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Hydrochemical Assessment of Groundwater in Ludhiana and Amritsar Districts of Punjab and Identification of Fluoride Hotspots using GIS

Abstract: High fluoride concentrations in soil, water, or air can pose serious environmental and health risks to plants, and animals. Along with other hydrochemical parameters, this study investigates fluoride concentrations in the groundwater in the Ludhiana and Amritsar districts of Punjab, India. A total of 222 water samples were uniformly collected at approximately five-kilometer intervals for hydrochemical analyses. Statistical methods such as inverse distance weighting (IDW) and correlation matrices were used to assess the fluoride distribution and its relationships with other parameters. According to WHO guidelines, most fluoride concentrations were below 0.6 ppm in Ludhiana (84.30%) and Amritsar (77.23%). Fluoride levels that were within the permissible range (0.6–1.5 ppm) were found in 15.70% of Ludhiana's samples and 21.78% of Amritsar's samples; only 1% of Amritsar's samples exceeded the permissible limit (>1.5 ppm). The water quality index (WQI) analysis indicated that 0.83% of the groundwater samples from the Ludhiana district and 4.95% from the Amritsar district were unfit for consumption. This study demonstrates the importance of standardized sample collection and the use of GIS technology for comprehensive hydrochemical assessments, raising awareness and reducing health risks.

Keywords: hydrochemistry, groundwater, geographic information system (GIS), water quality index (WQI)

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1. Introduction

Fluoride is naturally present in various minerals, soils, water bodies, and even in some foods. Several studies have demonstrated that areas with fluoride contamination in groundwater are mostly characterized by the presence of crystalline basement rocks [1–4]. The consumption of a small quantity of fluoride (0.60 mg/L) is essential for the human body. When consumed in high doses (>1.5 mg/L), it can lead to dental fluorosis, and fluoride concentrations that are too high (>3.0 mg/L) can cause skeletal fluorosis [5]. Children under the age of 12 years old are most likely to exhibit high indicators of dental fluorosis [6]. Developing countries rely predominantly on groundwater for their potable water needs [7]. According to the UN World Water Development Report 2022, groundwater provides 50% of the world's household water needs, including the drinking water for the great majority of the people who live in rural areas. In addition to drinking water, groundwater is a crucial natural resource that affects several economic sectors, including agriculture, industry, fisheries, forestry, and animal production [8]. Fluoride contamination in groundwater is influenced by the climate, natural sources, and geochemical processes, along with human activities like irrigation, industrial waste leaks, and surface water infiltration that can further accelerate this pollutant [9–11]. Groundwater quality varies with depth and is influenced by physical, chemical, and biological processes, seepage, rock sediment interactions, and the chemical composition of dissolved rocks [8, 12, 13]. In recent decades, the demand for groundwater for drinking has significantly increased due to population growth and rising living standards, thus leading to declines in both water quality and its quantity [14]. Poor drinking water quality and unsanitary conditions are responsible for around 80% of water-borne diseases in developing countries like India [15]. Drinking water is the primary source of fluoride for humans. Fluoride in groundwater has been widely studied due to its significant impact on human health [8, 16–19].

Using geographic information systems (GIS) to create spatial distribution maps is a valuable technique for generating interpolated maps of various hydrochemical parameters based on measurements that are taken at specific locations. This approach allows researchers to estimate the values of these parameters at unsampled locations, providing a more comprehensive understanding of an area [5]. High concentrations of fluoride have been detected in the groundwaters across various districts of India; these districts rely heavily on agriculture, with maize, wheat, and rice being the primary crops that are cultivated [2, 8, 17, 20, 21]. So, it is critical to model groundwater quality and assess the paths of pollution and its related human health hazards. Fluoride levels in drinking water are significantly higher than the acceptable limit in various states of India, including Andhra Pradesh, Tamil Nadu, Rajasthan, Punjab, Bihar, Uttar Pradesh, Madhya Pradesh, and West Bengal [2, 10, 22]. According to the available literature, most regions of Punjab, India, have not been thoroughly investigated for groundwater fluoride levels – especially concerning low fluoride consumption and the associated health risks to the local populations. Several studies that have been conducted in various parts of Punjab have found significant amounts of fluoride in groundwater; this is used not only for irrigation but also as a primary source of drinking water in the state [23]. Therefore, it is necessary to examine the impacts of the consumption of such water on human health. A large number of studies have focused on assessing groundwater quality in specific areas, but only a few studies have been carried out using uniform sample collection for hydrochemical analyses of groundwater. Numerous researchers worldwide have conducted hydrogeochemical studies in order to gain a deeper understanding of groundwater quality [2, 12, 13, 24–26]. Despite the extensive use of both shallow and deep groundwaters, there is a lack of comprehensive research on the groundwater conditions of the study area. As a result, protecting these resources (both in terms of quality and quantity) is critical in the current situation, and conducting health risk assessments that are related to high and low fluoride levels is a crucial part of the study.

The study aims to address the fluoride levels and other hydrochemical parameters in the Ludhiana and Amritsar districts of Punjab, India. It is also intended to demonstrate the importance of a uniform distribution of sample collection on a regional scale. The study covers a wide variety of parameters in order to provide an extensive understanding of the groundwater quality in these areas. The study uses advanced statistical approaches such as inverse distance weighting (IDW) for geographical analyses and correlation matrices in order to find correlations among fluoride and other hydrochemical parameters [5, 16, 18, 27]. This analytical technique improves the accuracy and consistency of the results. Using IDW, the study provides a complex geographic distribution map of fluoride concentrations. This geostatistical approach enables the exact interpolation of fluoride levels across the districts, which helps us detect hotspots and those areas that are at risk of fluoride pollution [16, 28, 29]. The study not only finds places with high fluoride concentrations but also links these findings to significant public health concerns. The study's double focus on the environmental impact and public health makes it extremely relevant and practical. This research contributes to the scientific understanding of groundwater quality, highlighting the use of advanced technologies (GIS and remote sensing) to assess the potential health and environmental risks that are associated with fluoride contamination and the WQI [18, 30–33]. The study's focus on Ludhiana and Amritsar (two agriculturally and industrially key areas in Punjab) increases its regional importance. The findings can help to shape local water management practices and regulations, which will directly benefit the local communities. Additionally, it provides actionable insights for policymakers and stakeholders who are involved in water-resource management and public health initiatives.

2. Study Area

Among India's 29 states, the northwestern state that is known as Punjab occupies 50,362 km^2, or around 1.6% of the country's total landmass [34]. The Indian state of Punjab depends largely on groundwater for industrial, drinking, and agricultural uses. The region's groundwater resources are facing serious challenges to their sustainability and quality due to a combination of natural and anthropogenic influences [35]. To shed light on the quality, sources, and levels of pollution of Punjab's groundwater, this paper attempts to compile the body of knowledge that is currently available on the hydrochemical properties of water. The Ludhiana district is centrally located in the state of Punjab, which is on the Grand Trunk Road from Delhi to Amritsar at a latitude of 30° 55′ N and a longitude of 75° 54′ E in Northern India. It is situated next to the Sutlej River – one of the area's principal rivers. The Amritsar district in the Indian state of Punjab is pinpointed at 31° 38′ 2.3280′′ N and 74° 52′ 20.1396′ E in the country of India (specifically, in the category of cities). Amritsar is situated on the international border with Pakistan in the northwest part of Punjab. The study area is situated on the rich Indo-Gangetic plain, which facilitates a wide range of agricultural activities (including the production of vegetables, grains, and wheat). The study region has a semi-arid environment that ranges from dry to sub-humid conditions (Fig. 1). Annual rainfall normally varies between 400 and 500 mm and is unevenly distributed over the region.

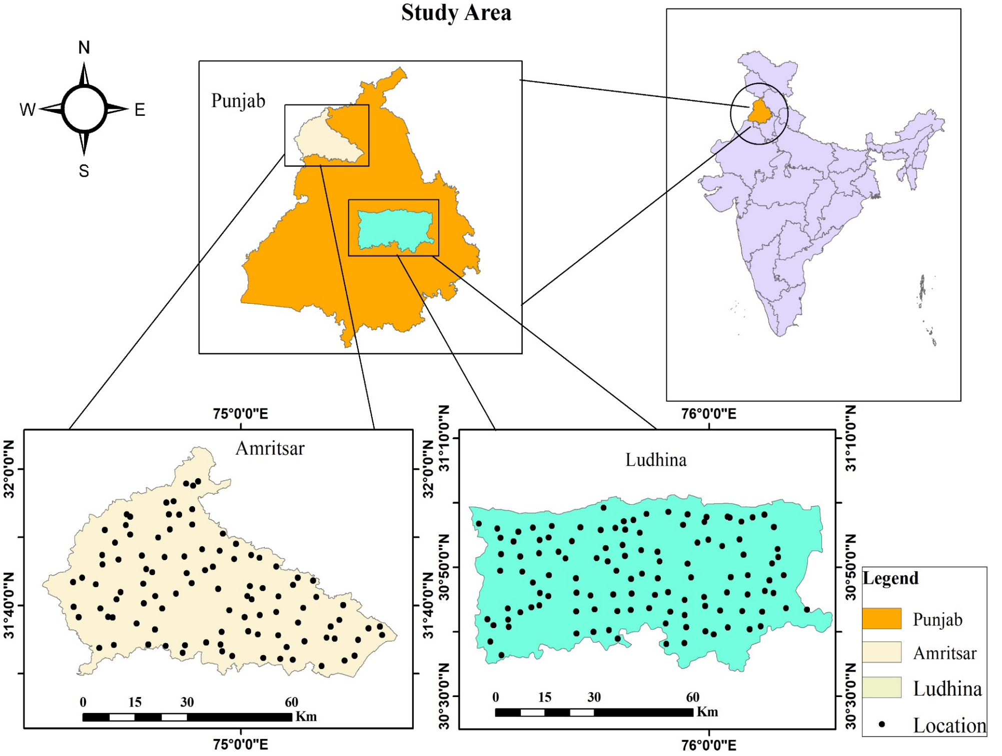


Fig. 1. Study area location maps of Amritsar and Ludhiana (generated using ArcGIS 10.5 software)

The southwest monsoon (which runs from July to September) contributes to more than 82% of the total annual rainfall of the area [36]. Summers are hot and muggy, with highs reaching 45°C (113°F) during the warmest months. Winters are cold, but not very cold; the range of winter temperatures is 0–15°C (32–59°F). The groundwater table in the Ludhiana district has progressively fallen, with depths reaching 20–30 m in certain regions; this has been the result of significant extraction for agricultural and industrial uses. Over the last few decades, the water table has dropped 0.5 to 1.0 m each year (CGWB, 2021) [37]. Similarly, groundwater levels have fallen to around 15 to 25 m in the Amritsar district, with an annual reduction of 0.3 to 0.8 m; this has been mainly attributable to agricultural needs [37]. Groundwater is a vital resource for both the Ludhiana and Amritsar districts in Punjab, which is heavily relied upon for agricultural and domestic use. However, both districts face significant challenges with groundwater depletion due to over-extraction – particularly for irrigation [38–40]. Sustainable management practices and conservation efforts are urgently needed in order to protect and preserve the groundwater resources in these regions.

2.1. Lithology

The lithology of the study area was downloaded from the open Alluvial plains, which are characterized by the deposition of sediments that have been transported by rivers like the Indus, Sutlej, Beas, and Ravi; these dominate most of Punjab (including Ludhiana and Amritsar). These expanses consist of highly productive unconsolidated sediments that have been deposited by river actions. As they are comprised of sand, silt, clay, and gravel, they are suitable for intensive agriculture [41]. The downcutting of river valleys over time has created terraces along the banks of major rivers such as the Sutlej, Beas, and Ravi. The gravel, sand, and silt layers that form these terraces were deposited by historic river systems, providing a well-drained terrain that is conducive to significant agricultural activity [42]. Those sediments that have been brought by those rivers that originate from the mountains have formed alluvial fans in the northeastern Punjabi foothills of the Shivalik Range. These fans transition from coarse sediments (like boulders and gravel) to finer materials downstream [43]. Part of the outermost range of the Himalayas, the Shivalik Hills are a distinctive feature of northeastern Punjab (bordering Himachal Pradesh). Agriculture occupies approximately 60% of the total area in the Shivaliks, with forests covering 27% and horticulture crops accounting for 2%. However, the Shivaliks' sediments are subjected to various land uses and are prone to erosion risks [44]. Fossils of marine life that have been found in these rocks indicate their origins in the sea, and Punjab is situated in the Kandi area (the Piedmont zone); this is comprised of the foothill border of the Shivalik hills [43]. Tertiary basaltic lava flows are exposed in several areas of Punjab – particularly in the central and southern portions [42]. The study area (Ludhiana and Amritsar) classifies five lithological classes: gray micaceous sand, silt, and clay; grey sand, silt, and clay; oxidized silt-clay with kankar and micaceous sand; and yellowish-brown loose sand with/without kankar (Fig. 2). The lithology map of the study was analyzed using the ArcGIS 10.5 software, and the data that is presented in Figure 2 was sourced from the Bhukosh Geological Survey of India (GSI).

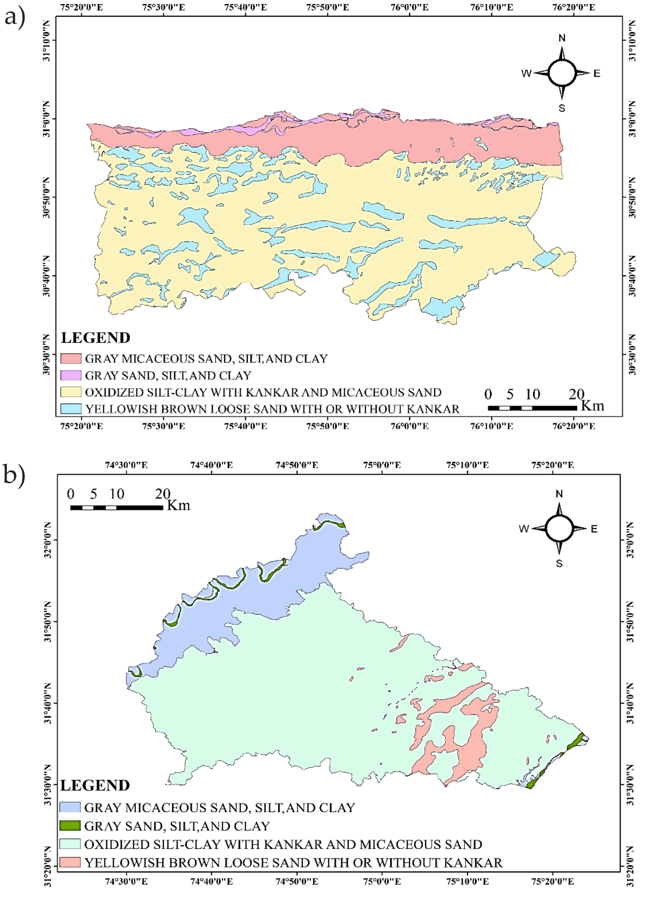


Fig. 2. Lithology maps of study area:
a) Ludhiana district; b) Amritsar district (generated using ArcGIS 10.5 software)

Source: based on GSI Bhukosh data

3. Materials and Methods

3.1. Sample Collection and Physiochemical Analysis

In this research, water samples were collected using high-density polyethylene (HDPE) bottles. These bottles were chosen due to their chemical resistance and non-reactive properties, which were critical for maintaining the integrity of the groundwater samples [45]. The manufacturer of these bottles (Nalgene) is renowned for producing laboratory-grade containers that ensure the reliability of any collected data. The accuracy of HDPE bottles in groundwater sample collection is their ability to preserve the chemical composition of the groundwater samples without contamination [46]. HDPE is known for its low permeability to gases and liquids, making these bottles ideal for storing samples. The leak-proof screw-on caps further ensure that no external substances can alter the sample's condition during transportation and storage. For the groundwater sample collection for the study area, a total of 222 groundwater samples were collected across the Ludhiana (121) and Amritsar (101) districts in Punjab, India. The samples were collected from borewells and handpumps that were strategically located at approximately five-kilometer intervals in order to ensure a uniform coverage of the study area. The sampling locations were precisely mapped using QGIS – open-source GIS software. A grid system that measured 5 km × 5 km was generated across the two districts in order to guide the sampling process, thus ensuring that the samples were collected systematically and representatively. To minimize contamination, the HDPE bottles were pre-washed with a solution of HNO_3 (nitric acid), followed by distilled water [47]. This cleaning process was repeated two or three times following the standardized procedures that are outlined by the American Public Health Association [47]. Before collecting the water samples from the borewells, the wells were pumped for 5–10 minutes; this step was crucial for flushing out any stagnant water within the pipeline, thus ensuring that the collected samples were truly representative of the groundwater and not influenced by any residual water that could have skewed the results. Once collected, the water samples were immediately sealed in the HDPE bottles and transported to the laboratory. To preserve the integrity of the samples, they were stored at 4°C until been analyses [3, 32, 48]. This low-temperature storage was critical for preventing any biochemical changes in the samples that could have affected the accuracy of the subsequent analyses [46]. The samples were carefully transported under controlled conditions in order to maintain their temperatures and prevent any potential contamination or degradation. The use of HDPE bottles combined with the standardized preservation methods ensured that the samples arrived at the laboratory in optimal conditions for accurate testing [47–49].

The quantitative analyses of the groundwater samples that were collected from the two districts (i.e., Ludhiana and Amritsar) were tested for 12 physicochemical parameters; namely, pH, electrical conductivity (EC), fluoride (F^-), chloride (Cl^-), sulfate (SO_4^{2-}), nitrate (NO_3^-), calcium (Ca^{2+}), magnesium (Mg^{2+}), total alkalinity (TA), total hardness (TH), carbonate (CO_3^{2-}), and bicarbonate (HCO_3^-). Fluoride determination was conducted using a Thermo ISE (ion-selective electrode) that was calibrated with a set of standard fluoride solutions. The electrode potential response of the fluoride ion-selective electrode was measured at various fluoride concentrations for our calibrations; the sample that was tested was prepared by diluting it with a TISAB reagent at a 1:1 proportion. For the analysis of the physicochemical parameters, a titration method with an acid of a known concentration was used. The titration process involved gradually adding the acid to the water samples until color changes occurred, thus indicating their endpoints: TH, Ca^{2+}, and Mg^{2+} were measured by using a titration method with ethylenediaminetetraacetic (EDTA) acid; TA, HCO_3^-, and CO_3^{2-} were measured using a titration method with sulfuric acid (H_2SO_4); Cl^- was measured using a titration method with silver nitrate ($AgNO_3$) (which was carried out slowly with the swirling of the flask until the color of the indicator changed); SO_4^{2-} and NO_3^- were calculated using a UV-VIS spectrophotometer; and pH and EC were measured using a pH and EC meter. Standard protocols for the aforementioned parameters were referenced from the American Public Health Association (APHA) manual and standardized in the lab before conducting the tests on the sample water [47].

3.2. Fluoride Correlation Analysis

Pearson's correlation coefficient matrix was used to understand the correlation between fluoride and the other hydrochemical parameters for the Amritsar and Ludhiana districts of Punjab. Often denoted as R, the Pearson correlation coefficient is a statistical measure that quantifies the strength and direction of the linear relationship between two continuous variables (where R is the correlation coefficient, and R is always a number between –1 and 1; $R > 0$ indicates a positive association, while $R < 0$ indicates a negative association) [50, 51]. The significance of R lies in its ability to summarize the degree and direction of any association between variables, making it a fundamental tool in statistical analysis [52, 53]. Figure 3 shows the correlation coefficients of all of the hydrochemistry parameters for the Ludhiana and Amritsar districts of Punjab, India. Pearson's correlation coefficient is a useful statistical technique for assessing and understanding the correlations between variables, giving insights that are critical for decision-making and research in a variety of fields.

3.3. Saturation Index (SI)

The groundwater SI is a metric that is used to assess the equilibrium state of water in terms of certain minerals, thus determining whether it is in balance, undersaturated, or oversaturated. This measure aids in understanding the capacity of the water to either dissolve minerals from the aquifer it traverses or deposit minerals back into the water. The calculation of this index is particularly valuable in assessing the potential for mineral precipitation or dissolution in geological and hydrogeological settings, thus shedding light on crucial processes within these areas [21]. In this investigation, the focus was on evaluating fluoride levels in groundwater where the solubility or precipitation of fluoride were contingent upon specific conditions. The SI plays a pivotal role in monitoring water quality, ensuring the safe and efficient utilization of water for industrial, agricultural, and domestic purposes [54].

a)

N=121

R = -1 | -0.80 | -0.60 | -0.40 | -0.20 | 0 | 0.20 | 0.40 | 0.60 | 0.80 | 1

Variable	Fluoride (ppm)	Total Hardness (ppm)	Calcium (ppm)	Magnesium (ppm)	Total Alkalinity (ppm)	Carbonate (ppm)	Bicarbonate (ppm)	Chloride (ppm)	pH	EC	Sulphate (ppm)	Nitrate (ppm)
Fluoride (ppm)	1.000	-0.142	-0.143	-0.116	-0.126	-0.129	-0.020	0.079	0.112	0.125	0.149	0.019
Total Hardness (ppm)	-0.142	1.000	0.889	0.919	-0.071	-0.122	0.041	0.037	-0.466	0.364	0.056	0.373
Calcium (ppm)	-0.143	0.889	1.000	0.638	-0.044	-0.092	0.052	0.090	-0.423	0.245	0.119	0.392
Magnesium (ppm)	-0.116	0.919	0.638	1.000	-0.082	-0.126	0.024	-0.015	-0.422	0.402	-0.008	0.292
Total Alkalinity (ppm)	-0.126	-0.071	-0.044	-0.082	1.000	0.865	0.122	-0.191	0.128	-0.017	-0.146	0.074
Carbonate (ppm)	-0.129	-0.122	-0.092	-0.126	0.865	1.000	-0.197	-0.073	0.146	-0.075	-0.149	-0.049
Bicarbonate (ppm)	-0.020	0.041	0.052	0.024	0.122	-0.197	1.000	-0.091	-0.007	0.047	-0.003	0.103
Chloride (ppm)	0.079	0.037	0.090	-0.015	-0.191	-0.073	-0.091	1.000	-0.036	0.016	0.041	0.002
pH	0.112	-0.466	-0.423	-0.422	0.128	0.146	-0.007	-0.036	1.000	-0.150	0.051	-0.246
EC	0.125	0.364	0.245	0.402	-0.017	-0.075	0.047	0.016	-0.150	1.000	0.396	0.355
Sulphate (ppm)	0.149	0.056	0.119	-0.008	-0.146	-0.149	-0.003	0.041	0.051	0.396	1.000	0.280
Nitrate (ppm)	0.019	0.373	0.392	0.292	0.074	-0.049	0.103	0.002	-0.246	0.355	0.280	1.000

b)

N=101

R = -1 | -0.80 | -0.60 | -0.40 | -0.20 | 0 | 0.20 | 0.40 | 0.60 | 0.80 | 1

Variable	Fluoride (ppm)	Total Hardness (ppm)	Calcium (ppm)	Magnesium (ppm)	Total Alkalinity (ppm)	Carbonate (ppm)	Bicarbonate (ppm)	Chloride (ppm)	pH	EC	Sulphate (ppm)	Nitrate (ppm)
Fluoride (ppm)	1.000	-0.067	-0.175	0.052	0.392	0.361	0.272	0.008	0.045	0.514	-0.131	0.171
Total Hardness (ppm)	-0.067	1.000	0.263	0.772	0.100	-0.261	0.179	0.201	-0.516	0.142	-0.070	0.224
Calcium (ppm)	-0.175	0.263	1.000	-0.410	0.091	-0.385	0.208	0.085	-0.279	0.000	0.094	-0.010
Magnesium (ppm)	0.052	0.772	-0.410	1.000	0.035	0.007	0.032	0.134	-0.304	0.134	-0.128	0.218
Total Alkalinity (ppm)	0.392	0.100	0.091	0.035	1.000	0.090	0.951	0.162	-0.068	0.613	-0.104	-0.179
Carbonate (ppm)	0.361	-0.261	-0.385	0.007	0.090	1.000	-0.221	0.107	0.433	0.113	-0.175	-0.030
Bicarbonate (ppm)	0.272	0.179	0.208	0.032	0.951	-0.221	1.000	0.126	-0.200	0.566	-0.047	-0.166
Chloride (ppm)	0.008	0.201	0.085	0.134	0.162	0.107	0.126	1.000	-0.049	0.203	-0.034	-0.077
pH	0.045	-0.516	-0.279	-0.304	-0.068	0.433	-0.200	-0.049	1.000	-0.083	-0.054	-0.177
EC	0.514	0.142	0.000	0.134	0.613	0.113	0.566	0.203	-0.083	1.000	-0.149	-0.154
Sulphate (ppm)	-0.131	-0.070	0.094	-0.128	-0.104	-0.175	-0.047	-0.034	-0.054	-0.149	1.000	0.085
Nitrate (ppm)	0.171	0.224	-0.010	0.218	-0.179	-0.030	-0.166	-0.077	-0.177	-0.154	0.085	1.000

Fig. 3. Correlation coefficient of each hydrochemistry parameter for Ludhiana (a) and Amritsar (b) districts in Punjab (generated using Satistica software)

The calculation for SI is computed using Equation (1):

$$SI = \log 10 \frac{IAP}{K_{sp}} \tag{1}$$

where SI represents the saturation index, IAP signifies the ion activity product of the fluoride ions, and K_{sp} denotes the solubility product constant of the fluoride.

3.4. Water Quality Index (WQI)

The weight arithmetic water quality index (WAWQI) method was implemented to analyze the quality of the water from the Amritsar and Ludhiana districts of Punjab. WAWQI provides a comprehensive assessment by considering multiple parameters for a holistic understanding of water quality. The WAWQI uses a weighted arithmetic technique in which each water quality metric is allocated a weight based on its relative relevance [55]. This weighting illustrates how different metrics affect the overall water quality. Brown et al. [56] classified WQI into five groups: excellent, good, poor, extremely poor, and unsuitable (when the values of the index fall between 0–25, 26–50, 51–75, 76–100, and >100, respectively). This is shown in Table 1.

Table 1. Weight arithmetic WQI

Water quality index	Water quality status
>100	Unfit for consumption
76–100	Very poor
51–75	Poor
26–50	Good
0–25	Excellent

Source: [56]

This approach gives information on determining the quality of a water body and is computed using the following formula:

$$\text{WAWQI} = \frac{\sum w_i q_i}{\sum W_i} \tag{2}$$

Ranging from 0 to 100, WAWQI reflects the water quality, with q_i representing the relative quality for each parameter. Variable i signifies the number of parameters that are considered, while W_i measures a parameter's significance.

For the calculation of q_i, Equation (3) is used:

$$q_i = 100 \cdot \frac{V_i - V_0}{S_i - V_0} \tag{3}$$

where V_i represents the value that is determined experimentally for analyzed parameter i, V_0 represents the ideal value for this parameter, and S_i stands for the standard legally accepted value that corresponds to the water category in which the analyzed sample belongs. Furthermore, the W_i factor is calculated by using Equation (4):

$$W_i = \frac{K}{S_i} \tag{4}$$

where K is a constant that can result after applying Equation (5):

$$K = \frac{1}{\sum \frac{1}{S_i}} \tag{5}$$

3.5. Geospatial Distribution

GIS software was used to map and analyze the spatial data, allowing for the display and investigation of the geographical distributions in the research region. This facilitated the integration and assessment of heterogeneous information, offering clear insights into the spatial patterns and linkages [57]. The use of GIS software for geographic distribution analysis was critical for correctly mapping and displaying the spatial patterns throughout the study area; the application enabled the combination and analysis of various bits of information (including topography, lithology, and groundwater levels) to find patterns and connections. GIS techniques were also used to examine the spatial distribution of the geological features and other important criteria for clarity and a deeper understanding of the geographical characteristics [58, 59]; this improved the precision and dependability of the study results. In this study, the geospatial distribution of fluoride and WQI was conducted for two districts of Punjab using the inverse distance weighting (IDW) method. These spatial-interpolation techniques were employed in order to estimate the fluoride and water-quality-index values at unsampled locations based on nearby measurements, resulting in continuous surfaces of fluoride and water-quality distribution throughout the research region. A spatial analysis was beneficial for hotspot analysis, helping us identify areas with unusually high or low concentrations of pollutants using spatial statistical techniques. Using GIS software, maps of the fluoride and WQI were created to represent the spatial distribution of the fluoride and water-quality metrics with suitable symbology and color gradient that graphically indicated the concentration levels or categories [23, 60, 61]. These spatial maps can be overlaid with different geographical layers to help understand the correlations and discover any probable sources of pollution or environmental factors.

4. Results and Discussion

The present study examines the hydrochemical parameters (particularly, fluoride concentrations) in the groundwaters in the Ludhiana and Amritsar districts of Punjab, India, using methods like GIS and statistical analyses to assess their distributions and correlations with other hydrochemical parameters. Similar studies have also focused on groundwater quality in various regions, employing GIS technology to map fluoride distribution and assess its environmental and public health impact. Similar studies that were conducted by researchers such as Kumar et al. [62], Singh et al. [63], and Paikaray and Chander [64] analyzed the groundwater quality in Punjab and found high fluoride levels that were linked to geochemical processes. Another study by Kaur et al. [23] also highlighted the issue of fluoride contamination in Punjab and emphasized the need for comprehensive groundwater assessments using uniform sampling methods. These studies highlight the critical necessity of understanding groundwater quality for public health and environmental sustainability, however, the present research not only identifies fluoride hotspots but also uses advanced geostatistical approaches such as inverse distance weighting to generate detailed geographic distribution maps of the fluoride and WQI concentrations. This method makes it possible for the precise identification of contamination risk regions, providing policymakers and stakeholders with valuable insights about water-resource management. Furthermore, the study demonstrates the need for standardized sample-collection practices over a vast region; this is in contrast to the previous studies that may have focused on smaller specialized areas or employed less-consistent sampling approaches. This comprehensive method provides a broader understanding of the region's groundwater quality and its effects on public health and provides a significant contribution to the knowledge of hydrochemical assessments.

4.1. Data Exploration and Descriptive Statistics

The work focused on a statistical analysis of the hydrochemical data, which was critical for understanding the water quality trends and influencing the management methods. The first phase required the careful collection and organization of the data that was relevant to the essential characteristics for parameters such as Mg^{2+}, Ca^{2+}, TH, CO_3^{2-}, HCO_3^-, Cl^-, NO_3^-, SO_4^{2-}, TA, pH, EC, and F^-. Descriptive statistics such as the minimums, maximums, means, and standard deviations of all of the parameters were determined using statistic software, ArcGIS software, and SPSS. Descriptive statistics such as histograms and scatter plots were crucial tools for clarifying the distributions and determining the patterns within the data set. Figure 4 (on the interleaf) shows a histogram that depicts the hydrochemistry parameters for the study area.

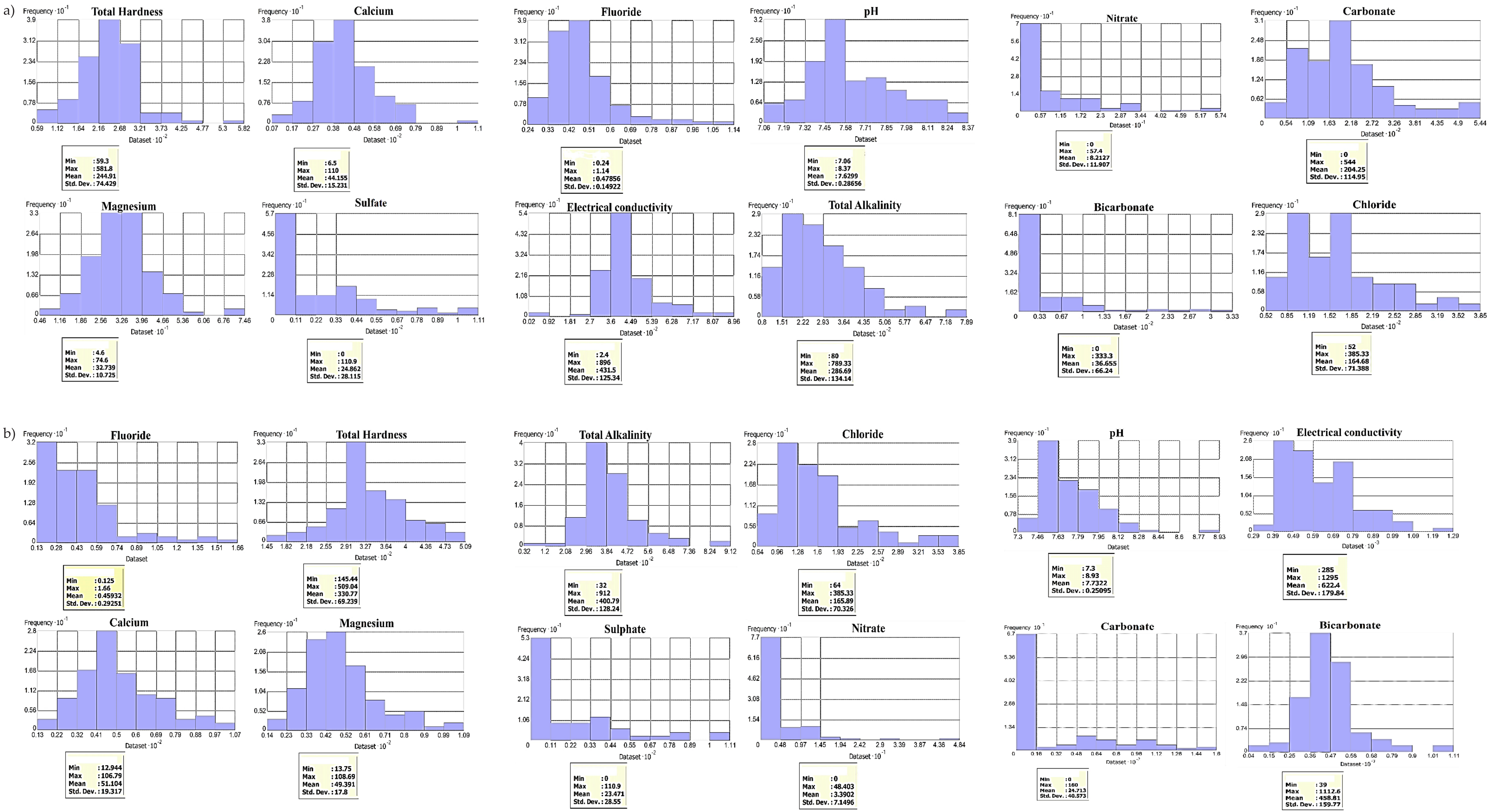


Fig. 4. Histogram representation for Ludhiana (a) and Amritsar (b) districts in Punjab, India (generated using ArcGIS software)

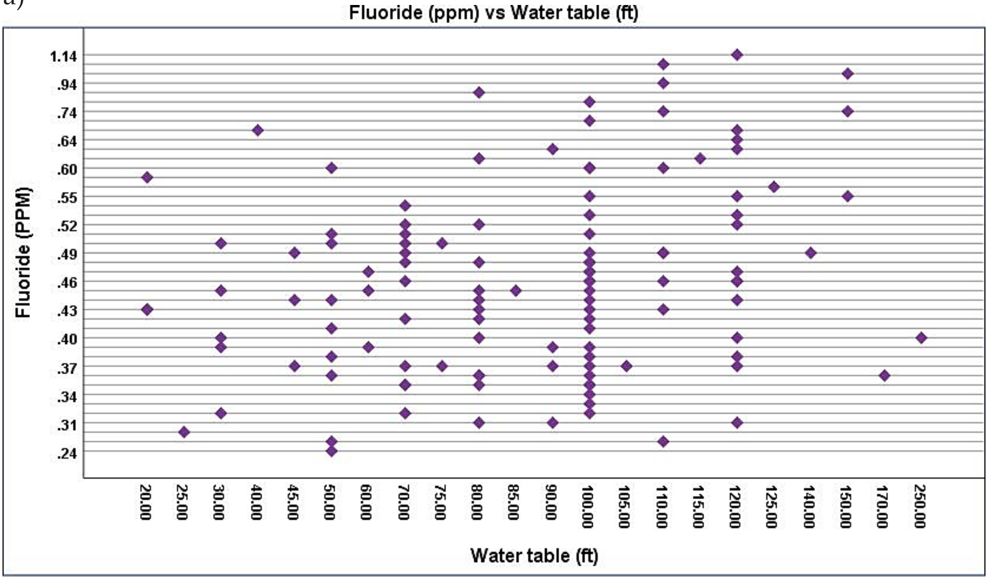
A data overview of the hydrochemical parameters for the Ludhiana and Amritsar districts is presented in Table 2. In the study area, it can be observed that the fluoride concentrations in Ludhiana ranged from 0.24 to 1.14 ppm, with a mean of 0.47, a standard deviation of 0.14, and a median of 0.45. Similarly, the fluoride concentrations for Amritsar ranged from 0.12 to 1.66 ppm, with a mean of 0.45, a standard deviation of 0.29, and a median of 0.38.

Table 2. Descriptive statistics for Ludhiana and Amritsar (study area)

Statistics	Parameter										
	F^-	TH	Ca^{2+}	Mg^{2+}	Cl^-	TA	pH	EC	CO_3^{2-}	HCO_3^-	NO_3^-	SO_4^{2-}
Number of samples = 121 (Ludhiana)												
Min	0.24	80.00	6.50	4.60	52.00	59.30	7.06	2.40	0	0	0	0
Max	1.14	789.33	110.00	74.60	385.30	581.80	8.37	896.00	544.00	333.30	57.40	110.90
Mean	0.47	286.69	44.15	32.73	164.60	244.90	7.62	431.50	204.25	36.65	8.21	24.86
SD	0.14	134.14	15.23	10.72	71.38	74.42	0.28	125.34	114.95	66.24	11.90	28.11
Median	0.45	268.00	44.20	32.10	153.30	242.40	7.56	404.00	192.00	0	2.50	15.35
Number of samples = 101 (Amritsar)												
Min	0.12	145.44	12.94	13.75	64.00	32.00	7.30	285.00	0	39	0	0
Max	1.66	509.04	106.70	108.60	385.30	912.00	8.93	1,295.00	160.00	1,112.00	48.40	110.90
Mean	0.45	330.77	51.10	49.39	165.8	400.70	7.73	622.40	24.71	458.81	3.39	23.47
SD	0.29	69.23	19.31	17.80	70.32	128.24	0.25	179.80	40.57	159.70	7.14	28.55
Median	0.38	323.20	48.54	45.17	152.00	376.00	7.66	587.00	0	449.00	0	10.85

The relationships between the fluoride levels and the water tables were analyzed for the study area using scatter plots, as were the depths of the water sources. Several studies have suggested that the depths of wells significantly influence the fluoride levels in the groundwater [16, 65]. In the Ludhiana district, it was noted that high fluoride concentrations were present in the water table at depths that ranged from 80 to 150 feet, and elevated fluoride levels were detected at depths of approximately 250 to 550 feet (Fig. 5). Similarly, elevated fluoride concentrations in the Amritsar district could be observed in the water table at depths that ranged from 35 to 75 feet, and higher fluoride levels were found at depths of around 70 to 90 feet (Fig. 6). Correlating fluoride concentrations with the water tables and water depths may have revealed the probable sources of fluoride pollution and a more-thorough evaluation of the groundwater quality and any related concerns [66]. Monitoring the fluoride concentrations about the water tables and depths over time might indicate seasonal or long-term patterns in the quality of the groundwater. Changes in groundwater levels or hydrological conditions may affect the flow and distribution of fluoride within the aquifers, thus influencing its concentration patterns [67].

a)



b)

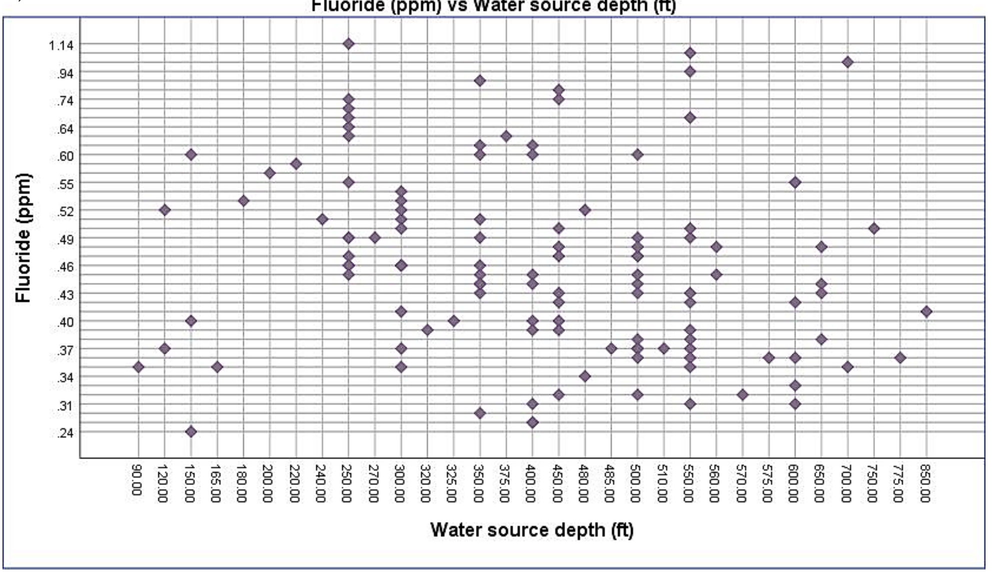
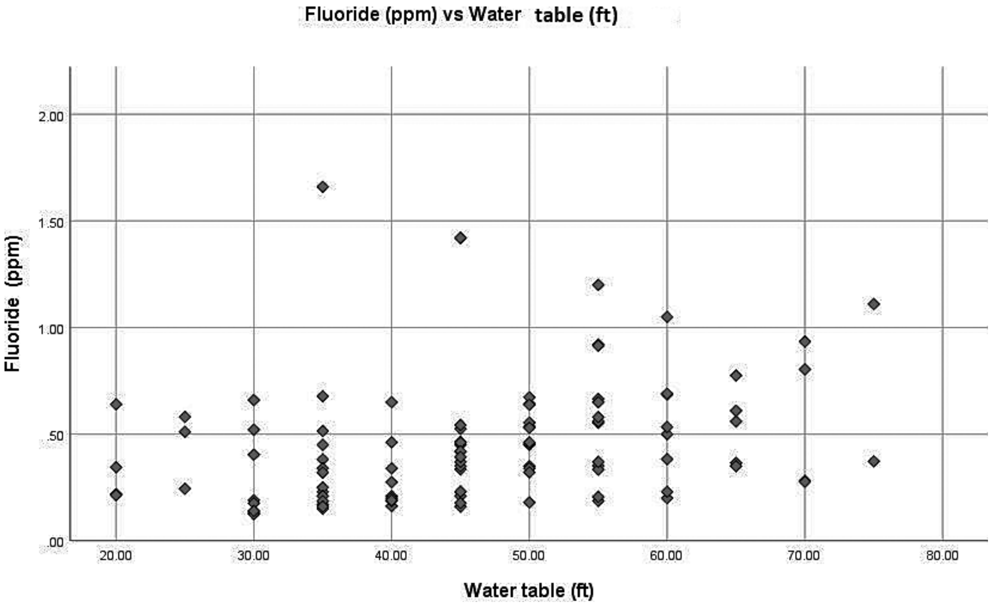


Fig. 5. Fluoride correlation with water table (a) and water source depth (b) of Ludhiana district (generated using ArcGIS software)

a)



b)

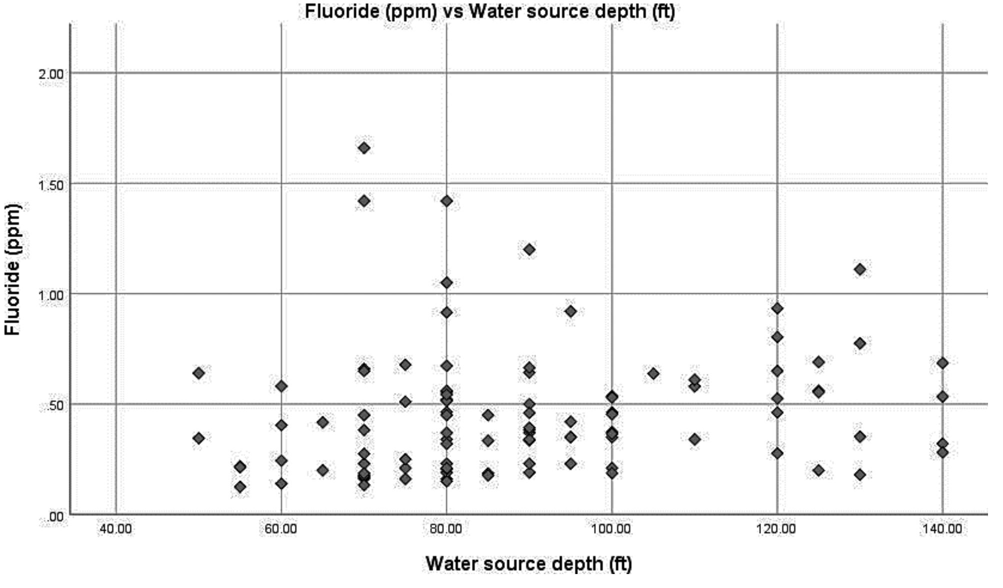


Fig. 6. Fluoride correlation with water table (a) and water source depth (b) for Amritsar district (generated using ArcGIS software)

4.2. Fluoride Correlation with Other Hydrochemistry Parameters

According to the correlation coefficient for the Ludhiana district, it could be observed that, for fluoride, there was a positive correlation with parameters such as sulfate (R = 0.149), EC (R = 0.125), and pH (R = 0.112), whereas EC (R = 0.514), total alkalinity (R = 0.392), carbonate (R = 0.361), and bicarbonate (R = 0.272) had high positive associations in the Amritsar district (Fig. 3). To explore the associations among fluoride and the other hydrochemical parameters, correlation matrices were generated for the study area. These matrices displayed correlation coefficients visually, providing insights into the statistical relationships among fluoride and the different geochemical factors. This aided us in identifying the factors that were responsible for regulating the fluoride enrichment in the groundwater as well as the underlying processes thereof [68, 69]. Parameters such as sulfate, electrical conductivity (EC), pH, total alkalinity, carbonate, and bicarbonate are frequently positively associated with fluoride levels in groundwater. These relationships have been highlighted in many studies, with a focus on the interactions of fluoride with other hydrochemical factors [16, 70]. In our research region, sulfate ions can increase fluoride solubility by forming compounds with fluoride ions. These compounds enhance the mobility and transport of fluoride in groundwater, resulting in greater fluoride concentrations. Higher EC values can result from greater mineral dissolution, which may release fluoride into the groundwater (also resulting in higher fluoride levels). pH levels influence the chemical distribution of fluoride ions in water. In alkaline environments (higher pH levels), fluoride remains soluble (fluoride ions), resulting in increased fluoride concentrations in groundwater, whereas fluoride can precipitate or form insoluble compounds under acidic conditions (lower pH levels), thus reducing its concentration in groundwater [71]. Alkaline substances such as carbonate and bicarbonate ions may increase fluoride's solubility by complexing with fluoride ions and increase the stability and mobility of fluoride in groundwater, thus leading to higher concentrations. Furthermore, total alkalinity in groundwater can buffer pH levels, generating conditions that are favorable to enhanced fluoride solubility.

4.3. Fluoride Saturation Index (FSI) for Ludhiana and Amritsar Districts in Punjab

When the FSI falls below 0 ($SI < 0$), this indicates an inadequate amount of fluoride in the groundwater, thus implying that the fluoride ion concentration is below equilibrium. This situation suggests that fluoride might dissolve into the water. When the SI is equal to zero ($SI = 0$), the groundwater has reached equilibrium with the fluoride, thus suggesting that no more fluoride dissolution or precipitation will occur. When the SI exceeds 0 ($SI > 0$), the groundwater becomes oversaturated with fluoride, thus indicating that the fluoride ion concentration has exceeded the equilibrium threshold. Under such conditions, fluoride might precipitate from the water. The regulation of fluoride (F^-) in groundwater is influenced by several factors, including the saturation levels of the fluoride, calcite, and HCO_3^- as well as the presence of Ca^{2+} and Na^+ ions in the groundwater [72].

Table 3. Fluoride saturation indexes for Ludhiana and Amritsar districts in Punjab

District	Total number of samples (*N*)	Mean	SD	Maximum	Minimum
Ludhiana	121	–2.35	0.275	–0.92	–2.35
Amritsar	101	–2.77	0.506	–0.69	–2.77

The FSI for the two districts was calculated using Phreeqc software [73]. In Table 3, we observed the maximums, minimums, means, and standard deviations (SD) of the fluoride saturation indexes (FSIs) for the two districts. According to the analysis, the FSI for the Ludhiana district ranged from –2.35 to –0.92; this ranged from –2.77 to –0.69 for the Amritsar district. All of the samples were observed to be undersaturated in the study area, with 121 water samples for Ludhiana and 101 water samples for Amritsar. The figure that is depicted in Figure 7 represents a graphical representation of the FSI values for the two districts. This visualization offers a clear depiction of which fluoride SI values were oversaturated and undersaturated.

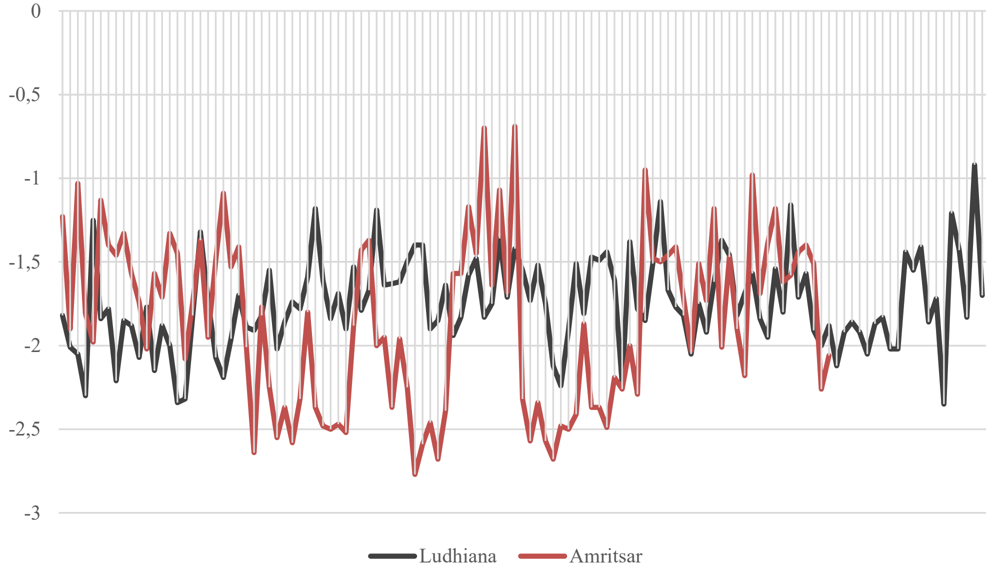


Fig. 7. FSI for Ludhiana and Amritsar districts (generated using MS Excel)

4.4. Geospatial and Data Analysis of Fluoride

Whether in high or low amounts, fluoride in groundwater may affect human health. The fluoride concentrations in the study area were analyzed and calculated for the two districts. Fluoride assessments in the groundwater were carried out for the Ludhiana and Amritsar districts in order to determine those concentrations that were below the recommended level (<0.6 ppm), within permissible limits (0.6–1.2 ppm), and that exceeded permissible limits (more than 1.2 ppm; specifically >1.5 ppm). Research has indicated that a region with F^- concentrations that are below 0.6 ppm may lead to tooth decay and poor bone growth. The recommended fluoride content includes those regions with levels of 0.6–1.2 ppm. F^- concentrations that are between 1.2 and 3.0 ppm increase the incidence of dental fluorosis, whereas concentrations that are above 3.0 ppm contribute considerably to both dental and skeletal fluorosis. From the two districts, it could be observed that the fluoride levels that were below 0.6 ppm accounted for 84.30% (102 samples) for Ludhiana and 77.23% (78 samples) for Amritsar; these were below the recommended fluoride concentration. Those fluoride levels that were within a range of 0.6–1.2 ppm for the study area accounted for 15.70% (19 samples) for Ludhiana and 21.78% (22 samples) for Amritsar; these were within the recommended range of fluoride concentration. However, only 1% (1 sample) of the water samples from the Amritsar district could be observed to exceed the permissible limit (>1.5 ppm), and none were observed in the Ludhiana district (Table 4).

Table 4. Fluoride content in groundwater for Ludhiana and Amritsar districts in Punjab

Content	Ludhiana (N = 121)		Amritsar (N = 101)	
	no. of sample	percentage [%]	no. of sample	percentage [%]
<0.6 ppm (F^- below recommendation)	102/121	84.30	78/101	77.23
0.6–1.5 ppm (F^- as per permissible limit)	19/121	15.70	22/101	21.78
>1.5 ppm (F^- more than permissible limit)	0/121	0	1/101	0.99

A spatial distribution map of the fluoride levels was prepared for the two districts in Punjab by analyzing the fluoride concentrations in the 121 samples for Ludhiana and the 101 samples for Amritsar. This was done using the interpolation technique of inverse distance weighting (IDW) under a common GIS environmental platform. The spatial maps of the fluoride concentrations for the Ludhiana and Amritsar districts (Fig. 8) indicate fluoride concentrations that ranged from 0.24–1.14 ppm and 0.12–1.66 ppm, respectively. From an Indian perspective, the concentrations of fluoride were fixed between 0.6 and 1.2 ppm [5]. The spatial map depicts both high and low fluoride concentrations, those that exceeded the permissible limit (i.e., >1.2 ppm), and those that were below the recommended limit (>0.6 ppm) for the study region. The spatial map indicates a serious health risk for those populations that reside in fluoride hotspots as well as in fluoride-depleted areas. According to this study, the populations in those regions with fluoride concentrations that are above the desirable and permissible limits are prone to skeletal and dental fluorosis; appropriate precautions should be taken. Additionally, the study revealed that the populations of those regions that showed fluoride levels that were below the recommended limit (0.0–0.6 ppm) should supplement their diets with extra fluoride intakes. The fluoride concentration across the Ludhiana district was divided into three zones (0.0–0.6 ppm, 0.61–1.2 ppm, and >1.21 ppm), whereas Amritsar was classified into four zones (0.0–0.6 ppm, 0.61–1.2 ppm, 1.21–1.5 ppm, and >1.51 ppm); this provides valuable information for further mitigation steps (Fig. 8).

4.5. Water Quality Index (WQI) and Geospatial Distribution

The water quality indexes (WQI) for Ludhiana and Amritsar was classified into five classes; namely, excellent (0–25), good (26–50), poor (51–75), very poor (76–100), and unfit for human consumption (>100); these classes were proposed by Brown et al. [56]. The classification revealed that, for the Ludhiana district, 3 samples (2.48%) fell into the good zone, 92 samples (76.03%) – the poor zone, 29 samples (23.97%) – the very poor zone, and 1 sample (0.83%) – the unfit-for-consumption zone (Fig. 9a). In the Amritsar district, 4 samples (3.96%) fell into the excellent zone, 59 samples (58.42%) – the good zone, 27 samples (26.73%) – the poor zone, 6 samples (5.94%) – the very poor zone, and 5 samples (4.95%) – the unfit-for-consumption zone (Fig. 9b). The statistical measures of the WQI for the Ludhiana and Amritsar districts are represented in a table that provides clear and supplementary information (Table 5).

Table 5. WQI classification (weight arithmetic method) of two districts in Punjab

WQI	Class of water	Ludhiana (*N* = 121)		Amritsar (*N* = 101)	
		sample count	percentage of samples [%]	sample count	percentage of samples [%]
0–25	Excellent	–	–	4	3.96
26–50	Good	3	2.48	59	58.42
51–75	Poor	92	76.03	27	26.73
76–100	Very poor	29	23.97	6	5.94
>100	Unfit for consumption	1	0.83	5	4.95

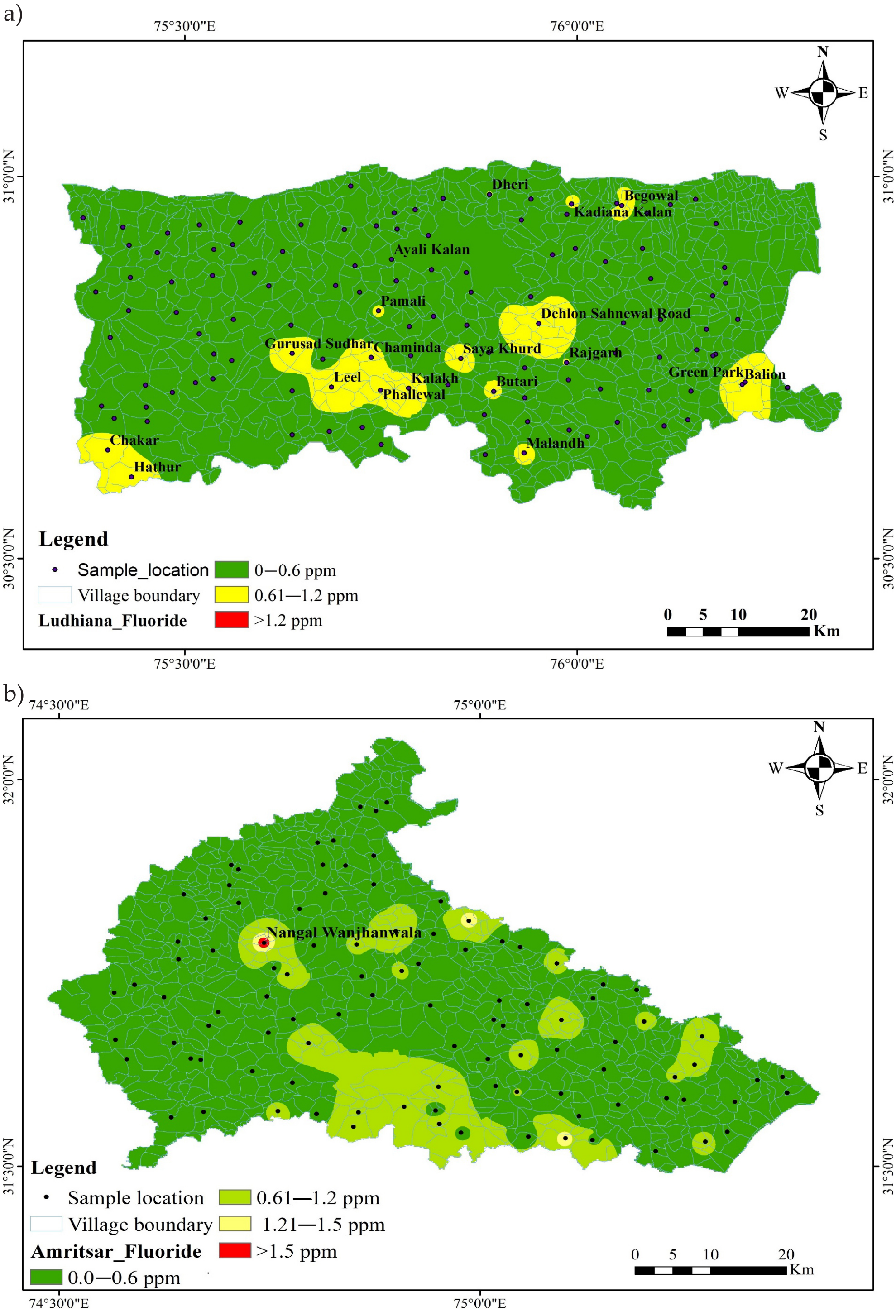


Fig. 8. Geospatial distributions of fluoride for Ludhiana (a) and Amritsar (b) districts in Punjab (generated using ArcGIS software)

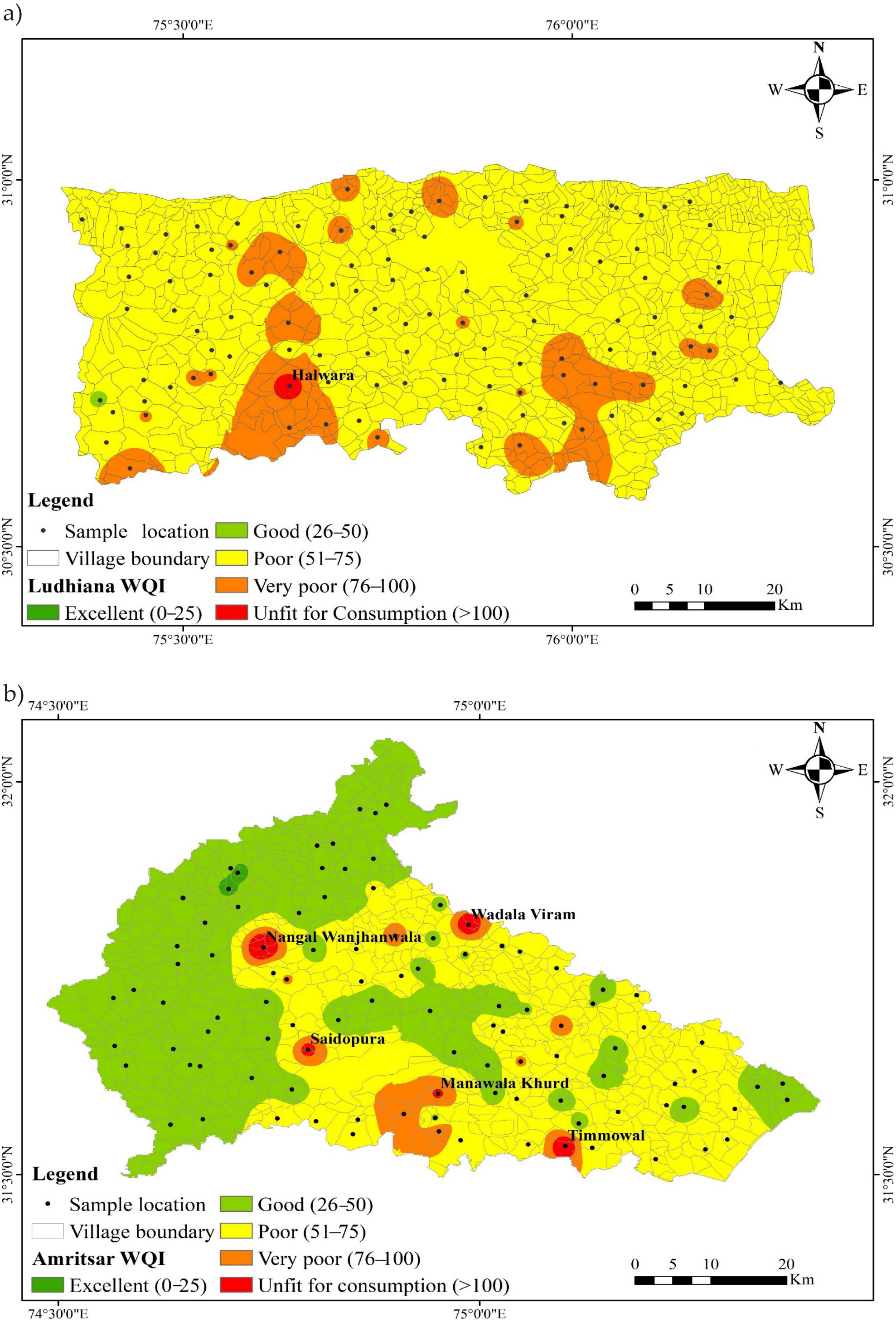


Fig. 9. Geospatial distribution of WQI for Ludhiana (a) and Amritsar (b) districts in Punjab (generated using ArcGIS software)

The WQI plays a crucial role in assessing and communicating the overall state of a water quality within a specific geographical region. It presents a reliable and uniform approach for assessing various water parameters, thus aiming to ascertain the suitability and safety of water for diverse uses. The WQI values for the groundwater samples in the two districts of Punjab (that is, Ludhiana and Amritsar districts) ranged from 43.96 to 120.52 in Ludhiana (with an average level of 68.20), whereas it ranged from 21.78 to 155.38 in Amritsar (with an average level of 50.67). The geospatial form of the WQI is significant for the study area, as it mapped the quality of the water over an area, thus offering a visual picture of the differences in quality (Fig. 9). These maps assisted in identifying areas of concern and making decisions about water-resource management and environmental preservation.

4.6. Health-Risk Assessment

The health effects of fluoride contamination (especially in drinking water) vary according to the concentration and length of exposure. The following are some of the primary health risks that are related to fluoride contamination:

- Dental fluorosis. This condition affects teeth and causes changes to the surface and color of the enamel. In moderate cases, teeth may show white patches or streaks. Severe occurrences may cause enamel pitting and brown discolorations. When children consume excessive fluoride during their tooth-growth periods, they often get dental fluorosis.
- Skeletal fluorosis. Prolonged exposure to high fluoride levels can cause skeletal fluorosis (a bone disease). Skeletal anomalies, joint immobility, stiffness, and bone soreness are all possible outcomes. Severe skeletal fluorosis can raise the risk of fractures and cause debilitating disabilities.
- Negative neurological effects. Research suggests that fluoride exposure may have harmful neurological consequences – particularly in youngsters. Early exposure to excessive fluoride levels may harm children's brain development and lower their IQs. These kinds of issues have been discussed by many researchers, along with some other health risks that are related to fluoride contamination [17, 74, 75]. Even so, further research is needed in order to establish a conclusive association. It is crucial to highlight that the degrees of the health effects vary according to individual sensitivities, durations of exposure, and other variables. Fluoride levels in drinking water must be regulated and monitored in order to avoid overexposure and reduce the possibility of negative health consequences.

The geospatial distribution of fluoride in the Ludhiana and Amritsar districts in Punjab is crucial for understanding the prevalence of fluoride contamination in the water sources and identifying those areas that may be at risk. The analysis revealed that only one water sample location exceeded the permissible limit (>1.5 ppm) out of the 222 water samples. The hotspot of fluoride that exceeded the permissible limit could be observed in Nangal Wanjhanwala village in the Amritsar district in Punjab. This geospatial representation of the fluoride map will facilitate analyses of fluoride-level distributions across specified geographical areas. Similarly, a geospatial representation provides a visual depiction of WQI values across various locations, helping stakeholders to understand overall water qualities quickly. The WQI study indicated that one water sample from Ludhiana and five water samples from Amritsar were unfit for consumption. The affected WQI villages that featured water that was unfit for consumption were Halwara (in the Ludhiana district) and Nangal Wanjhanwala, Wadala Viram, Saidopura, Manawala Khurd, and Timmowal (in the Amritsar district). To address this serious problem, an integrated approach must be applied in those locations that were identified as hotspots (where the fluoride concentrations and WQIs in the water exceeded permissible limits). For example, a robust monitoring program must be developed to periodically evaluate the fluoride levels in water sources, thus ensuring that any deviations are detected on time. Concurrently, extensive public awareness programs should be implemented in order to educate local communities about the health concerns that are associated with fluoride ingestion and promote safe water-consumption practices.

5. Validation for Fluoride and WQI Map

The interpolated inverse distance weighting maps for the fluoride concentrations and water quality indexes were validated using the receiver operating characteristic (ROC) curves in Figures 10 and 11. The ROC curve is a powerful tool for evaluating the prediction performance of the IDW model by displaying the true positive rate versus the false positive rate at various threshold values. In this study, the ROC curve was used to assess the consistency of the predicted values that were provided by the IDW model and the actual groundwater data.

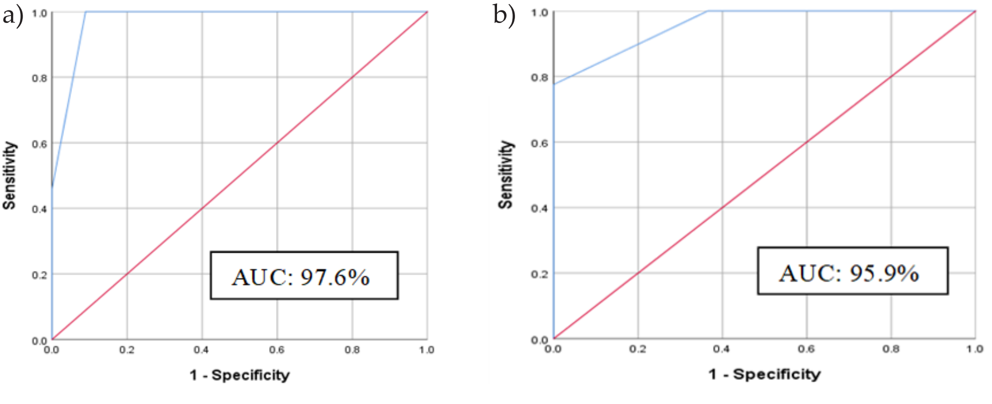


Fig. 10. ROC curves for fluoride IDWs:
a) Ludhiana district; b) Amritsar district (generated using SPSS software)

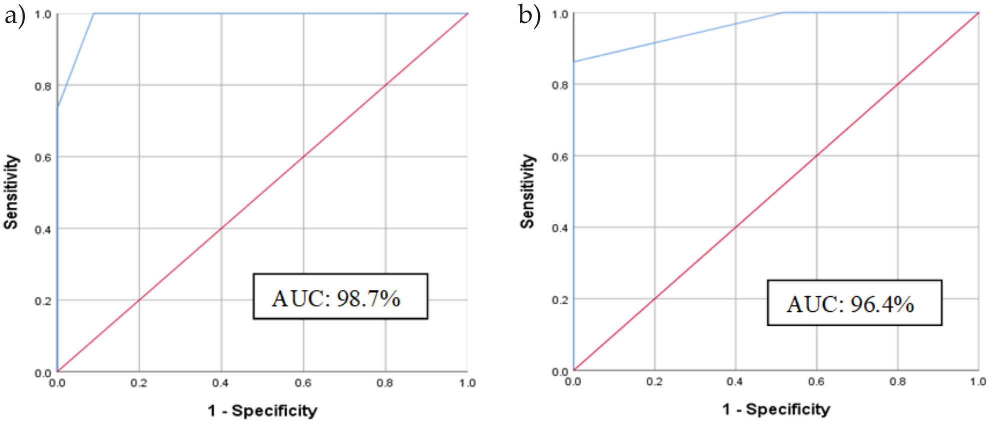


Fig. 11. ROC curves for WQI IDWs:
a) Ludhiana district; b) Amritsar district (generated using SPSS software)

The area under the ROC curve (AUC) was used to determine the model's accuracy in Tables 6 and 7. A higher AUC value implies that the IDW model was significantly predictive, ensuring that the spatial-distribution maps can accurately represent the fluoride concentrations and WQIs in the study area.

Table 6. Area under curves for fluoride IDWs for Ludhiana and Amritsar districts

Ludhiana district		Amritsar district	
test result	percentage [%]	test result	percentage [%]
0.976	97.6	0.959	95.9

Table 7. Areas under curves for WQI IDWs for Ludhiana and Amritsar districts

Ludhiana district		Amritsar district	
test result	percentage [%]	test result	percentage [%]
0.987	98.7	0.964	96.4

6. Conclusion

The groundwater assessment in the Ludhiana and Amritsar districts of Punjab, India, provided valuable information about the factors that affected the water qualities in these areas. The study involved gathering and examining 222 water samples in order to understand the key factors that contributes to the fluoride concentrations in the region. The results indicated that the majority of the fluoride concentrations in the two districts were less than 0.6 ppm, with only 1% of the groundwater samples from Amritsar exceeding the permissible limit of >1.5 ppm. Similarly, the WQI study revealed that 0.83 and 4.95% of the collected groundwater samples were unfit for consumption in the Ludhiana and Amritsar districts, respectively. Geographic information system (GIS) technology played a critical role in identifying hotspots and mapping the geographical distribution of the fluoride and WQI levels in the research region. Spatial interpolation techniques were employed in order to predict the fluoride and WQI values in unsampled areas, thus providing a comprehensive understanding of regional water quality changes. These spatial maps not only depicted the concentration levels but also helped identify those regions with exceptionally high or low contaminant concentrations. The study highlighted the need for standardized sample collection and thorough hydrochemical analysis in order to ensure accurate water quality assessments. Water samples were carefully gathered from borewells and handpumps at approximately five-kilometer intervals, and analyses were performed for 12 parameters: Mg^{2+}, Ca^{2+}, TH, CO_3^{2-}, HCO_3^-, Cl^-, NO_3^-, SO_4^{2-}, TA, pH, EC, and F^-. While most of the fluoride levels were within safe limits, some samples in Amritsar exceeded permissible limits; this can lead to health issues like dental and skeletal fluorosis. The WAWQI was used to evaluate the overall water quality in both districts and provide a detailed assessment. This study improves our understanding of the groundwater quality and fluoride pollution in Ludhiana and Amritsar. By using advanced GIS technology and detailed data analysis, it offers valuable insights for policymakers and stakeholders on effectively monitoring and managing water quality. Future work should focus on expanding the study to include more districts and incorporating additional parameters that could influence the water quality. The constant monitoring and improvement of data-collection methods will further enhance the understanding and management of groundwater resources.

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CRediT Author Contribution

K. K.: investigation, methodology, formal analysis, writing – original draft.
N. R. S.: conceptualization, methodology, formal analysis.
R. K.: validation – review & editing, supervision.
I. C. D.: formal analysis, supervision.
R. S.: methodology, supervision.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data Availability

The original contributions that were presented in the study are included in the article; further inquiries can be directed to the corresponding authors.

Use of Generative AI and AI-assisted Technologies

No generative AI or AI-assisted technologies were employed in the preparation of this manuscript.

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