

Article



Assessment of Groundwater Quality beneath Agriculturally Advanced Region of Northern Alluvial Plain, India

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Abstract: In the present study, groundwater suitability for domestic and irrigation purposes was analyzed in the alluvial aquifers of the Bist-Doab region of Punjab, India, using various indices such as WQI, WAWQI, MCDA, RSC, SAR, PI, %Na, KR, MH, PS, K, and K_a. Since it is difficult to assess the suitability of groundwater for irrigation based on various indices individually, a composite groundwater quality index for irrigation (CGQII) was used in the study which transforms nine indices to a single value for each sample. Results reveal that the groundwater of a few blocks was found unsuitable for domestic use due to chemical leaching from fertilizers, pesticides, and agricultural and industrial wastes. Whereas, the groundwater of mainly southwestern parts was found unsuitable for irrigation due to long-term water accumulation in aquifers and continuous use of sodium-ion-rich groundwater. The findings conclude that anthropogenic activities have played a significant role in making groundwater unfit for domestic and irrigation purposes in the study area. The present study also emphasizes continuous monitoring and evaluation of groundwater resources in the region.

Keywords: anthropogenic activities; over-extraction; groundwater quality; composite groundwater quality index for irrigation

1. Introduction

Groundwater has become a significant source of water to fulfill the everyday water requirement of booming human civilization in all parts of the globe. The impotable nature of surface water as a result of rapid industrialization, urbanization, and unsustainable development has forced the population to depend on the largest freshwater storage of the world for meeting domestic, industrial, and irrigational needs. In most megacities, households directly depend on fresh groundwater resources to meet their domestic needs. In Mexico City, about 90% of the domestic water supply comes from groundwater [1]. In most of the regions around the globe, especially arid, semi-arid, and alluvial, the uncontrolled extraction of groundwater has led to a continuous decrease in groundwater table [2,3], which has become a threat to the sustainability of agricultural production and hence human civilization.

Sustainable groundwater development is not only constrained by resource availability but also by quality deterioration [4,5]. Groundwater quality is greatly influenced by the nature of recharging water, chemical constituents of precipitation, surface and subsurface water, and groundwater chemistry acquired in the aquifer environment [6]. Among these factors, groundwater chemistry plays a significant role in determining the quality of groundwater; controlled by the dissolution of minerals (mainly carbonates and dolomite in alluvial aquifers), seawater intrusion in coastal areas, and nitrate, leachate, and other microbial contamination in the areas of unsustainable urban, industrial, and agricultural growth [7–9]. Therefore, looking at the magnitude of groundwater dependency by the hu-



Citation: Gautam, A.; Rai, S.C.; Rai, S.P. Assessment of Groundwater Quality beneath Agriculturally Advanced Region of Northern Alluvial Plain, India. *Sustainability* 2021, *13*, 7053. https://doi.org/ 10.3390/su13137053

Academic Editors: Mohammed Mainuddin, Mohammad A. Mojid and Sreekanth Janardhanan

Received: 14 May 2021

Accepted: 22 June 2021 Published: 23 June 2021

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Copyright: © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). man population, the analysis of chemical constituents of groundwater becomes a necessary task for the research community, government organizations, and other stakeholders.

Various studies have focused on monitoring and evaluation of the groundwater quality for drinking, irrigation, and industrial purposes using individual parameters (physico-chemical) and various suitable indices (WQI, WAWQI, MCDA, RSC, SAR, PI, %Na, KR, MH, PS, K, and K_a) [10–15]. The studies have reported degradation in groundwater quality mainly due to sodium hazard, excessive salt concentration, and nitrate contamination [16–18]. Higher sodium concentration in groundwater has been found to limit a plant's healthy growth by decreasing porosity and permeability in clay-dominant soil [11–13]. The studies also reported that the concentration of salts impacts agricultural productivity to a large extent [12,14,19]. Excessive salt concentration limits water transportation, whereas its deficiency reduces water infiltration in the soil. Studies have also found nitrate contamination in groundwater as a problem worldwide due to high input of chemical fertilizers; a by-product of organic compounds from agriculture, poultry wastes, leaky waste disposal, unlinked severe lines, and livestock manure [20,21].

The alluvial tract of north India is geomorphologically formed by the sediments carried by the Indus, Ganga, and Brahmaputra river systems. This makes the region hydrogeologically very rich. The availability of sufficient groundwater resources and fertile soil have made the region a laboratory for successful implementation of the green revolution in the 1960s, which fulfilled the food needs of the rapidly growing population. However, greater extraction of groundwater for agricultural irrigation and the intensive use of chemical fertilizers, pesticides, and insecticides by the farmers initiated the degradation in groundwater quality in the region [22–24]. Therefore, to have a micro-level analysis to assess the suitability of groundwater for domestic and irrigation purposes, the Bist-Doab region of Punjab (locally known as Doaba) was considered as the area of interest for the present study, which truly represents the agriculturally active northern alluvial plains of India. The Bist-Doab region of Punjab is very rich in fertile soil and groundwater resources due to its geomorphic formations; it is structured by the sediments of Satluj and Beas rivers of the Indus river system.

With this background, the main aims and objectives of the study include (i) physicochemical analysis of the ions present in the groundwater of the Bist-Doab region of Punjab; (ii) analyzing groundwater suitability in the region for domestic and irrigation purposes; and (iii) comparison of various existing indices for assessment of groundwater suitability for domestic and irrigation purposes.

2. Materials and Methods

2.1. Site Description

Located in the northwestern parts of India, the Bist-Doab region of Punjab covers an area of 9022 km², extending from 30°58' to 32°5' N and 74°57' to 76°31' E (Figure 1). It is bounded by Rivers Beas and Satluj to the north, west, and south, and Siwalik hills to the east. The region shares state boundaries with Himachal Pradesh to the east and on the other side by the other districts of the state of Punjab, i.e., Rupnagar, Ludhiana, Moga, and Firozepur to the south, and Tarn Taran, Amritsar, and Gurdaspur to the west. The region shares about 17.91% of the state's area and 18.77% of its total population. About 60% of the urban population of Punjab resides in this region. With a moderate climate, the region receives about 750 mm of annual rainfall. The study area has a high population density due to rich fertile soil and good agricultural harvest as water-rich aquifers are present beneath due to the geological advantage of the slope. Tube wells and extensive canal network dominate the sources of agricultural irrigation as the region is the moderate recipient of rainfall which mainly depends upon the monsoon wind system. The study area is undergoing a fast rate of development with a rising level of urbanization, construction of highways and expressways, setting up of industries, and increasing rate of agricultural development.



Figure 1. Physiography and administrative divisions of the Bist-Doab region of Punjab, India.

The study area can be divided into Siwalik hills and alluvial plains based on altitude and relief. Hills with the highest point at 735 m from mean sea level (msl) are about 10 km wide along the eastern boundary line of the study area. Hills have developed undulating topography due to erosion activities of rainwater and seasonal streams, soil characteristics, vegetation cover, and human activities. The areas parallel to Siwalik foothills have an average elevation of 400 m whereas, the alluvial tracts are below 300 m from msl. The alluvial plain is almost homogenous but the slope is towards the west and southwest. Geologically, the alluvial plain areas are covered by quaternary sediments brought down by the rivers and streams of the Indus river system, mainly by the rivers Sutlej, Beas, Kali Bein, and White Bein, and deposited on semi-consolidated tertiary rocks or metamorphic and igneous rocks of pre-Cambrian origin [24]. Most of these have been covered with sand, silt, loam, clay, and kankar. However, the areas adjoining foothills are covered with subangular unsorted pebbles, gravel, and cobbles. Hydrogeologically, two groups of aquifers have been reported in the region. The top unconfined layer consists of coarse sand beds, separated by thin and less extensive clay horizontal layers with a varying thickness between 72 m to 94 m. This thickness decreases as one moves towards the west and southwest. The next confined layer with around 250 m thickness is composed of gravel, sand, clay, and kankar with alternating sequences of sand and clay [25].

2.2. Database and Sampling Design

A total of 148 groundwater samples were collected in June–July 2019 from a combination of 94 irrigation tube wells, 38 domestic water supply submersible pumps, and 16 handpumps. A grid-based random sampling method was used to collect the data for homogenous representation of groundwater of the study area. The screening depth of sources of groundwater, i.e., tube well, submersible pumps, and handpumps, varied within various parts of the study area, depending upon the current status of the groundwater table. However, the present study analyses the groundwater suitability considering its daily use for irrigation and domestic consumption, irrespective of regional variation in depths of groundwater level in the Bist-Doab region of Punjab, India. The screening depth of most of the tube wells and submersible pumps was found at intermediate depth of ~30 m to 120 m in an alluvial aquifer environment. Whereas, the handpumps had their source of water in shallow aquifers, i.e., <30 m depth. The tube wells, submersible pumps, or handpumps were continuously operated for 10 min before the collection of groundwater samples in 250 mL amber narrow mouth bottles, manufactured by Tarson Products Pvt. Limited. The physical parameters, such as temperature, pH, and EC, were immediately measured in the field to overcome the environmental impact. Utmost care was taken in carrying the groundwater samples to the laboratory so that their chemical characteristics remained conserved.

2.3. Physico-Chemical Analysis

The analysis of cations (calcium, magnesium, sodium, potassium, and lithium) and anions (sulphate, chloride, fluoride, nitrate, nitrite, and bromide) of all the groundwater samples was carried out with the help of ion-chromatography technique using Dionex IC 5000+ instrument. A mixture of 4.5 mM Na₂CO₃ and 0.8 mM NaHCO₃ was used as an eluent for analysis of anions, and 30 mM of methanesulphonic acid (MSA) was used as an eluent for cations analysis. Bicarbonate concentration in the groundwater samples was measured with the help of an auto-titrator (Metrohm, Switzerland; model: 877 Titrino Plus). These analyses were carried out in the Institute of Environment and Sustainable Development (IESD), Banaras Hindu University, Varanasi, Uttar Pradesh, India. To avoid atmospheric influence on the physical parameters of the groundwater samples, temperature, pH, and EC were measured in the field itself by using a digital field thermometer, pH meter, and EC meter, respectively.

2.4. Water Quality Evaluation for Domestic Use

Water Quality Index (WQI) is a quality rating technique widely used to show the composite influence of all the water quality parameters by regenerating a single score to represent the water quality for either domestic or irrigation purposes [26,27]. There are two widely used indices for computing water quality index, i.e., Water Quality Index (WQI) and Weighted Arithmetic Water Quality Index (WAWQI) [28,29]. These indices are based on the quality rating scale of each parameter and their unit weight. The calculation of the quality rating scale for both indices is the same (Equation (1)). However, there is a difference in the calculation of the unit weight for each parameter in both indices. In WQI, unit weight is calculated by assigning a weight ranging between 1 to 5 to each parameter on the knowledge and experience of the researcher/user. The higher value is assigned to the parameter which has more impact on water quality. The weight to each parameter has to be assigned with the utmost care, otherwise the result would be misleading. Then the unit weight is calculated by using Equation (2). Whereas, unit weight for WAWQI is directly calculated using Equation (3), depending upon the standard value of each parameter as prescribed by WHO (2011). However, the final calculation for determining the water quality is the same in both the indices; it is calculated using Equation (4).

$$Q_n = \frac{C_n}{S_n} \times 100 \tag{1}$$

$$W_n = \frac{w_n}{\sum_n w_n} \tag{2}$$

$$W_n = \frac{K}{S_n} \tag{3}$$

$$WQI = \frac{\sum Q_n W_n}{\sum W_n} \tag{4}$$

where Q_n is the quality rating scale for *n*th water quality parameter, C_n is the observed value of the *n*th parameter, S_n is the standard value of the *n*th parameter, w_n is the assigned weight to *n*th parameter, W_n is the unit weight of *n*th parameter, and *K* is the proportionality constant, calculated by Equation (5).

$$K = \frac{1}{\sum_{n} \frac{1}{S_{n}}} \tag{5}$$

In the present study, for calculating WQI, the quality standard for each parameter is considered as per WHO (2011) specifications (Supplementary Table S1). Weight (w_n) and unit weight (W_n) for WQI and WAWQI are also mentioned in Supplementary Table S1. This was followed by the analysis of water quality concerning both indices. Further, groundwater quality for drinking has also been analyzed by a method of multi-criteria decision analysis (MCDA) by combining weights assigned to each parameter using ranking. Rank was assigned within each parameter based on its quality criteria and classification scheme.

2.5. Water Quality Evaluation for Irrigation

Based on the ionic characteristics of the groundwater samples, the groundwater suitability for irrigation was calculated using various indices such as Residual Sodium Carbonate (RSC) (Equation (6)), Sodium Adsorption Ratio (SAR) (Equation (7)), Sodium Percentage (%Na) (Equation (8)), Permeability Index (PI) (Equation (9)), Kelly's Ratio (KR) (Equation (10)), Magnesium Hazard (MH) (Equation (11)), Potential Salinity (PS) (Equation (12)), Irrigation Coefficient (K_a) (Equation (13)) and Synthetic Harmful Coefficient (K) (Equation (14)).

$$RSC = (HCO_3^- + CO_3^{2+}) - (Ca^{2+} + Mg^{2+})$$
(6)

$$SAR = \frac{Na^+}{\sqrt{(Ca^{2+} + Mg^{2+})/2}}$$
(7)

$$\% Na = \frac{(Na^{+} + K^{+}) \times 100}{(Ca^{2+} + Mg^{2+} + Na^{+} + K^{+})}$$
(8)

$$PI = \frac{Na^{+} + \sqrt{HCO_{3}^{-}}}{(Ca^{2+} + Mg^{2+} + Na^{+} + K^{+})} \times 100$$
(9)

$$KR = \frac{Na^+}{(Ca^{2+} + Mg^{2+})}$$
(10)

$$MH = \frac{Mg^{2+}}{(Ca^{2+} + Mg^{2+})} \times 100$$
(11)

$$PS = Cl^{-} + \frac{1}{2}SO_4^{2-}$$
(12)

$$K_{a} = \begin{cases} \frac{\frac{288}{5Cl^{-}} \text{ if } Na^{+} < Cl^{-}}{\frac{288}{10Na^{+} + 4Cl^{-}} \text{ if } Cl^{-} < Na^{+} < Cl^{-} + 2SO_{4}^{2-}}{\frac{288}{10Na^{+} - 5Cl^{-} - 9SO_{4}^{2-}} \text{ if } Na^{+} > Cl^{-} + 2SO_{4}^{2-}} \end{cases}$$
(13)

where all ionic concentrations are expressed in meq/L, and

$$K = 12.4M + SAR \tag{14}$$

where *M* represents the TDS (in g/L).

Since it is difficult to make a final decision on the suitability of groundwater for irrigation based on these indices individually, the present study has developed a Composite Groundwater Quality Index for Irrigation (CGQII) to evaluate the overall quality of

groundwater for irrigation using a single index value. The composite index is based on all the above mentioned indices. This was done to remove the doubt over the quality of groundwater samples which were qualified for use by one index and disqualified by the other. CGQII for each groundwater samples was calculated using the following formulas:

$$Q_n = \frac{C_n}{S_n} \times 100 \begin{bmatrix} When the water quality decreases \\ with increase in index value \end{bmatrix}$$
(15)

$$Q_n = \left(\frac{C_n}{S_n}\right)^{-1} \times 100 \begin{bmatrix} When \ the \ water \ quality \ decreases \\ with \ decrease \ in \ index \ value \end{bmatrix}$$
(16)

$$W_n = \frac{K}{S_n} \tag{17}$$

$$CWQII = \frac{\sum Q_n W_n}{\sum W_n}$$
(18)

where Q_n is the quality rating scale for the *n*th irrigation index, C_n is the calculated value of *n*th irrigation index, S_n is the standard upper limit of the *n*th irrigation index for classifying the groundwater as unsuitable, W_n is the unit weight for the *n*th irrigation index, and *K* is the proportionality constant, calculated by Equation (19).

$$K = \frac{1}{\sum_{n} \frac{1}{S_n}} \tag{19}$$

The unsuitability limit for each index was considered as the standard upper limit for groundwater to be unsuitable for irrigation. The standard limit, proportionality constant, and unit weight for each irrigation index are listed in Supplementary Table S1.

2.6. Geospatial Analysis

Spatial distribution of the physico-chemical parameters and various indices were carried out using the Inverse Distance Weighting (IDW) interpolation method of spatial analysis tool in ArcGIS 10.2.2 software. IDW was chosen over Krigging and other interpolation methods, as the region is almost homogenous with less irregularity in the measured and calculated values of the parameters and indices.

3. Results

3.1. Physico-Chemical Parameters

Results reveal that the pH of groundwater ranges between 6.8 to 8.4 (Figure 2a), which is acceptable for domestic use. The concentration of EC was found more in the southern areas of the region (Figure 2b). Very high salinity (measured by EC) was recorded in the groundwater samples of Nangal Ambian, Baloki, and Taunsa blocks. Only 32% of the study area recorded a TDS level below 300 mg/L (Figure 2c and Supplementary Table S2). About 95% of the region recorded a TH value of more than 200 mg/L, which is of great concern. The groundwater of about one-fifth of the study area (Shahkot, Nakodar, Jalandhar East, and Jalandhar West blocks of Jalandhar district and areas around Taunsa in Balachaur block of SBS Nagar district) recorded a TH value even greater than 400 mg/L (Figure 2d and Supplementary Table S2).



Figure 2. Spatial distribution of (**a**) pH, (**b**) EC, (**c**) TDS, and (**d**) TH in groundwater of the Bist-Doab region of Punjab, India.

The concentration of Ca²⁺ ions ranged between 16.65 mg/L and 330.18 mg/L with higher concentrations in the Kandi belt and Jalandhar district (Figure 3a and Supplementary Table S2). Sodium with a mean of 63.48 mg/L \pm 79.44 was found dominating in the groundwater of southwestern blocks of Sultanpur Lodhi, Lohian Khas, Shahkot, and parts of Phagwara and Balachaur districts (Figure 3b and Supplementary Table S2). The groundwater of around 96% of the region recorded magnesium concentration below the acceptable limit of 50 mg/L (Figure 3c and Supplementary Table S2). However, a higher concentration of potassium ion was limited to the shallow aquifers of Taunsa and Jaijjon (Figure 3d). The higher concentration of Li⁺ ion corresponded to the higher concentration of Mg²⁺ ion at Taunsa, Lohian Khas, and Shahkot blocks (Figure 3d).

The concentration of bicarbonate ranged between 108.68 mg/L and 748.11 mg/L with about 97% of the groundwater samples having concentrations below 600 mg/L (Figure 4a and Supplementary Table S2). Chloride concentration was found higher than 1000 mg/L in three groundwater samples from Taunsa, Baloki, and Nangal Ambian (Figure 4b). Higher SO_4^{2-} concentration was recorded in part of Lohian Khas and Shahkot blocks of Jalandhar district (Figure 4c). The concentration of nitrate ranged between 0.02 mg/L and 203.69 mg/L with its higher concentration in the groundwater of agriculturally productive blocks of Jalandhar, Rukra Kalan, Nurmahal, and parts of the Hoshiarpur district, representing about 9% of the study area (Figure 4d and Supplementary Table S2). NO₂⁻ concentration higher than 1 mg/L at some places in SBS Nagar district (Figure 4f) may be injurious to health in a similar way as nitrate concentration beyond 45 mg/L, i.e., harmful to pregnant women, children, and the elderly. Fluoride levels higher than 1.5 mg/L was recorded in groundwater samples of just one location, i.e., Mukundpur (Figure 4e). In the Bist-Doab region of Punjab, bromide was the least commonly found anion in all the groundwater samples (Figure 4g).



Figure 3. Spatial distribution of cations (**a**) Ca²⁺, (**b**) Na⁺, (**c**) Mg²⁺, (**d**) K⁺, and (**e**) Li⁺ in groundwater of the Bist-Doab region of Punjab, India.

3.2. Groundwater Quality for Domestic Use

A groundwater sample sometimes becomes suitable for domestic consumption concerning one ion and sometimes becomes unfit concerning the other. Therefore, the present study analyzes the groundwater quality of the study area concerning the combination of physical and chemical parameters by using various indices.

As per WQI, the groundwater of most of the Hoshiarpur and Kapurthala districts was found to be of excellent quality, comprising about one-third of the study area. Good-quality groundwater was found in about two-thirds of the study area, mostly in the southern parts (Figure 5a and Supplementary Table S3). However, poor quality of groundwater was found in 23 samples of Shahkot block and parts of Nakodar, Noormahal, Jalandhar East, Jalandhar West, Phagwara, Mahilpur, Nawanshahr, and Balachaur blocks. The poor quality of groundwater in these areas is caused by the combined effect of high concentration of EC, TDS, TH, calcium, magnesium, sodium, chloride, nitrite, nitrate, sulphate, and bromide. It should be noted that these physico-chemical parameters were assigned a greater weight (w_n) in WQI calculation. Hence, the result is the proportional representation of the weight assigned to each parameter for evaluating the groundwater quality of the region.



Figure 4. Spatial distribution of anions (**a**) HCO_3^- , (**b**) Cl^- , (**c**) SO_4^{2-} , (**d**) NO_3^- , (**e**) F^- , (**f**) NO_2^- , and (**g**) Br^- in groundwater of the Bist-Doab region of Punjab, India.



Figure 5. Groundwater quality of the Bist-Doab region of Punjab, India calculated by (**a**) WQI, (**b**) WAWQI, (**c**) WAWQI excluding Br⁻ and NO₂⁻, and (**d**) MCDA.

As per WAWQI, the groundwater of about 95% of the Doaba region was found to be of excellent quality (Supplementary Table S3). Poor to unsuitable quality of groundwater was observed in areas around Nurmahal, Banga, and Taunsa blocks (Figure 5b). Two groundwater samples of Taunsa and Kahma in the SBS Nagar district were found unsuitable for domestic use. The higher concentration of EC, TDS, TH, chloride, nitrite, nitrate, bromide, and magnesium was found to be responsible for the poor quality of groundwater in these regions.

A comparison of the results from WQI and WAWQI shows that in the former index, no groundwater sample was found to be unsuitable for domestic use. On the other hand, two samples were found to be unsuitable concerning WAWQI. The difference in the groundwater quality using both indices has resulted from differences in the calculation of their unit weight and the difference in their classification criteria. In WQI, if the weight assigned to each parameter is changed, then the overall result will change. Whereas, no alteration in the calculated value of the groundwater quality index is possible in WAWQI, as it considers the standard value specified by the water quality certifying agencies like WHO. However, if we modify the classification criteria of WQI and keep it the same as WAWQI, then 23 samples representing about 3.5% of the study area would be found unsuitable for domestic purposes. However, a detailed consideration has to be made before changing the classification criteria as it may alter the basic aim of the development of the WQI method.

In WAWQI, a change in the number of parameters under consideration for quality evaluation can have an impact on the overall analysis of groundwater quality to some extent. In Figure 5b, the consideration of bromide and nitrite have led to a high correlation between the areas having a higher concentration of bromide and nitrite, and the areas with poor to unsuitable groundwater quality. If these ions are left out in calculating WAWQI, significant change can be observed (Figure 5b,c). The areas of excellent quality groundwater were limited to the parts of northern Hoshiarpur district and western Kapurthala district which have comparatively less ionic concentration and are better concerning all the individual physico-chemical parameters. In Figure 5c, more than two-thirds of the region can be found to have a good quality of groundwater. However, despite the exclusion of nitrite and

bromide, there has not been much change in the poor to unsuitable groundwater quality in the respective regions.

A detailed comparison between WQI and WAWQI methods reveals that the evaluation of groundwater quality using WAWQI seems much better as compared to the WQI method, as the WQI may result in doubtful quality evaluation with doubtful weights assigned to each parameter by the respective researcher.

The groundwater quality in the area was also evaluated using MCDA, taking into consideration significant parameters such as pH, TDS, TH, Ca²⁺, Mg²⁺, Cl⁻, SO₄²⁻, F⁻, and NO₃⁻ (Supplementary Table S4). Results reveal that more than two-thirds of the study area has a good quality of groundwater (Supplementary Table S5). Bad-quality groundwater was found in Shahkot, Nakodar, Balachaur, and Mahilpur blocks of the study area (Figure 5d). The water quality evaluation by this method depends upon the detailed pre-knowledge about the specific parameter having a significant impact on the groundwater quality for drinking. There seems always a chance of leaving some of the important parameters which can make the groundwater unsuitable for domestic consumption.

3.3. Groundwater Quality for Irrigation

The relatively high concentration of one ion over the other leads to a negative impact on soil, water, and ultimately plants' health. Therefore, the present study analyses the groundwater quality of the region concerning various indices such as Residual Sodium Carbonate (RSC), Sodium Adsorption Ratio (SAR), Permeability Index (PI), Sodium Percentage (%Na), Kelly's Ratio (KR), Magnesium Hazard (MH), Potential Salinity (PS), Synthetic Harmful Coefficient (K), and Irrigation Coefficient (K_a).

About 88% of the study area has good-quality groundwater for irrigation concerning SAR (Supplementary Table S6). However, the groundwater of about 3% of areas including parts of the Phagwara, Bhulath, and Sultanpur Lodhi blocks of Kapurthala district have been found unsuitable for the use of irrigation (Figure 6a and Supplementary Table S6). Higher RSC leads to Na⁺ ion adsorption, leading to swelling of the soil which adversely affects soil permeability and thus productivity. The groundwater of the Doaba region was found suitable for irrigation concerning SAR (Supplementary Table S6). However, the groundwater of parts of Sultanpur Lodhi, Lohian Khas, Shahkot, Balachaur, Bhulath, and Phagwara has a comparatively higher value of SAR (Figure 6b). USSL diagram of SAR against EC gives further insight into the irrigation quality of groundwater (Figure 7). The groundwater samples which have been classified as either C1S1 or C2S1, indicate low to medium salinity and low SAR. Hence, these groundwater samples are suitable for irrigation. Few groundwater samples have also been classified as C3S1. These could only be used to irrigate certain soil-tolerant crops. The groundwater samples falling under C3S2 are unsuitable for irrigation due to high salinity and medium sodium hazards.

%Na best indicates the sodium hazard in irrigation water. The excess of sodium has a direct effect on the growth of plants. The calculated value for sodium percentage in the groundwater of the study area was found well within the unsuitability limit of 80% (Supplementary Table S6). However, the areas at the receiving end of groundwater have a higher value of %Na than the other (Figure 6c). The long residence time of water at these places tends to initiate a cation exchange process, leading to an increase in sodium concentration in the groundwater. The Wilcox diagram also shows that few groundwater samples fall under the permissible to doubtful category for agricultural irrigation (Figure 8).



Figure 6. Groundwater quality for irrigation in the Bist-Doab region of Punjab, India, concerning various irrigation indices (a) RSC, (b) SAR, (c) %Na, (d) KR, (e) MH, (f) PS, (g) Synthetic Harmful Coefficient K, and (h) Irrigation Coefficient K_a.



Figure 7. USSL diagram for assessment of groundwater quality for irrigation in the Bist-Doab region of Punjab, India.



Figure 8. Wilcox diagram for assessment of groundwater quality for irrigation in the Bist-Doab region of Punjab, India.

Concerning KR, about 90% of the study area has good-quality groundwater for irrigation (Supplementary Table S6). The groundwater of the southwestern parts of the

Bist-Doab region, i.e., Sultanpur Lodhi and Lohian Khas blocks, has a higher concentration of sodium ions as compared to calcium and magnesium combined, making it unsuitable for agricultural irrigation (Figure 6d). Apart from these blocks, the groundwater of the Bhulath block has also been found unsuitable for irrigation.

Groundwater with a high concentration of calcium, magnesium, sodium, and bicarbonate should not be used for irrigation for a longer period. It can reduce soil aeration and permeability of the soil. A Doneen diagram (1964) was used to represent the permeability index of the samples (Figure 9). The results reveal that few groundwater samples of the Sultanpur Lodhi, Balachaur, Bhulath, Phagwara, and Dhilwan blocks lie in class III, being unsuitable for the use of agricultural irrigation.



Figure 9. Doneen diagram from an assessment of groundwater quality for irrigation in the Bist-Doab region of Punjab, India.

Contrary to the above mentioned indices, which have a major influence on sodium ion concentration, MH considers the Mg²⁺ ion concentration in total Ca²⁺ and Mg²⁺ ions. In general, calcium and magnesium must maintain equilibrium for good crop yield. Excess of Mg²⁺ ion increases the hardness of the soil, makes it alkaline, and adversely impacts soil productivity and crop yield. About 95.6% of the study area has groundwater with 50% MH, representing acceptable quality for irrigation (Supplementary Table S6). Whereas, parts of Phagwara, Banga, Mahilpur, Nawanshahr, Saroya, Nurmahal, and Bhogpur blocks have recorded above 50% MH value, making the groundwater of these regions unsuitable for irrigation (Figure 6e).

PS value above 5 is considered as injurious to plant growth and hence unsuitable for irrigation use. The groundwater of about 94% of the study area was found suitable for irrigation (Supplementary Table S6). Whereas, Shahkot and Balachaur blocks have a high value of PS due to high chloride and sulphate concentration in their groundwater, making it unsuitable for irrigation (Figure 6f).

K alone can reflect salinity and alkalinity hazards in the groundwater as it is calculated using TDS and SAR values. In the present study, the value of k for all the groundwater samples was found below 25, indicating the excellent quality for agricultural irrigation (Supplementary Table S6). However, the groundwater of Hoshiarpur district was comparatively better for irrigation than the other parts of the study area (Figure 6g). As per the irrigation coefficient, the groundwater of about 80% of the study area was found to have excellent quality. However, nine groundwater samples have been classified as having doubtful conditions for irrigation (Supplementary Table S6). The groundwater of most of the Kapurthala district was classified under the permissible category for irrigation use (Figure 6h).

3.4. Composite Groundwater Quality Index for Irrigation (CGQII)

It can be seen from the above indices that the groundwaters of mostly Kapurthala and other parts of the region were found suitable for one index and found unsuitable for another. Hence, to remove the confusion, the CGQII method takes into account all the above-mentioned indices and generates a single value to analyze the groundwater quality for irrigation. Results reveal that about two-thirds of the study area comprising most of Hoshiarpur, Jalandhar, and SBS Nagar district were found of excellent quality for irrigation (Figure 10 and Supplementary Table S7). Whereas, six groundwater samples of Sultanpur Lodhi, Nakodar, Phagwara, Bhulath, and Balachaur blocks were found unsuitable for the use of irrigation.



Figure 10. Groundwater quality for irrigation in the Bist-Doab region of Punjab, India, calculated by CGQII.

4. Discussion

Anthropogenic activities reflected in demographic characteristics, change in landuse/cover pattern, change in sources of irrigation, application of chemical fertilizers, level of urbanization, industrial and infrastructural growth have significantly contributed to declining the groundwater resources in the alluvial tract of Punjab [3]. The area under paddy increased by around 30% from 317,000 ha in 1996 to 409,000 ha in 2016, whereas the area under wheat cultivation recorded an increase of about 10% from 453,000 ha to 500,000 ha in the same period. However, in the same period, the yield of paddy increased by about 40% from 2960 Kg/ha to 4122 Kg/ha, and that of wheat increased from 3652 Kg/ha to 4593 Kg/ha [30]. The increase in the yield of paddy is directly linked to the amount of water used for irrigation and the application of chemical fertilizers [3]. To meet the water needs of paddy, the farmers of the region mainly depend on groundwater irrigation as the region is not a good recipient of rainfall that could facilitate paddy cultivation. These unsustainable developmental activities to fulfill the unending need of the fast-growing population have not only led to a reduction in the available fresh groundwater resources but also led to a decline in the groundwater quality of the region. The present analysis reveals that these activities have not only led to changes in the physico-chemical characteristics of groundwater resources but have also influenced the groundwater suitability of the region for domestic and irrigation uses.

In the study area, the only pH was found under the permissible limit of 8.5 among the physical parameters in the groundwater. In most of the groundwater samples, parameters like EC, TDS, and TH were above the permissible limit as prescribed by WHO (2011). This is because EC, TDS, and TH are highly controlled by the chemical constituents present in the groundwater. In the present study, a strong link was found between TDS and evapotranspiration in the southern areas of the region which has higher TDS attributed to the higher evapotranspiration due to massive irrigation in scorching summer. A similar type of relation was established in the hydrochemical analysis of groundwater resources in the alluvial aquifer of the Condamine River in Queensland, Australia [31].

In the present study, the distribution of cations shows some similarities. Higher concentrations of calcium, magnesium, sodium, and lithium ions have coincided in few pockets of the region, which may be linked to the weathering and dissolution of carbonates and silicate rocks present in the region. In Punjab, under similar geological, hydrological, and anthropogenic characteristics, the previous studies have also asserted the significant role of rock–water interaction in attributing chemical characteristics to the groundwater of alluvial aquifers of the region [24,31,32].

The spatial distribution of anions shows the higher concentration of bicarbonate, chloride, sulphate, and nitrate in certain limited pockets of the study area. At these places, humans are susceptible to many adverse health effects following the intake of groundwater with a higher concentration of some specific ion. In the groundwater of Shahkot and Taunsa, chlorine concentrations above 1000 mg/L have been recorded due to the presence of fertilizers and pharmaceutical companies, respectively, in its vicinity. In these areas, children are susceptible to physiological damage [33]. The groundwater of southern parts of Nakodar has a higher concentration of sulphate due to the presence of fertilizer and pesticide factories. At these places, domestic use of water with higher sulphate concentration may cause changes in taste and lucrative effects [34].

In the present study, the spatial pattern of nitrate concentration in the groundwater of the region was largely controlled by the prevailing agriculturally dominant land-use practices and higher application of chemical fertilizers. Nitrate concentration beyond the suitable limit was observed in major parts of the Jalandhar district. Here, the source of nitrate is highly anthropogenic and is directly linked to the level of urbanization and prevailing intensive agricultural practices such as application of nitrogenous fertilizers and untreated discharge of solid wastes in the region. At these places, people are susceptible to diseases like methemoglobinemia in infants, blue baby syndrome, and cancer, due to long-term intake of groundwater [35,36]. Similar results have also been reported in the agriculturally active regions of the world [37,38]. Apart from agricultural sources, sewage effluent has also been observed as a prominent source of nitrate contamination in groundwater in the growing city of Ulaanbaatar, Mongolia [39], which stands true for this region of Jalandhar as well. Similar to most of the cities of the world, Jalandhar, Phagwara, and Kapurthala also do not have a proper waste disposal system. Therefore, leachate contamination may be one of the significant sources of groundwater contamination in this region. The closing of these pollutants' sites may play a significant role in decreasing groundwater contamination in the study area. In southern Norway, the closing of the Revdalen landfill site has resulted in a decrease in groundwater contamination [40].

Evaluation of groundwater for irrigation purposes is similarly important for domestic consumption because continuous use of higher EC and sodium-rich ion alters soil porosity and permeability, inversely affecting the fertility of the soil and healthy growth of plants.

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Fortunately, groundwater of most of the region was found suitable for irrigation use, but it may not be so in near future due to the increasing anthropogenic activities, mainly in the southern parts. The RSC was found higher in the groundwater of Sultanpur Lodhi, Bhulath, and Phagwara, due to the greater possibility of sodium ion adsorption due to cation exchange in clayey soil present in the area. This may further lead to the deposition of sodium carbonate making the soil alkaline, reducing soil productivity [41,42]. Excess of sodium ion in comparison to calcium and magnesium damages soil texture and structure, inhibiting the absorption of water by soil. This reduction in permeability obstructs the growth of seedlings and harms agricultural productivity [43,44]. Fortunately, the groundwater of most of the places in the study area has sodium concentration in a balanced state concerning calcium and magnesium ions.

The concentration of sodium to the total cations should not exceed 80% of the total cations present in the irrigation water. It alters soil structure, causes deflocculation and impairment of the tilth, and reduces soil permeability and aeration [45–47]. Sodium percentage was found to be greater in some pockets of Sultanpur Lodhi blocks and Bhulath. These places have also recorded higher KR values, i.e., greater than 1. The main reason for sodium hazard in the groundwater at these places can be identified as the accumulated groundwater having a longer residence time. The study relating to the groundwater table fluctuation between 1996 and 2016 in the Bist-Doab region revealed that Sultanpur Lodhi blocks have experienced some rise in the groundwater table due to its location at the receiving end of groundwater flow from all directions, and Bhulath has undergone a minimum change in groundwater table fluctuation in these two decades [3]. This aquifer setting and hydrological characteristics provide enough space for cation exchange reaction, leading to an increase in the sodium ions.

The composite index developed in the present study to evaluate groundwater for irrigation finds that six groundwater samples of Sultanpur Lodhi, Nakodar, Phagwara, Bhulath, and Balachaur blocks are unsuitable for the purpose of irrigation. In these areas, over-irrigation is one of the key factors to make the groundwater unsuitable for irrigation. It leads to greater evapotranspiration and an increase in irrigation-return flow in agriculturally active alluvial plains. These two dominant processes in turn lead to enrichment of certain ions in the groundwater, the longer use of which makes it unsuitable for agricultural use.

5. Conclusions

The assessment of groundwater quality in the Bist-Doab region of Punjab concludes that though at present, the groundwater of most of the region is fit for domestic and irrigation use, it may not be the same in near future. Higher chloride-induced EC in Taunsa and Nakodar are of great concern because here the source of chloride is not natural, but anthropogenic, i.e., the untreated waste discharge of chemical factories and pharmaceutical industries in these areas, respectively. Densely populated areas around Jalandhar have higher nitrate concentrations due to the large urban setup, industrial areas, and high use of chemical fertilizers. The study showed that the ion concentration increases in the direction of groundwater flow, i.e., from north to south and east to west. As a result, the groundwater gets accumulated in the southwestern parts, where long-term water accumulation in aquifers and continuous use of ion-rich water for a long time was found to be responsible for the unsuitability of groundwater for irrigation. Here, a higher concentration of ions, especially sodium, may have a significant impact on the soil porosity and permeability, leading to a probable reduction in crop production and yield in near future.

The results of the present study also show that in Sultanpur Lodhi, Phagwara, and Bhulath blocks, groundwater was found to be suitable for domestic use but unsuitable for irrigation. This difference is due to sodium hazards. The permissible limit of sodium concentration in groundwater for domestic use is 200 mg/L (9 meq/L), whereas that of calcium and magnesium is 75 mg/L (3.7 meq/L) and 30 mg/L (2.5 meq/L), respectively. Even in this condition, the concentration of sodium exceeds that of calcium and magnesium

combined, indicating a KR value greater than 1 that makes it unsuitable for irrigation. The study concludes that continuous monitoring and evaluation of groundwater quality is a must to assess its adverse impact on the human population. Accordingly, strategic plans can be made to minimize the over-extraction of groundwater for irrigation and minimize the intensive use of chemical fertilizers. Further, a holistic comprehensive regional plan can be made for sustainable development concerning land-use patterns (residential, agricultural, and industrial) so that the precious freshwater resources can be conserved for future generations, as well.

Supplementary Materials: The following are available online at https://www.mdpi.com/article/ 10.3390/su13137053/s1, Table S1: Quality standard (WHO, 2011), weight (wn) and unit weight (Wn) for each parameter for calculating WQI and CGQII for groundwater samples in the Bist-Doab region of Punjab, India. Table S2: Area under various physico-chemcial parameters of groundwater samples (n = 148) of the Bist-Doab region of Punjab, India. Table S3: Classification of groundwater of the Bist-Doab region of Punjab as per WQI and WAWQI (percentage in pa-renthesis). Table S4: Weights assigned to various parameters of groundwater in the Bist-Doab region of Punjab (modified after Bhuiyan and Ray, 2017). Table S5: Classification of groundwater of the Bist-Doab region of Punjab as per MCDA (percentage in parenthesis). Table S6: Classification of groundwater for irrigation concerning various indices in the Bist-Doab region of Punjab (percentage in parenthesis). Table S7: Classification of groundwater of the Bist-Doab region of Punjab as per CGQII (percentage in parenthesis).

Author Contributions: Conceptualization, A.G., S.C.R. and S.P.R.; data curation, A.G. and S.P.R.; formal analysis; A.G. and S.C.R.; methodology, A.G., S.C.R. and S.P.R.; resources, A.G., S.C.R. and S.P.R.; software, A.G.; supervision, S.C.R. and S.P.R.; writing—original draft, A.G.; writing—review and editing, S.C.R. and S.P.R. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: The data presented in this study are available on request from the corresponding author. The data are not publicly available due to privacy.

Acknowledgments: The authors are thankful to Kripa Ram for providing necessary lab facilities and Sanny for helping in carrying out chemical analysis of groundwater samples in their laboratory at the Institute of Environment and Sustainable Development (IESD), Banaras Hindu University (BHU), Varanasi. The first author is also thankful to the Head, Department of Geography, Delhi School of Economics, University of Delhi, for providing necessary facilities to carry out the research work, and to the University Grants Commission for providing a research fellowship under the UGC NET/JRF scheme.

Conflicts of Interest: The authors declare no conflict of interest.

Abbreviations

WQI	Water Quality Index
WAWQI	Arithematic Weighted Water Quality Index
MCDA	Multi-criteria Decision Analysis
RSC	Residual Sodium Carbonate
SAR	Sodium Adsorption Ratio
PI	Permeability Index
%Na	Sodium Percentage
KR	Kelly's Ratio
MH	Magnesium Hazard
PS	Potential Salinity
K	Synthetic Harmful Coefficient
Ka	Irrigation Coefficient

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