

Article

Evaluation of Water Quality of Groundwater of Sanghar District, Sindh, Pakistan: Chemical and Multivariate Analysis

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Abstract: Sanghar District is located in the central part of Sindh Province and shares a boarder with India to the east. This work examines the water quality of the groundwater of three subdistricts, Sanghar, Khipro, and Jan Nawaz Ali, mostly used for human consumption, cattle farming, and irrigation. A total of 74 representative samples were collected and analyzed for 26 different parameters, including anions, cations, trace, and toxic elements. The total dissolved salts (TDSs) contained in 41 samples (55.4%), the major cations, K, Na, Mg, and Ca, in 44.6–93.2% of samples, and the major anions, Cl, HCO₃, and SO₄, in 68.6–81.0% of samples were within the permissible guidelines of the World Health Organization (WHO). The samples containing elements Cr (24.0%), Pb (29.7%), Ni (39.2%), Cd (40.5%), As (10.8%), and F (39.18%) were above the permissible limits of the WHO. The groundwater samples were examined for water quality index (WQI), contamination index (C_d), chronic daily intake indices (CDIs), hazard quotient indices (HQ), principal component analysis (PCA), piper diagrams, Gibbs diagrams, and cluster analysis to ascertain nature of the groundwater present in the study area. The samples were also examined for suitability for irrigation by sodium percentage (Na%), sodium adsorption ratio (SAR), Kelly's index (KI), permeability index (PI), and Wilcox diagrams. Samples in the range of 0 to 58.33% were inappropriate for irrigation.

Keywords: water quality; chemical assessment; groundwater; water quality index; health hazard



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1. Introduction

Water is the most abundant chemical substance and is a basic source for the lives of people, plants, and animals on Earth. Water has a central role to play for every cell and organ in the human body. The main sources of water for human consumption are surface and groundwater [1]. Water may become hazardous if it does not meet the required standards for drinking, irrigation, and industries [2]. Groundwater is broadly used in rural areas as a source of drinking water, mostly in third-world countries; thus, the quality of groundwater needs to be tested for possible health effects [3]. A number of studies have been conducted to examine the quality of groundwater from many parts of the world, including Sindh Province of Pakistan. One study analyzed 218 samples from Sindh Province and evaluated them for irrigation and drinking purposes [4]. The results of the physicochemical analysis indicated that 17.8–62.8% of samples were not suitable for drinking. Higher values were reported from Southern Sindh due to the effects of sea intrusion. Lanjwani et al. [5] analyzed 21 samples from the district of Qambar Shahdadkot and reported water quality for human consumption and irrigation. The TDSs in 81% of samples, major cations in 50% of samples, and Cd, Pb, and Ni in 28.5–57.1% of samples

exceeded the permissible limits of the WHO. Lanjwani et al. [6] analyzed 25 samples from Ratodero subdistrict, Larkana district, Sindh, for their physicochemical parameters. The results of the analysis based on the water quality index (WQI) indicated that 35% of samples were of the poor water category. Another work assessed [7,8] 425 samples for the water quality of the primary schools of selected districts of Sindh. Groundwater samples made up 62% of the total samples used for drinking in schools, and the results of the WQI indicated that 26% of schools were supplied poor to very poor drinking water. Rind et al. [9] analyzed 30 groundwater samples for 26 different parameters from Hala subdistrict, Matiari district, Sindh. Fluoride and arsenic were reported to be 40% and 43% above the WHO limits, and the results of the WQI suggested that 57.7% of samples were poor to very poor for drinking water. Another study [10] reported the contamination of arsenic in the groundwater of Indus Valley, Pakistan. Nearly 1200 samples were analyzed for a number of physicochemical parameters. The mobilization of arsenic in groundwater was related to elevated pH dissolution. Higher arsenic contents were reported near the Indus river and its tributaries. Khuhawar et al. [11] assessed the quality of the groundwater of the Thar Desert of Sindh Province, where 2193 samples were taken from dug wells. The TDSs of 57.5% samples were higher than 3000 mg/L, 14% were within 1500–3000 mg/L, and 27% were below 1500 mg/L. Ullah et al. [12] analyzed 61 samples from different sites in Sanghar District and analyzed for 12 different parameters, including arsenic. Arsenic was reported to be in the range of 5–25 µg/L. Bashed et al. [13] analyzed 39 groundwater samples for 11 different parameters from the subdistrict of Khipro, Sanghar District. The results of the analysis indicated that the majority of the samples were suitable for cultivation, except for a few samples. Another study [14] examined the groundwater quality of Hangu district, Pakistan, for the purposes of drinking and irrigation. The water quality was suitable for cultivation, except for 5% of the sampling sites. Another study [15] evaluated the groundwater quality of Northern Algeria using the WQI and GIS. The results indicated that nitrate ions exceeded the WHO limits in all water samples, and calcium, chloride, and sulphate occurred at alarming concentrations. Kaur et al. [16] analyzed 24 groundwater samples in Malawi, Southwestern Punjab, India, for major cations, anions, and other physicochemical parameters. The results indicated a major number of parameters above the Indian standards. Adimalla et al. [17] analyzed 105 groundwater samples from Central Telangana, India, for drinking and irrigation. The samples were suitable for drinking, but 51% and 71% exceeded the permissible limits for fluoride and nitrate, respectively. Li et al. [18] analyzed 74 groundwater samples for irrigation purposes from Pengyang, China. The quality of the groundwater for irrigation was reported to be excellent to good. Fifty groundwater samples were assessed for drinking water quality from Qorveh and Dehgolan, Kurdistan, Iran. The results based on the WQI indicated that 36% of the samples were excellent and 64% were good for drinking [19].

The present work critically examines the groundwater quality by analyzing 74 samples collected from 3 subdistricts of Sanghar District for drinking, domestic, and irrigation purposes. A total of 26 different physicochemical parameters were analyzed, and results were compared with WHO permissible limits. The results were analyzed on multivariate statistical procedures, including WQI, C_d , CDI, HQ, PCA, Gibbs diagrams, and coefficient of correlation (r), to ascertain the nature of groundwater available in the study area. The work also reports the quality of groundwater for irrigation.

Geography and Geology

Sanghar District lies between 25°58'13" N latitude and 69°24'4" E longitude. The area of the district is 10,608 km² with a total population of about 2.049 million [20]. It is located at the Centre of Sindh and has a common border with India in the east. The Sanghar town is the district headquarter and is at a distance of about 56 km from Benazirabad (Nawabshah) and Mirpurkhas cities. The main industry of the district is agriculture. The district is administratively divided into six subdistricts: Jam Nawaz Ali, Khipro, Sanghar, Shahdadpur, Singhro, and Tando Adam Khan. The district is also divided into 70 union

councils. The areas of Sanghar District mainly consists of semiarid land, a part of the great Thar desert (mostly in the subdistrict of Khipro), and cropped areas, irrigated by the Mithrao and Nara canal system, connected with the river Indus. The main crops cultivated are rice, wheat, and cotton. The climatic conditions of district Sanghar are subtropical. The average monthly temperature varies within 21.2–39.11 °C with an average yearly temperature of 32.3 °C. It receives about 15.87 millimeters of precipitation annually.

Sanghar District is located in the lower Indus basin; the stratigraphic sequence drilled in the southern part of the Indus basin indicates from Jurassic to recent and the sediments source is the Indian craton [21]. The lower Goru formation of the southern Indus basin was deposited in a shallow to deep marine environment, with seven distinct lithological units composed of various sand and shale intervals [22]. The study area has composition of silts, sand, and clay of tertiary rocks [23]. The significance of soil differs from one place to another by sand and clay, with approximately 250 to 450 feet thickness of sandy layers under a shallow aquifer [24]. They are satisfactory to intermediate micaceous sands having well-sorted bands and lenses of clay and silt [25]. The water tables have a mean depth 3.93 m and range between 1.39–12.76 m [26]. Shakir et al. examined Cretaceous sands of Khipro, Sanghar District area, by integrated seismic structural analysis, and studied Naimat Basal 01 and Siraj South 01 wells using petrophysical interpretation [27].

2. Materials and Methods

2.1. Sample Collection

The 74 samples were collected from three subdistricts of the districts Sanghar (32), Khipro (30), and Jam Nawaz Ali (12), from villages and populated towns randomly from most of the union councils to cover the study area, where the groundwater for human needs is used for drinking and agriculture (Table 1) (Figure 1). The water samples were gathered from hand pumps, motor pumps, and tube wells. Two clean plastic bottles (1.5 L) were filled from each sampling station, after allowing water from the source to drain for 5 min. A bottle was used for physicochemical analysis, and another was used for metal analysis [28,29]. The bottles for metal analysis were acidified with 1.5 mL hydrochloric acid or nitric acid. Hand pumps and motor pumps were bored at 75–150 feet and tube wells at 150–350 feet depth [30].



Figure 1. Pakistan, Sindh, and Sanghar subdistricts.

Table 1. Water analysis of Sanghar with descriptive statistics ($n = 74$).

Parameters	Minimum	Maximum	Mean	Std. Deviation	Std. Error
pH	6.74	8.65	7.7284	0.34037	0.03957
Conductivity $\mu\text{s}/\text{cm}$	346	5730	1675	1231	143
Salinity g/L	0.2	3.1	0.858	0.6697	0.0779
TDS mg/L	221	3667	1072	787	91
NO ₂ $\mu\text{g}/\text{L}$	0.09	400	42	95	11
NO ₃ mg/L	0.65	6.39	2.8199	1.26219	0.14673
T.PO ₄ mg/L	0.26	7.76	1.4619	1.40125	0.16289
O.PO ₄ mg/L	0.14	3.07	0.7942	0.75109	0.08731
T.H mg/L	1	800	244	170	19
Na mg/L	20	1349	185	254	29
K mg/L	5	103	20	21	2.5
Ca mg/L	44	272	98	45	5
Mg mg/L	10	149	36.39	27	3.212
Chloride mg/L	28	1230	211	227	26
Alkalinity mg/L	104	820	265	127	14
SO ₄ mg/L	27	1319	216	256	29
Mn $\mu\text{g}/\text{L}$	3	282	36	40	4
As $\mu\text{g}/\text{L}$	0	10	4	7.8	0.9
Fe $\mu\text{g}/\text{L}$	1.2	256	27	41	4
Co $\mu\text{g}/\text{L}$	9.8	48	26	9	1
Cu $\mu\text{g}/\text{L}$	0	113	24	38	4
Ni $\mu\text{g}/\text{L}$	0	155	45	38	4
Pb $\mu\text{g}/\text{L}$	0	66	14	15	2
Cd $\mu\text{g}/\text{L}$	0	107	19	27	3
F mg/L	0.1	26	4	5.4	0.6
Cr $\mu\text{g}/\text{L}$	0	96	29	31	3.6
KI meq/L	0.2	76	24	22	2.6
SAR meq/L	0.4	4.9	1.3	0.84	0.0984
PI meq/L	67	112	94	8.6	1.0068
Na% meq/L	27	82	52	11.5	1.3386

2.2. Sample Analysis

The samples were analyzed for 26 different parameters (Table S1) following standard analytical procedures. The analyses were carried out at least in triplicate, and average values are reported. The electrical conductivity (EC), salinity, total dissolved salts (TDS), and pH were measured utilizing an Orion 115 conductivity meter (Orion Pvt Ltd., Boston, MA, USA). Chloride, alkalinity, and total hardness were determined by titrimetric methods [31]. Nitrate, nitrite, total phosphate, orthophosphate, sulphate, and fluoride were measured using spectrophotometric procedures utilizing a Hitachi 220 double beam spectrophotometer (Hitachi (Pvt) Ltd., Tokyo, Japan). Na, K, Ca, Mg, Cu, Ni, Mn, Co, Fe, Cd, Pb, and Cr were determined by flame atomic absorption spectrometry (Perkin Elmer, AA 800, Singapore) at the conditions recommended by the manufacturer. The equipment was controlled by the computer with Winlab 36 software. The analyses were carried out in triplicate ($n = 3$) with integration time of 4 s and time of delay of 4 s. For the analysis of Ca, Mg, K, and

Na, the samples were diluted 10–25 times with distilled water. For determination of trace elements, the samples were preconcentrated by the factor of 10 by evaporation of water at 80–90 °C on an electrical hot plate. The solutions were filtered if required before analysis. The arsenic was estimated using the E. Merck kit method.

The standard deviation (SD), relative standard deviation (RSD), mean, scatter diagrams, Gibbs diagrams, and Wilcox diagrams were drawn on the Excel 2013 program. Coefficient of correlation[®], principal component analysis (PCA), and cluster analysis were carried out on SPSS 20 (SPSS Inc., Chicago, IL, USA) program. The piper diagrams were drawn on Aquachem software 11.

2.3. Water Quality Index (WQI)

WQI was calculated using the reported procedure [32]. The parameters for water quality were ascribed the weight (wi) corresponding to their hazardous effects. The weight of 5 was given to As, Pb, and Cd owing to their expressing effects on water quality [28,29]. The K, Na, and Ca were allowed a weight (wi) of 3. The relative weight (Wi) is accounted from the following relation, where n designates the number of parameters [33,34].

$$Wi = wi / \sum_{i=1}^n wi. \quad (1)$$

Quality rating (Qi) is determined by dividing the concentration of each sample (Ci) with the WHO standard (Si) of the corresponding parameter for drinking water, then multiplying the equation by 100.

$$Qi = (Ci/Si) \times 100. \quad (2)$$

Then,

$$WQI = \sum Wi \times Qi. \quad (3)$$

2.4. Gibbs Diagrams

The Gibbs diagrams are used to calculate the sources of anions (Cl^- , HCO_3^-) and cations (Na^+ , Ca^{2+} , K^+) in groundwater by plotting against TDS in the Origin program. The values are evaluated with the aid of the following formula:

$$\text{Anions} = Cl^- / (Cl^- + HCO_3^-). \quad (4)$$

$$\text{Cations} = (Na^+ + K^+) / (Na^+ + K^+ + Ca^{2+}). \quad (5)$$

All the concentrations are in milliequivalent (m.eq/L).

2.5. Contamination Index (C_d)

Contamination index (C_d) was calculated by Backman et al.'s [35] method to evaluate the harmful effect of the parameters on the human health and environment, by comparing the observed values of the parameters with WHO permissible limits. The C_d is estimated by using the following Formula (6) [5]:

$$Cfi = (CAi/CNi) - 1. \quad (6)$$

where Cfi = Contamination factor of the ith parameters; CAi = observed value of ith parameter; CNi = higher permissible level of ith parameter by the WHO for human consumption.

2.6. Chronic Daily Intake Indices (CDIs)

Metal ions enter the human body by different ways: food, drinking, and inhalation. However, by the drinking water is considered more important. The CDIs of Sanghar District were estimated by using the following relation (7) [36]:

$$CDI = C \times DI/BW. \quad (7)$$

where C stands for the values of the parameters, DI represents daily intake (2 L/day), and BW is the average body weight (72 kg).

2.7. Hazard Quotient Indices (HQ)

The HQ is calculated for noncarcinogenic effects of metal ions on the human body. HQ was estimated from the following relation (8):

$$HQ = CDI/RfD. \quad (8)$$

CDI stands for chronic daily intake indices and RfD for reference dose of oral harmfulness. The values described by US EPA are for Cd 5.0×10^{-4} , Ni 2.0×10^{-2} , Cu 2.7×10^{-2} , Pb 3.5×10^{-3} , Cr 3.0×10^{-3} , Zn 3.0×10^{-1} , As 3.0×10^{-4} , Mn 2.4×10^{-2} , and Fe 3.0×10^{-1} mg/kg-day [37]. The value of HQ less than 1 is considered safe, and an HQ value above 1 is considered unsafe [34].

2.8. Suitability of the Groundwater for Irrigation

The parameters sodium percent (% Na), sodium adsorption ratio (SAR), Kelly's index (KI), and permeability index (PI) were calculated by using the following Equations (9)–(12). All the concentrations were in m.eq/L.

$$\text{Na\%} = [(\text{Na}^+ + \text{K}^+)/(\text{Ca}^{2+} + \text{Mg}^{2+} + \text{Na}^+ + \text{K}^+)] \times 100. \quad (9)$$

$$\text{SAR} = [\text{Na}^+]/[(\text{Ca}^{2+} + \text{Mg}^{2+})/2]^{1/2}. \quad (10)$$

$$\text{KI} = \text{Na}^+ / (\text{Ca}^{2+} + \text{Mg}^{2+}) \quad (11)$$

$$\text{PI} = [(\text{Na}^+ + \text{HCO}_3^-)/(\text{Na}^+ + \text{Ca}^{2+} + \text{Mg}^{2+})] \times 100. \quad (12)$$

3. Results and Discussion

The results describe the physicochemical analysis of 74 groundwater samples from the Sanghar (32), Khipro (30), and Tando Jam Nawaz Ali (12) subdistricts of Sanghar District, Sindh.

3.1. Sanghar Subdistrict

The samples collected were from hand pumps, 20 (62.5%), motor pumps, 8 (25%), and tube wells, 4 (12.5%). The water from hand pumps and motor pumps was mostly used for the drinking of humans as well as cattle, but the water from tube wells was consumed for irrigation. The results of analysis are summarized in Table 1 and the results with mean, minimum–maximum, and standard deviation are summarized in Table 1. All the results obtained were compared with the permissible limits of WHO [36]. The pH of the Sanghar subdistrict ranged from 6.74–8.65, and two samples (6.2%) crossed the upper limit of 8.5, which may be due to the presence of carbonate salts in the groundwater. More samples were slightly on the alkaline side. EC and TDS were observed within 399–5730 $\mu\text{S}/\text{cm}$ and 255.4–3667.2 mg/L. EC of 16 (50%) and TDS of 13 (40.6%) samples crossed the WHO limits (EC 1562.5 $\mu\text{S}/\text{cm}$ and TDS 1000 mg/L). Higher amount of TDS gives an unpleasant taste to the water. Total hardness was between 120–788 mg/L, and only one sample crossed the limit 500 mg/L. The high concentration of total hardness is objectionable for aesthetic sense and may cause gastrointestinal problems. The alkalinity was indicated within 120–362 mg/L, and 8 (25%) samples crossed the permissible limit of 300 mg/L. High amounts of alkalinity may cause dry skin by dissolving skin oil. The chloride is highly soluble in water and is distributed in groundwater as salts of sodium, potassium, and calcium. The sources of sulphate may be associated with agriculture activities, including the use of the fertilizers. The chloride and sulphate were observed between 28–750 mg/L and 27–762 mg/L, and 13 (40.6%) for chloride and 5 (15.6%) for sulphate were above the limit for both 250 mg/L. Based on average values, $\text{Cl}^- > \text{SO}_4^{2-} > \text{HCO}_3^-$. The high concentration of nitrate-N may cause a disease commonly known as blue baby in children. High concentration of nitrite-N

may cause cancer due to the formation of N-nitroso and nitrosamine compounds [38]. The application of fertilizers for irrigation and the use of detergents for washing purposes may be responsible for the higher concentration of phosphate-P in groundwater. The results of nitrate, nitrite, total phosphate, and orthophosphate for all samples were observed within WHO permissible limits (Table S1) [39]. Sodium is required for the muscles and nerve functioning, but the higher concentration of sodium may be responsible for high blood pressure and kidney damage in humans. High concentration of potassium may be due to mineral dissolution, agricultural activities, and plant material decomposition. Sodium and potassium were observed within 22–390 mg/L and 6–117 mg/L. The sodium in 13 (40.6%) and potassium in 21 (65.6%) samples were above the permissible limits of 200 mg/L and 12 mg/L, respectively. Calcium and magnesium have similar functions in the human body. High concentration of magnesium may cause vomiting or diarrhea. The results of calcium and magnesium were within 44–272 mg/L and 10–130 mg/L, and calcium in 01 (3.1%) and magnesium in 5 (15.6%) samples crossed the limits of 150 mg/L and 75 mg/L, respectively. Based on the average values, $\text{Na}^+ > \text{Ca}^{2+} > \text{Mg}^{2+} > \text{K}^+$. Iron and copper are essential elements for humans, but higher intake of copper may be responsible for neurological or liver complications. Manganese is mostly present in groundwater together with iron, but high amounts of manganese may account for lungs, eyes blindness, and nerve damage. The concentrations of Fe, Cu, Mn, and Co for all samples were within the limits of WHO. Chromium is present in a number of oxidation states, but chromium (VI) is more present in natural waters. It can enter cell tissues and may prove hazardous. Lead is a main pollutant and is considered as toxic. Lead is harmful for multiple body systems and can particularly affect children [40]. Cadmium is also toxic and can act as an agent to cause cancer. Nickel affects the absorption of iron in the human body, and higher concentrations of nickel in the human body may be responsible for causing vomiting and headaches. The concentrations of Cr for 15 (46.8%), Pb for 10 (31.2%), Cd for 15 (46.8%), and Ni for 13 (40.6%) samples crossed WHO guidelines (Table S2). The arsenic in inorganic form is widely present on Earth. The arsenic contamination of groundwater is reported from different countries, including Pakistan [41]. The initial poisonous effects of arsenic are skin and nail abnormalities like hyperpigmentation. The arsenic concentration in 3 (9.4%) crossed the limit of 10 µg/L. Fluoride at low levels is beneficial for dental caries, but fluoride concentration above 1.5 mg/L in water causes dental fluorosis. The fluoride concentrations above 4 mg/L in water causes bones fluorosis, where the skeleton is affected. The concentration of fluoride was found to be between 0.21–10.7 mg/L and the fluoride in 16 (50%) samples was above the limit of 1.5 mg/L. The values of standard deviation (SD) for a number of parameters present are high (Table 1), indicating that a wide variation in the parameter may be due to the changes in the geological settings within the study area.

Suitability of Groundwater for Irrigation

The groundwater of Sanghar subdistrict was evaluated for irrigation based on Na%, SAR, KI, and PI. The sodium% (Na%) was calculated within 21.48–60.46%. Samples 7 (21.8%) were of good quality for irrigation with Na% within 20–40%. Samples 24 (74%) were permissible with Na% within 40–60%. Sample 01 (3.1%) was in the uncertain category with Na% 60–80 (Table S3). The results of sodium adsorption ratio (SAR) for 32 groundwater samples were observed within 0.47–2.84 and the indicated values were below the required sodium adsorption ratio value of 6. All the samples based on SAR values were suitable for irrigation. The Kelly's index (KI) of samples were calculated within 0.24–1.42, and 75% of samples indicated KI values less than 01 and were considered suitable for irrigation. However, 25% samples showed KI values more than 01 and were not considered suitable for irrigation. The permeability index (PI) was calculated within 23.83–142.09. A total of 62.5% of the samples were observed with PI values above 75% and were considered as class I, good for irrigation. A total of 21.9% samples were within PI values between 75–50% and were considered as class II, suitable for irrigation. However, 15.6% of the samples indicated PI values below than 50% and were classified as class III, as inappropriate for agriculture.

3.2. Khipro Subdistrict

The groundwater (30) samples were collected from Khipro subdistrict, comprising 10 samples from motor pumps, 18 from hand pumps, and 2 from dug wells. The samples were gathered from villages and towns used for drinking. The pH of all samples was within WHO guidelines of 6.5–8.5 [40]. The EC and TDS were observed between 385–5710 $\mu\text{S}/\text{cm}$ and 246–3654 mg/L. EC and TDS of 12 (40%) samples were observed above WHO limits (EC 1500 $\mu\text{g}/\text{cm}$ and TDS 1000 mg/L). The total hardness was detected within 140–800 mg/L, and 3 (10%) samples were found above the limit of 500 mg/L. The alkalinity was indicated between 138–820 mg/L, and 7 (23.3%) samples crossed the limit (300 mg/L). Chloride and sulphate were observed within 40–1230 mg/L and 32–1319 mg/L. The chloride for 9 (30%) and sulphate for 6 (20%) samples crossed the limit of 250 mg/L. Based on the average values, $\text{SO}_4^{2+} > \text{Cl}^- > \text{HCO}_3^-$ (Table S1). Nitrate in all the samples was within permissible limits, but nitrite in 01 sample, orthophosphate in 02 samples, and total phosphates in 04 samples crossed the limits of WHO. The sodium was detected within 22–1349 mg/L and 9 (30%) samples were above the limit of 200 mg/L. Potassium was found between 5–103 mg/L and 15 (50%) samples crossed the limit of 12 mg/L. The calcium was observed within 46–260 mg/L and 4 (13.3%) samples were beyond the limit of 150 mg/L. The magnesium was within 10–149 mg/L and 3 (10%) samples were above the limit of 75 mg/L. Based on the average values, $\text{Na}^+ > \text{Ca}^{2+} > \text{Mg}^{2+} > \text{K}^+$ (Table S2). The concentrations of Fe, Cu, Mn, and Co for all the (30) samples were within the permissible limits, but 9 (30%) samples for Cr and Pb and 11 (36.6%) samples for Ni and Cd crossed the limits of WHO for drinking water. The arsenic contents in 3 (10%) samples crossed the permissible limit of 10 $\mu\text{g}/\text{L}$. The contents of fluoride in groundwater samples varied between 0.11–18.0 mg/L, and 10 (33.3%) samples were above the acceptable limit of 1.5 mg/L. The area is devoid of industrial activities and the livelihood of most of the inhabitants depends on the agriculture. Thus, high concentrations of salts and fluoride may be due to geological reasons.

Quality of the Water for Irrigation

The Na% was calculated within 18.3–76.55%, and 9 (30%) samples were within the range of 20 to 40%, indicating good quality. Eighteen samples (60%) were in the range of 40 to 60% and were acceptable for irrigation. Three (10%) samples were found within 60–80% and were indicated as doubtful. The SAR values were observed within 0.39–6.26. A total of 29 (96.6%) samples were within acceptable limits of SAR (6) for irrigation, and only one sample crossed the limit. The KI values were calculated within 0.19–3.3, and 76.7% of samples indicated KI values less than 1, and were good for irrigation. A total of 23.3% samples had KI values more than 01 and were not suitable. PI of the samples were indicated within 19.75–312.79, and 43.3% of samples were in class I, with PI values greater than 75%. A total of 36.7% of samples were within class II, with PI values of 50–75% (Table S3). However, 20% samples were in class III, with PI values less than 50%, and were inappropriate for irrigation.

3.3. Jam Nawaz Ali Subdistrict

Twelve samples were collected from Jam Nawaz Ali subdistrict: 3 from motor pumps, 01 from dug well, and 8 from hand pumps. Two samples were gathered from Jam Nawaz Ali town and 10 samples from different villages, mostly used for drinking purposes. The pH of all the samples was observed within the limits 6.5–8.5. EC and TDS of the samples were observed within 346–2798 $\mu\text{S}/\text{cm}$ and 221–1791 mg/L. Seven (58.3%) samples for EC and eight (66.6%) samples for TDS were within WHO limits (Table S1). The total hardness and alkalinity were noted within 126–400 mg/L and 104–304 mg/L, respectively. All the samples for total hardness and 11 (91.2%) samples for alkalinity were within limits of drinking water. The chloride and sulphate were indicated between 35–257 mg/L and 43–414 mg/L, respectively. Eleven (91.2%) samples for chloride and nine (75%) samples for sulphate were within permissible limits of 250 mg/L for both. The nitrate and nitrite for all samples and orthophosphate and total phosphate for 10 (83.3%) samples were

within limits. Sodium and potassium were observed within 20–272 mg/L and 5–32 mg/L, respectively. Na in 9 (75%) and K in 7 (58.3%) samples were within acceptable limits. Similarly, calcium and magnesium were indicated within 45–140 mg/L and 13–50 mg/L. The Ca and Mg contents in all the samples were within permissible limits for drinking water. The concentrations of Fe, Cu, Mn, and Co in all (12) samples were in acceptable limits, but concentrations of Cr and Ni in 7 (58.3%), Ni in 9 (75%), and Cd in 8 (66.6%) samples were within agreeable limits for drinking. The arsenic contents in 10 samples (83.3%) were within 10 µg/L, and fluoride in 9 (75%) samples were within permissible limits of 1.5 mg/L (Table S2).

Water Quality for Irrigation

The Na% for Jam Nawaz Ali subdistrict varied from 18.42–47.04. Seven (58.3%) samples were within Na% 20–40 and were of good quality. Five (41.66) samples were calculated within Na% 40–60 and were considered of acceptable quality for irrigation (Table S3). The SAR values varied from 0.52–2.21 and were within the acceptable limit of 6 for irrigation. The KI values were calculated between 0.88–3.8. 4 (33.3%) and samples indicated that KI values were less than 1 and were acceptable for irrigation. Eight (66.66%) samples showed KI values more than 1 and were doubtful for irrigation. PI values for the samples were observed within 84–106 and were above 75%. All the samples were considered good for irrigation.

3.4. Water Quality Index (WQI)

WQI provides a numerical value that indicates the quality of drinking water. The calculated values of WQI are categorized into five groups for drinking water: excellent < 50, good 50–100, poor 100–200, very poor 200–300, and unfit > 300 [42]. The values of WQI for the collected samples ($n = 74$) from Sanghar, Khipro, and Jam Nawaz Ali subdistricts of district Sanghar were within 22.47–374.25 (Table 2). The samples were divided into categories: excellent, 26 (35.14%), good, 31 (41.89), poor, 12 (16.22%), very poor, 2 (2.70%), and unfit, 3 (4.05%). The results indicated that more samples were present in excellent to good water categories for drinking.

Table 2. Water Quality Index of Sanghar District.

Sanghar Sub District			Khipro Sub District			Jam Nawaz Ali Sub District		
Sample ID	WQI	State	Sample ID	WQI	State	Sample ID	WQI	State
S1	75	Poor	K1	49	Good	J1	43	Good
S2	48	Good	K2	42	Good	J2	112	Unfit
S3	212	Unfit	K3	65	Poor	J3	74	Poor
S4	46	Good	K4	49	Good	J4	83	Very Poor
S5	22	Excellent	K5	105	Unfit	J5	108	Unfit
S6	128	Unfit	K6	374	Unfit	J6	35	Good
S7	99	Very Poor	K7	345	Unfit	J7	19	Excellent
S8	91	Very Poor	K8	323	Unfit	J8	81	Very Poor
S9	119	Unfit	K9	96	Very Poor	J9	42	Good
S10	65	Poor	K10	65	Poor	J10	64	Poor
S11	37	Good	K11	96	Very Poor	J11	30	Good
S12	29	Good	K12	67	Poor	J12	34	Good
S13	117	Unfit	K13	51	Poor			
S14	167	Unfit	K14	70	Poor			
S15	43	Good	K15	98	Very Poor			

Table 2. Cont.

Sanghar Sub District			Khipro Sub District			Jam Nawaz Ali Sub District		
Sample ID	WQI	State	Sample ID	WQI	State	Sample ID	WQI	State
S16	55	Poor	K16	30	Good			
S17	73	Poor	K17	64	Poor			
S18	38	Good	K18	135	Unfit			
S19	69	Poor	K19	28	Good			
S20	73	Poor	K20	53	Poor			
S21	57	Poor	K21	57	Poor			
S22	28	Good	K22	34	Good			
S23	81	Very Poor	K23	43	Good			
S24	80	Very Poor	K24	134	Unfit			
S25	107	Unfit	K25	64	Poor			
S26	37	Good	K26	44	Good			
S27	39	Good	K27	50	Good			
S28	33	Good	K28	52	Poor			
S29	73	Poor	K29	247	Unfit			
S30	51	Poor	K30	128	Unfit			
S31	42	Poor						
S32	102	Unfit						

3.5. Contamination Index (C_d)

The individual parameters above the permissible limit of WHO are added up to obtain the contamination index (C_d). The values of parameters indicate whether the sample is hazardous for drinking purposes. The C_d values calculated for all 74 samples varied within 0–42.8 (Table 3). The 59 (79.7%) samples had C_d values less than 1, and were considered suitable for drinking. Seven samples (9.4%) had C_d values within 3 and were considered moderately acceptable for drinking. Eight (10.8%) samples were above the value of 3 and were not considered suitable for drinking.

Table 3. Water analysis of Sanghar for contamination index.

Sanghar Sub District		Khipro Sub District		Jam Nawaz Ali Sub District	
Sample ID	Contamination Index	Sample ID	Contamination Index	Sample ID	Contamination Index
S1	−1	K1	−8	J1	−5
S2	−7	K2	−10	J2	−0.7
S3	19	K3	−7	J3	−2
S4	−7	K4	−9	J4	−1
S5	−9	K5	−2	J5	0.7
S6	8.5	K6	42	J6	−7.3
S7	−1	K7	38	J7	−9.2
S8	0.2	K8	37	J8	0.2
S9	2	K9	−0.101	J9	−7
S10	−2	K10	−0.5	J10	−3
S11	−7	K11	−2	J11	−8

Table 3. Cont.

Sanghar Sub District		Khipro Sub District		Jam Nawaz Ali Sub District	
Sample ID	Contamination Index	Sample ID	Contamination Index	Sample ID	Contamination Index
S12	2	K12	−7	J12	−9
S13	0.85	K13	−8		
S14	11	K14	−4		
S15	−7	K15	−2		
S16	−5	K16	−13		
S17	−0.2	K17	−5		
S18	−10	K18	1		
S19	−3	K19	−10		
S20	−2	K20	−8		
S21	−8	K21	−8		
S22	−11	K22	−6		
S23	3	K23	−8		
S24	−1	K24	2		
S25	2	K25	−3		
S26	−3	K26	−10		
S27	−8	K27	−8		
S28	−9	K28	−8		
S29	−0.4	K29	16		
S30	−5	K30	1		
S31	−9				
S32	2				

3.6. Gibbs Diagrams

The Gibbs diagrams [43] are used to assess the sources of cations and anions (m.eq/L) against TDS (mg/L). The Gibbs diagrams are mostly used to examine the relationships between water quality and aquifer characteristics. The allotment of cations or anions versus TDS are used to evaluate the dominance of rock, evaporation, or precipitation in Gibbs diagrams (Figure 2). The cations and anions were predominantly within rock–water dominance and a few samples (samples 3, 4.0%) were within evaporation dominance. The samples within precipitation dominance were not observed. The rock–water dominance showed synergy between the chemistry of the rocks and leaching of the water under the subsurface.

3.7. Chronic Daily Intake Indices (CDIs)

Human health risk assessment is determined from the magnitude of negative effects on human health due to the exposure to heavy metals, mainly through the path of drinking water. The CDI values for the drinking water of three subdistricts of Sanghar District for iron varied from 3.3×10^{-5} to 7.1×10^{-3} with an average value of 7.7×10^{-4} , copper $0\text{--}3.1 \times 10^{-3}$ with an average value of 6.7×10^{-4} , cadmium $0\text{--}2.97 \times 10^{-3}$ with an average value of 5.3×10^{-4} , chromium $0\text{--}2.66 \times 10^{-3}$ with an average value of 8.2×10^{-4} , manganese 8.3×10^{-5} to 7.83×10^{-3} with an average value of 1.03×10^{-3} , nickel $0\text{--}4.3 \times 10^{-3}$ with an average value of 1.27×10^{-3} , lead $0\text{--}1.87$ with an average value of 0.40, and arsenic $0\text{--}6.94 \times 10^{-4}$ with an average value of 1.16×10^{-4} $\mu\text{g}/\text{kg}\text{-day}$. The CDI values of the elements decreased in the following order: Pb > Ni > Mn > Cr > Fe > Cu > Cd > As. The

mean values of CDI of all the elements were below 1, but the CDI values for Pb at some locations were higher than 1 (Table 4). The area is mostly based on agricultural lands, and high value of CDI for Pb at some locations may be due to geological reasons owing to rock–water interactions.

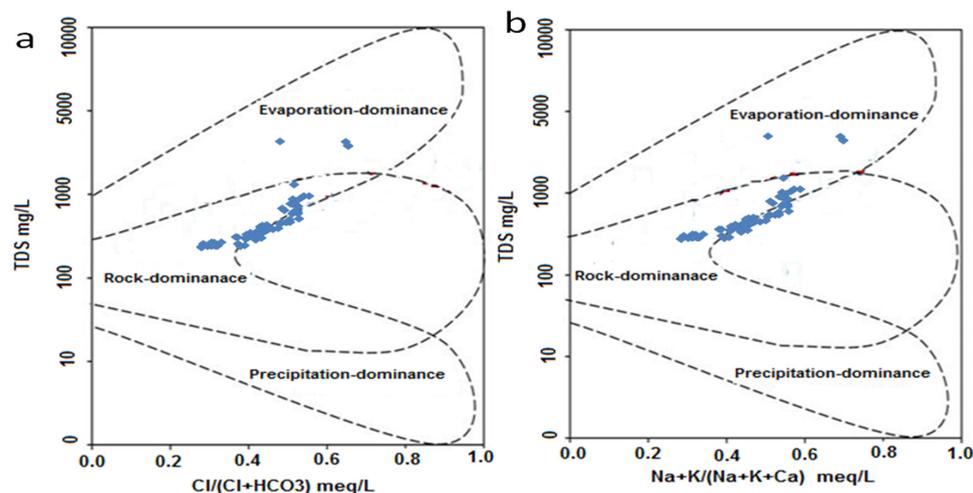


Figure 2. Gibbs diagram: (a) Cl/(Cl + HCO₃) vs. TDS, (b) Na + K/(Na + K + Ca) vs. TDS.

Table 4. Water analysis of Sanghar for chronic daily index (CDI).

Samples No.	Fe	Cu	Cd	Cr	Mn	Ni	Pb	As
S1	5.80×10^{-4}	1×10^{-3}	1×10^{-4}	1×10^{-3}	1.3×10^{-3}	$4. \times 10^{-4}$	2.14×10^{-1}	1×10^{-4}
S2	5.30×10^{-4}	1×10^{-4}	0	1.9×10^{-3}	1.9×10^{-3}	3×10^{-4}	0	0
S3	3.22×10^{-3}	0	7×10^{-4}	0	2.2×10^{-3}	2.7×10^{-3}	1.92×10^{-1}	0
S4	7.12×10^{-3}	5×10^{-4}	0	1.1×10^{-3}	6×10^{-4}	1×10^{-3}	2.44×10^{-1}	0
S5	1.74×10^{-3}	2.50×10^{-3}	0	1.3×10^{-3}	1.3×10^{-3}	0	1.97×10^{-1}	7×10^{-4}
S6	3.70×10^{-4}	1×10^{-4}	7×10^{-4}	1.5×10^{-3}	1.4×10^{-3}	2.1×10^{-3}	12.2×10^1	0
S7	8.0×10^{-4}	2×10^{-4}	3×10^{-4}	0	4×10^{-4}	2.4×10^{-3}	3×10^{-1}	0
S8	1.57×10^{-3}	2.5×10^{-3}	2×10^{-4}	1.8×10^{-3}	1.9×10^{-3}	1.5×10^{-3}	2.47×10^{-1}	0
S9	2.51×10^{-3}	0	0	1.5×10^{-3}	2.2×10^{-3}	3.1×10^{-3}	0	0
S10	0	2×10^{-4}	0	1.1×10^{-3}	6×10^{-4}	2.6×10^{-3}	9.64×10^{-1}	1×10^{-4}
S11	0	0	0	2×10^{-3}	1.3×10^{-3}	4×10^{-4}	3.44×10^{-1}	3×10^{-4}
S12	9.20×10^{-4}	1×10^{-4}	0	2.7×10^{-3}	1.4×10^{-3}	5×10^{-4}	2.03×10^{-1}	1×10^{-4}
S13	1.41×10^{-3}	1×10^{-4}	3×10^{-4}	0	4×10^{-4}	1.5×10^{-3}	1.78×10^{-1}	0
S14	3.50×10^{-4}	1×10^{-4}	5×10^{-4}	1.2×10^{-3}	3×10^{-4}	2.6×10^{-3}	9.58×10^{-1}	0
S15	7.30×10^{-4}	2×10^{-4}	0	1.3×10^{-3}	5×10^{-4}	3×10^{-4}	2.17×10^{-1}	1×10^{-4}
S16	2.70×10^{-4}	3.1×10^{-3}	0	9×10^{-4}	2×10^{-4}	1.5×10^{-3}	2.33×10^{-1}	1×10^{-4}
S17	1.20×10^{-4}	2.7×10^{-3}	3×10^{-4}	1.4×10^{-3}	7×10^{-4}	1.3×10^{-3}	8.19×10^{-1}	1×10^{-4}
S18	8.70×10^{-4}	1×10^{-4}	0	0	8×10^{-4}	0	1.19×10^{-1}	0
S19	3.30×10^{-4}	1×10^{-4}	0	0	2.9×10^{-3}	4.3×10^{-3}	7.75×10^{-1}	7×10^{-4}
S20	5.60×10^{-4}	2×10^{-4}	1×10^{-4}	1.9×10^{-3}	1.8×10^{-3}	4×10^{-4}	2.06×10^{-1}	3×10^{-4}
S21	2.40×10^{-4}	1×10^{-4}	1×10^{-4}	0	1.3×10^{-3}	4×10^{-4}	1.64×10^{-1}	0
S22	2.70×10^{-4}	2×10^{-4}	3×10^{-5}	1.2×10^{-3}	2.1×10^{-3}	1×10^{-3}	2.14×10^{-1}	1×10^{-4}
S23	5.60×10^{-4}	0	3×10^{-4}	1×10^{-3}	1×10^{-3}	4×10^{-4}	17.6×10^1	0
S24	3.70×10^{-4}	1.6×10^{-3}	2×10^{-4}	2.3×10^{-3}	6×10^{-4}	3×10^{-4}	1.58×10^{-1}	0

Table 4. Cont.

Samples No.	Fe	Cu	Cd	Cr	Mn	Ni	Pb	As
S25	4.25×10^{-3}	2.8×10^{-3}	2×10^{-4}	1.8×10^{-3}	3×10^{-4}	1.6×10^{-3}	0	1×10^{-4}
S26	2.50×10^{-4}	$1. \times 10^{-4}$	0	2×10^{-3}	1.8×10^{-3}	1.7×10^{-3}	12.3×10^1	7×10^{-4}
S27	1.20×10^{-4}	0	0	1.6×10^{-3}	4×10^{-4}	7×10^{-4}	2.17×10^{-1}	0
S28	3.40×10^{-4}	3×10^{-3}	0	1.3×10^{-3}	3×10^{-4}	4×10^{-4}	2.42×10^{-1}	0
S29	1.90×10^{-4}	1×10^{-4}	2×10^{-4}	2.4×10^{-3}	6×10^{-4}	3×10^{-4}	4.28×10^{-1}	1×10^{-4}
S30	1.60×10^{-4}	0	0	1.4×10^{-3}	3×10^{-4}	8×10^{-4}	2.42×10^{-1}	3×10^{-4}
S31	2.88×10^{-3}	2.9×10^{-3}	0	1.2×10^{-3}	1.8×10^{-3}	1.8×10^{-3}	0	0
S32	5.80×10^{-4}	2×10^{-4}	3×10^{-4}	1.8×10^{-3}	2.2×10^{-3}	1×10^{-3}	2.42×10^{-1}	1×10^{-4}
K1	6.67×10^{-5}	0	0	0	5×10^{-4}	5×10^{-4}	2.03×10^{-1}	1×10^{-4}
K2	1.80×10^{-4}	1×10^{-4}	2.50×10^{-3}	0	4×10^{-4}	9×10^{-4}	2.44×10^{-1}	0
K3	3.30×10^{-4}	2×10^{-4}	0	0	3×10^{-4}	2.5×10^{-3}	8.61×10^{-2}	0
K4	3.60×10^{-4}	2×10^{-4}	$4. \times 10^{-4}$	0	7.8×10^{-3}	9×10^{-4}	2.28×10^{-1}	0
K5	1.10×10^{-4}	3×10^{-4}	1.5×10^{-3}	1×10^{-4}	2.1×10^{-3}	2.5×10^{-3}	0	0
K6	3.33×10^{-5}	2×10^{-4}	3×10^{-4}	5×10^{-4}	8×10^{-4}	2.6×10^{-3}	10.8×10^1	0
K7	1.06×10^{-3}	2.0×10^{-4}	1.3×10^{-3}	5×10^{-4}	2.4×10^{-3}	9×10^{-4}	2.19×10^{-1}	0
K8	5.10×10^{-4}	2.0×10^{-4}	7×10^{-4}	4×10^{-4}	0	2.6×10^{-3}	9.33×10^{-1}	0
K9	1.60×10^{-4}	2.2×10^{-3}	2.8×10^{-3}	0	4×10^{-4}	2.1×10^{-3}	9.22×10^{-1}	0
K10	5.0×10^{-4}	1×10^{-4}	2.2×10^{-3}	0	9×10^{-4}	4×10^{-4}	18.4×10^1	0
K11	3.40×10^{-4}	0	0	0	2×10^{-4}	4×10^{-4}	1.75×10^{-1}	0
K12	5.28×10^{-5}	3×10^{-4}	2.1×10^{-3}	0	4×10^{-4}	3.8×10^{-3}	2.31×10^{-1}	0
K13	1.30×10^{-3}	3.1×10^{-3}	0	0	2.4×10^{-3}	1.4×10^{-3}	2.47×10^{-1}	0
K14	2.80×10^{-4}	2×10^{-4}	0	0	4×10^{-4}	2.5×10^{-3}	9.0×10^{-1}	0
K15	1.80×10^{-4}	1×10^{-4}	2.6×10^{-3}	1×10^{-4}	1.1×10^{-3}	4×10^{-4}	2.19×10^{-1}	0
K16	6.94×10^{-5}	0	3×10^{-3}	0	8×10^{-4}	6×10^{-4}	1.97×10^{-1}	0
K17	2.80×10^{-4}	1×10^{-4}	9×10^{-4}	0	3×10^{-4}	4×10^{-3}	2.11×10^{-1}	7×10^{-4}
K18	4.80×10^{-4}	2×10^{-4}	1.4×10^{-3}	1×10^{-4}	4×10^{-4}	1×10^{-3}	2.42×10^{-1}	0
K19	5.60×10^{-4}	2×10^{-4}	8×10^{-4}	0	2.2×10^{-3}	4×10^{-4}	2.06×10^{-1}	7×10^{-4}
K20	2.40×10^{-4}	1×10^{-4}	1.1×10^{-3}	1×10^{-5}	6×10^{-4}	4×10^{-4}	1.64×10^{-1}	0
K21	2.70×10^{-4}	2×10^{-4}	3×10^{-4}	0	3×10^{-4}	1×10^{-3}	2.14×10^{-1}	0
K22	5.60×10^{-4}	0	1.1×10^{-3}	0	2×10^{-4}	4×10^{-4}	17.6×10^1	1×10^{-4}
K23	3.70×10^{-4}	1.6×10^{-3}	1×10^{-3}	0	9×10^{-4}	3×10^{-4}	1.58×10^{-1}	7×10^{-4}
K24	4.25×10^{-3}	2.8×10^{-3}	1.2×10^{-3}	2×10^{-4}	1.1×10^{-3}	1.6×10^{-3}	0	0
K25	2.50×10^{-4}	1×10^{-4}	3×10^{-4}	0	1.3×10^{-3}	1.7×10^{-3}	12.3×10^1	1×10^{-4}
K26	1.20×10^{-4}	0	6×10^{-4}	0	0	7×10^{-4}	2.17×10^{-1}	0
K27	3.40×10^{-4}	3×10^{-3}	1.7×10^{-3}	0	4×10^{-4}	4×10^{-4}	2.42×10^{-1}	0
K28	1.90×10^{-4}	1×10^{-4}	1.1×10^{-3}	0	8×10^{-4}	3×10^{-4}	4.28×10^{-1}	1×10^{-4}
K29	4.80×10^{-4}	2×10^{-4}	1.9×10^{-3}	3×10^{-4}	3×10^{-4}	1×10^{-3}	2.42×10^{-1}	0
K30	5.28×10^{-5}	0	0	2×10^{-4}	2.9×10^{-3}	4×10^{-4}	3.42×10^{-1}	0
J1	9.20×10^{-4}	1×10^{-4}	0	2.6×10^{-3}	2.1×10^{-3}	5×10^{-4}	2.03×10^{-1}	0
J2	1.41×10^{-3}	1×10^{-4}	2×10^{-4}	0	0	1.5×10^{-3}	1.78×10^{-1}	0
J3	3.50×10^{-4}	1×10^{-4}	2×10^{-4}	0	6×10^{-4}	2.6×10^{-3}	9.58×10^{-1}	0
J4	7.30×10^{-4}	2×10^{-4}	2×10^{-4}	1.7×10^{-3}	2.1×10^{-3}	3×10^{-4}	2.17×10^{-1}	0
J5	2.70×10^{-4}	3.10×10^{-3}	2×10^{-4}	3×10^{-4}	2×10^{-4}	1.5×10^{-3}	2.33×10^{-1}	0
J6	1.20×10^{-4}	2.70×10^{-3}	0	1×10^{-3}	2×10^{-4}	1.3×10^{-3}	8.19×10^{-1}	1×10^{-4}

Table 4. Cont.

Samples No.	Fe	Cu	Cd	Cr	Mn	Ni	Pb	As
J7	8.70×10^{-4}	1×10^{-4}	0	2.4×10^{-3}	4×10^{-4}	0	1.19×10^{-1}	7×10^{-4}
J8	3.30×10^{-4}	1×10^{-4}	0	2.2×10^{-3}	2×10^{-4}	4.3×10^{-3}	7.75×10^{-1}	1×10^{-4}
J9	1.60×10^{-4}	0	0	2.1×10^{-3}	4×10^{-4}	8×10^{-4}	2.42×10^{-1}	0
J10	2.88×10^{-3}	2.9×10^{-3}	0	2.4×10^{-3}	2×10^{-4}	1.8×10^{-3}	0	0
J11	5.80×10^{-4}	2×10^{-4}	0	1×10^{-3}	2×10^{-4}	1×10^{-3}	2.42×10^{-1}	7×10^{-4}
J12	0	0	0	1.9×10^{-3}	3×10^{-4}	5×10^{-4}	2.03×10^{-1}	0
Min	0	0	0	0	0	0	0	0
Max	7.12×10^{-3}	3.1×10^{-3}	3×10^{-3}	2.7×10^{-3}	7.8×10^{-3}	4.3×10^{-3}	18.4×10^1	7×10^{-4}
Mean	7.70×10^{-4}	7×10^{-4}	5×10^{-4}	8×10^{-4}	1×10^{-3}	1.3×10^{-3}	4.07×10^{-1}	1×10^{-4}

3.8. Hazard Quotient Indices (HQ)

HQ for noncarcinogenic effect is related to dose received at risk point as compared to the reference dose (RfD) and is calculated by dividing chronic daily intake (CDI) by RfD [7]. HQ calculated for the groundwater samples were in the range for iron of 4.3×10^{-5} to 1.01×10^{-2} with average value of 1.20×10^{-3} , copper 0–0, cadmium 0–5.94 with average value of 1.11, chromium 0– 1.8×10^{-3} with average value of 5.59×10^{-4} , manganese 5.95×10^{-4} to 5.59×10^{-2} with average value of 7.95×10^{-3} , nickel 0– 2.15×10^{-1} with average value of 6.47×10^{-2} , lead 0–118 with average value of 15.97, and As 0–16.2 with average value of 2.85×10^{-1} mg/kg-day (Table 5). The average values of cadmium and lead crossed the safe limit of 1 and may be considered hazardous for human health [44]. The average values of HQ were observed in the following decreasing order: Pb > Cd > As > Ni > Mn > Fe > Cr.

Table 5. HQ results of heavy metals.

Samples No.	Fe	Cd	Cr	Mn	Ni	Pb	As
S1	8.20×10^{-4}	2.61×10^{-1}	7×10^{-4}	9.30×10^{-3}	1.79×10^{-2}	1.18×10^2	3.23×10^{-1}
S2	7.60×10^{-4}	1.61×10^{-1}	1.20×10^{-3}	1.39×10^{-2}	1.51×10^{-2}	5.43×10^1	0
S3	4.60×10^{-3}	13.7×10^1	0	1.57×10^{-2}	1.35×10^{-1}	5.72×10^1	0
S4	1.02×10^{-2}	1.17×10^{-1}	7×10^{-4}	4.60×10^{-3}	5.19×10^{-2}	5.65×10^1	0
S5	2.49×10^{-3}	6.11×10^{-2}	8×10^{-4}	8.90×10^{-3}	0	5.25×10^1	16.2×10^1
S6	5.30×10^{-4}	13.5×10^1	1×10^{-3}	9.70×10^{-3}	1.07×10^{-1}	0	0
S7	1.15×10^{-3}	6.61×10^{-1}	0	2.80×10^{-3}	1.21×10^{-1}	0	0
S8	2.24×10^{-3}	4.94×10^{-1}	1.20×10^{-3}	1.39×10^{-2}	7.65×10^{-2}	0	0
S9	3.58×10^{-3}	1.28×10^{-1}	1×10^{-3}	1.57×10^{-2}	1.56×10^{-1}	0	0
S10	0	1.44×10^{-1}	8×10^{-4}	4.60×10^{-3}	1.28×10^{-1}	59.4×10^1	3.23×10^{-1}
S11	0	1×10^{-1}	1.30×10^{-3}	8.90×10^{-3}	2.13×10^{-2}	0	6.46×10^{-1}
S12	1.31×10^{-3}	6.67×10^{-2}	1.80×10^{-3}	9.70×10^{-3}	2.74×10^{-2}	53.2×10^1	3.23×10^{-1}
S13	2.02×10^{-3}	6.33×10^{-1}	0	2.80×10^{-3}	7.74×10^{-2}	67.9×10^1	0
S14	5×10^{-4}	10.5×10^1	8×10^{-4}	2.20×10^{-3}	1.32×10^{-1}	54.8×10^1	0
S15	1.05×10^{-3}	1.39×10^{-1}	9×10^{-4}	3.40×10^{-3}	1.61×10^{-2}	3.40×10^1	3.23×10^{-1}
S16	3.80×10^{-4}	1.28×10^{-1}	6×10^{-4}	1.20×10^{-3}	7.42×10^{-2}	83.3×10^1	3.23×10^{-1}
S20	7.90×10^{-4}	2.94×10^{-1}	1.30×10^{-3}	1.29×10^{-2}	2.22×10^{-2}	95.7×10^1	6.46×10^{-1}
S21	3.40×10^{-4}	2.33×10^{-1}	0	8.90×10^{-3}	1.75×10^{-2}	56.3×10^1	0

Table 5. Cont.

Samples No.	Fe	Cd	Cr	Mn	Ni	Pb	As
S17	1.70×10^{-4}	5.44×10^{-1}	1×10^{-3}	5×10^{-3}	6.35×10^{-2}	68.7×10^1	3.23×10^{-1}
S18	1.24×10^{-3}	1.28×10^{-1}	0	6×10^{-3}	0	0	0
S19	4.70×10^{-4}	6.11×10^{-2}	0	2.04×10^{-2}	2.15×10^{-1}	2.68×10^1	16.2×10^1
S22	3.90×10^{-4}	5×10^{-2}	8.00×10^{-4}	1.51×10^{-2}	4.82×10^{-2}	49.4×10^1	3.23×10^{-1}
S23	8.00×10^{-4}	6.94×10^{-1}	6.00×10^{-4}	6.90×10^{-3}	2.04×10^{-2}	2.66×10^1	0
S24	5.20×10^{-4}	4.78×10^{-1}	1.50×10^{-3}	4.60×10^{-3}	1.65×10^{-2}	60.2×10^1	0
S25	6.07×10^{-3}	4.06×10^{-1}	1.20×10^{-3}	2.20×10^{-3}	7.83×10^{-2}	64.8×10^1	3.23×10^{-1}
S26	3.50×10^{-4}	6.67×10^{-2}	1.30×10^{-3}	1.29×10^{-2}	8.50×10^{-2}	2.28×10^1	16.2×10^1
S27	1.70×10^{-4}	7.22×10^{-2}	1.10×10^{-3}	3.20×10^{-3}	3.44×10^{-2}	33.2×10^1	0
S28	4.90×10^{-4}	1.06×10^{-1}	9.00×10^{-4}	2.20×10^{-3}	2.03×10^{-2}	2.15×10^1	0
S29	2.70×10^{-4}	3.78×10^{-1}	1.60×10^{-3}	4.2×10^{-3}	1.72×10^{-2}	57.1×10^1	3.23×10^{-1}
S30	2.30×10^{-4}	1.50×10^{-1}	1.00×10^{-3}	2×10^{-3}	3.83×10^{-2}	45.5×10^1	6.46×10^{-1}
S31	4.11×10^{-3}	6.11×10^{-2}	8.00×10^{-4}	1.29×10^{-2}	8.78×10^{-2}	59.4×10^1	0
S32	8.20×10^{-4}	5.50×10^{-1}	1.20×10^{-3}	1.59×10^{-2}	5.06×10^{-2}	4.89×10^1	3.23×10^{-1}
K1	0	0	0	3.80×10^{-3}	2.26×10^{-2}	44.0×10^1	3.23×10^{-1}
K2	2.60×10^{-4}	49.4×10^1	0	3×10^{-3}	4.61×10^{-2}	0	0
K3	4.70×10^{-4}	0	0	1.80×10^{-3}	1.24×10^{-1}	3.42×10^1	0
K4	5.10×10^{-4}	8.56×10^{-1}	0	5.60×10^{-2}	4.65×10^{-2}	60.2×10^1	0
K5	1.50×10^{-4}	29.4×10^1	0	1.53×10^{-2}	1.24×10^{-1}	67.1×10^1	0
K6	0	5×10^{-1}	3×10^{-4}	5.40×10^{-3}	1.29×10^{-1}	1.19×10^1	0
K7	1.51×10^{-3}	25.6×10^1	3×10^{-4}	1.73×10^{-2}	4.69×10^{-2}	67.1×10^1	0
K8	7.30×10^{-4}	13.9×10^1	3×10^{-4}	6×10^{-4}	1.29×10^{-1}	0	0
K9	2.20×10^{-4}	5.67×10^1	0	2.80×10^{-3}	1.07×10^{-1}	67.1×10^1	0
K10	7.20×10^{-4}	44.8×10^1	0	6.30×10^{-3}	1.92×10^{-2}	56.3×10^1	0
K11	4.90×10^{-4}	0	0	1.60×10^{-3}	2.19×10^{-2}	67.9×10^1	0
K12	0	42.8×10^1	0	2.80×10^{-3}	1.88×10^{-1}	23.9×10^1	0
K13	1.86×10^{-3}	0	0	1.75×10^{-2}	7.14×10^{-2}	63.3×10^1	0
K14	4×10^{-4}	0	0	3×10^{-3}	1.24×10^{-1}	0	0
K15	2.50×10^{-4}	52.8×10^1	0	7.90×10^{-3}	1.88×10^{-2}	3×10^1	0
K16	0	59.4×10^1	0	5.80×10^{-3}	3.11×10^{-2}	61×10^1	0
K17	3.90×10^{-4}	17.2×10^1	0	2×10^{-3}	2.01×10^{-1}	2.59×10^1	16.2×10^1
K18	6.80×10^{-4}	27.2×10^1	0	3×10^{-3}	4.79×10^{-2}	2.56×10^1	0
K19	7.90×10^{-4}	15×10^1	0	1.57×10^{-2}	2.22×10^{-2}	5.11×10^1	16.2×10^1
K20	3.40×10^{-4}	2.22×10^0	0	4.60×10^{-3}	1.75×10^{-2}	48.6×10^1	0
K21	3.90×10^{-4}	5.56×10^{-1}	0	2×10^{-3}	4.82×10^{-2}	64.0×10^1	0
K22	8×10^{-4}	21.7×10^1	0	1.20×10^{-3}	2.04×10^{-2}	68.7×10^1	3.23×10^{-1}
K23	5.20×10^{-4}	19.4×10^1	0	6.70×10^{-3}	1.65×10^{-2}	2.50×10^1	16.2×10^1
K24	6.07×10^{-3}	24.4×10^1	2×10^{-4}	7.90×10^{-3}	7.83×10^{-2}	61×10^1	0
K25	3.50×10^{-4}	6.11×10^{-1}	0	8.90×10^{-3}	8.50×10^{-2}	54.8×10^1	3.23×10^{-1}

Table 5. Cont.

Samples No.	Fe	Cd	Cr	Mn	Ni	Pb	As
K26	1.70×10^{-4}	11.7×10^1	0	6×10^{-4}	3.44×10^{-2}	58.6×10^1	0
K27	4.90×10^{-4}	34.4×10^1	0	3×10^{-3}	2.03×10^{-2}	67.1×10^1	0
K28	2.70×10^{-4}	21.1×10^1	0	6×10^{-3}	1.72×10^{-2}	57.1×10^1	3.23×10^{-1}
K29	6.80×10^{-4}	37.2×10^1	2×10^{-4}	2.20×10^{-3}	4.79×10^{-2}	45.5×10^1	0
K30	0	0	1×10^{-4}	2.04×10^{-2}	2.13×10^{-2}	59.4×10^1	0
J1	1.31×10^{-3}	1.22×10^{-1}	1.70×10^{-3}	1.51×10^{-2}	2.74×10^{-2}	4.89×10^1	0
J2	2.02×10^{-3}	4.50×10^{-1}	0	6×10^{-4}	7.74×10^{-2}	44×10^1	0
J3	5×10^{-4}	4.28×10^{-1}	0	4.60×10^{-3}	1.32×10^{-1}	0	0
J4	1.05×10^{-3}	4×10^{-1}	1.20×10^{-3}	1.51×10^{-2}	1.61×10^{-2}	3.42×10^1	0
J5	3.80×10^{-4}	4.39×10^{-1}	2×10^{-4}	1.60×10^{-3}	7.42×10^{-2}	62×10^1	0
J6	1.70×10^{-4}	3.94×10^{-2}	7×10^{-4}	1.40×10^{-3}	6.35×10^{-2}	6.71×10^1	3.23×10^{-1}
J7	1.24×10^{-3}	3.33×10^{-2}	1.60×10^{-3}	3×10^{-3}	0	1.19×10^1	16.2×10^1
J8	4.70×10^{-4}	9.44×10^{-2}	1.40×10^{-3}	1.40×10^{-3}	2.15×10^{-1}	67.1×10^1	3.23×10^{-1}
J9	2.30×10^{-4}	1.06×10^{-1}	1.40×10^{-3}	3.20×10^{-3}	3.83×10^{-2}	94.9×10^1	0
J10	4.11×10^{-3}	1.28×10^{-1}	1.60×10^{-3}	1.40×10^{-3}	8.78×10^{-2}	56.3×10^1	0
J11	8.20×10^{-4}	4.50×10^{-2}	7×10^{-4}	1.40×10^{-3}	5.06×10^{-2}	49.4×10^1	16.2×10^1
J12	0	1.17×10^{-1}	1.20×10^{-3}	2.20×10^{-3}	2.26×10^{-2}	2.66×10^1	0
Min	0	0	0	6×10^{-4}	0	0	0
Max	1.02×10^{-2}	59.4×10^1	1.80×10^{-3}	5.60×10^{-2}	2.15×10^{-1}	1.18×10^2	16.2×10^1
Mean	1.20×10^{-3}	11.1×10^1	6×10^{-4}	8×10^{-3}	6.47×10^{-2}	1.60×10^1	2.85×10^{-1}

3.9. Scatter Diagrams for Weathering Processes

The scatter diagrams were drawn using Microsoft Excel 2013 using the concentrations of cations and anions in meq/L. The graph of Na against HCO_3 indicated that Na and HCO_3 were balanced with each other and showed a linear relationship along the trend line. The results of HCO_3 increased with the increase in Na, with $r^2 = 0.9466$ (Figure 3a). The sample dots above the trend line show carbonate weathering, and dots below the trend line indicate silicate weathering [45]. The scatter diagram of $\text{HCO}_3 + \text{SO}_4$ against Ca + Mg (Figure 3b) indicates that points fell on both sides of the equiline. The points falling above the equiline indicate weathering of anions (HCO_3 and SO_4), mainly HCO_3 , and points falling along and below the equiline are due to the silicate weathering [45,46]. More sample dots fell along and below the equiline and the silicate weathering was considered to be responsible for the calcium in groundwater. The scatter diagram of SO_4 against Ca (Figure 3c) indicates sample dots on both the sides of the trend line, suggesting weathering of both gypsum and silicate. However, more sample dots fell below the trend line due to silicate weathering. The scatter diagram of Na versus Ca + Mg (Figure 3d) indicates sample dots on both the sides along the trend line. The dots below the trend line may be designated as direct cation exchange, and those above as reverse cation exchange. The scatter diagram of Na against Cl (Figure 3e) indicates that most of the sample dots fell along the trend line, but a few sample dots fell away from the trendline on both the sides. The coefficient of determination (r^2) of Na versus Cl was observed to be 0.9444, indicating dissolution of halite [47]. The diagram of EC against Na/Cl (Figure 3f) did not indicate a straight line, but the trend line was inclined upward, suggesting that evaporation may not be the major process involved in the hydrochemistry of groundwater. The sample dots were scattered on both sides of the trend line, but more sample dots were present above the trend line,

indicating that silicate weathering or forward ion exchange process was dominant over sodium reduction process or reverse ion exchange represented by the sample dots below trend line.

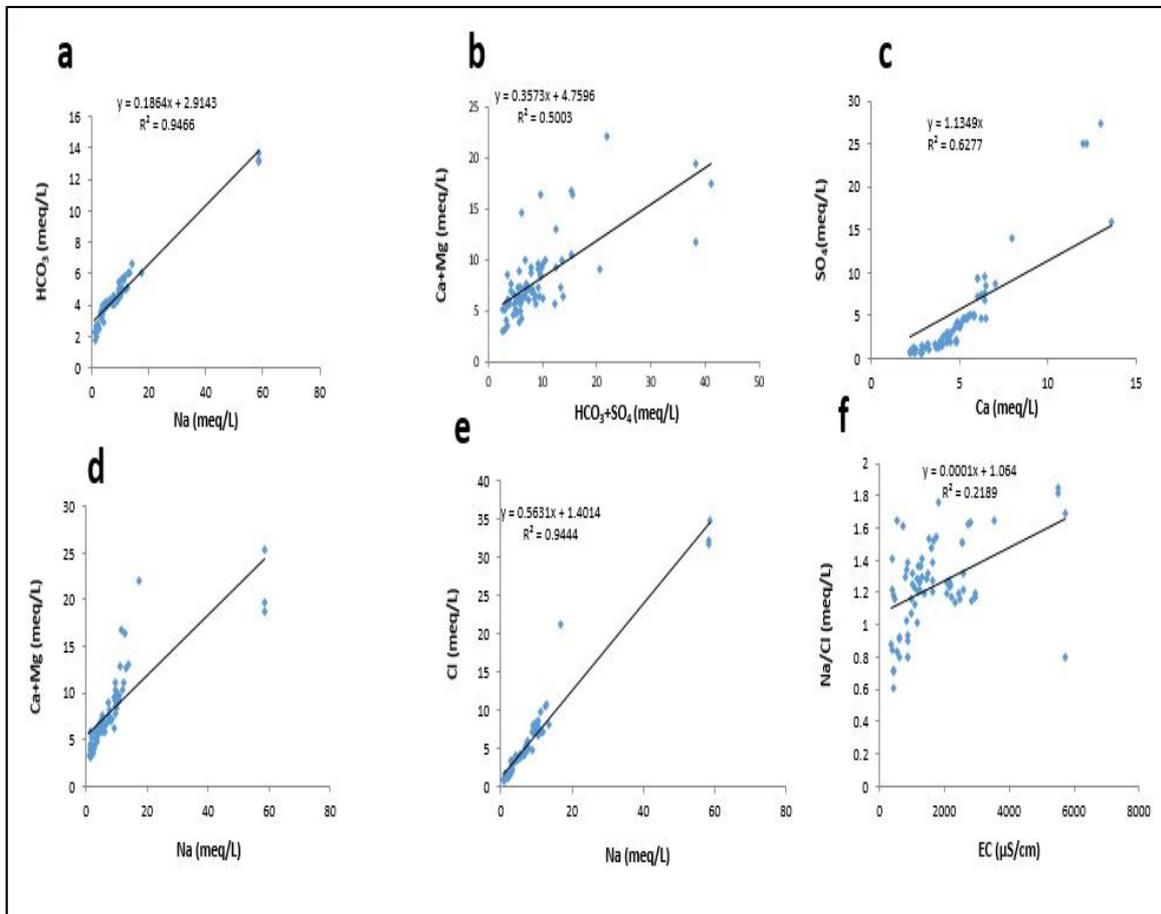


Figure 3. Scatter diagrams: (a) Na vs. HCO₃, (b) Ca + Mg vs. HCO₃ + SO₄, (c) Ca vs. SO₄, (d) Na vs. Ca, (e) Na vs. Cl, (f) EC vs. Na/Cl. All concentrations are in meq/L.

3.10. Cluster Analysis (CA)

The CA indicates similarities and dissimilarities among the samples based on the linkage distance method. Similar results for the samples are grouped in the same cluster. The dendrogram (Figure 4) indicated three clusters. Cluster 1 is again divided into two (clusters 1A and 1B). Cluster 1A comprised 35 and 1B 14 samples. Cluster 2 was based on 21 samples, whereas Cluster 3 consisted of 4 samples. Clusters 1 and 2 are connected by a common line and these have some similarities. Cluster 3 had higher values than clusters 1 and 2, and Cluster 2 had a higher value than Cluster 1. Similarly, Cluster 1A had the lowest values for water quality. The majority of the samples indicated as excellent for water quality in WQI were present in Cluster 1A.

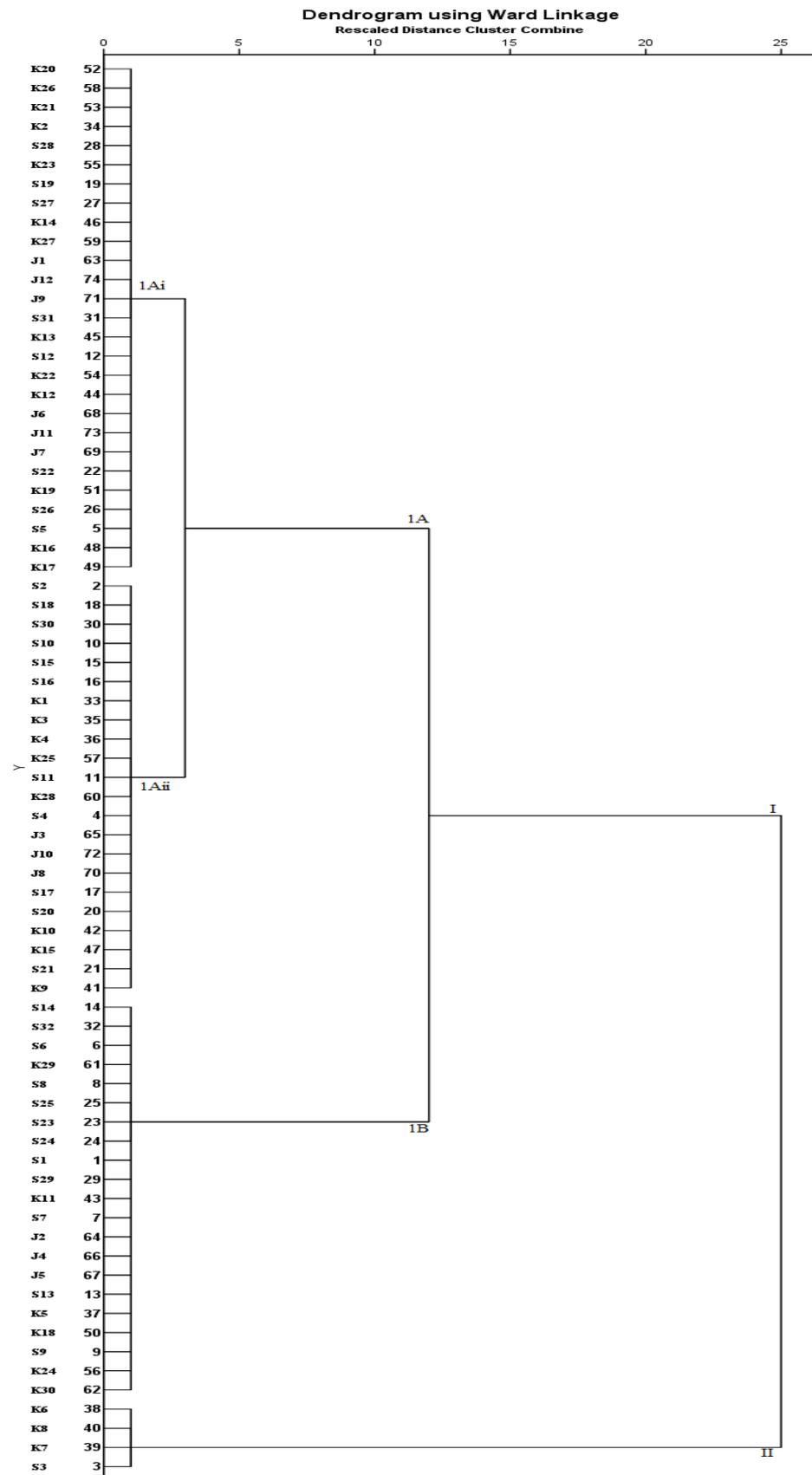


Figure 4. Cluster analysis of sampling stations.

3.11. Piper Diagrams

The Piper diagrams were drawn by using anions (HCO_3^- , Cl^- , SO_4^{2-}) and cations (Na^+ , K^+ , Ca^{2+} , Mg^{2+}) values to obtain a triangle on the right side for anions and the left side for cations. The plots in the triangles show the composition of cations and anions in water samples [48]. The symbols indicated blue, black and red were from Jam Nawaz Ali, Sanghar and Kot Ghulam Muhammad. The Piper diagrams indicate the geochemistry of the area. Some samples in the cations triangle are gathered at the middle and are of mixed type (Figure 5). More samples are towards $\text{Na}^+ + \text{K}^+$ and others are towards Ca^{2+} . The right-side triangle for anions also indicates some samples in the middle and these are due to mixed type, but more are towards HCO_3^- and a few towards Cl^- . The quality of groundwater is controlled by rock–water interactions and anthropogenic activities due to agriculture. The diamond shape indicates some samples within mixed-type water, and others in the NaCl zone. Some samples are also in the $\text{Ca}(\text{HCO}_3)_2$ area.

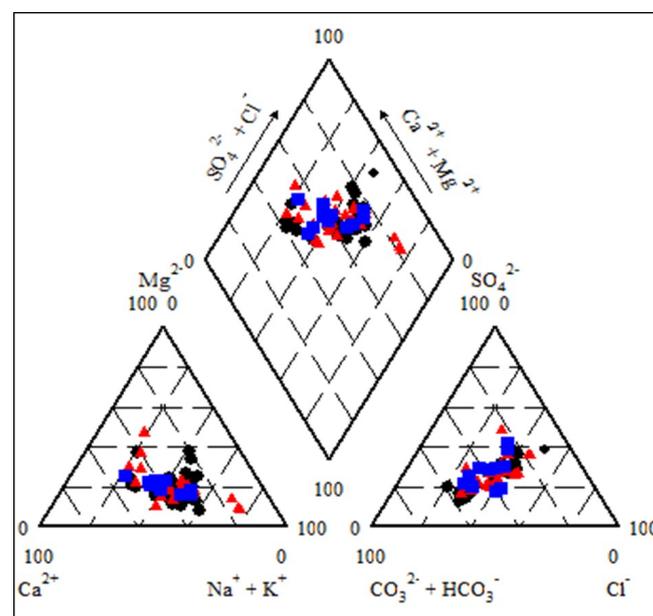


Figure 5. Piper diagrams of water analysis of Sanghar District.

3.12. Principal Component Analysis (PCA)

PCA was calculated based on 26 different parameters, and seven components were obtained with eigenvalues greater than 1 with total cumulative% of 80.07. Component 1 had an eigenvalue of 10.964 with variance% and cumulative% 42.168 (Figure 6, Table 6). Salinity, chloride, conductivity, TDS, sulphate, calcium, alkalinity, sodium, potassium, fluoride, total hardness, and magnesium indicated strong correlation (0.847–0.979) and supported the results of the coefficient of correlation. Other parameters indicated low to negative correlation. Component 2 had an eigenvalue of 2.811 with variance% 10.812 and cumulative% 52.979. Orthophosphate, nitrite, and total phosphate indicated strong to medium correlation (0.696–0.945) and showed anthropogenic activity due to the use of fertilizers in agricultural lands. Component 3 had an eigenvalue of 1.998 with variance% 7.683 and cumulative% 60.663. Cadmium and nitrate indicated medium correlation (0.520–0.530). Component 4 was observed with eigenvalue of 1.319 with variance% 5.074 and cumulative% 66.396. Cobalt and arsenic indicated medium correlation (0.531–0.553). Component 5 had an eigenvalue of 1.319 with variance% 5.074 and cumulative% 71.470. Lead indicated medium correlation (0.602). Component 6 was observed with eigenvalue 1.128 with variance% 4.338 and cumulative% 75.809. Nickel indicated medium correlation (0.619). Component 7 showed an eigenvalue of 1.261 with variance% 4.261 and cumulative% 80.070. pH indicated medium correlation (0.670). The maximum loading was obtained

with maximum positive correlations in PCA1, and loading decreased continuously from PCA1 to PCA 7.

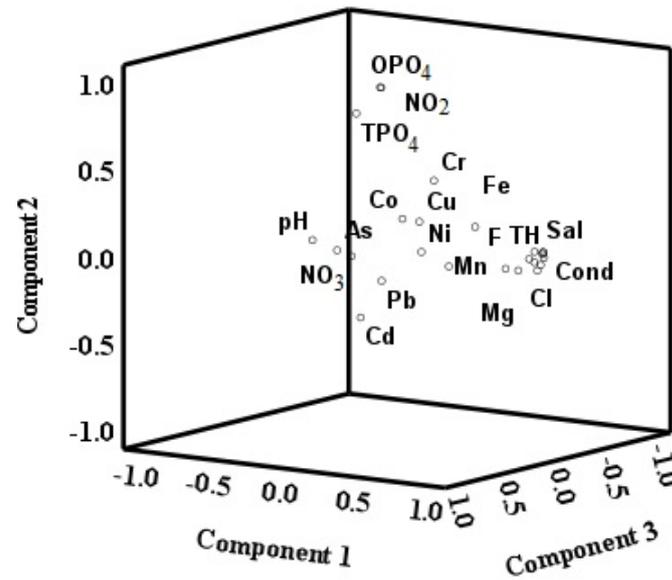


Figure 6. Dendrogram with three components.

3.13. Correlation Coefficient

The correlation coefficient is used to examine nearness among the parameters [48]. The results of correlation coefficient were obtained by plotting the average values of 26 parameters for 74 samples (Table 7). Conductivity and TDS indicated strong correlation with TH, Ca^{2+} , Mg^{2+} , Na^+ , K^+ , Cl^- , alkalinity, SO_4^{2-} , and F^- (0.799–0.981), indicating that these have a similar origin, mostly due to geology. Nitrate and total phosphate had strong correlation (0.864), but these had low to negative correlations with other parameters, indicating the effect of fertilizers on the agricultural lands. Na^+ and Cl^- were strongly correlated (0.972), indicating possible dissolution of halite in an underground aquifer. Calcium indicated strong correlation with alkalinity (0.90), supporting the dissolution of calcite and dolomite. The pH, trace metals, and arsenic had low to negative correlation with most of the parameters.

Table 6. Water analysis for PCA of Sanghar District for 3 subdistricts for total variance.

Component	Initial Eigenvalues			Extraction Sums of Squared Loadings			Rotation Sums of Squared Loadings		
	Total	% of Variance	Cumulative%	Total	% of Variance	Cumulative%	Total	% of Variance	Cumulative%
1	10.96	42.17	42.17	10.96	42.17	42.17	10.67	41.06	41.06
2	2.81	10.81	52.98	2.81	10.81	52.98	2.78	10.71	51.77
3	1.998	7.68	60.66	1.998	7.68	60.66	1.80	6.91	58.67
4	1.49	5.73	66.40	1.49	5.73	66.40	1.55	5.95	64.63
5	1.32	5.07	71.47	1.32	5.07	71.47	1.44	5.55	70.17
6	1.13	4.34	75.81	1.13	4.34	75.81	1.37	5.27	75.44
7	1.11	4.26	80.07	1.11	4.26	80.07	1.204	4.630	80.070
8	0.898	3.45	83.52						
9	0.83	3.18	86.70						
10	0.68	2.60	89.31						
11	0.59	2.27	91.58						
12	0.51	1.98	93.56						
13	0.43	1.66	95.21						
14	0.36	1.40	96.61						
15	0.30	1.14	97.76						
16	0.20	0.78	98.54						
17	0.17	0.64	99.18						
18	0.09	0.34	99.53						
19	0.06	0.25	99.78						
20	0.02	0.09	99.86						
21	0.020	0.08	99.94						
22	0.01	0.05	99.99						
23	0.002	0.007	99.995						
24	0.001	0.004	99.999						
25	0.000	0.001	100.000						
26	2.202×10^{-6}	8.468×10^{-6}	100.000						

Table 7. Water analysis of Sanghar for correlation matrix.

Parameters	pH	Cond	NO ₃	T.PO ₄	TH	Na	K	Ca	Mg	Cl	Alk	SO ₄	Mn	As	Fe	Cu	Ni	Pb	Cd	F	Cr	
pH	1.00																					
Conduct	−0.309	1.00																				
TDS	−0.309	1.00																				
NO ₃	−0.011	0.022	1.00																			
T.PO ₄	0.082	−0.106	0.105	1.00																		
T.H	−0.298	0.799	0.000	−0.417	1.00																	
Na	−0.249	0.864	0.034	−0.105	0.724	1.00																
K	−0.255	0.854	−0.076	−0.161	0.780	0.864	1.00															
Ca	−0.325	0.981	0.030	−0.112	0.806	0.863	0.876	1.00														
Mg	−0.325	0.830	0.052	−0.176	0.737	0.702	0.689	0.783	1.00													
Cl	−0.291	0.933	0.019	−0.148	0.804	0.972	0.921	0.935	0.796	1.00												
Alk	−0.320	0.906	0.042	−0.132	0.769	0.973	0.847	0.900	0.763	0.965	1.00											
SO ₄	−0.265	0.947	0.068	−0.052	0.765	0.954	0.874	0.934	0.813	0.970	0.955	1.00										
Mn	−0.309	0.040	−0.045	−0.091	0.132	0.012	0.110	0.050	0.055	0.044	0.021	0.026	1.00									
As	0.361	−0.384	0.071	0.122	−0.284	−0.249	−0.259	−0.417	−0.283	−0.293	−0.349	−0.284	0.191	1.00								
Fe	−0.166	0.147	−0.203	0.006	0.121	0.025	0.101	0.154	0.045	0.083	0.042	0.068	0.152	−0.090	1.00							
Cu	0.045	−0.108	−0.224	0.047	−0.147	−0.098	−0.116	−0.116	−0.171	−0.132	−0.111	−0.104	0.054	−0.034	0.293	1.00						
Ni	−0.032	0.207	0.018	−0.096	0.129	0.172	0.167	0.182	0.259	0.199	0.200	0.196	0.013	0.021	0.073	−0.009	1.00					
Pb	0.033	0.074	−0.052	−0.059	0.105	0.152	0.113	0.065	0.166	0.126	0.126	0.134	−0.028	.017	−0.257	−0.164	0.196	1.00				
Cd	0.068	0.069	0.118	−0.026	0.189	0.064	0.054	0.068	0.118	0.073	0.085	0.105	−0.132	−0.176	−0.135	−0.031	0.007	0.107	1.00			
F	−0.186	0.848	0.189	−0.008	0.733	0.841	0.724	0.829	0.719	0.839	0.865	0.902	−0.025	−0.293	0.027	−0.104	0.146	0.103	0.250	1.00		
Cr	−0.011	−0.097	−0.225	−0.062	−0.229	−0.089	−0.059	−0.135	−0.042	−0.095	−0.109	−0.103	0.107	0.120	0.129	0.083	−0.164	−0.100	−0.464	−0.216	1.00	

3.14. Wilcox Diagrams for Quality of Groundwater

The quality of groundwater is tested on the basis of the Wilcox diagram for irrigation. Two parameters are used to draw the Wilcox diagram: (1) salinity, represented as C by conductivity ($\mu\text{S}/\text{cm}$); and (2) sodium adsorption ratio (SAR), represented by (S) (Figure 7). Ten samples (13.5%) were present in C_1S_1 (low salinity and low SAR values), which were suitable for all purposes. A total of 36 (48.6%) samples were in C_2S_1 with medium salinity and low SAR (Figure 7). These samples can be used for irrigation, where moderate percolation. A total of 24 samples (32.4%) were located in C_3S_1 (high salinity and low SAR) and required salinity control and drainage facilities for irrigation. One sample (1.4%) was in C_4S_2 (very high salinity and moderate SAR), and three samples (4%) were present in C_4S_3 (very high salinity and high SAR). These samples were unsuitable for irrigation. The results of the Wilcox diagram indicated that 5.4% samples were unsuitable for irrigation, and more samples can be used for irrigation with some drainage facilities. Another Wilcox diagram was also drawn based on two parameters: (1) conductivity ($\mu\text{S}/\text{cm}$) and (2) Na% (Figure 8). The results indicated that 14 (18.9%) samples were in the excellent category and can be used for all the irrigational purposes. A total of 26 samples (35%) were in the good category and can also be used for irrigation. A total of 20 samples (27%) were in the doubtful category and could be used with some drainage facilities. A total of 13 samples (17.5%) were in the doubtful to unfit category and 1 sample (1.4%) was unfit for irrigation. The results indicated that 54% samples were present in the excellent to good category for irrigation.

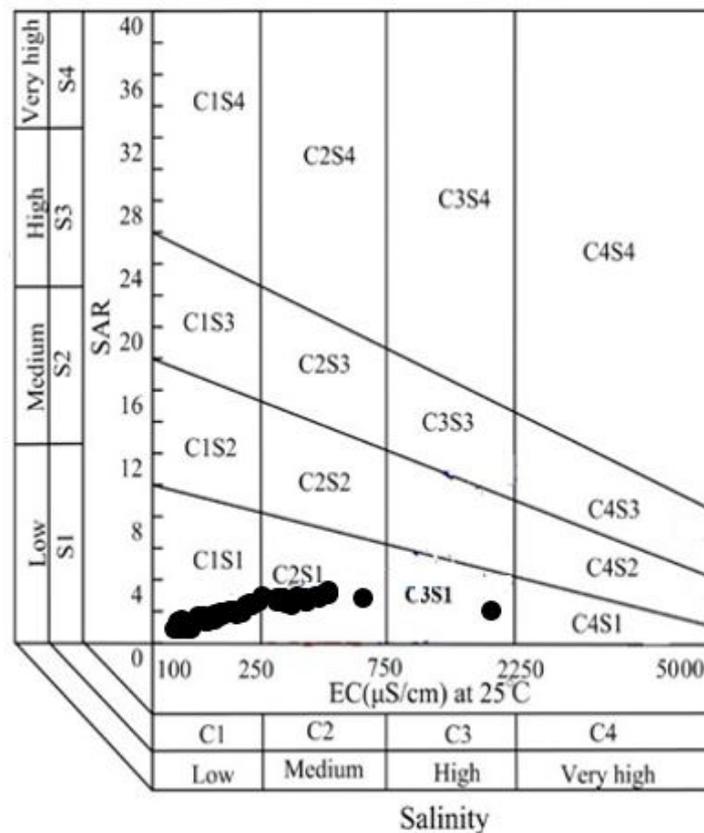


Figure 7. Wilcox diagram EC vs. SAR.

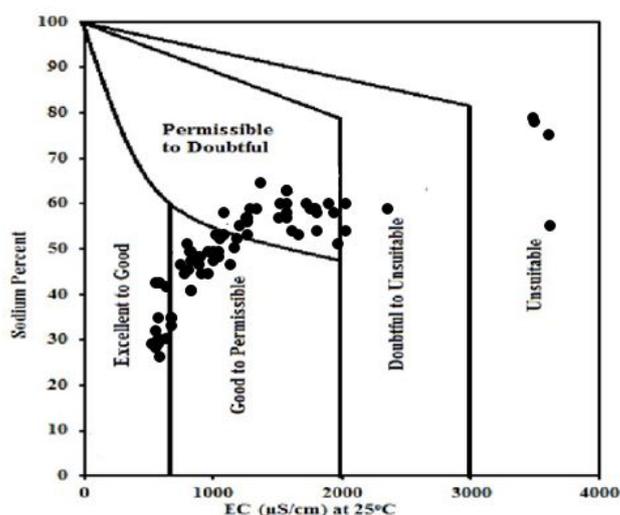


Figure 8. Wilcox diagram EC vs. Na percent.

4. Conclusions

Three subdistricts (Sanghar, Khipro, and Jam Nawaz Ali) of Sanghar District were examined for water quality for drinking and irrigation. The results of water quality were compared with WHO permissible limits. A number of parameters at different sampling stations crossed the permissible limits and were not considered suitable for human consumption. A total of 77% of the samples based on WQI were in excellent to good water quality. The results of contamination index (C_d) also indicated that 89% of the samples had C_d less than 3 and were considered suitable for drinking. The sources of contamination are mostly geological, except at the towns where some anthropogenic contamination can be expected. Gibbs diagrams indicated that the hydrochemistry of the groundwater was mostly based on rock–water interactions. The results of coefficient of correlation indicated that major cations and anions had good correlation among each other and supported that samples had a similar geochemical setting. The results of CDI and HQ indicated that the presence of lead in groundwater was a concern for human health. The water quality for irrigation indicated 54–100% suitability for irrigation.

Recommendations:

- (1) Awareness programs may be initiated to inform the inhabitants about the locations of the contaminated groundwater and their possible health effects.
- (2) Alternate sources of drinking water may be used for drinking, particularly surface water from the river Indus.
- (3) If a dependable source of drinking water is not available, then the groundwater may be joined to suitable filters to reduce the concentrations of contaminants.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/w16060856/s1>.

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References

- Brohi, R.O.Z.; Khuhawar, M.Y.; Mahar, R.B.; Ibrahim, M.A. Novel bimetallic nano particles for sorption of mercury (II) from drinking water: Adsorption experiment and computational studies. *J. Water Process Eng.* **2021**, *39*, 101727. [CrossRef]
- Singh, A.; Sharma, A.; Verma, R.K.; Chopade, R.L.; Pandit, P.P.; Nagar, V.; Aseri, V.; Choudhary, S.K.; Awasthi, G.; Awasthi, K.K.; et al. Heavy Metal Contamination of Water and Their Toxic Effect on Living Organisms. In *The Toxicity of Environmental Pollutants*; IntechOpen: Rijeka, Croatia, 2022.
- Daud, M.K.; Nafees, M.; Ali, S.; Rizwan, M.; Bajwa, R.A.; Shakoor, M.B.; Arshad, M.U.; Chatha, S.A.S.; Deeba, F.; Murad, W.; et al. Drinking water quality status and contamination in Pakistan. *BioMed Res. Int.* **2017**, *2017*, 7908183. [CrossRef] [PubMed]
- Shahab, A.; Shihua, Q.; Rashid, A.; Hasan, F.U.; Sohail, M.T. Evaluation of water quality for drinking and agricultural suitability in the lower Indus plain in Sindh province, Pakistan. *Pol. J. Environ. Stud.* **2016**, *25*, 2563–2574. [CrossRef]
- Lanjwani, M.F.; Khuhawar, M.Y.; Jahangir Khuhawar, T.M.; Lanjwani, A.H.; Jagirani, M.S.; Kori, A.H.; Rind, I.K.; Khuhawar, A.H.; Muhammad Dodo, J. Risk assessment of heavy metals and salts for human and irrigation consumption of groundwater in Qambar city: A case study. *Geol. Ecol. Landsc.* **2020**, *4*, 23–39. [CrossRef]
- Lanjwani, M.F.; Khuhawar, M.Y.; Khuhawar, T.M.J. Assessment of groundwater quality for drinking and irrigation uses in taluka Ratodero, district Larkana, Sindh, Pakistan. *Int. J. Environ. Anal. Chem.* **2022**, *102*, 4134–4157. [CrossRef]
- Ahmed, J.; Wong, L.P.; Chua, Y.P.; Channa, N. Drinking water quality mapping using water quality index and geospatial analysis in primary schools of Pakistan. *Water* **2020**, *12*, 3382. [CrossRef]
- Ahmed, J.; Wong, L.P.; Chua, Y.P.; Yasmin, A.; Channa, N.; VanDerslice, J.A. Estimation of hepatitis a virus infection prevalence through drinking water supply of primary schools of Sindh, Pakistan. *Hepat. Mon.* **2020**, *20*, e98412. [CrossRef]
- Rind, I.K.; Khuhawar, M.Y.; Lanjwani, M.F.; Khuhawar, T.M.J.; Samtio, M.S.; Soomro, W.A.; Baloch, A.R. Spatial variability of hydrochemistry and health risk assessment of groundwater of taluka Hala, district Matiari, Sindh, Pakistan. *Arab. J. Geosci.* **2023**, *16*, 99. [CrossRef]
- Podgorski, J.E.; Eqani, S.A.M.A.S.; Khanam, T.; Ullah, R.; Shen, H.; Berg, M. Extensive arsenic contamination in high-pH unconfined aquifers in the Indus Valley. *Sci. Adv.* **2017**, *3*, e1700935. [CrossRef]
- Khuhawar, M.; Ursani, H.; Khuahwar, T.; Lanjwani, M.; Mahessara, A. Assessment of water quality of groundwater of Thar Desert, Sindh. *Pakistan J. Hydrogeol. Hydrol. Eng.* **2019**, *7*, 2.
- Ullah, Z.; Talib, M.A.; Rashid, A.; Ghani, J.; Shahab, A.; Irfan, M.; Rauf, A.; Bawazeer, S.; Almarhoon, Z.M.; Mabkhot, Y.N. Hydrogeochemical investigation of elevated arsenic based on entropy modeling, in the aquifers of District Sanghar, Sindh, Pakistan. *Water* **2021**, *13*, 3477. [CrossRef]
- Bashir, E.; Huda, S.N.-U.; Naseem, S.; Hamza, S.; Kaleem, M. Geochemistry and quality parameters of dug and tube well water of Khipro, District Sanghar, Sindh, Pakistan. *Appl. Water Sci.* **2017**, *7*, 1645–1655. [CrossRef]
- Din, I.U.; Muhammad, S.; Faisal, S.; Rehman, I.U.; Ali, W. Heavy metal (loid) s contamination and potential risk assessment via groundwater consumption in the district of Hangu, Pakistan. *Environ. Sci. Pollut. Res.* **2023**, *30*, 33808–33818. [CrossRef]
- Selmane, T.; Dougha, M.; Djerbouai, S.; Djemiat, D.; Lemouari, N. Groundwater quality evaluation based on water quality indices (WQI) using GIS: Maadher plain of Hodna, Northern Algeria. *Environ. Sci. Pollut. Res.* **2023**, *30*, 30087–30106. [CrossRef]
- Kaur, T.; Bhardwaj, R.; Arora, S. Assessment of groundwater quality for drinking and irrigation purposes using hydrochemical studies in Malwa region, southwestern part of Punjab, India. *Appl. Water Sci.* **2017**, *7*, 3301–3316. [CrossRef]
- Adimalla, N.; Dhakate, R.; Kasarla, A.; Taloor, A.K. Appraisal of groundwater quality for drinking and irrigation purposes in Central Telangana, India. *Groundw. Sustain. Dev.* **2020**, *10*, 100334. [CrossRef]
- Li, P.; Wu, J.; Qian, H. Assessment of groundwater quality for irrigation purposes and identification of hydrogeochemical evolution mechanisms in Pengyang County, China. *Environ. Earth Sci.* **2013**, *69*, 2211–2225. [CrossRef]
- Soleimani, H.; Nasri, O.; Ojaghi, B.; Pasalari, H.; Hosseini, M.; Hashemzadeh, B.; Kavosi, A.; Masoumi, S.; Radfard, M.; Adibzadeh, A.; et al. Data on drinking water quality using water quality index (WQI) and assessment of groundwater quality for irrigation purposes in Qorveh & Dehgolan, Kurdistan, Iran. *Data Brief* **2018**, *20*, 375–386. [PubMed]
- P.B.O. Statistics. Available online: https://www.pbs.gov.pk/sites/default/files/tables/district_at_glance/Sanghar.pdf (accessed on 5 December 2023).
- Kadri, I.B. *Petroleum Geology of Pakistan*; Pakistan Petroleum Limited: Karachi, Pakistan, 1995.
- Baig, M.O.; Harris, N.; Ahmed, H.; Baig, M. Controls on reservoir diagenesis in the Lower Goru sandstone formation, Lower Indus Basin, Pakistan. *J. Petrol. Geol.* **2016**, *39*, 29–47. [CrossRef]
- Ashraf, U.; Zhang, H.; Anees, A.; Mangi, H.N.; Ali, M.; Zhang, X.; Imraz, M.; Abbasi, S.S.; Abbas, A.; Ullah, Z.; et al. A core logging, machine learning and geostatistical modeling interactive approach for subsurface imaging of lenticular geobodies in a clastic depositional system, SE Pakistan. *Nat. Resour. Res.* **2021**, *30*, 2807–2830. [CrossRef]
- Ashraf, U.; Zhu, P.; Yasin, Q.; Anees, A.; Imraz, M.; Mangi, H.N.; Shakeel, S. Classification of reservoir facies using well log and 3D seismic attributes for prospect evaluation and field development: A case study of Sawan gas field, Pakistan. *J. Pet. Sci. Eng.* **2019**, *175*, 338–351. [CrossRef]
- Li, M.; Ma, H.; Pan, H.; Ashraf, U.; Jiang, R. Building a rock physics model for the formation evaluation of the Lower Goru sand reservoir of the Southern Indus Basin in Pakistan. *J. Petrol. Sci. Eng.* **2020**, *194*, 107461.

26. Ashraf, U.; Zhang, H.; Anees, A.; Ali, M.; Zhang, X.; Shakeel Abbasi, S.; Nasir Mangi, H. Controls on reservoir heterogeneity of a shallow-marine reservoir in Sawan Gas Field, SE Pakistan: Implications for reservoir quality prediction using acoustic impedance inversion. *Water* **2020**, *12*, 2972. [[CrossRef](#)]
27. Shakir, U.; Hussain, M.; Mahmood, M.F.; Amjad, M.R.; Mehood, W.A.Z.S.; Abideen, Z.U.; Tahir, A.R.; Barron, M. Prospect generation studies of Cretaceous sands, Kipro area by integrating seismic and well data. *Nucleous* **2020**, *57*, 67–75.
28. Shahab, A.; Qi, S.; Zaheer, M. Arsenic contamination, subsequent water toxicity, and associated public health risks in the lower Indus plain, Sindh province, Pakistan. *Environ. Sci. Pollut. Res.* **2019**, *26*, 30642–30662. [[CrossRef](#)] [[PubMed](#)]
29. Jacobs, H.L.; Gabrielson, I.N.; Horton, R.K.; Lyon, W.A.; Habbard, E.C.; McCallum, G.E. Water quality criteria-stream vs. effluents standards. *J. Water Pollut. Control. Fed.* **1965**, *37*, 292–315.
30. American Public Health Association (APHA); WEF (Water Environment Federation). *Standard Methods for the Examination of Water and Wastewater*, 22nd ed.; American Public Health Association: Washington, DC, USA; American Water Works Association: Denver, CO, USA; Water Environment Federation: Washington, DC, USA, 2012; ISBN 978-087553-013-0.
31. Greenberg, A.E.; Clesceri, L.S.; Eaton, A.D. *Standard Methods for the Examination of Water and Wastewater*. Available online: <https://www.standardmethods.org/doi/book/10.2105/SMWW.2882> (accessed on 5 December 2023).
32. Baird, R.; Eaton, A.D.; Rice, E.W.; Bridgewater, L.; American Public Health Association (APHA); American Water Works Association, Water Environment Federation. *Standard Methods for the Examination of Water and Wastewater*; American Public Health Association: Washington, DC, USA, 2017.
33. Masood, A.; Aslam, M.; Pham, Q.B.; Khan, W.; Masood, S. Integrating water quality index, GIS and multivariate statistical techniques towards a better understanding of drinking water quality. *Environ. Sci. Pollut. Res.* **2022**, *29*, 26860–26876. [[CrossRef](#)] [[PubMed](#)]
34. US EPA. Risk Assessment for Carcinogenic Effects. Available online: <https://www.epa.gov/fera/risk-assessment-carcinogenic-effects> (accessed on 5 December 2023).
35. Backman, B.; Bodiš, D.; Lahermo, P.; Rapant, S.; Tarvainen, T. Applications of a groundwater contamination index in Finland and Slovakia. *Environ. Geol.* **1998**, *36*, 55–64. [[CrossRef](#)]
36. Zabin, S.A.; Foad, M.; Al-Ghamdi, A.Y. Non-carcinogenic risk assessment of heavy metals and fluoride in some water wells in the Al-Baha Region, Saudi Arabia. *Hum. Ecol. Risk Assess.* **2008**, *14*, 1306–1317. [[CrossRef](#)]
37. Muhammad, S.; Usman, Q.A. Heavy metal contamination in water of Indus River and its tributaries, Northern Pakistan: Evaluation for potential risk and source apportionment. *Toxin Rev.* **2022**, *41*, 380–388. [[CrossRef](#)]
38. Moldovan, Z. Spectrophotometric determination of nitrite by its catalytic effect on the oxidation of Congo red with bromate. *Bull. Chem. Soc. Ethiop.* **2012**, *26*, 159–169. [[CrossRef](#)]
39. WHO. *Guidelines for Drinking-Water Quality: First Addendum to the Fourth Edition*; WHO: Geneva, Switzerland, 2017.
40. Abadin, H.; Llanos, F.; Stevens, Y.W. *Toxicological Profile for Lead*; US Department of Health and Human Services, Agency for Toxic Substances and Diseases Registry: Atlanta, GA, USA, 2007.
41. Ketata, M.; Gueddari, M.; Bouhlila, R. Use of geographical information system and water quality index to assess groundwater quality in El Khairat deep aquifer (Enfidha, Central East Tunisia). *Arab. J. Geosci.* **2012**, *5*, 1379–1390. [[CrossRef](#)]
42. Gibbs, R.J. Mechanisms controlling world water chemistry. *Science* **1970**, *170*, 1088–1090. [[CrossRef](#)] [[PubMed](#)]
43. Khan, S.; Cao, Q.; Zheng, Y.; Huang, Y.; Zhu, Y. Health risks of heavy metals in contaminated soils and food crops irrigated with wastewater in Beijing, China. *Environ. Pollut.* **2008**, *152*, 686–692. [[CrossRef](#)]
44. Mgbenu, C.N.; Egbueri, J.C. The hydrogeochemical signatures, quality indices and health risk assessment of water resources in Umunya district, southeast Nigeria. *Appl. Water Sci.* **2019**, *9*, 22. [[CrossRef](#)]
45. Datta, P.; Deb, D.; Tyagi, S. Stable isotope (^{18}O) investigations on the processes controlling fluoride contamination of groundwater. *J. Contam. Hydrol.* **1996**, *24*, 85–96. [[CrossRef](#)]
46. Egbueri, J.C.; Mgbenu, C.N.; Chukwu, C.N. Investigating the hydrogeochemical processes and quality of water resources in Ojoto and environs using integrated classical methods. *Model. Earth Syst. Environ.* **2019**, *5*, 1443–1461. [[CrossRef](#)]
47. Jankowski, J.; Acworth, R.I. Impact of debris-flow deposits on hydrogeochemical processes and the development of dryland salinity in the Yass River Catchment, New South Wales, Australia. *Hydrogeol. J.* **1997**, *5*, 71–88. [[CrossRef](#)]
48. Piper, A.M. A graphic procedure in the geochemical interpretation of water-analyses. *Eos Trans. Am. Geophys. Union* **1944**, *25*, 914–928.

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