Spatial distribution of groundwater quality and risk indices in the Mirpur district, Pakistan

Said Muhammad[1*], Rizwan Ullah[2], Sehrish Amin[3], Haseeb Haroon[1], Ashfaq Ahmad[4]

[1]National Centre of Excellence in Geology, University of Peshawar 25130, Pakistan
[2]Helmholtz Centre for Environmental Research-UFZ, Department of River Ecology, Brückstra.3a, 39114 Magdeburg, Germany
[3]Department of Environmental Sciences, University of Peshawar 25120, Peshawar, Pakistan
[4]Department of Chemistry, College of Science, King Saud University, P.O. Box, 2455, Riyadh-11451, Saudi Arabia

Corresponding author: Dr. Said Muhammad, National Centre of Excellence in Geology, University of Peshawar 25130, Pakistan, Email: saidmuhammad1@gmail.com, Tel: +92 91 9221254; Fax: +92 919221228

Abstract

Groundwater is a valuable source for drinking and irrigation use and is the main concern of developing countries. Therefore, the current study investigated groundwater in the Mirpur District of Azad Jammu and Kashmir, Pakistan, for drinking and irrigation purposes. Groundwater was sampled from the Jatlan, Mirpur, and Dadyal towns and analyzed for physicochemical parameters. Groundwater results revealed that the WHO's upper limits were not surpassed for physiochemical parameters, except for pH value (11.7% samples). Groundwater was evaluated for various quality and risk indices. Based on the water quality index (WQI), groundwater was categorized as excellent to good for drinking use. For irrigation uses, 11.7% of Mirpur and 5.8% of Dadyal water were unsuitable, and the rest was found in the good category as evaluated by sodium adsorption ratio and sodium hazards. The groundwater was classified as calcium sulfate ($CaSO_4$), and mixed types and hydrogeochemistry were predominantly influenced by surrounding rock weathering. The groundwater showed a maximum level of hazard quotient of 0.20±0.05 via fluoride intake in the Dadyal town. Based on studied parameters and risk indices, groundwater is recommended for drinking, domestic and agricultural purposes.

Keywords: Drinking water; hazard quotient; hydrogeochemistry; irrigation water; water quality index

Abbreviations: Average daily dose (ADD), atomic absorption spectrometer (AAS), Azad Jammu and Kashmir (AJK), body weight (BW), calcium (Ca), calcium sulfate ($CaSO_4$), chloride (Cl), concentration of fluoride (C), concentration of individual parameters (Ci), electrical conductivity (EC), Fluoride (F), Global positioning system (GPS), hazard quotient (HQ), ingestion rate (IR), iodide (I), magnesium (Mg), maximum allowable limits (MAL), multi-parameter analyzer (MPA), number (n), optimal values (Cip), oxidation-reduction potential (ORP), potassium (K), relative weight (Wi), sodium (Na), sodium adsorption ratio (SAR), sodium percentage (Na%), sulfate (SO_4), temperature (T), total dissolved solids (TDS), total hardness (TH), water quality index (WQI), weight of the individual parameter (wi), and world health organization (WHO)

1. Introduction

Access to clean and safe water has become increasingly significant worldwide in recent years due to its critical role in human growth and economic development (Muhammad et al., 2024; Pacheco and Ortiz, 2024). However, water availability is often scarce, particularly in arid and semi-arid regions, where the demand for drinking and irrigation purposes is high (Masoud et al., 2016; Tang et al., 2023; Zhou et al., 2023; Zhou et al., 2022; Zhou and Liu, 2022). Rapid population growth, increased per capita consumption, urbanization, and extensive agricultural and industrial activities led to a depletion of water availability and quality (Gugulothu et al., 2022; Tokatlı et al., 2024; Wang et al., 2023; Zhang et al., 2022; Zhao et al., 2024). Several other factors impact water quality, including contamination from urban waste, treatment plants, agricultural runoff, leakage from underground septic tanks, and improper waste disposal practices (Subba Rao et al., 2022a; Verma et al., 2023). These sources introduce contaminants such as fertilizers, organic matter, and heavy metals that increase or decrease water quality parameters, leading to a decline in quality (Tuan et al., 2024; Ullah and Muhammad, 2022). The geogenic sources reported for water contamination were weathering and erosion of bedrock (Amin et al., 2021; Subba Rao et al., 2022b). Over-extraction of groundwater exacerbates the problem by lowering of water table, making it more susceptible to contamination from deeper geological formations and saline water intrusion (Dai et al., 2005; Dai et al., 2007; Navarro-Hernández et al., 2023). Using such contaminated groundwater for drinking and other purposes could pose severe risks to humans and the ecosystem (Biswas et al., 2024; Chandnani et al., 2022; Lan et al., 2022; Rao et al., 2021).

Regular monitoring and evaluation of water quality are crucial to ensure that the reservoirs remain free from contamination, which could otherwise pose risks to human health and degrade ecosystems (Dippong and Resz, 2024; Muhammad et al., 2024). Water quality monitoring gathers essential information regarding suitability for drinking, domestic, industrial use, and agricultural activities (Haq and Muhammad, 2023; Haq et al., 2023). This information is highly valuable for resource management, conservation, and policymaking decisions (Bennett, 2016; McKinley et al., 2017). High-quality water sustains biodiversity and supports ecosystem vital functions like water purification, nutrient cycling, and mitigation of climate change impacts (Muruganandam et al., 2023; Zhang et al., 2023). Several studies have documented quality monitoring techniques, such as calculating the WQI for drinking and irrigation uses and potential risks (Tokatli et al., 2024; 2023). However, this information on water quality needs to be improved in Pakistan, especially in the AJK region. Apart from WQI, other techniques like geospatial distribution and statistical analyses are also utilized to formulate comprehensive strategies for protecting scarce water resources (Ravindra et al., 2023; Subba Rao et al., 2024).

Pakistan, like many other developing countries, is grappling with significant challenges related to the deterioration of water quality, affecting both drinking water sources and agricultural activities (Shaheen and Konain, 2024; Shaibur, 2019; Shaibur et al., 2019; Shaibur et al., 2023; Shaibur and Das, 2022; Shaibur et al., 2021a; Shaibur et al., 2021b). However, regular water quality monitoring faces limitations due to a need for more awareness and economic constraints, particularly in the AJK region. The Mirpur district is the southeastern part of the region and is renowned for its extensive agricultural and irrigation practices. Mangla Dam reservoir is also in the vicinity, which makes the water resources of Mirpur vulnerable to contamination, especially salination, in case of water storage saturation. Despite this, studies on water quality monitoring in this region still need to be available. Radon contamination in groundwater and associated risks were reported by Haroon and Muhammad (2022) and highlighted the attention toward its drinking and irrigation WQI. Therefore, it becomes more profoundly essential to ascertain the water quality status, especially concerning its suitability for domestic and irrigation uses. Therefore, the current study aimed 1) to determine the physicochemical parameters of groundwater, 2) to evaluate the drinking and irrigation WQI, 3) to evaluate the potential health risk assessment via consumption of groundwater, 4) to the geospatial distribution of physicochemical parameters, drinking and irrigation WQI, and health indices.

2. Material and Methods

2.1. Study area

The study area is the Mirpur district of AJK, with a latitude of 32–33° and longitudes of 73–74°, the southeastern region of Pakistan (Fig. 1). The study area has three main towns: Jatlan, Dadyal, and Mirpur (Haroon and Muhammad, 2022). The study area has a lot of agricultural activities, an increasing population, and a diverse geological site. Major geological faults, including the Jhelum fault, Siwalik group, and Neogene rocks, dominate the study area. The area also hosts sandstone, sediment of clastic origin, and argillaceous rocks. The diverse geology, higher population density, and irrigation activities contribute major water quality ions (Shah, 1977).

The area is arid to semi-arid based on precipitation and temperature variations. Higher temperatures are observed between April and October, while in December and January, the temperature usually falls. The area has two dominant drainages of the Poonch and Jhelum rivers; however, in heavy rainfall, the groundwater is also recharged by seasonal nalla, which joins the main rivers by mainstream tributaries. Furthermore, Mangla water reservoirs are the dominant groundwater recharge source (Haroon and Muhammad, 2022).

2.2. Sampling and field analyses

For sampling, the Mirpur district was divided into three locations: Jatlan (n=12), Mirpur (n=17), and Dadyal (n=7) as show in Figure 1. Water samples were collected from these predetermined locations identified using Google Maps. The exact locations were then cross-checked with the help of a GPS (Garmin eTrex 10) for each sample. Samples were taken in 1L bottles from different groundwater water sources in pre-cleaned and pre-labelled recommended by APHA (2005) during spring season 2022. EC, pH, T, TDS, and ORP were investigated on the spot using a MPA (CONSORT 6030, Belgium).

2.3. Analytical procedure

The major negatively charged ions, including Cl, I, and F, were analyzed using MPA. Major positively charged ions such as Na, K, Ca, and Mg were analyzed using an AAS (Perkin Elmer, USA). Water hardness parameters, including TH and total alkalinity with titration method and SO_4 using a UV-spectrophotometer (UV-1900i, Shimadzu Co., Japan) (APHA, 2017).

2.4. Drinking water quality index

The WQI is extensively used for monitoring and assessing water quality status (Nath et al., 2024) for drinking and irrigation purposes (Ullah et al., 2024). The WQI evaluates various physiochemical parameters to determine their suitability for drinking purposes and provides valuable information regarding associated human health problems. The WQI was adapted from Yenugu et al. (2020). It consists of four steps; the equations are provided below to better understand the entire process.

$$Wi = \frac{wi}{\Sigma_n^i wi} \qquad (1)$$

$$Qi = \frac{(Ci - Cip)}{Si - Cip} \times 100 \qquad (2)$$

$$Sli = Wi \times Qi \qquad (3)$$

$$WQI = \Sigma_n^i SLI \qquad (4)$$

Where Cip=7 for pH and Cip=0 for all other parameters in this study.

2.5. Irrigation water quality index

Irrigation WQI was evaluated using Na% and SAR. Evaluation of SAR is a substantial method described by El-Defan et al. (2016).

The SAR provides valuable information about sodium hazards of irrigation water but doesn´t consider the impact of anionic composition on irrigation water hazards. Nonetheless, it is a reliable indicator for predicting the dominance of sodium cations adsorbed onto soil particles from prevalent sodium in irrigation water. The equations for Na% and SAR were taken from (Richards, 1954; Todh, 1980), and the parameters were expressed as meq/L.

$$SAR = \frac{Na}{\sqrt{Ca + Mg/2}} \qquad (5)$$

$$Na\% = \frac{(Na+K)100}{(Na+K+Ca+Mg)} \quad (6)$$

2.6. Health risk assessment

Average daily dose (ADD) for F intake via groundwater was measured by equation adapted from the (Din et al., 2024; US-EPA, 2011).

$$\mathrm{ADD} = \frac{\mathrm{C\ x\ IR}}{\mathrm{BW}} \quad (7)$$

Where IR is 2L per day and BW 72 kg for adults and 30.6 kg for children, as adapted from Din et al. (2024). Similarly, the noncarcinogenic risk, i.e., HQ, is a potential risk estimation of F for adults and children as in equation 8 (Haq et al., 2023; US-EPA, 2011).

$$HQ = \frac{CDI}{RfD} \quad (8)$$

2.7. Hadrochemical and geospatial analyses

The data processing and interpretation were conducted using Microsoft Office Excel, and the data were prepared for further analysis in other software programs. Basic statistical analyses, including determining data range, mean, and standard deviation. Geospatial analyses were performed using ArcGIS software (version 10.8.2). Water quality categorization and resource identification were illustrated using Wilcox and Piper plots created with an online scatterplot maker.

3. Results and discussion

3.1. Water characteristics

The descriptive statistics of groundwater sources are shown in Table 1. Furthermore, their spatial distributions are exhibited in Fig. 2. Water from Dadyal has the uppermost pH mean value of 7.73±0.13, followed by Mirpur, and the lowermost of 6.99±0.10 for Jatlan. However, 11.7% of the Mirpur water samples reached the highest recommended value (8.5) set by WHO.

Samples showed that mean pH values were under the WHO's recommended threshold. The geological formation of carbonate rocks such as limestone can contribute carbonate minerals to underground water, raising the water's pH to more alkaline (Haroon and Muhammad, 2022; TUČEK et al., 2017). The highest mean TDS and EC values, 482±39.5 mg/L and 971±74.1 µS/cm were noted in water of Dadyal, and the lowest 273±40.6 mg/L and 541±82.0 µS/cm in Jatlan. These lower and higher TDS and EC values could result from geogenic and anthropic factors (Subba Rao et al., 2024). Water showed lower TDS and EC values than the standard of both WHO and MAL. Higher values of TDS in water provide a sink to various water-quality deteriorated substances that are toxic to both human and aquatic life. The values of TDS and EC Mirpur district were noted as lesser than reported by Shaibur et al. (2021b) for the groundwater of Khulna district, Bangladesh. The maximum mean concentration of ORP was 439±112 in the water of Dadyal, and the minimum was 237±64 in Mirpur. However, the concentrations of ORP were found in the safe zone for all the water samples, indicating sustainable water quality. Other basic water quality parameters, including hardness and alkalinity, were below the recommended threshold for water quality in all three studied towns.

The concentrations of major ions such as Ca, Mg, Na, K, SO_4, I, Cl, and F are shown in Table 1 and distribution maps (Fig. 2). The uppermost mean concentrations of 83.6±7.9, 87.0±25.5, 3.02±0.60, 13.4±3.71 mg/L were noted for Ca, Na, K, Mg in water of Mirpur and the lowermost of 54.5±7.9, 23.8±6.5, 3.47±1.66, and 10.2±3.01 mg/L in the Jatlan, respectively (Table 1). Their concentrations were below the recommended values for these significant cations in water. F showed a maximum concentration of 0.19±0.04 mg/L in Dadyal and a minimum of 0.07±0.01 mg/L in Jatlan. F is one of the essential elements for bone development and dental enamel organ formation. However, its higher concentration is toxic and causes diseases such as fluorosis (Din et al., 2024). Similarly, the maximum average concentrations of 11.7±1.46, 141±16.0, and 34.9±8.56 mg/L were found for the I, SO_4, and Cl in the Mirpur and the minimum concentration of 5.42±0.80, 78.9±16.4, and 18.7±6.57 mg/L in Jatlan, respectively. The concentration of these anions was noted to be lower than the WHO-recommended guidelines values. The values of Ca, Mg, Na, K, SO_4 in present study were noted as lesser than reported by Shaibur et al. (2021b) for the groundwater of Khulna district, Bangladesh. Spatial distribution maps showed that Jatlan town noted lesser values for most of the studied physiochemical parameters, and Mirpur showed higher values. Elevated values of these parameters could be attributed to bedrock geology and domestic sewerage.

3.2. Drinking water quality index

The WQI values were determined and to characterize groundwater quality (Wen et al., 2024; Zahedi et al., 2017). Based on WQI classifications, water is described as excellent (WQI < 50), good ($50 \leq$ WQI ≤ 99.9), poor ($100 \leq$ WQI ≤ 199), very poor ($200 \leq$ WQI ≤ 299), and unsuitable for drinking purposes (WQI $\geq$ 300) (Boyacioglu, 2010). The average WQI values of groundwater for studied towns were noted to be excellent (Table 2). Spatial distribution of the WQI values showed that 5.8% of samples of Mirpur were in good category, while rest were in excellent category (Fig. 3). The spatial distribution maps of WQI showed that groundwater was found suitable for drinking purposes, indicating no harmful consequences for the dependent population. The WQI values in present study were noted as lesser than reported by Subba Rao et al. (2024) for the groundwater of Odisha, India.

3.3. Irrigation water quality index

The groundwater was evaluated for irrigation WQI through SAR and Na% using sodium hazards. The spatial distribution maps showed the distribution of SAR and Na% values. Water classifications based on SAR are excellent (< 10), good (10-18), doubtful (18-26), and unsuitable (> 26) categorizing the quality for irrigation purposes. The average SAR values were noted as an excellent category for groundwater (Table 2). The spatial distribution map showed that 5.8% and 14.2% of samples were in the good category in Mirpur and Dadyal towns, respectively (Fig. 3). Rest of the samples of studied town were observed to be in the excellent class. SAR values showed the suitability of groundwater for irrigation of agricultural fields. The SAR values were noted as lesser than those for groundwater, as reported by Din et al. (2023).

The average values of Na% for groundwater are summarized in Table 2. Higher values of Na% were noted for the Dadyal, followed by Mirpur, and the lowest values in Jatlan Town. The spatial distribution of the map of the Na% showed that 11.7% and 5.8% of samples showed unsuitable water for irrigation. The remaining samples in the studied towns were noted in good to excellent categories (Fig. 3). These Na% values were noted as less than reported by Shaibur et al. (2021b) for the groundwater of Khulna district, Bangladesh.

For the Wilcox diagram, the values of Na% and SAR were plotted in contrast to the EC, and the results are shown in Fig 4ab. The groundwater samples of the Mirpur district were noted to be in the excellent and good categories, and only three samples were in the admissible category. Water quality results showed no limitation for irrigation Fig. 4a. Similarly, the Riverside diagram classified water with low levels of SAR. Therefore, the salinity problem from the studied groundwater to irrigated soils will not impact agriculture fields (Fig. 4b). Hydrochemical properties were evaluated by assessing the significant ion concentrations in the groundwater. Groundwater chemistry is exposed to changes due to its interactions with different chemical and biological variability of the parent bedrock and soil. The weathering of bedrock and anthropogenic accelerated erosion brought changes in the groundwater chemistry. The study used a Piper diagram to understand the contributing agents and origins of the hydrogeochemistry of the groundwater (Ekbal and Khan, 2022; Siegel et al., 2015; Ullah et al., 2024). This study revealed that Ca was dominant in cations SO_4 in the anion part of the piper diagram, and groundwater facies were Ca-SO_4 and mix types (Fig. 4c). This indicates that the groundwater is complex, with a higher contribution from Ca, which affects its uses. Furthermore, due to the predominance of SO_4, the groundwater was slightly acidic. However, no significant harmful threat is found for drinking purposes.

3.4. Health risk assessment

The ADD values of F via drinking water intake were summarized in Figure 5. Results noted that Dadyal town has the maximum average ADD values for F via groundwater intake, and Jatlan town showed the minimum values. Maximum ADD values in Dadyal town were attributed to the higher contamination of F in groundwater than in other towns. Among the human population, children showed higher ADD values than adults (Fig. 5). The spatial distribution of ADD values for F of adults and children was summarized in Figure 6ab. Spatial distribution maps showed that Dadyal town was observed with maximum ADD values. A higher intake and low body weight of children lead to maximum HQ values and potential risk than adults. Hence, the children of Dadyal town showed higher HQ values than those of other studied towns. The spatial distribution of HQ values for F of both adults and children was summarized in Figure 6cd. Spatial distribution maps revealed that Dadyal town was observed with elevated HQ values. Higher risks for children were noted, consistent with a previous study (Din et al., 2024). The HQ values through groundwater intake were less than in another study reported by the Khyber district of Pakistan (Ather et al., 2022). F contamination in the groundwater does not pose any potential risk and is recommended for drinking and domestic uses.

4. Conclusions

The present study concluded that Jatlan town of Mirpur district showed better groundwater than other towns. The physicochemical parameters, except for pH, were found under WHO drinking water guidelines. Spatial distribution showed higher contamination for most of the physicochemical parameters in Mirpur town. The physicochemical parameters, WQI, SAR, and Na%, showed a general trend that Mirpur > Dadyal > Jatlan. The Ca and SO_4 were dominant species with $CaSO_4$ and mixed water type. The HQ values through F intake in groundwater were noted as less than the threshold of 1. The drinking and irrigation WQI showed groundwater's suitability and recommendations for their uses. This study recommends future work on heavy metal contamination and potential risk assessment in the studied towns.

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Data Availability *The data supporting this study's findings are available from the corresponding author upon reasonable request.*

Conflict of Interest *The authors declare no competing interests.*

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Table 1. Physiochemical parameters in groundwater of the Mirpur district, Pakistan

	Jatlan				Mirpur				Dadyal					
Parameters	Mean	Std dev	Minimum	Maximum	Mean	Std dev	Minimum	Maximum	Mean	Std dev	Minimum	Maximum	WHO	MAL
pH	6.99	0.10	6.35	7.54	7.72	0.13	6.90	8.50	7.73	0.13	7.00	8.10	7.5	8.5
T	25.7	0.9	18.9	30.4	26.3	0.5	22.0	30.0	24.3	0.7	21.0	25.9		
TDS	273	40.6	110	531	359	29.3	127.0	623	482	39.5	356	647	1000	2000
EC	541	82.0	212	1045	719	59.0	252.0	1240	971	74.1	783	1293	1400	3000
ORP	271	10.1	210	325	239	15.9	101.0	297	439	36.8	296	591		
TH	148	12.0	98.0	240	221	20.6	76.0	430	117	22.7	34.0	188	500	
T Alk	155	15.3	59.0	220	215	19.4	60.0	430	279	25.7	210	430	500	
Ca	54.5	7.9	30.7	123	83.6	7.9	37.1	163	59.2	7.3	32.0	92.8	75	400
Na	23.8	6.5	3.2	69.6	87.0	25.5	3.8	390	80.9	37.0	17.6	316	200	919
K	3.47	1.66	0.90	21.3	3.02	0.60	0.50	11.2	2.19	0.32	1.20	4.00	15	2
Mg	10.2	3.01	1.54	37.2	13.4	3.71	1.92	56.4	5.94	0.72	4.00	9.60	50	60
F	0.07	0.01	0.00	0.18	0.16	0.02	0.08	0.31	0.19	0.04	0.07	0.45	1.5	
I	5.42	0.80	2.50	12.0	11.7	1.46	4.80	23.3	7.56	1.33	5.27	15.9	400	
SO_4	78.9	16.4	21.6	207	141	16.0	36.8	311	85.1	19.3	23.3	166	200	960
Cl	18.7	6.57	2.00	68.0	34.9	8.56	2.00	128	22.3	4.80	8.00	42.0	250	1063

calcium (Ca), chloride (Cl), electrical conductivity (EC), Fluoride (F), iodide (I), magnesium (Mg), maximum allowable limits (MAL), oxidation-reduction potential (ORP), potassium (K), sodium (Na), sulfate (SO_4), temperature (T), total dissolved solids (TDS), total hardness (TH), and world health organization (WHO). pH unitless, T measured in °C, EC µS/cm, I µg/L and the rest of the parameters in mg/L.

Table 2. Drinking and irrigation water quality indices of groundwater in the Mirpur district, Pakistan

Location	Statistics	WQI	SAR	%Na
Jatlan	Mean	25.3	1.03	20.1
	Stdev	8.11	0.89	13.1
	Minimum	17.5	0.17	6.2
	Maximum	41.6	2.88	41.7
Mirpur	Mean	37.4	3.31	32.6
	Stdev	8.74	4.23	21.3
	Minimum	23.4	0.16	4.61
	Maximum	56.3	17.0	81.2
Dadyal	Mean	34.6	3.76	42.1
	Stdev	19.1	4.59	7.38
	Minimum	17.0	0.76	27.5
	Maximum	78.3	14.0	49.4

sodium adsorption ratio (SAR), sodium percentage (Na%), and water quality index (WQI)

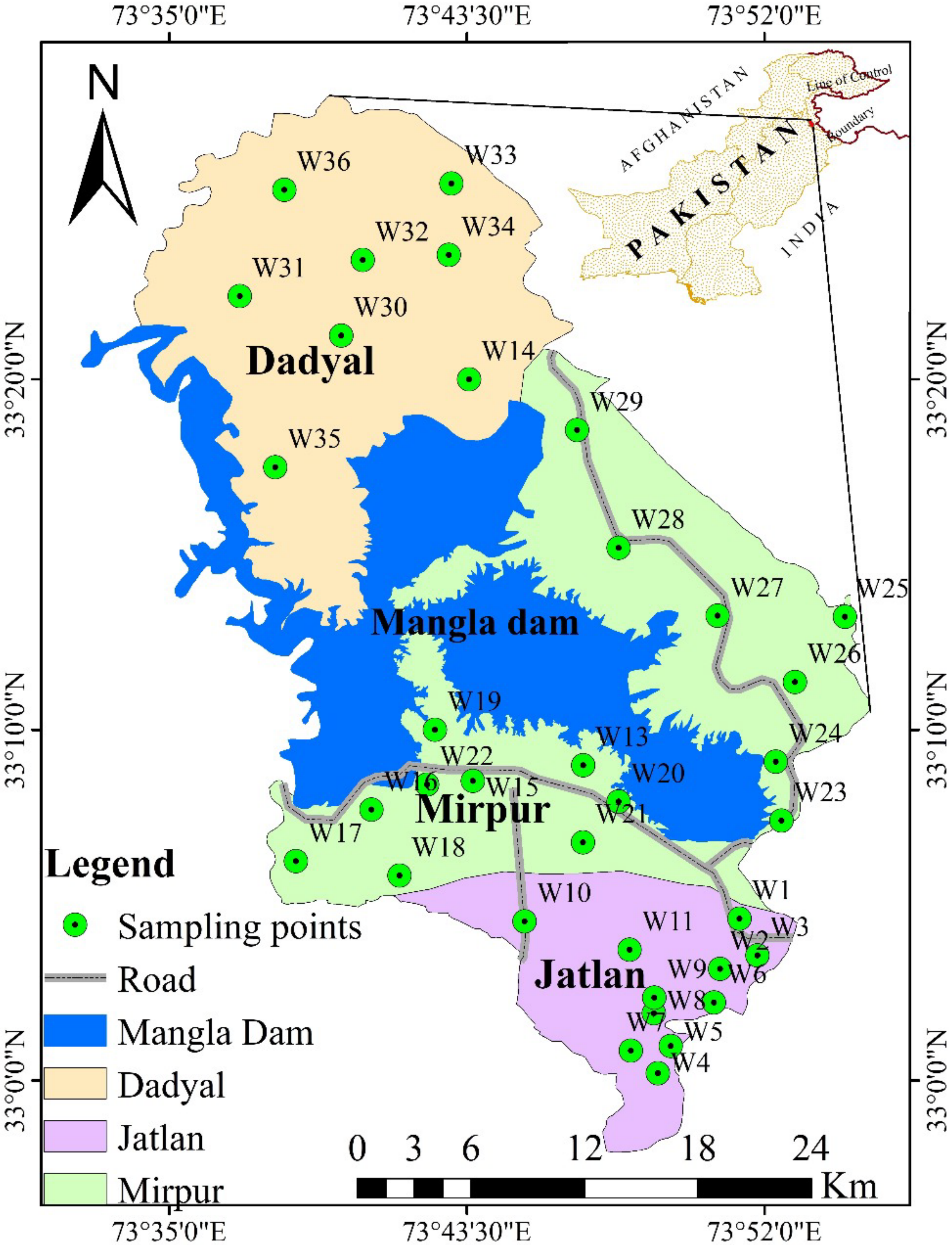

Fig. 1. Groundwater sampling location map in the Mirpur district, Pakistan

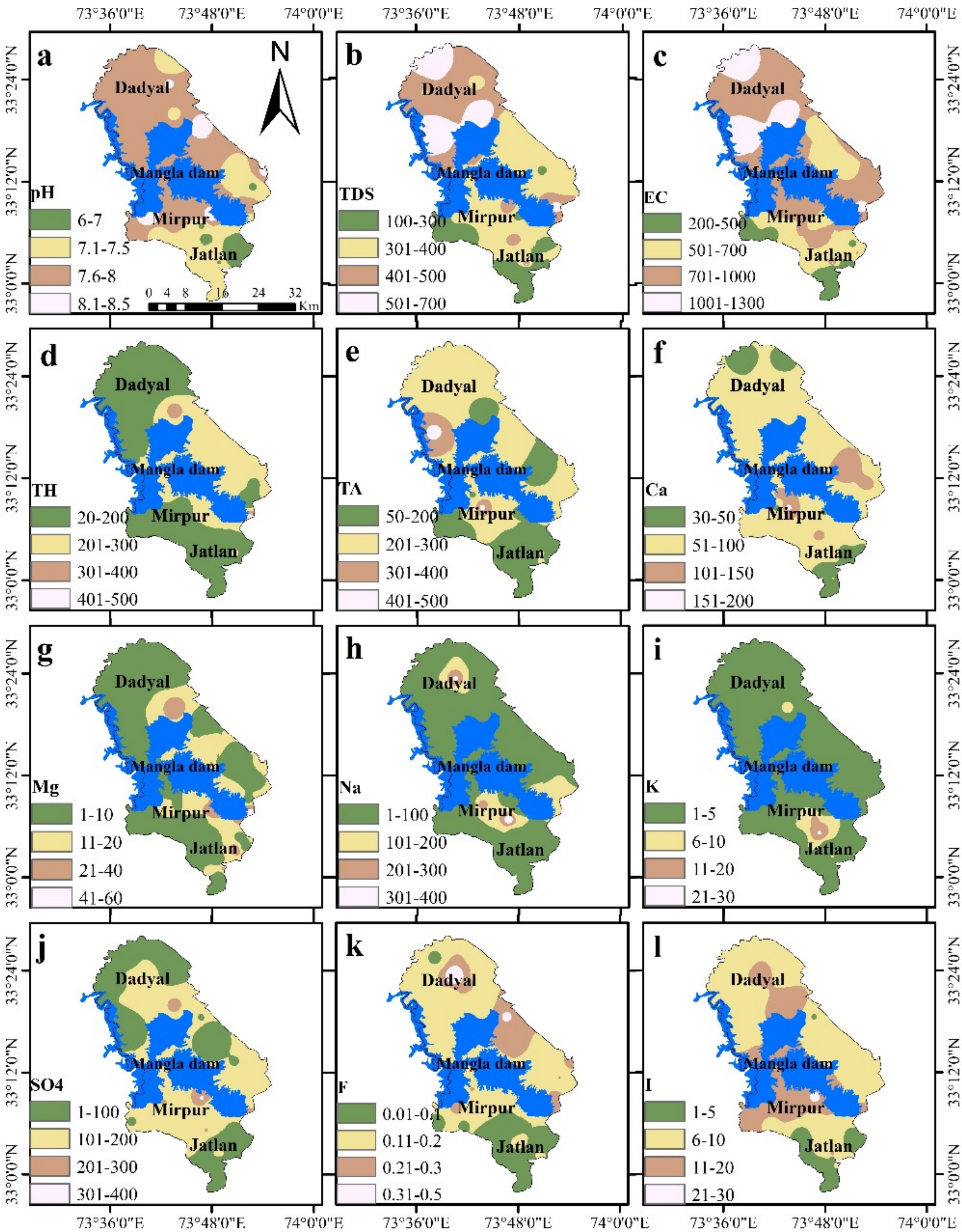

Fig. 2. Spatial distribution map of physiochemical parameters of groundwater in the Mirpur district, Pakistan. calcium (Ca), chloride (Cl), electrical conductivity (EC), Fluoride (F), iodide (I), magnesium (Mg), maximum allowable limits (MAL), oxidation-reduction potential (ORP), potassium (K), sodium (Na), sulfate (SO_4), temperature (T), total dissolved solids (TDS), total hardness (TH), and world health organization (WHO). pH unitless, T measured in °C, EC µS/cm, I µg/L and the rest of the parameters in mg/L.

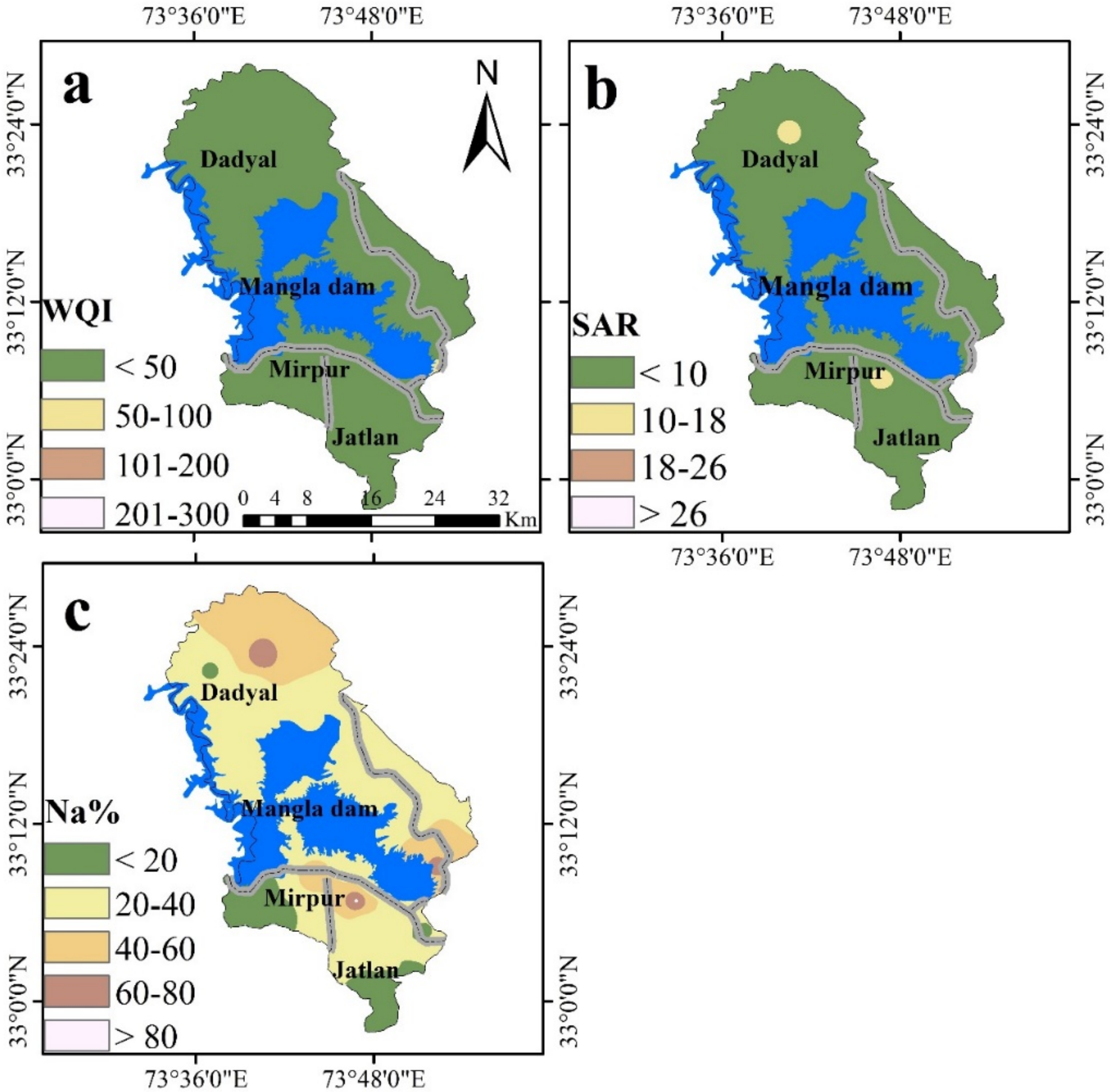

Fig. 3. Spatial distribution map of drinking and irrigation water quality indices for groundwater in the Mirpur district, Pakistan**.** sodium adsorption ratio (SAR), sodium percentage (Na%), and water quality index (WQI)

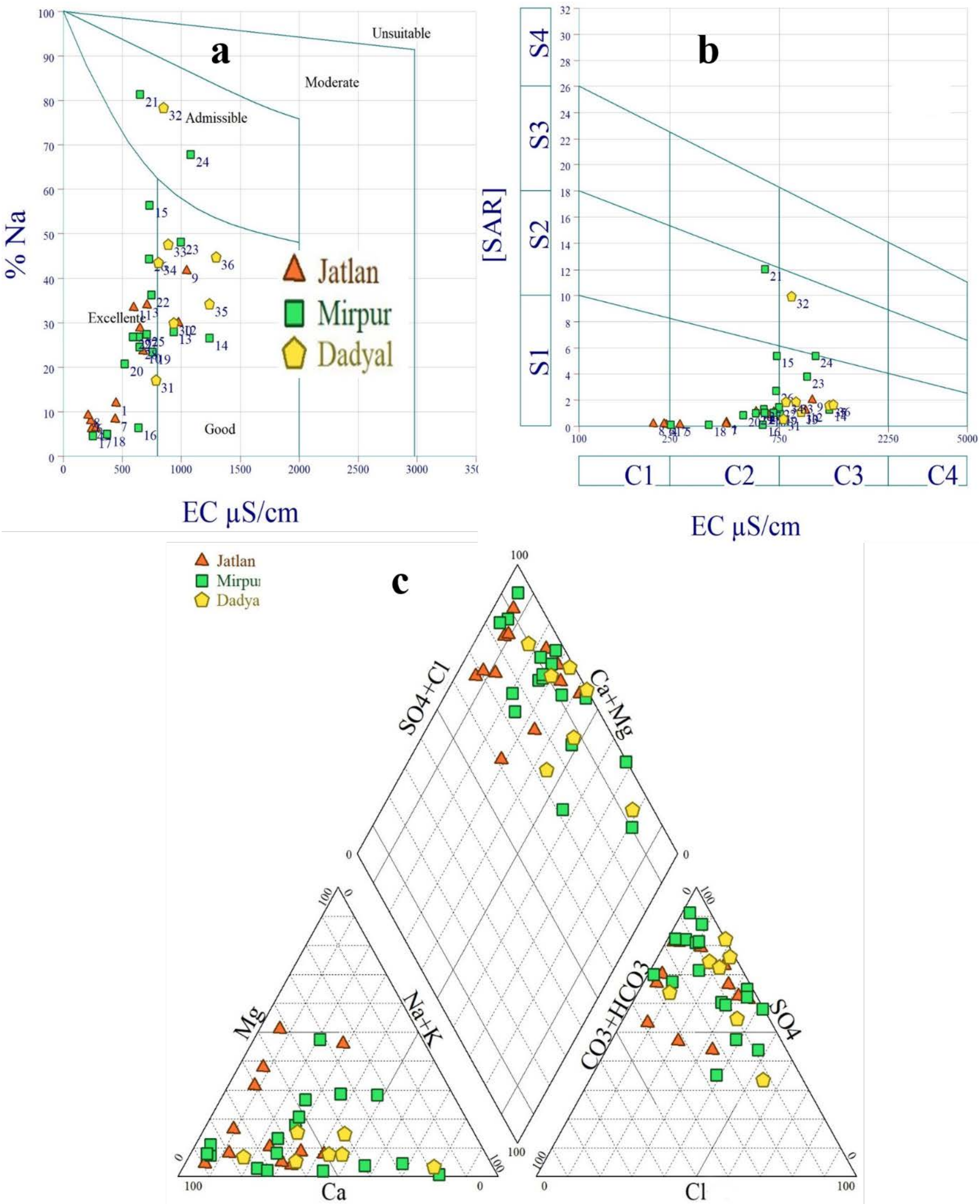

Fig. 4abc. Wilcox diagram of groundwater in the Mirpur district, Pakistan, a. Na% and EC ratio, b. SAR and EC ratio, c. Piper diagram, calcium (Ca), chloride (Cl), electrical conductivity (EC), Fluoride (F), iodide (I), magnesium (Mg), potassium (K), sodium (Na), sulfate (SO_4), sodium adsorption ratio (SAR), and sodium percentage (Na%)

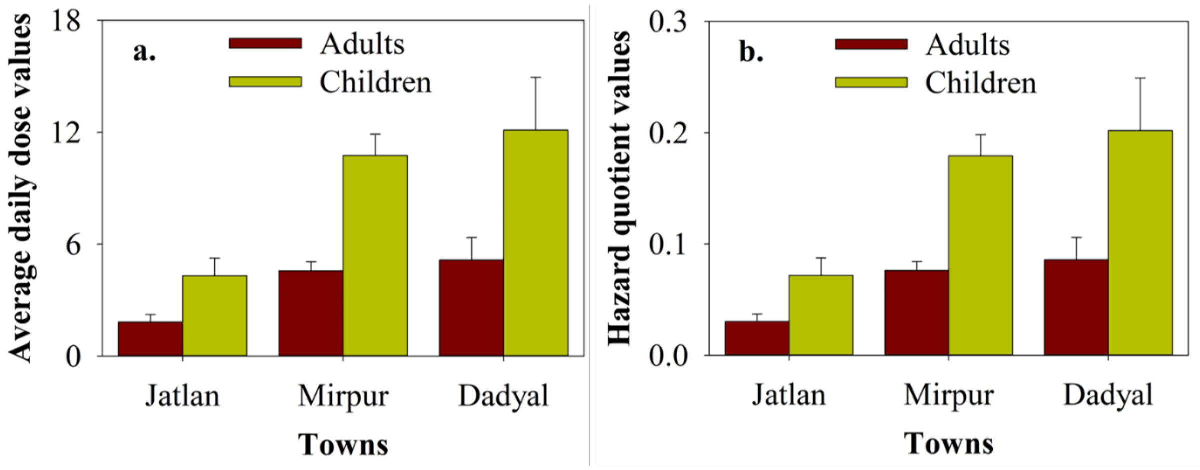

Fig. 5. Health risk assessment via consumption of groundwater in the Mirpur district, Pakistan

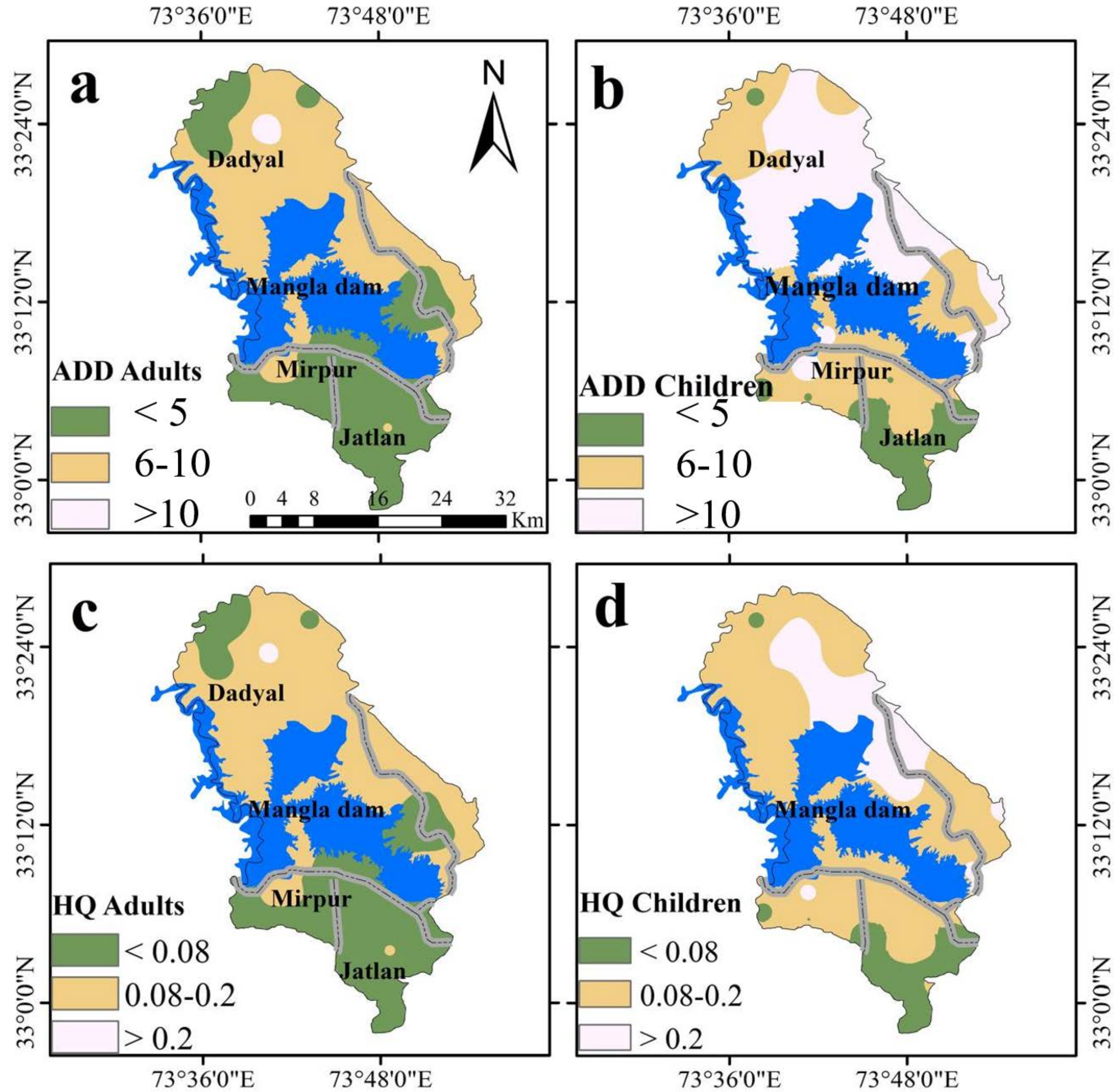

Fig. 6. Spatial distribution of averge daily dose (µg/kg-day) and hazard quotient via consumption of groundwater in the Mirpur district, Pakistan, average daily dose (ADD) and hazard quotient (HQ)