
65 result of changes in the water cycle brought about by climate change in different parts of the
66 world (Chen 2019). Due to water's ability to regulate energy on a planetary scale this
67 redistribution has the effect of intensifying weather patterns making dry seasons drier, summers
68 hotter and the natural recharge rates of reservoirs and aquifers decreasing (McMahon *et al.*
69 2011). As the recharge of subsurface freshwater supplies not being able to keep up with the pace
70 of withdrawal, agriculture is severely impacted and irrigation becomes less dependable
71 (Janakarajan and Moench 2018). The continued flow of saline wastewater into the groundwater
72 without treatment has posed a hazard to aquatic, terrestrial and wetland ecosystems. Currently
73 salinization affects around 33% of the world's irrigated farmland (Munns 2005). Irrigating with
74 saline water can cause salt to build up in the soil, reducing yield and deteriorating soil resources
75 (Feizi *et al.* 2010). Many more areas with good-quality groundwater are threatened with
76 contamination as a consequence of unnecessary withdrawals of groundwater (Roy and Shah
77 2002). Similarly, contamination of water bodies with heavy metals especially in developing
78 countries has become a matter of great concern (Gao and Chen 2012). Unlike organic pollutants

79 in the environment, heavy metals are more persistent and tend to accumulate in different parts of
80 the environment.

81 The problem of groundwater pollution in numerous parts of Pakistan has developed so severe
82 that without crucial steps are taken, extensive groundwater resources may be spoiled (Daud *et al.*
83 2017). According to a report by International Monetary Fund (IMF), Pakistan is listed in the top
84 countries facing severe water shortages. The Pakistan Council of Research in Water Resources
85 (PCRWR) declared that by 2025 most of the country will experience very little or no clean water
86 availability (Ahmed *et al.* 2020). At present, only 20% of population has admittance to clean
87 drinking water while remaining 80% of the country's population relies on polluted water mainly
88 by sewerage, pesticides, fertilizer and industrial effluents (Sahoutara 2017). Such level of water
89 pollution is responsible for nearly 30% of deaths and 80% of all diseases in Pakistan (Daud *et al.*
90 2017). Moreover about 17% area of Punjab and 75% in Sindh is underlain by saline groundwater
91 (TDS>3000 ppm) which cannot be used for both drinking and irrigations purposes.

92 The Bahawalpur district at the edge of Cholistan desert is a fast developing and urbanizing
93 district in the Punjab province, where groundwater is the main source for domestic and irrigation
94 purposes. A few studies have been conducted on groundwater quality in response to deterioration
95 due to overexploitation, excessive use of chemical fertilizers and other anthropogenic activities
96 (Aamer *et al.* 2014, Mohsin *et al.* 2019). However, a detailed geochemical analysis and
97 classification of groundwater quality has not been evaluated in the said district. Therefore, the
98 current study was planned to evaluate groundwater quality of Bahawalpur district where main
99 objectives were (1) to analyze various physicochemical parameters to pinpoint the suitable and
100 unsuitable groundwater quality areas for drinking and irrigation purposes, (2) to evaluate the
101 groundwater suitability by comparing the measured parameters with the guideline values, and (3)
102 to prepare the spatial distribution map of the Water Quality Index (WQI).

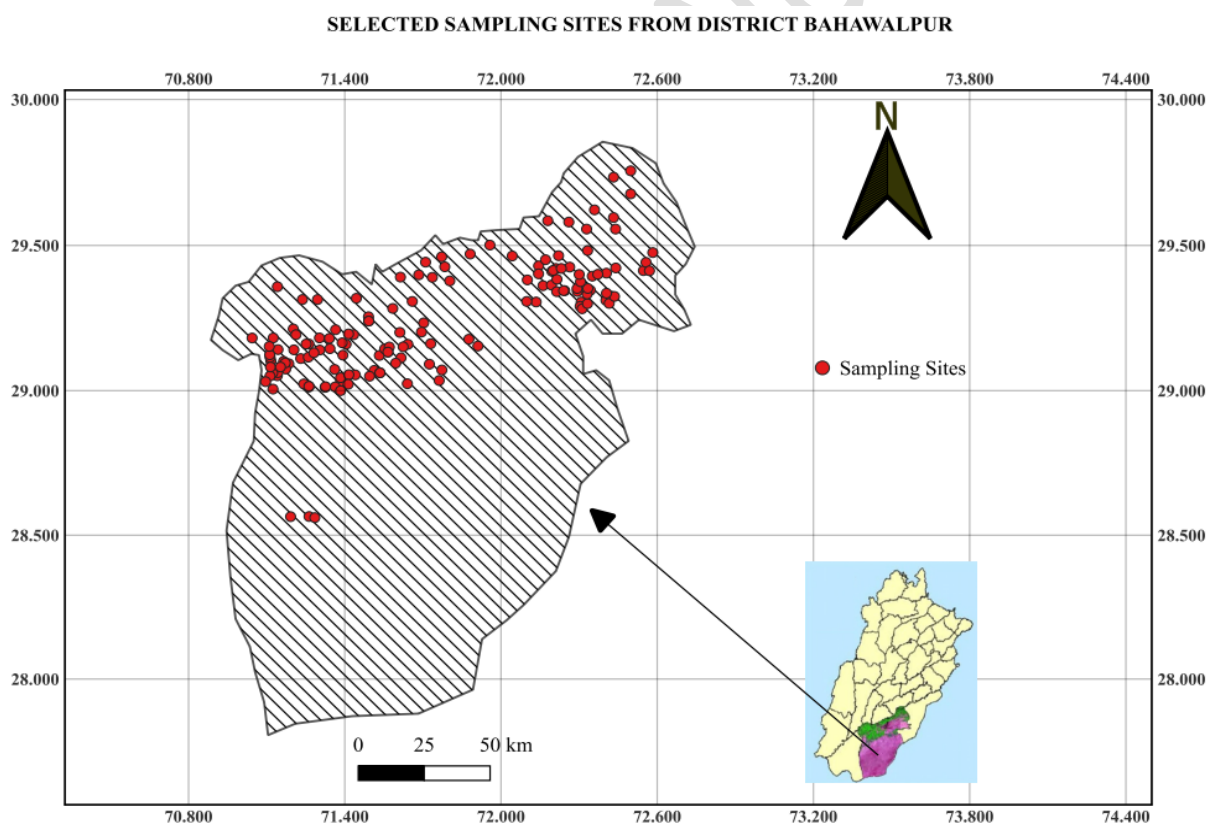
103 **2. Material and methods**

104 *2.1. Study Area*

105 Bahawalpur district is situated in southern part in Punjab province of Pakistan and lies between
106 27°-80' to 29°-70' N latitudes and 70°-54' to 72°-50' E longitude along the south eastern bank of
107 river Sutlej near the Cholistan desert. With the population size of 3.6 million people and

108 population density of 150 persons per km², it is 12th largest city of Pakistan (Pakistan Bureau of
109 Statistics 2017). It covers an area of almost 24,830 km² with small industries in urban areas and
110 temperature normally ranges between 13 to 48°C with annual rainfall around 150 mm (Govt. of
111 Punjab and World Bank 2006).

112 As the Bahawalpur is an agricultural district nearly 73% population in villages is involved in
113 agricultural production. Most of the suburban areas are irrigated with effluent released from the
114 industries as well as municipal waste water for the production of crops, vegetables and forages.
115 Moreover, groundwater extracted by either hand or electric pumps is the main source of drinking
116 water in the selected area. In this study 120 sampling sites with four replications for each were
117 selected from the study area on the basis of population density and groundwater consumption
118 (drinking or irrigation purpose) for the assessment of groundwater quality. The map of the
119 Bahawalpur district indicating the sampling points is shown in Figure 1.



120

121

Figure 1. Map of Bahawalpur district indicating sampling points.

122

2.2. Physiochemical and heavy metal analysis

123 Physiochemical analysis of water samples was carried out for the determination of cationic,
124 anionic and trace elements according to their standard procedures. All chemicals and reagents
125 used during the analysis were of the analytical grade. Moreover, all the instruments were
126 standardized before actual determination with accurate standards of each element/parameter.

127 In the field, water pH, electrical conductivity (EC), temperature and total dissolved solids (TDS)
128 were measured using pH meter (Milwaukee H0030229), EC meter (OHAUS ST3200C),
129 thermometer and TDS meter (Hanna TDS meter HI98311) respectively (Clesceri *et al.* 1998).
130 The concentrations of major cations (K^+ , Na^+ and Ca^{2+}) were measured through a specific
131 procedure using Flame Photometer (BWB XP made in UK) after calibrating the instrument with
132 standards of known concentrations. Four replications for each of the selected area were run for
133 cations determination and the instrument was calibrated after every 20 samples (Hameed *et al.*
134 2022). The combined concentration of Ca^{2+} and Mg^{2+} and hardness of water were measured by
135 titrating sample solution using ethylene diamine tetra acetic acid (EDTA, 0.01 N) in the presence
136 of eriochrome black T (EBT) and a buffer solution at pH 10 and 12 respectively (Nasrin *et al.*
137 2014). A titration method of USSL, (1954) was followed for the measurement of CO_3^- and
138 HCO_3^- using 0.1N H_2SO_4 as titrating agent and indicator solutions of phenolphthalein and methyl
139 orange respectively. Cl^- was also analyzed by titration method using 0.2N silver nitrate ($AgNO_3$)
140 in the presence of potassium chromate (K_2CrO_4) indicator. Anions including NO_3^- and SO_4^- were
141 measured through UV/VIS Spectrophotometer (CECIL CE7400S) at a wavelength of 229 and 420
142 nm respectively (APHA 1998).

143 The analysis of heavy metal (Fe, As, Cr, Pb, Ni) concentration were carried out through Atomic
144 Absorption Spectrophotometer (Agilent Technologies, AAS 200, USA). Quality control of heavy
145 metal determination was measured with blank, reference standard solutions and duplicate
146 samples and the analytical error was estimated to $\leq 10\%$ (Estefan 2013). Fluoride concentration
147 in collected water samples was determined through standard SPADNS colorimetric method using
148 UV/VIS Spectrophotometer (CECIL CE7400S) at a wavelength of 570 nm (Arancibia *et al.*
149 2004). Piper (1944) trilinear diagram and a Durov (1948) plot were used to understand the
150 geochemical progression of groundwater in particular. The diagrams in this study were plotted
151 using the AquaChem software (AquaChem v4.0). Gibbs (1970) projected two diagrams to know

152 the natural mechanisms of surface water chemistry. Gibbs diagrams basically depend on two
 153 ratios which are calculated by the following equations;

$$154 \quad \text{Gibbs ratio-I} = \frac{Cl^-}{(Cl^- + HCO_3^-)} \quad (1)$$

$$155 \quad \text{Gibbs ratio-II} = \frac{Na^+ + K^+}{Na^+ + K^+ + Ca^{2+}} \quad (2)$$

156 Where all the ionic concentrations are stated in meq L⁻¹.

157 2.3. Sodium Adsorption Ratio (SAR) and Residual Sodium Carbonate (RSC)

158 The Sodium Adsorption Ratio (SAR) (Lesch and Suarez 2009) and Residual Sodium Carbonate
 159 (RSC) were calculated by using the equations given below (USSSL 1954);

$$160 \quad \text{SAR (meq L}^{-1}\text{)} = \frac{Na^+}{\left[\frac{Ca^{2+} + Mg^{2+}}{2}\right]^{1/2}} \quad (3)$$

$$161 \quad \text{RSC (meq L}^{-1}\text{)} = (CO_3^{2-} + HCO_3^-) - (Ca^{2+} + Mg^{2+}) \quad (4)$$

162 Where Na⁺, Ca²⁺, Mg²⁺, CO₃²⁻ and HCO₃⁻ are all measured in meq L⁻¹.

163 2.4. Water Quality Index (WQI)

164 Water Quality Index (WQI) was used to assess the groundwater quality for drinking purposes in
 165 the selected region (Adimalla *et al.* 2018). It is calculated using the following equations;

$$166 \quad \text{WQI} = \frac{\sum W_n \times Q_n}{\sum W_n} \quad (5)$$

167 Where;

$$168 \quad \text{Quality rating (Qn)} = \frac{V_n - V_o}{S_n - V_o} \times 100 \quad (6)$$

$$169 \quad \text{Unit weight (Wn)} = \frac{K}{S_n} \quad (7)$$

170 Here, V_n is the assessed value of parameters, V_o is the ideal or reference value, S_n is the
 171 suggested allowable limit of the parameter and K is constant of proportionality. WQI was
 172 classified giving to the criteria defined by the WHO (2004), (Table 1).

173 **Table. 1.** Criteria for the classification of groundwater quality on the basis of WQI.

Classification of water quality	WQI
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Excellent quality water	0-25
Good quality water	26-50
Poor quality water	51-75
Very poor quality water	75-100
Unfit for drinking	>100

174

175 *2.5. Heavy Metal Pollution Index (HPI)*

176 The HPI signifies the total quality of groundwater with relation to heavy metals. The HPI model
 177 proposed is given by Mohan *et al.* (1996);

178
$$HPI = \frac{\sum_{i=1}^n W_i Q_i}{\sum_{i=1}^n W_i} \quad (8)$$

179 Where Q_i is the i th parameter's subindex. n is the number of constraints taken into consideration
 180 and w_i is the unit weightage of the i th parameter. The sub index (Q_i) of the parameter is derived
 181 by;

182
$$Q_i = \sum_{i=1}^n \frac{\{M_i(-)I_i\}}{S_i - I_i} \times 100 \quad (9)$$

183 Wherein S_i is the typical value of the i th parameter, I_i is the ideal value and M_i is the observed
 184 value of the heavy metal. Ignoring the algebraic sign, the sign (-) denotes the numerical variance
 185 between the two values. The critical heavy metal index value is 100 for drinking water.

186 **3. Results**

187 *3.1. Physicochemical properties of water samples*

188 *3.1.1. pH, EC and TDS*

189 The physicochemical parameters of the water samples collected from Bahawalpur district are
 190 shown in Table 2. pH, EC and TDS are the most basic parameters to identify the quality and
 191 usage of water. The guideline values for pH, EC and TDS for drinking water are 6.5 to 8.5, <400
 192 $\mu\text{S cm}^{-1}$ and <1000 mg L^{-1} respectively while recommended EC for irrigation water is <1150 μS
 193 cm^{-1} . The analyzed data showed that in the total 120 selected areas of Bahawalpur pH ranged
 194 from 6.81 to 8.42 while EC and TDS values were in the range of 144.8 to 5292.2 $\mu\text{S cm}^{-1}$ and
 195 226 to 8269 mg L^{-1} respectively. The frequency distribution of samples revealed that the pH of
 196 more than 80% samples were between 7 to 7.5, 14% between 7.5 to 8, 5% between 6.5 to 7 and
 197 nearly 1% between 8 to 8.5. On the other hand, EC of 40% samples were in the range of 100 to

198 500 $\mu\text{S cm}^{-1}$, 37% in the range of 500 to 1000 $\mu\text{S cm}^{-1}$, 9% in the range of 1000 to 1500 $\mu\text{S cm}^{-1}$
 199 and 11% above 1500 $\mu\text{S cm}^{-1}$. Similar trend was also observed in the values of TDS where 53%
 200 samples ranged between 200 to 1000 mg L^{-1} , 30% ranged between 1000 to 2000 mg L^{-1} , 8%
 201 ranged between 2000 to 3000 mg L^{-1} and nearly 8% samples were above 3000 mg L^{-1} . It can be
 202 seen from the Table 2 that a few sampling sites showed much more EC and TDS values as
 203 compared to average values of most of the samples. All such sites were observed to be far away
 204 from Sutlej River which indicates that groundwater in the vicinity of Sutlej River can be
 205 considered good quality but with the increase in the distance from the river water gradually
 206 becomes contaminated. Additionally, the availability of most of the water in this river is only
 207 restricted to monsoon season.

208 3.1.2. Major cations

209 The groundwater Na^+ concentrations in Bahawalpur district were found within the range of 66.5
 210 to 451.6 mg L^{-1} and according to the overall Na^+ distribution 53% samples showed less than 200
 211 mg L^{-1} , 36% within the range of 200 to 300 mg L^{-1} and a few locations (<11%) were exceeding
 212 300 mg L^{-1} . Comparatively K^+ concentrations in the groundwater samples were less than
 213 guideline value for drinking purpose except a few samples collected from selected sites of
 214 Bahawalpur. Almost 93% samples from Bahawalpur district were below 12 mg L^{-1} and 7%
 215 exceeding the line in terms of K^+ concentrations. The analysis of data showed that the Ca^{2+}
 216 concentration was uniformly distributed in all over the sampling sites ranging from 16.3 to 110.2
 217 mg L^{-1} (13% samples observed to be high in Ca^{2+} content than 75 mg L^{-1} and 87% were
 218 containing less than 75 mg L^{-1}). The Ca^{2+} concentrations were not restricted to a specific area in
 219 all the selected locations but mixed concentrations (low and high) were observed in equal
 220 proportions. This might be because of equal distribution of calcareous soils all over the arid to
 221 semiarid region of southern Punjab. The data presented in Table 2 depicts that the distribution of
 222 Mg^{2+} ions was also coincides with Ca^{2+} concentrations i.e., uniformly dispersed throughout the
 223 areas and the number of samples exceeding WHO guideline value were comparatively less (8%)
 224 in Bahawalpur.

225 **Table 2.** Physicochemical parameters of groundwater samples collected from Bahawalpur
 226 district. All values in mg L^{-1} except EC in $\mu\text{S cm}^{-1}$ and pH.

Parameters	pH	TDS	EC	Na^+	K^+	Ca^{2+}	Mg^{2+}	Cl^-	SO_4^{2-}	CO_3^-	HCO_3^-	NO_3^-
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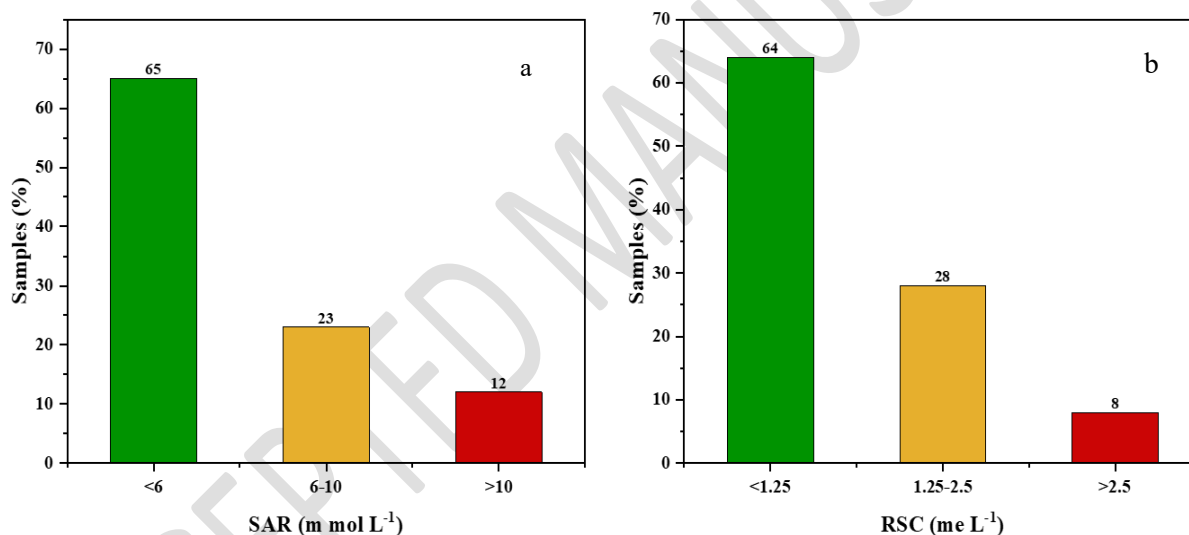
Mean	7.3	867	1356	210.6	6.9	50.1	30.9	188.0	135.7	0	359.2	3.59
Max	8.4	5292	8269	451.5	14.3	110.1	73.3	291.1	201.3	0	701.2	56.52
Min	6.8	144	226	66.5	0.9	16.3	8.1	83.7	46.1	0	151.1	0.01
SD	0.2	899	1406	84.1	3.0	21.3	12.6	50.07	32.81	0	102.9	6.6
Ideal v	7	0	0	0	0	0	0	0	0	0	0	0
CV	3.4	103	104	39.9	43.0	42.5	40.8	26.6	24.1	0	28.6	183.96
MOD	7.3	456	714	N/A	8.0	43.2	35.5	N/A	136.4	0	204.2	0.1
WHO	6.5-8.5	1000	400	250	12	75	50	250	250	-	500	10

227 3.1.3. Major anions

228 The Cl⁻ concentrations observed in the groundwater of Bahawalpur were in the range of 83.7 to
229 291.1 mg L⁻¹ where total of 74 (61%) samples contained Cl⁻ concentrations below 200 mg L⁻¹, 28
230 (23%) were in the range of 200 to 250 mg L⁻¹ and 18 (15%) were above 250 mg L⁻¹. Similar
231 ranges (46.1 to 201.3 mg L⁻¹) of SO₄²⁻ concentrations have also been observed in the
232 groundwater of Bahawalpur. The analyzed data reveals that >90% of samples from Bahawalpur
233 district were below 250 mg L⁻¹ and in fact most of the values were even below 200 mg L⁻¹ in
234 terms of SO₄²⁻ content which indicates only a little contamination to such extent prescribed by
235 WHO for SO₄²⁻ ion in drinking water (250 mg L⁻¹). In contrast HCO₃⁻ ions were present in higher
236 concentrations in most of the areas selected for sampling. The concentrations were found to be
237 varied among different locations but as a whole it ranged from 151.1 to 701.2 mg L⁻¹. Despite
238 higher threshold level for drinking purpose more that 10% sampling sites were exceeding the 500
239 mg L⁻¹ line recommended by WHO. The data arranged in the Table 2 depicts that most of the
240 sampling locations were in the safe line in terms of NO₃⁻ contamination as the average
241 concentration from maximum number of samples showed less than 10 mg L⁻¹ concentrations
242 except a few one from Bahawalpur district. As stated earlier almost 114 (95%) samples were
243 below 10 mg L⁻¹ and only 6 (5%) samples contained more that the said limit of NO₃⁻. The
244 fluoride concentrations in the case study were found in varying degrees ranging from 0.15 to 9.8
245 mg L⁻¹ in the groundwater samples (Table 2). The determined concentrations revealed that there
246 is a serious contamination of F⁻ in the groundwater of Bahawalpur as 29% of selected locations
247 were exceeding 1.5 mg L⁻¹ concentrations. Out of total 120 sampling sites 85 were in safe limit
248 and 35 were in toxic range.

249 3.2. Sodium Adsorption Ratio (SAR) and Residual Sodium Carbonate (RSC)

250 Sodium adsorption ratio and residual sodium carbonate are two important parameters for
 251 quantifying the suitability of irrigation water for growing crops. Both the parameters are
 252 calculated by the mathematical interactions (equations 3, 4) of major cations (Na^+ , Ca^{2+} , Mg^{2+})
 253 and anions (CO_3^- , HCO_3^-) occurring in the water. Data regarding SAR and RCS of groundwater
 254 is represented in Figure 2 (a and b). On the basis of these ions SAR and RSC of most of the
 255 sampling sites were found fit for irrigation but still a significant number of sampling areas were
 256 showing greater SAR and RSC. On an average the SAR of nearly 65% samples from
 257 Bahawalpur district were in acceptable limit ($<6 \text{ meq L}^{-1}$), while 12% sampling sites were found
 258 to be unfit for irrigation ($>10 \text{ meq L}^{-1}$). Likewise, results were also found for RSC values which
 259 depicts that 64% water samples were falling in the category of fit irrigation water from
 260 Bahawalpur and the number of unfit water samples were 8%.



261
 262 **Figure 2.** Distribution of SAR (a) and RSC (b) in selected areas of Bahawalpur. The graph bars
 263 in figure (a) are denoting percentage of samples (on the basis of SAR) falling in the category of
 264 fit (<6), marginal fit (6-10) and unfit (>10) for irrigation while graph bars in figure (b) are
 265 showing the percentage of samples (based on RSC) in the category of fit (<1.25), marginal fit
 266 (1.25-2.5) and unfit (>2.5) irrigation water.

267 3.3. Heavy Metal Pollution Index (HPI)

268 Heavy metal pollution index defines the overall contamination of water with a number of heavy
 269 metals including As, Pb, Cr, Ni and Fe etc. The classification of HPI of water includes five
 270 categories: <25 excellent, 25-50 good, 51-70 poor, 71-100 very poor and >100 hazardous water.

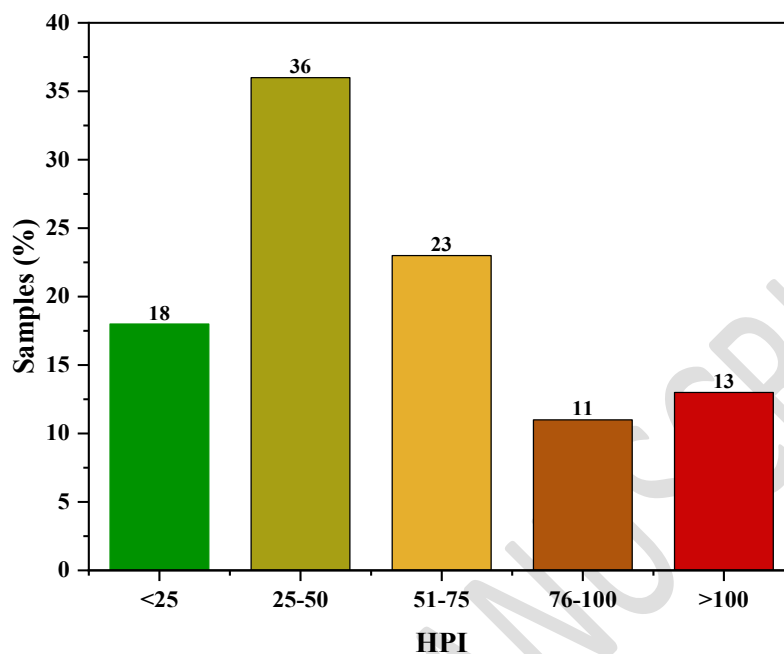
271 In the case study total of 18% samples were found excellent and 13% hazardous in terms of HPI.
 272 Moreover 36% samples were in the category of good and 11% in the very poor water (Figure 3).

273 According to overall heavy metal occurrence in groundwater samples in selected sites iron
 274 ranged from 0 to 2.06 mg L⁻¹. Out of 120 sampling sites of Bahawalpur only 2 sites showed Fe
 275 concentration more than 0.3 mg L⁻¹ while all other sites were below this limit. The data shown in
 276 the Table 3 indicates the As contamination in more than half of the sampling areas especially
 277 those areas which are comes under the effect of industrial units. High As contamination was also
 278 found to be linked with soil minerals such as Fe, Al and Mn oxyhydroxides which release As in
 279 groundwater due to changing soil pH and microbial actions. The overall range of As in
 280 groundwater was 0 to 100 µg L⁻¹ where 47.5% samples was found to be none contaminated (<10
 281 µg L⁻¹) while 52.5% samples were having As more than 10 µg L⁻¹. Data shown in the Table 3
 282 shows that Pb concentration in most of the sampling areas was more than 10 µg L⁻¹ and even
 283 greater than 50 and 100 µg L⁻¹ in some of the samples. In the groundwater samples of
 284 Bahawalpur district it ranged from 2.5 to 120 µg L⁻¹ and more than 100 (87%) samples were
 285 exceeding 10 µg L⁻¹, 5 out of them had Pb beyond 100 µg L⁻¹. The analyzed data for Cr
 286 concentrations reveals that there was only a certain number of samples showing more than 50 µg
 287 L⁻¹ Cr in water samples collected from selected district (ranged from 5 to 56 µg L⁻¹). Like other
 288 heavy metals the groundwater contamination with Ni was also reported from many of the
 289 sampling areas in the selected district. On an average it was found between 4 to 90 µg L⁻¹ in
 290 district Bahawalpur and out of 120 sampling sites nearly 5% were showing Ni concentration <70
 291 µg L⁻¹. It is important to mention that similar to Cr, Ni concentrations in maximum number of
 292 samples (54%) were in the range of 20 to 50 µg L⁻¹.

293 **Table 3.** Heavy metal concentrations and drinking as well as irrigation water quality indices
 294 determined in the groundwaters of Bahawalpur. F and Fe are given in mg L⁻¹, As, Pb, Cr and Ni
 295 in µg L⁻¹ while SAR and RSC in me L⁻¹. Remaining are index values.

Parameters	F	Fe	As	Pb	Cr	Ni	WQI	HPI	SAR	RSC
Mean	1.49	0.08	17	37	33	29	81	56	5.89	0.90
Max	9.80	2.06	100	120	56	90	442	162	16.00	3.30
Mini	0.15	0.00	0	2	5	4	20	6	2.00	0.01
SD	1.65	0.19	17	24	12	18	68	33	2.85	0.91
Ideal v	0.00	0.00	0	0	0	0				
CV	110.00	239.00	100	65	36	60	84	58	48.40	101.00
MOD	0.75	0.04	10	15	33	30	36	21	5.00	0.08

WHO	1.5	0.3	10	10	50	70
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296
 297 **Figure 3.** Range of HPI in the groundwater of Bahawalpur. Bars in the graphs are showing
 298 percentage of samples in the categories of excellent quality water (<25), good quality water (25-
 299 50), poor quality water (51-75), very poor quality water (76-100) and hazardous water (>100) on
 300 the basis of HPI.

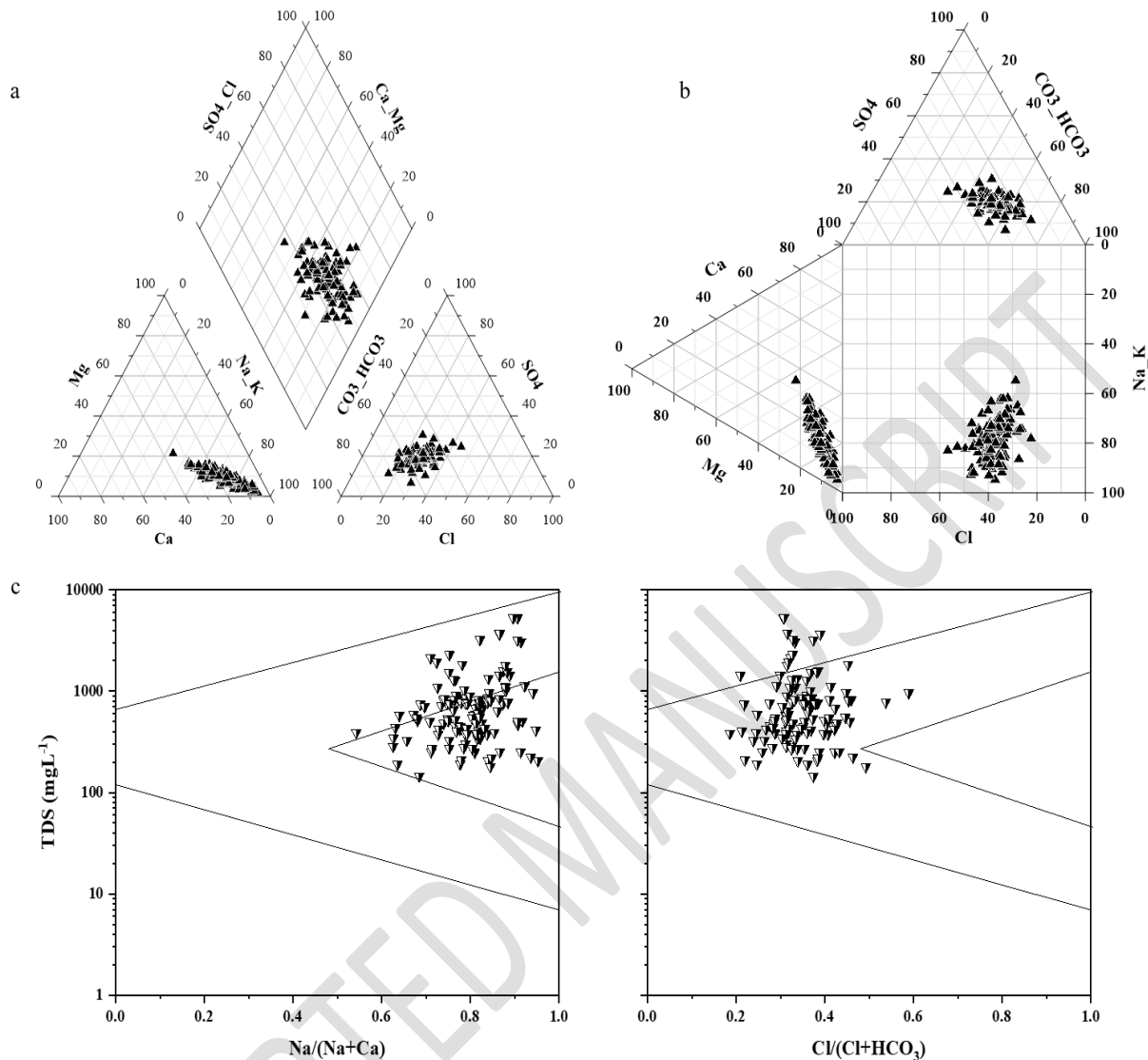
301 *3.4. Major water type in aquifers of Bahawalpur*

302 All the major water types determined in selected area of Bahawalpur district can be classified as
 303 sodium-potassium/sodium-bicarbonate type (Figure 4a) except a few samples having sodium-
 304 chloride type. As shown in the figure dominant major cation is Na and the remaining cations are
 305 in the sequence of $K^+ > Ca^{2+} > Mg^{2+}$. While HCO_3^- is found to be major anion and rest of the
 306 anions are in the sequence of $Cl^- > SO_4^{2-} > CO_3^-$. Some of the samples (<20%) appearing in the
 307 middle of diamond and lower triangles of Piper diagram are indicating no dominant type of
 308 water (mixed water type) in the Bahawalpur district. Moreover, none of the sample was observed
 309 to be SO_4^{2-} or Mg^{2+} type because of lower distribution of these ions. Above data also indicates a
 310 single aquifer source in most of the sampling area. The results plotted on the Durov diagram
 311 shows that more than 75% of the samples appear along the dissolving or mixing line of the
 312 Durov plot (Figure 4b), supporting the idea that a mixed variety of water types predominate in
 313 the research area. Fresh recharge water with simple dissolving or mixing and no dominating

314 large anion or cation is responsible for this tendency. Furthermore, a small percentage of samples
315 (~13%) with Cl^- and Na^+ as the predominant anion/cation suggested a connection between the
316 ground waters and the reverse ion exchange of Na-Cl waters.

317 The functional dissolution sources of ions were also determined by plotting Gibbs diagram
318 (Figure 4c) of variability ratios of $\text{Na}/(\text{Na} + \text{Ca})$ and $\text{Cl}/(\text{Cl} + \text{HCO}_3)$ as a function of TDS. A
319 clear interaction can be observed from the plot between rock and groundwater chemistry and
320 more specifically the major ions concentrations in the groundwater mainly resulted from rock-
321 water interaction (weathering of rocks, formation of minerals and precipitation of carbonates)
322 and evaporative sedimentation. The moderate TDS values and ions concentration is indicating
323 dominancy of rock-water interaction as well as evaporative sedimentation. On the other hand,
324 precipitation is not influencing the ion chemistry i.e., low precipitation causes high ion
325 concentrations and moderate to low TDS, opposite is true for high precipitation.

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328 **Figure 4.** Piper plot in figure (a) is representing major water types while Durov diagram (b) is
 329 indicating major processes involved in the dissolution of major ions in the water systems in
 330 Bahawalpur. Occurring of clusters towards centers and Na-k to HCO₃ lines in Piper plots
 331 indicating the dominancy of sodium bicarbonate type water and mixed water type. Similarly
 332 points appearing near the middle line in Durov diagram reveals simple dissolution or mixing is
 333 the main process in groundwater chemistry. Gibbs diagram constructed between TDS and major
 334 cations and anions found in the groundwater of Bahawalpur is shown in figure (c). The points in
 335 the diagrams are showing that rock-water interactions and evaporative sedimentation are
 336 influencing the groundwater composition.

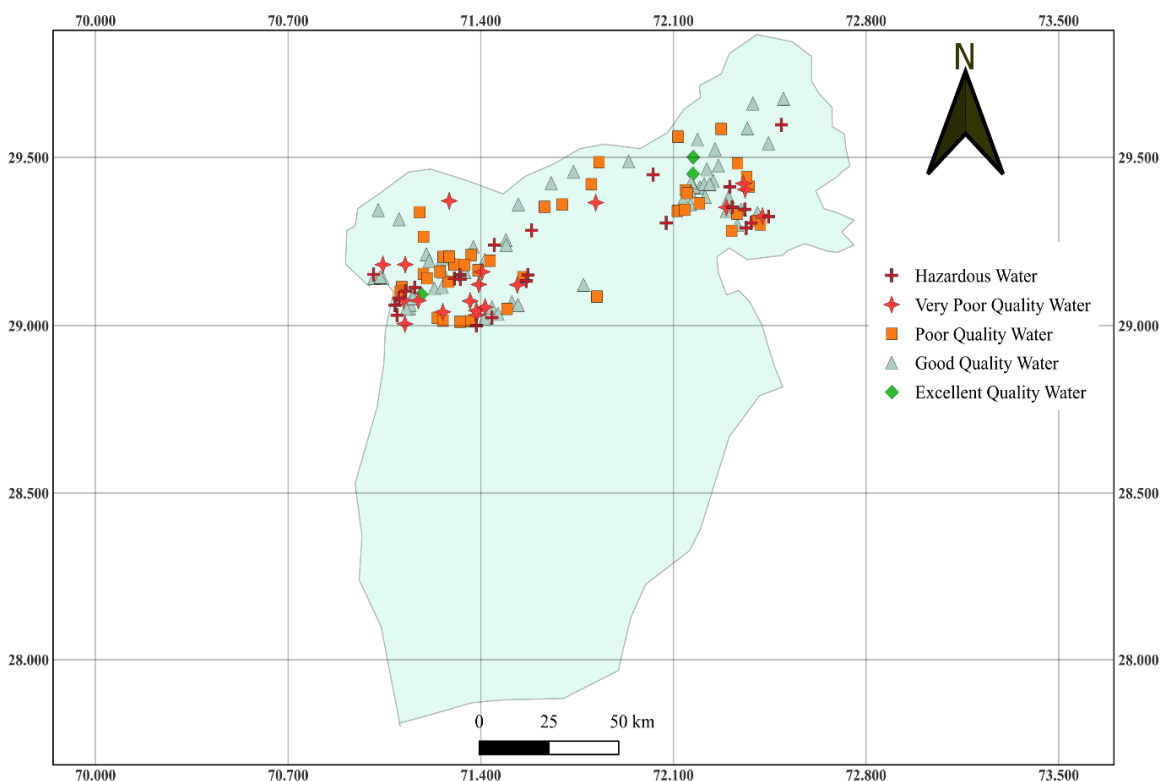
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340 3.5. Water Quality Index (WQI)

341 Water quality index can be considered as a complete set of water quality which includes all the
342 physicochemical and heavy metal constituents. Similar to HPI the classification of WQI also
343 include five categories: <25 excellent, 25-50 good, 51-70 poor, 71-100 very poor and >100
344 hazardous water. WQI of selected site of Bahawalpur is shown in the Figure 5 and Table 3. Out
345 of total 120 sampling sites in Bahawalpur the number of excellent and hazardous water samples
346 were 3 (~2%) and 22 (18%) respectively. Moreover, the number of samples in categories of
347 good, poor and very poor quality water were 44 (36%), 35 (29%) and 16 (13%) respectively.

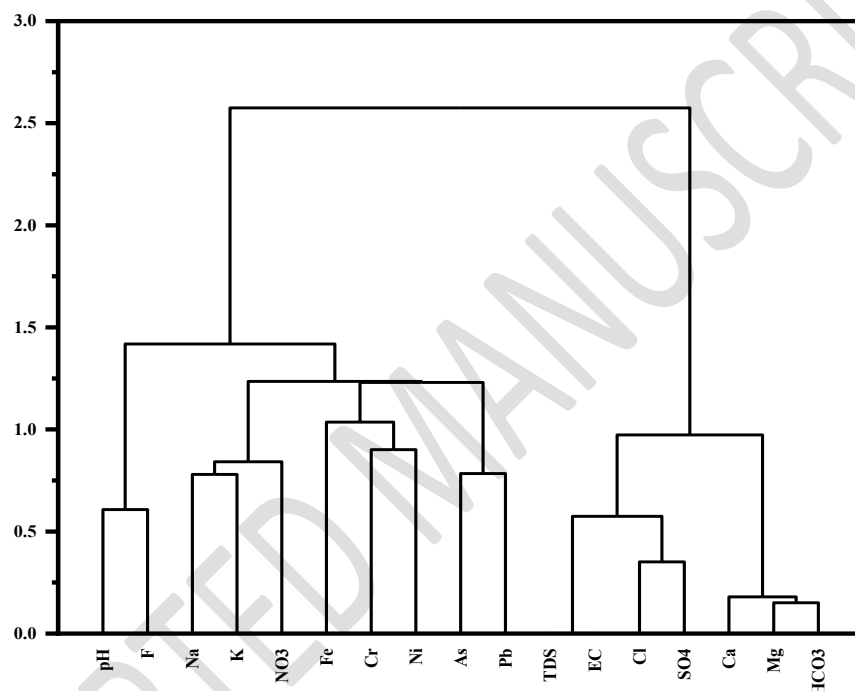


348
349 **Figure 5.** Spatial geographical distribution of WQI in the selected areas of Bahawalpur.

350 3.6. Correlation and cluster analysis

351 The correlation matrix of physicochemical characteristics and heavy metals of water samples
352 collected from Bahawalpur is given in Table 4. A number of parameters determined in the water
353 samples can be seen having a positive correlation between each other like EC and TDS ($r = 1$),
354 Ca^{2+} and HCO_3^- ($r = 0.85$), Mg^{2+} and HCO_3^- ($r = 0.84$), Ca^{2+} and Mg^{2+} ($r = 0.80$), Cl^- and SO_4^{2-} (r

355 = 0.65), Cl⁻ and EC (r = 0.64), Na⁺ and TDS (r = 0.61), Ca²⁺ and SO₄²⁻ (r = 0.52). In addition to
 356 correlation matrix a dendrogram of cluster analysis was also constructed to further verify the
 357 grouping and correlation of different physicochemical and heavy metal constituents (Figure 6).
 358 Which generated four groups of sites having similar characteristics and same source of
 359 contamination in Bahawalpur area, group (G1) includes pH, F⁻, Na⁺ and K⁺, group (G2) includes
 360 NO₃⁻, Fe, Cr and Ni, group (G3) includes As and Pb and the group (G4) includes TDS, EC, Cl⁻,
 361 SO₄²⁻, Ca²⁺, Mg²⁺ and HCO₃⁻.

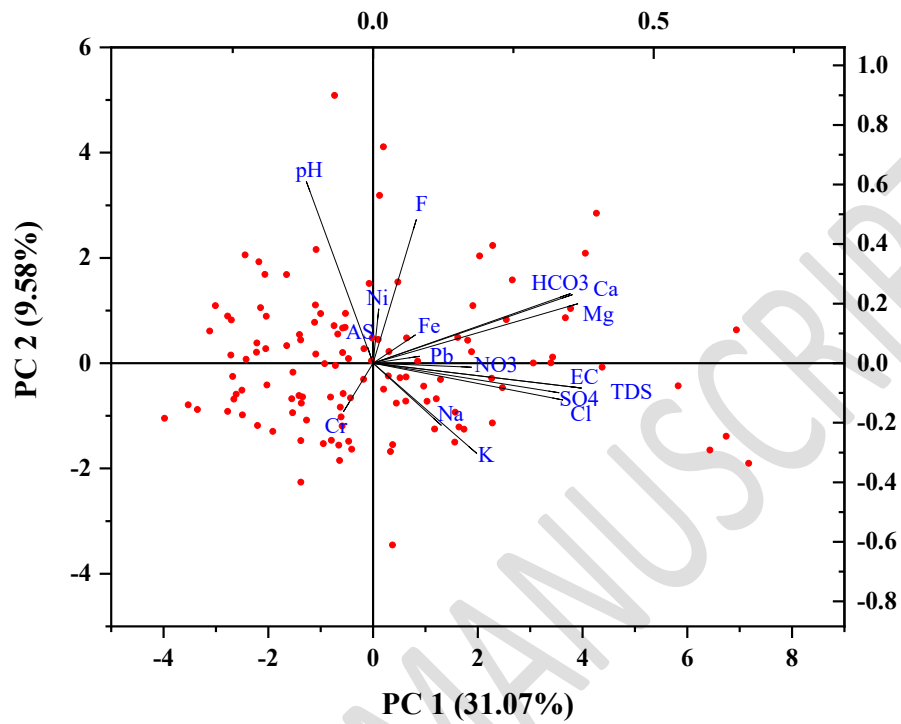


362
 363 **Figure 6.** Dendrogram of cluster analysis (CA) of water samples collected from Bahawalpur
 364 constructed using Ward's method. The figure is indicating three distinct groups (parameters
 365 correlate within the group but differ from other group) of alike water samples from each site.

366 3.7. Principle Component Analysis (PCA)

367 The scores plots using principle component analysis were also generated between factor 1 (PC1)
 368 and 2 (PC2) to evaluate the enrichment of physicochemical parameters and heavy metals of
 369 water samples collected from the selected district. The scores plots obtained from water samples
 370 of Bahawalpur (Figure 7) demonstrated little variation in the relative dominance of main ions
 371 and other water quality criteria, such as trace metals. Groundwater samples were found to be
 372 substantially concentrated in main ions and metal contamination, as indicated by the score plots

373 in the right side quadrants, which can be either lower or higher. However, pH and Cr were more
374 prevalent in the distribution of sample in the left quadrants, either upper or lower.



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376 **Figure 7.** Score plot indicating the enrichment of different parameters found in the ground water
377 of Bahawalpur district.

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387 **Table 4.** Correlation matrix of all the physicochemical and heavy metal constituents in water samples (n=120) of Bahawalpur area.
 388 Highlighted values are indicating significance level at $P \leq 0.05$.

	<i>pH</i>	<i>EC</i>	<i>TDS</i>	<i>Na⁺</i>	<i>K⁺</i>	<i>Ca²⁺</i>	<i>Mg²⁺</i>	<i>Cl⁻</i>	<i>SO₄²⁻</i>	<i>HCO₃⁻</i>	<i>NO₃⁻</i>	<i>F⁻</i>	<i>Fe</i>	<i>As</i>	<i>Pb</i>	<i>Cr</i>	<i>Ni</i>
pH	1.00																
EC	-0.05	1.00															
TDS	-0.05	0.99	1.00														
Na⁺	-0.08	0.61	0.61	1.00													
K⁺	-0.28	0.28	0.28	0.22	1.00												
Ca²⁺	0.01	0.58	0.58	0.16	0.20	1.00											
Mg²⁺	-0.11	0.58	0.58	0.17	0.26	0.81	1.00										
Cl⁻	-0.24	0.63	0.63	0.28	0.39	0.51	0.56	1.00									
SO₄²⁻	-0.26	0.61	0.61	0.15	0.38	0.52	0.50	0.65	1.00								
HCO₃⁻	-0.08	0.56	0.56	0.16	0.18	0.85	0.85	0.50	0.50	1.00							
NO₃⁻	-0.15	0.24	0.24	0.18	0.17	0.25	0.37	0.25	0.24	0.29	1.00						
F⁻	0.39	0.10	0.10	-0.01	0.05	0.14	0.20	0.10	0.13	0.16	0.15	1.00					
Fe	-0.01	0.17	0.17	-0.11	0.01	0.10	0.11	0.13	0.17	0.08	-0.03	0.11	1.00				
As	0.05	-0.02	-0.02	-0.02	0.05	-0.09	-0.03	0.01	0.02	0.01	-0.10	0.03	-0.01	1.00			
Pb	-0.04	0.11	0.11	0.11	0.04	0.12	0.18	0.06	0.10	0.24	0.03	-0.08	0.04	0.22	1.00		
Cr	-0.04	-0.11	-0.11	0.15	-0.04	-0.08	-0.09	0.01	-0.17	-0.10	0.06	-0.09	0.03	-0.16	-0.06	1.00	
Ni	0.12	0.02	0.02	-0.04	-0.08	0.07	0.09	0.03	-0.11	0.09	0.05	-0.07	-0.03	-0.01	0.02	0.10	1.00

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394 4. Discussion

395 Groundwater quality assessment is a crucial process to evaluate the physical, chemical and
396 biological characteristics of groundwater to ensure its fitness for numerous uses, such as drinking
397 water, agriculture, industrial processes and environmental conservation. The analysis of water
398 samples revealed that the ground water pH of water samples were slightly alkaline but values of
399 most samples were within permissible limit for drinking water rendering to WHO defined range
400 (6.5-8.5). The presence of HCO_3^- in the study area is responsible for alkaline pH of water which
401 released from the weathering of carbonaceous rocks (López-Pazos *et al.* 2010). Parallel to pH,
402 EC is also a significant parameter for the characterization of groundwater (Ouarekh *et al.* 2021).
403 The EC of >90% water samples showed elevated values owing to the presence of dissolved salts
404 in the water (Aamer and Sabir, 2014). The increasing EC also resulted in an increase of TDS
405 because of ion exchange between groundwater and soil minerals (Baig *et al.* 2010). The majority
406 of the contaminated water samples were unfit for human consumption because their TDS levels
407 were beyond the WHO's recommended threshold of 1000 mg L^{-1} (WHO, 1993). According to
408 Abbas *et al.* (2014), there is mounting evidence that water EC rises with residency duration and
409 increased rock-water contact. Results of pH, EC and TDS found in line with those described by
410 Alam *et al.* (2021).

411 Hydrochemical parameters showed that Na^+ , K^+ , Ca^{2+} and Mg^{2+} were major cations that were
412 determined in the collected water samples. The main source of the higher Ca^{2+} and Na^+ levels in
413 groundwater was the infiltration of soluble soil salts from irrigation or precipitation that
414 contaminated surface water. High levels of Ca^{2+} and Na^+ can also result from sewage effluent
415 contamination of drinking water (Abbas *et al.* 2014). On the other hand, Ca^{2+} and Na^+ are
416 released on the weathering of silicate minerals, which may accumulate these types of ions in
417 groundwater by water-rock interactions, leading to greater concentrations of Ca^{2+} and Na^+ in
418 groundwater samples (Ramkumar *et al.* 2010). The overall groundwater K^+ concentrations were
419 comparatively low in the water samples because K^+ have a tendency to be locked on the surface
420 of clay minerals and disintegrates at a slower pace than Na^+ minerals (Mishra, 2020). The
421 concentrations of Mg^{2+} were slightly above the permissible limits in a few samples collected
422 from selected district. High concentrations of Mg^{2+} were caused due to diffusion of leachate from
423 industrial, household and landfills sites (Abbas *et al.* 2014). Mehmood *et al.* (2012) conducted a

424 selective study on the groundwater in parts of Bahawalpur city where they found similar trends
425 as found in the current study for the heavy metal contamination as well as physicochemical
426 parameters especially Cl^- , SO_4^{2-} , Ca^{2+} and Mg^{2+} .

427 The occurrence of anions was also observed in the similar pattern that of cations throughout the
428 sampling sites. Out of all the anions HCO_3^- concentrations were in higher levels followed by Cl^- ,
429 SO_4^{2-} , NO_3^- and F^- because of the growing population and the significant increase in agricultural
430 and residential waste in the examined area (Rasool *et al.* 2016). It is possible that the higher
431 HCO_3^- concentrations were caused by local inputs such as fertilizers and household waste
432 materials. The weathering of carbonaceous rocks is another possible reason behind elevated
433 levels of HCO_3^- in the studied areas (Li *et al.* 2019). Nitrate is another anion dominating in the
434 groundwater of selected sites especially in countryside areas of district Bahawalpur which
435 primarily may occurred due to agricultural activities, decay of dead plants, sewage discharges
436 and feces (Akhtar *et al.* 2021). The use of synthetic fertilizers such as DAP and urea for intensive
437 agriculture is another source of contribution in soil and groundwater contamination with NO_3^- .
438 FAO (2004) reports that during the past 30 years, Pakistan has grown its fertilizer usage, with
439 Punjab Province accounting for the majority of this growth due to its enormous agricultural area.

440 The analysis of data also represented relatively higher to moderate levels of Cl^- , SO_4^{2-} and F^-
441 contamination in samples. The possible reasons behind increased levels of Cl^- and SO_4^{2-} in
442 groundwater are thought to be anthropogenic activities such as municipal seepage and sewage
443 and other biowaste materials contributed in groundwater pollution. Additionally, the sampling
444 sites come under the low lands of arid to semi-arid region where water naturally flows from
445 North to South West, thus adding more concentrations of Cl^- and SO_4^{2-} in groundwater. When
446 paired with Na^+ or Mg^{2+} , SO_4^{2-} overload can be corrosive and laxative, imparting an unpalatable
447 taste (Ashraf and Foolad 2007). Groundwater contamination with SO_4^{2-} has been linked to
448 anthropogenic causes, such as detergent use and seepage from city areas (Arshad and Umar
449 2022). Groundwater fluoride content rises as a result of prolonged water-rock interaction brought
450 on by the low groundwater recharge sources such as rainfall in arid climate. Conversely, elevated
451 evaporation leads to the precipitation of less soluble minerals (CaCO_3), hence diminishing the
452 calcium ion availability in groundwater and facilitating the dissolving of fluoride minerals
453 (Vithanage and Bhattacharya 2015). The presence of moderate to high concentrations of these

454 cations and anions are responsible for high SAR and RSC values in few sampling locations of
455 the selected areas. While most of the sampling locations showed SAR and RSC values in
456 acceptable range which are in line with Mohsin *et al.* (2019).

457 By using the data attained from above mentioned parameters a Piper plot, Durov and Gibbs
458 diagrams were designated to study major water types, sources of contamination and its
459 interaction with external factors like precipitation and evaporation respectively. The Gibbs plot
460 of data from the study area (Figure 4c) indicated the interaction between rock-percolation waters
461 chemistry under subsurface. These plots revealed that weathering has a greater impact on the
462 local groundwater quality just like evaporation. This implies that water-rock interactions cause
463 concentrations of the main ions Na^+ , Ca^{2+} and Mg^{2+} in water to rise. The main processes
464 involved in water-rock interactions are ion exchange between clay minerals and water, chemical
465 weathering of rock-forming minerals and dissolution-precipitation of secondary carbonates
466 (Moghaddam and Fijani, 2008). Low rainfall (225-400 mm annually), considerable evaporation
467 (>2000 mm annually) and low hydraulic conductivity of groundwater are characteristics of dry
468 and semiarid climatic zones (Su *et al.* 2020, Khan *et al.* 2013a,b).

469 The spatial distribution of trace metals can be used to distinguish between zones with varying
470 metal concentrations and to assess potential enrichment sources (Wang *et al.* 2020). Spatial
471 distribution of elevated concentrations of As in the current study was mainly confined in the
472 sampling locations chosen from urban areas especially near the industrial sites. High As
473 contamination was also found to be linked with soil minerals such as Fe, Al and Mn
474 oxyhydroxides which release As in groundwater due to changing soil pH and microbial actions.
475 Transportation, intensive use of agricultural insecticides and leaching of weathered mafic and
476 ultramafic rocks are the reasons behind increasing level of Pb in groundwater samples. The
477 occurrence and distribution of moderate to lower concentrations of Fe and Ni were also
478 attributed to the river inflows (Zhang *et al.* 2022). High concentrations of heavy metals are
479 commonly summarized as heavy metal pollution index (HPI) which depends on the overall
480 concentrations of the metal ions. Additionally, the increased use of pesticides and fertilizers in
481 Punjab province is a key source of As, Pb, Ni, Cd, Cr and Fe in drinking water of the study area
482 (NFDC 2016). The body of research makes clear that excessive use of agrochemicals, such as

483 fertilizers and pesticides can result in high quantities of metals which can contaminate
484 groundwater and have negative health effects on people (Singh 2011).

485 5. Conclusion

486 In conclusion majority of the analyzed groundwater samples are acceptable and suitable for
487 drinking as well as irrigation purposes. The distribution of the major cations and anions showed
488 that they are below the guideline/permissible limits and the predominant ions are Na^+ , Ca^{2+} ,
489 HCO_3^- , Cl^- and SO_4^{2-} . It was observed that more than 50% of the groundwater samples are Na-
490 HCO_3 water, less than 10% are Ca- SO_4 and Mg- SO_4 water while 30% samples showed mixed
491 water type. On the basis of these ions SAR and RSC of most of the sampling sites are found fit
492 for irrigation but still a significant number of sampling areas are showing greater SAR and RSC.
493 The SAR and RSC of more than half of the samples (65 and 64% respectively) collected from
494 Bahawalpur are in acceptable limit ($<6 \text{ meq L}^{-1}$), while 12% and 8% samples are found to be
495 unfit for irrigation ($>10 \text{ meq L}^{-1}$) respectively. The heavy metal distribution in the groundwater
496 samples collected from the study area is in the order $\text{Fe} > \text{Pb} > \text{Cr} > \text{Ni} > \text{As}$. The WQI of all the
497 water samples showed that out of total 120 sampling sites in Bahawalpur the number of excellent
498 water samples are only 2% while 18% samples are in the category of hazardous water samples.
499 The remaining water samples shows WQI in the range of good (36%), poor (29%) and very poor
500 quality (13%) water. Therefore, this research suggests the treatment of contaminated
501 groundwater before human consumption. Also, the use of groundwater for irrigation purposes
502 should be considered according to the level of groundwater contamination and soil quality.

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