Spatial distribution of physico-chemical parameters for groundwater quality evaluation in a part of Satluj River Basin, India

Akshay Kumar Chaudhry, Kamal Kumar and Mohammad Afaq Alam

ABSTRACT

The rising population, contamination and mismanagement of groundwater worldwide require sustainable management techniques and strategies to prevent misuse of groundwater resources especially in the semi-arid regions of the world. The aim of the present study is to assess the distribution of contaminants in groundwater at a spatial level by using a geostatistical method, namely ordinary kriging. For this, a physico-chemical parameter data set at 14 sampling locations for a period over 25 years was assessed. Three semi-variogram models, namely exponential, Gaussian and spherical, fitted well for the data set and were cross-validated using predictive statistics. Based on nugget/sill ratio, which characterizes the overall spatial dependence of water quality parameters, it was observed that, apart from nitrate, all the other parameters showed moderate to weak spatial dependence (i.e. total hardness), indicating significant influence of urbanization, fertilization and industrialization. Spatial distribution maps of all the parameters were generated. Concentration of most of the parameters reported high values in the northern region, while silicon dioxide and potassium recorded high values in the southern and central regions of the study area respectively. The study highlighted the depleting groundwater resources in various regions of the study area, indicating that the groundwater quality is in a declining state.

Key words | kriging, nugget, physico-chemical parameters, Satluj, semi-variogram, sill

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INTRODUCTION

Groundwater is one of the vital resources of consumable water on earth, particularly in semi-arid regions. Nowadays, it is the most threatened resource, as the rate of extraction of groundwater is growing endlessly due to the increase in population growth, and agronomic and industrial-related activities. Hence, it has become an essential commodity in the recent past due to the increase in such activities. However, rapid development in the recent past in agronomic and industrial sectors poses a great risk to the safety and well-being of people due to release of wastewater from industries and municipal sewage (Olayinka 2004; Ntengwe 2006). Wastewater released (directly or indirectly) if not properly treated and controlled can cause a serious threat to groundwater resources and can cause a wide range of damage to human health (Shankar *et al.* 2008). The most common diseases that can be transmitted through intake of contaminated water, inadequate sanitation and poor hygiene are diarrheal diseases (WHO 2004). Groundwater, once contaminated, stays in an unusable condition for quite a long time or even hundreds of years. So, the issues related to groundwater contamination are a huge problem, which has caught the attention of social activists and researchers all around the world (Mishra *et al.* 2005).

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Variation and knowledge of physico-chemical parameters in an area play an important role in evaluating water quality and potability. They also help in planning sustainable management of groundwater resources and thus involve handling huge amounts of spatial data (that can be directly or indirectly referenced to a location on the Earth's surface) and non-spatial data (that cannot be directly or indirectly referenced to a location on the Earth's surface). The primary and most important tool for handling such types of data is the Geographical Information System, using geostatistical methods (Kitanidis 1999; Chang 2012). Geostatistical methods are considered as an important tool for autocorrelation between sampling locations and in assessing the spatial variability of contaminants in water and soils (Clark 1979; Trangmar *et al.* 1986). Such information is also vital in studying the occurrence, movement and contaminant migration history for source identification along with their spatial variability at different sampling locations. The spatial variability of water quality parameters provide a relative assessment of the variability of groundwater quality and check for any sort of relationship amongst the parameters used for sustainable safe use. This information depends on many parameters such as topography, geology, hydrometeorology, land-use pattern, climatic conditions and interrelationship amongst these parameters. Since these parameters play a vital role in determining the spatial variability of water quality in groundwater, the interpolation technique can be best used to find the concentration at unmeasured locations and can create points to depict groundwater contamination sources. Detailed explanations of different geostatistical methods are enumerated in the literature (Clark 1979; Isaaks & Srivastava 1989; Goovaerts 1997; Kitanidis 1999; Webster & Oliver 2001), hence, to prevent unnecessary paper length it is avoided here.

The quick pace of industrialization has turned Rupnagar District, Punjab, into a major source of groundwater contamination. Most of the industries discharge their wastewater (indirectly or directly) without proper treatment into nearby places or open pits, which travel forward through low-lying depressions on the land surface, resulting in groundwater contamination (Purandara & Varadarajan 2003). In April 2016, the Punjab Pollution Control Board came out with a report, post-testing water quality from 37 locations where the Satluj River flows in the state. The river, which enters Rupnagar district in Punjab, begins to deteriorate as it runs its course in the state (Dutta 2017). Thus, a few past studies made by Singh *et al.* (2011b; 2014), have used a deterministic technique (inverse distance weighted) to quantify and alleviate groundwater contamination in Rupnagar District, while the present study uses one of the geostatistical techniques, i.e. ordinary kriging (OK), to study and understand various hydrogeochemical, anthropogenic and geogenic processes occurring in the region, which brings novelty to this work. It is the most widely used geostatistical technique and can predict spatial variability more accurately and gives better cross-validation results (Environmental Systems Research Institute (ESRI) 2016). It assumes that the data are normally distributed and do not contain any trends and come from a stationary stochastic process (Audu & Usman 2015). Thus, z-scale transformation was performed to standardize the data. Further, OK fits a mathematical function to a certain number of data set points within a certain specified radius, to get the values at unknown locations by forming weights from neighbouring measured values. These weights come from semi-variogram modeling and depend on the distance between the sample and estimated point. They are calculated using the minimum variance method (Gandhi & Sarkar 2016). Predictions at each sampling location in the study area are made based on semi-variogram and on the arrangement of spatially measured values that are close to each other. The theoretical explanation of the OK technique can be found in the literature (Isaaks & Srivastava 1989; Oliver & Webster 1990; Goovaerts 1997; Kitanidis 1999; Merino *et al.* 2001; Webster & Oliver 2001), hence, it is omitted here to avoid unnecessary paper length. The only limitation lies in the case of outliers and non-stationary data (Weise 2001). Henceforth before proceeding with this method, these limitations should be addressed.

MATERIALS AND METHODOLOGY

Study area and data procurement

Rupnagar district, Punjab, is a part of Satluj River Basin. The project area lies between E longitude 76°16′26″ to 76°43′21″ and N latitude 30°44′21″ to 31°25′53″, and covers an area of 1,414 km^2 (Figure 1). It is located in the eastern part of the

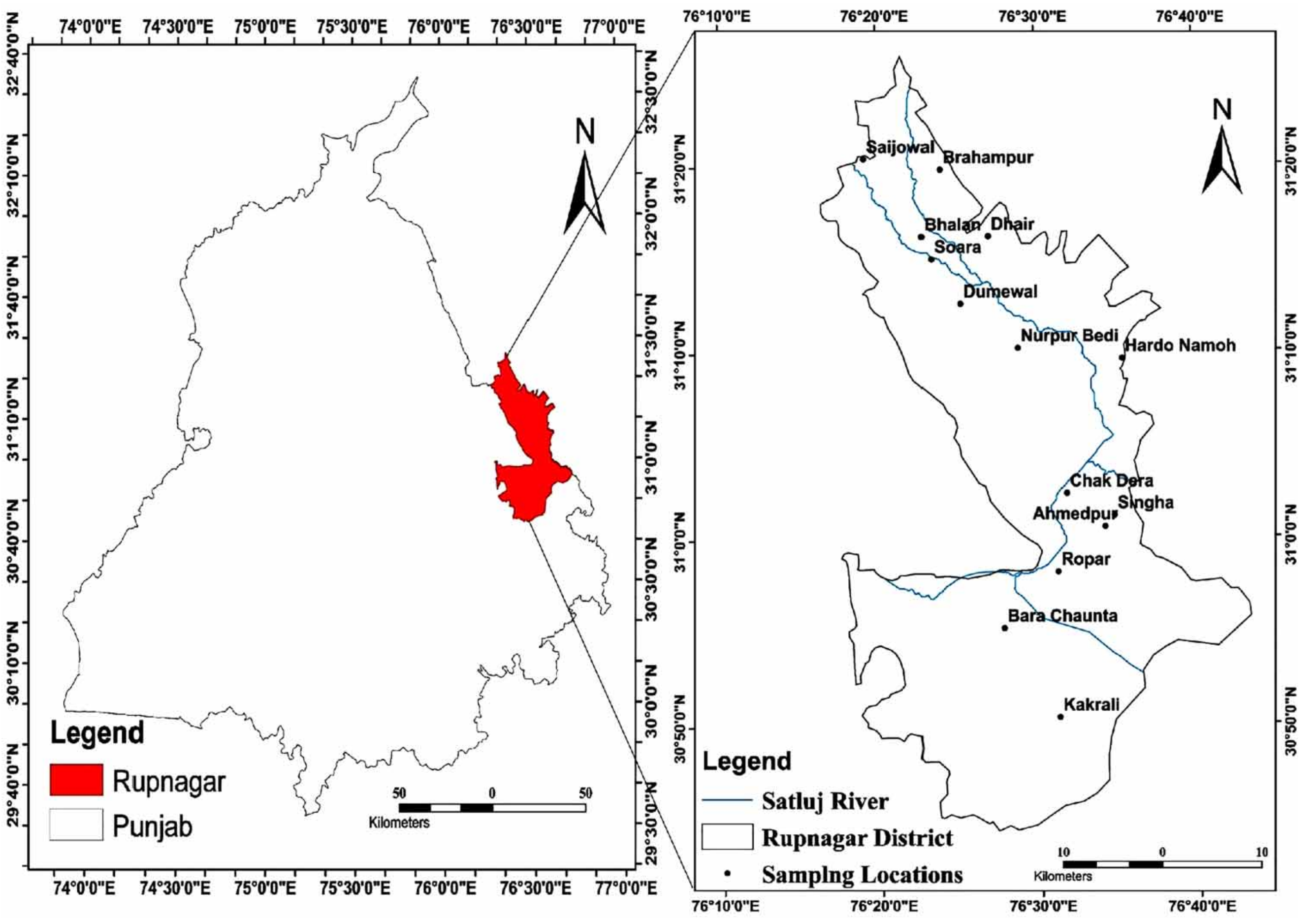

Figure 1 | Map of the study area along with sampling locations.

Punjab State. Agriculture is the most important source of economy in the state, covering almost 55% of the area (Central Groundwater Board (CGWB) 2017). The River Satluj is the chief source of water in the area. It is the longest river in the Punjab region. It starts from west of Lake Rakshastal in Tibet, enters Punjab through the Nangal region in the north and streams southeasterly and after that wanders south and southwest over the peripheral Siwalik Hills to emerge into fields. The climate is semi-arid, with warm summers and cold winters. The temperature varies from a maximum of 45 °C in summer to 5 °C in winter. The district gets its rainfall through the southwest monsoon, which contributes about 78% of the total rainfall (CGWB 2017).

CGWB is a national agency working under the Ministry of Water Resources, Government of India. It monitors and analyses data related to physico-chemical parameters of groundwater resources in the country in its chemical laboratory using standard methods for the examination of water and wastewater as per American Public Health Association (APHA) (1998) and Bureau of Indian Standards (BIS) IS: 3025 (2004). Therefore, the monthly data related to 11 physico-chemical parameters (i.e. pH, electrical conductivity (EC), chloride (Cl), nitrate (NO_3), sulphate (SO_4), total hardness (TH), potassium (K), sodium (Na), calcium (Ca), silicon dioxide/silica (SiO_2), and magnesium (Mg)) that had continuity in their data set for the 14 sampling locations that the study area covers was procured from the board for a period over 25 years (1990–2015). All concentrations (except pH) are in mg/L; EC in μS/cm at 25 °C. The sampling locations from which the data were taken included various dug wells and bore wells and were from the adjoining areas of National Fertilizers Limited,

Table 1 | Descriptive statistical analysis of physico-chemical parameters included in the present study

Physico-chemical parameters	Min.	Max.	Mean	Std. dev.	BIS acceptable limits (IS: 10500)
pH	7.61	7.88	7.74	0.08	6.5–8.5
Electrical conductivity, (μS/cm)	439.38	1,159.46	710.29	197.99	–
Chloride, (mg/L)	20.25	123.15	48.10	28.46	250
Nitrate, (mg/L)	2.98	78.76	27.32	23.29	45
Sulphate, (mg/L)	9.77	153.38	51.72	36.15	200
Total hardness, (mg/L)	183.92	343.92	251.65	41.46	200
Potassium, (mg/L)	1.91	39.98	11.53	10.51	–
Sodium, (mg/L)	11.78	205.92	63.47	44.73	–
Calcium, (mg/L)	33.81	67.15	53.50	8.21	75
Silicon dioxide/silica, (mg/L)	22.00	28.75	25.71	2.07	–
Magnesium, (mg/L)	13.34	46.85	28.34	10.62	30

–: No such guidelines are established for these parameters in drinking water.

Punjab Alkalies and Chemicals Limited, Ropar Thermal Power Plant and Ambuja Cement Plant. The descriptive statistics and acceptable limits as per BIS IS: 10500 (1991) for various parameters that are analysed are listed (Table 1). From the descriptive statistics result it was apparent that the concentrations of NO_3 and TH well exceeded the acceptable limits of 45 mg/L and 200 mg/L respectively. Geographic coordinates of each sampling location were linked to the quality data of various parameters. ArcGIS 10.4 was used to formulate a geodatabase to keep the data integrated and perform the OK technique.

Cross-validation and best-fit models

Cross-validation based on predictive statistics was done to determine the best-fit semi-variogram models (Gorai & Kumar 2013). For this, we compared the root mean square error (RMSE), mean error (ME), mean square error (MSE), average standard error (ASE) and root mean square standardized error (RMSSE) values (Table 2). As per ESRI (2016), best-fit models are those which attain RMSSE close to unity and result in minimum values of ASE, ME, MSE and RMSE when

Table 2 | Semi-variogram models used and cross-validation

Physico-chemical parameters	Model used	ME	MSE	RMSSE	RMSE	ASE
pH	Spherical	−0.003	−0.024	0.998	0.085	0.086
Electrical conductivity (μS/cm)	Exponential	1.592	−0.008	0.991	209.634	209.929
Chloride (mg/L)	Exponential	0.480	−0.090	0.998	29.591	29.891
Nitrate (mg/L)	Spherical	−1.398	−0.030	0.995	21.318	22.793
Sulphate (mg/L)	Gaussian	0.856	−0.055	0.990	35.860	38.089
Total hardness (mg/L)	Gaussian	−1.690	−0.037	0.998	45.244	45.293
Potassium (mg/L)	Exponential	−0.378	−0.201	0.984	12.297	14.900
Sodium (mg/L)	Exponential	0.561	−0.081	0.998	57.628	58.531
Calcium (mg/L)	Spherical	−0.228	−0.023	0.996	9.206	9.409
Silicon dioxide/silica (mg/L)	Exponential	−0.077	−0.034	0.992	2.158	2.196
Magnesium (mg/L)	Spherical	−0.158	−0.015	0.990	11.422	11.612

compared with other models. If the RMSE values of two methods are equal, then the MSE value is considered for determining the best-fit method (Hooshmand *et al.* 2011). Johnston *et al.* (2001) stated that, on examining the cross-validation results if the ASE value is close to the RMSE value, then the predicted standard errors are appropriate. Thus, three semi-variogram models are used in this study:

$$Spherical\,Model: \gamma(h) = N_o + P_o\left(\frac{3h}{2r} - \frac{1}{2}\left(\frac{h}{r}\right)^3\right) \quad (1)$$

$$Exponential\,Model: \gamma(h) = N_o + P_o\left(1 - \mathrm{Exp}\left(-\frac{h}{r}\right)\right) \quad (2)$$

$$Gaussian\,Model: \gamma(h) = N_o + P_o\left(1 - \mathrm{Exp}(-)\left(\frac{h}{r}\right)^2\right) \quad (3)$$

where: N_o is the nugget, P_o is the partial sill, h is the lag distance (m) and r is the range (m). It is important to note that, when the nugget value is relatively small, it results in a nugget effect model. This occurs when the data are widely spaced (Figure 2):

$$Nugget\,Effect\,Model: \gamma(h) = \begin{pmatrix} 0 & for\ h = 0 \\ P_o & for\ h \neq 0;\ P_o \geq 0 \end{pmatrix} \quad (4)$$

RESULTS AND DISCUSSION

Analysis of spatial structure of physico-chemical parameters

OK, like most interpolation techniques, is built on the assumption that things that are close to one another are more alike than those that are farther apart. Semi-variogram modeling is a way to explore this relationship (ESRI 2016). Thus, analysis of the spatial structure of physico-chemical parameters depends on semi-variogram modeling and expresses the relationship between measured values. Semi-variogram portrays the spatial autocorrelation at each sampling location. It tends to level out at a certain distance,

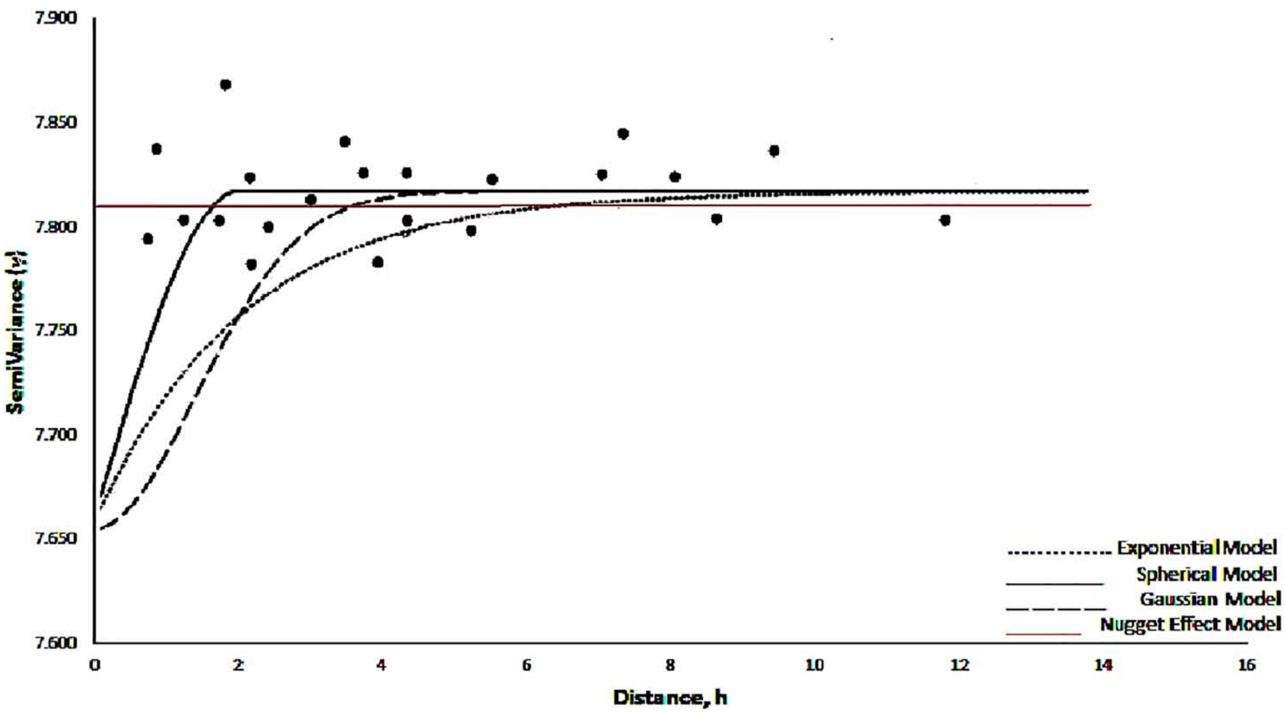

Figure 2 | Different theoretical semi-variogram models used in the study.

known as the range. There is no correlation in the data beyond the range. The value at which the model attains the maximum upper limit value is called the sill (Webster & Oliver 2001). The sill represents the nugget plus the partial sill. Trangmar *et al.* (1986) stated that the nugget is that value which indicates the random variation and is derived from the inaccuracy of measurements that cannot be found in the sample range. The nugget/sill ratio is determined and represents the overall spatial variation of water quality parameters (Table 3). In these studies (Cambardella *et al.* 1994; Emadi *et al.* 2008) it was stated that if the nugget/sill ratio is greater than 75%, it represents weak spatial dependence in the data used. A ratio between 25% and 75%, represents moderate spatial dependence; and a ratio less than 25%, indicates strong spatial dependence in the data used. In this respect, a ratio less than 25% was found for nitrate parameter, indicating a strong spatial dependency and can be attributed to intrinsic properties of soil (Yang *et al.* 2009). For total hardness, a high ratio (≥80%) was found indicating weak spatial dependency and can be the result of extrinsic factors (Mahmoudabadi *et al.* 2015). As per Yang *et al.* (2009), the moderate spatial dependency for the rest of the parameters can be attributed to anthropogenic factors (like industrialization, fertilization and soil management practices) in the study region. The semi-variograms of all the physico-chemical parameters are shown (Figure 3(a)–3(k)).

Table 3 | Analysis of spatial structure of physico-chemical parameters

Physico-chemical parameters	Nugget, N_o	Sill, S_o	Range, r	N_o/S_o
pH	0.005	0.008	33,498	72.63
Electrical conductivity (μS/cm)	29,201.000	42,201.000	15,558	69.20
Chloride (mg/L)	0.135	0.343	16,317	39.43
Nitrate (mg/L)	0.157	0.697	17,173	22.53
Sulphate (mg/L)	0.292	0.511	42,031	57.07
Total hardness (mg/L)	1,777.600	2,196.600	62,185	80.93
Potassium (mg/L)	0.259	0.850	16,558	30.52
Sodium (mg/L)	0.316	0.486	15,558	64.99
Calcium (mg/L)	68.990	98.990	50,985	69.69
Silicon dioxide/silica (mg/L)	2.016	4.625	14,958	43.60
Magnesium (mg/L)	106.110	154.937	58,985	68.49

Assessment of spatial variability maps of physico-chemical parameters

The spatial variability maps of all the parameters are shown in Figure 4(a)–4(k) along with the varied ranges (or simply attribute classes) for them. The study area is divided into five attribute classes, namely region 1, region 2, region 3, region 4 and region 5 (Table 4). From the variability map of pH (Figure 4(a)), it was observed that the pH values occurred mostly in region 3 with the values in the range 7.73–7.77. Thus, the groundwater is of alkaline nature in the study region. The EC values varied in the range 439.38–1,359.46 μS/cm. High concentration was observed in the Soara region in the north (Figure 4(b)) which may be due to ion exchange and solubilization in the aquifer medium (Sánchez-Pérez & Trémolières 2003; Todd 2014). Chloride exhibits a somewhat similar trend as that of EC (Figure 4(c)). Magnesium concentration exhibited high values in the northern region (Figure 4(d)), thus limiting the usage of drinking water before proper treatment in that region. From the variability map of calcium (Figure 4 (e)), it is observed that most of the concentration occurred in regions 4 and 5. This is due to weathering of rocks and ion exchange in groundwater (Fernandes *et al.* 2008). Thus, ascendency of cations like Ca, Na, and Mg in the groundwater of the region is attributed to dissolution of minerals, ion exchange, and agronomic and industrial-related activities (Davis & Dewiest 1966; Singh *et al.* 2011a). The variability map of TH concentration indicated Bhalan and Ahmedpur regions to be the most affected, thus limiting the usage of drinking water before proper treatment in these regions (Figure 4(g)). Hardness in water results in stains on glassware, water pipes, heaters, sinks and faucets and is due to minerals, such as calcium and magnesium (Sawyer & McCarty 1978; Craig & Anderson 1979). Other ill effects include skin and hairs to feel sticky and dull, stain in fabrics and deterioration of bathtub rings. The variability map of nitrate concentration indicated that the high concentration (>53.20 mg/L) in the study area is due to the collective outcome of contamination from sewage, unlined drains, cattle sheds and runoff from fertilized fields (Figure 4(h)). Similarly, from the variability map of sulphate, it was observed that a high concentration of sulphate is found in the northern region (Figure 4(i)). Sulphate occurs

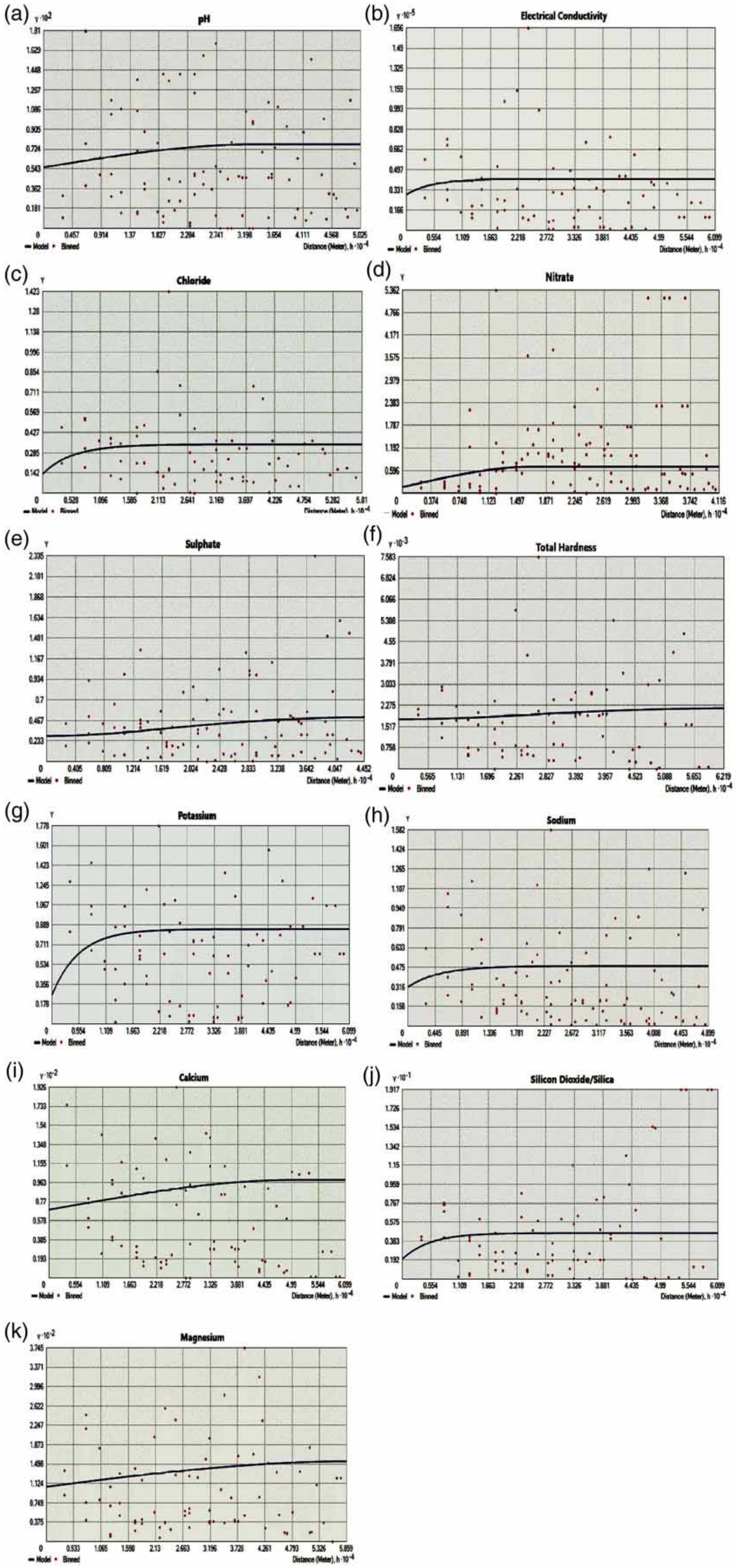

Figure 3 | Best-fit semi-variogram models of physico-chemical parameters.

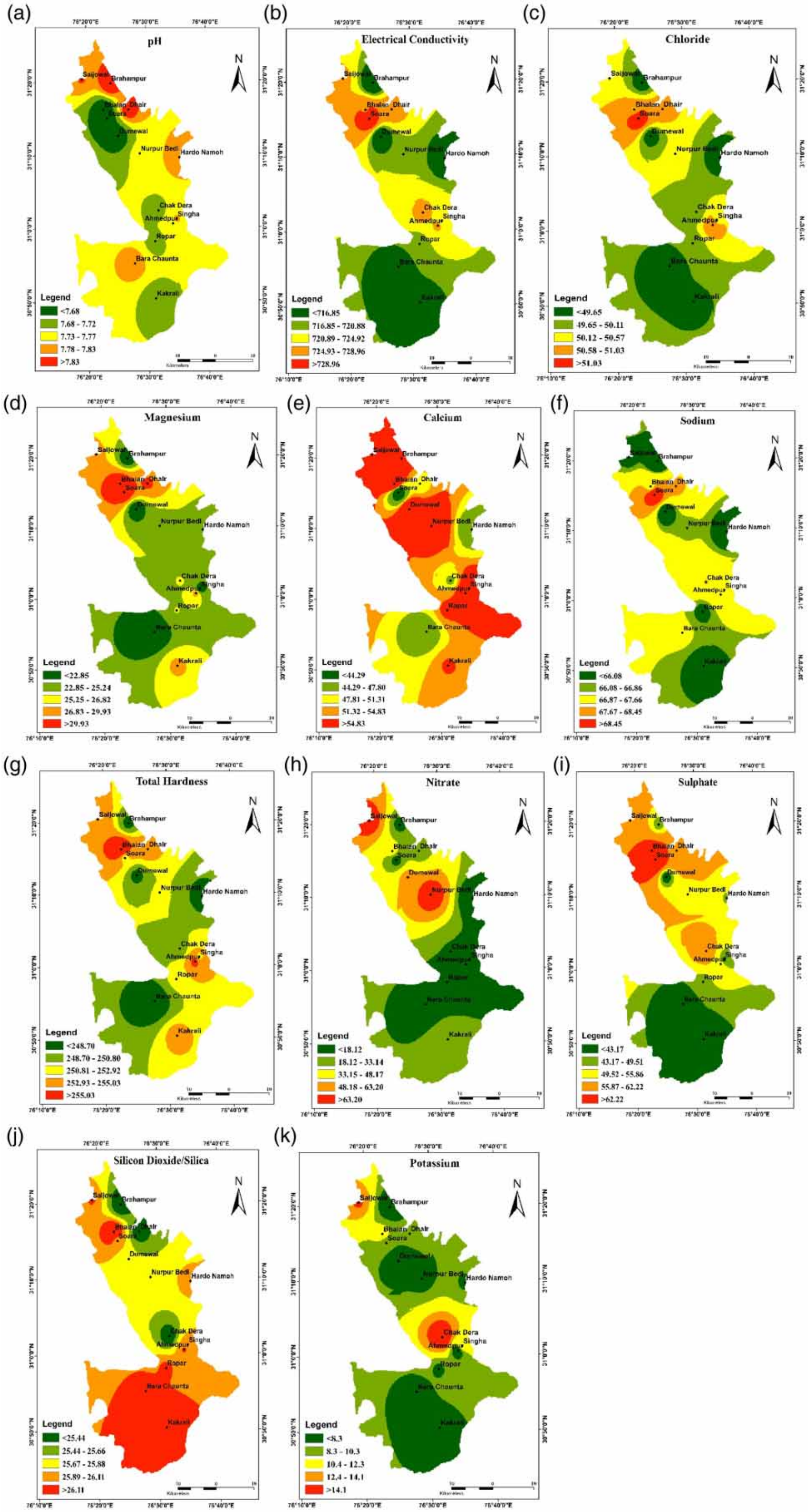

Figure 4 | Kriged maps showing spatial distribution of physico-chemical parameters.

Table 4 | Regional classification of physico-chemical parameters

Physico-chemical parameters	Region 1	Region 2	Region 3	Region 4	Region 5
pH	<7.68	7.68–7.72	7.73–7.77	7.78–7.83	>7.83
Electrical conductivity (μS/cm)	<716.85	716.85–720.88	720.89–724.92	724.93–728.96	>728.96
Chloride (mg/L)	<49.65	49.65–50.11	50.12–50.57	50.58–51.03	>51.03
Nitrate (mg/L)	<18.12	18.12–33.14	33.15–48.17	48.18–63.20	>63.20
Sulphate (mg/L)	<43.17	43.17–49.51	49.52–55.86	55.87–62.22	>62.22
Total hardness (mg/L)	<248.70	248.70–250.80	250.81–252.92	252.93–255.03	>255.03
Potassium (mg/L)	<8.3	8.3–10.3	10.4–12.3	12.4–14.1	>14.1
Sodium (mg/L)	<66.08	66.08–66.86	66.87–67.66	67.67–68.45	>68.45
Calcium (mg/L)	<44.29	44.29–47.80	47.81–51.31	51.32–54.83	>54.83
Silicon dioxide/silica (mg/L)	<25.44	25.44–25.66	25.67–25.88	25.89–26.11	>26.11
Magnesium (mg/L)	<22.85	22.85–25.24	25.25–26.82	26.83–29.93	>29.93

naturally in potable water and is considered useful for irrigation purposes in the presence of calcium. There are some reports from researchers that address the ill effects (dehydration and diarrhea) associated with the ingestion of drinking water containing high sulphate concentration (Sawyer & McCarty 1978; EPA 1999; WHO 2003). From the variability map of SiO_2 (Figure 4(j)), it was observed that a high concentration occurred in the southern part of the study area. This may be attributed to crushing or milling of natural resources. At the moment, there are no suggested health-based guidelines for SiO_2 but exposure to water contaminated with SiO_2 for a long period of time can lead to polyuria (excessive urination) and lower blood sugar (Kerkar 2017). From the map of potassium it was observed (Figure 4(k)) that the central part of study area is mostly affected by it. Since, there are no health-based guidelines for K, exposure to water contaminated with K for a long period of time can lead to health concerns in individuals with kidney dysfunction, hypertension, diabetes, and pre-existing hyperkalaemia) (WHO 2009). Thus, the study highlighted the depleting groundwater quality in various regions of the study area. Concentration of most of the parameters reported high values in the northern region, while silicon dioxide and potassium recorded high values in the southern and central regions of the study area respectively. Apart from NO_3 and TH all the parameters exhibited concentration values well within acceptable limits as per BIS (1991) (Table 1). Thus, the resulting variability maps provided information on the spatial variation and possible sources of occurrence of the parameters used.

CONCLUSION

Physical examination of occurrence, movement and distribution of groundwater contamination is difficult and involves a huge amount of data handling. Thus, in order to ease groundwater quality evaluation, spatial variability maps play a key role in it. The paper addressed the spatial variability of 11 physico-chemical parameters and from the results it was apparent that all the parameters reported increase in their concentration values in the northern region, while silicon dioxide and potassium recorded increasing concentration in the southern and central parts of the study area respectively. From the descriptive statistics result it was apparent that the concentration of nitrate and total hardness well exceeded the acceptable limits of 45 mg/L and 200 mg/L respectively as per BIS. Different semi-variogram models were tested and three amongst them, namely spherical, exponential and Gaussian, fitted well for the data set and were cross-validated using predictive statistics. Based on nugget/sill ratio, it was observed that, apart from nitrate, all the other parameters showed moderate to weak (total hardness) spatial dependence indicating significant influence of industrialization, fertilization and soil management practices in the study region.

The study highlights the depleting groundwater resources in various regions of the study area indicating that groundwater quality is in a declining state and is the result of various hydrogeochemical, anthropogenic, and geogenic processes occurring in the study region. In order to avoid wastage and misuse, as well as promoting better utilization of existing resources, the authors feel that a continuous groundwater quality-monitoring program along with regular hydrochemical analysis should be implemented not in the study area, but for the entire Punjab region.

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