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Identifying sources of groundwater contamination in a hard-rock aquifer system using multivariate statistical analyses and GIS-based geostatistical modeling techniques

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ABSTRACT

Study region: The study area is Udaipur district, which is situated in hard-rock hilly terrain of Rajasthan, India.
Study focus: In this study, spatio-temporal variations of fifteen groundwater quality parameters are explored by box–whisker plots, trends are detected and quantified, and GIS-based groundwater quality index (GQI) is computed. For the first time, scores of principal component analysis (PCA) are combined with GIS-based geostatistical modeling by following a sound methodology in comprehensive manner to identify sources of groundwater contamination.
New hydrological insights for the region: Box–whisker plots revealed linkages between rainfall and groundwater quality, which were further verified by GQI ranging from 69 to 76 in Cluster I and from 73 to 78 in Cluster II. Cluster analysis identified two clusters of sites based on groundwater contamination controlled by geology. Significantly increasing trends are indicated ($p < 0.05$) at most sites in fluoride, sodium, EC and TDS, but significantly decreasing trends in silica at 40% sites indicate a possibility of replacement of older groundwater with recent rainfall recharge. Spatial distribution of increasing trends is affected by anthropogenic processes. Sen's method indicated increasing rates for calcium, magnesium, sodium, iron, bicarbonate, sulphate, fluoride, TDS, hardness and EC. PCA results indicated occurrence of groundwater contamination in Cluster I by anthropogenic sources and presence of natural/geogenic processes in Cluster II. Significant PCs, viz. major ion and soil leaching pollution factors, govern overall evolution of geochemical processes.

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1. Introduction

In many semi-arid and arid regions of the world, water is limited by quality rather than quantity. Water quality is vital not only because of its impact on the availability of freshwater and human health but also because of its intrinsic value (McCutcheon et al., 1993). The dramatically growing pollution of freshwater resources worldwide during past few decades necessitates comprehensive and proper knowledge of contamination levels and accurate assessment of trends in water quality for protecting this vital resource from pollution as well as for identifying efficient and cost-effective measures to control present and future threats of pollution at local/regional levels (Bartram and Ballance, 1996). In dry regions, most of the water demands are met by groundwater supplies as the factors of mainly population growth and climate change cause severe stress to surface water supplies in these areas (Edmunds et al., 2003; Kulkarni et al., 2015). Groundwater quality in an area is greatly controlled by the natural processes (e.g., geology, groundwater movement, recharge water quality, and soil/rock interactions with water), anthropogenic activities (e.g., agricultural production, industrial growth, urbanization with increasing exploitation of water resources) and atmospheric input (Helena et al., 2000; Chan, 2001). Hence, the assessment of groundwater quality at both spatial and temporal scales is imperative for managing this vital resource, especially in water-scarce regions.

Udaipur district (study area of this study), situated in the hard-rock hilly terrain of western India, suffers from severe droughts, low rainfall, high summer temperature and inadequate water resources (Bhuiyan et al., 2006). In western India, droughts occur very frequently and one of the severest historical droughts was seen in the year 2002 (Samra, 2004). At that time, the annual rainfall of the Udaipur district was deviated by as high as −33% from the normal annual rainfall (UNDP, 2002). Consequently, groundwater levels declined significantly in this district (Machiwal and Jha, 2014a), and the diminishing groundwater levels caused deterioration in groundwater quality. Moreover, future climate change and variability may exacerbate the pressure on hydrologic and hydrogeologic systems, which may further deteriorate groundwater quality (Mukherjee et al., 2015). Besides the natural processes, anthropogenic activities prevailing in the area are also degrading groundwater quality at a much faster rate than the former one. The area is well known for its mining and smelting industries, which are probably the potential sources for contaminating surface water as well as groundwater resources. On the other hand, rising population, growing urbanization, and irrigated agriculture are among the other factors responsible for the poor quality of groundwater. The groundwater quality in vast areas is reported to be hard, brackish and with high fluoride levels (CGWB, 2010). This situation calls for an urgent need for developing appropriate strategies to mitigate the effects of groundwater contamination. Management of groundwater resources in hard-rock regions requires understanding of natural and anthropogenic factors, which govern geologic/hydrogeologic processes of the hard-rock aquifer system.

Many conventional tools/techniques for the graphical and statistical interpretation of groundwater quality are described in standard textbooks on groundwater or hydrogeology (e.g., Freeze and Cherry, 1979; Karanth, 1987; Sara and Gibbons, 1991). However, the natural and anthropogenic factors may not be easily distinguished from the chemical composition of groundwater alone. Hence, the need for the application of modern approaches and tools such as multivariate statistical techniques, namely principal component analysis (PCA) and hierarchical cluster analysis (HCA), time series modeling (e.g., trend identification) and GIS techniques has been emphasized for the efficient management of groundwater quality (e.g., Jha et al., 2007; Steube et al., 2009; Machiwal and Jha, 2010). The multivariate statistical techniques offer a valuable tool for the evaluation of spatio-temporal variations and interpretation of complex water quality datasets, apportionment of pollution sources/factors (natural or anthropogenic) and the design of a monitoring network for the efficient management of water resources as well as for finding pragmatic solution to pollution problems (Jeong, 2001; Güler and Thyne, 2004; Valdes et al., 2007). For example, Demirel and Güler (2006) identified anthropogenic factors affecting groundwater chemistry in a Mediterranean coastal aquifer, Mersin–Erdemli basin (Turkey) by applying HCA, PCA and geochemical modeling techniques. The results indicated that anthropogenic factors are responsible for the presence of seasonality in the area where water has been contaminated due to fertilizer and fungicide applications made during early summer season. Cloutier et al. (2008) applied PCA and HCA to identify geochemical processes controlling geochemistry of groundwater in a sedimentary rock aquifer system of the Paleozoic Basses-Laurentides (Canada). Based on loadings of principal components (PCs), the first two PCs were defined as 'salinity' and 'hardness' of groundwater. Lin et al. (2012) evaluated temporal variability and factors governing shallow groundwater chemistry using analysis of variance, PCA, HCA and geostatistical techniques in the tropical Manukan Island's aquifer of Malaysia. Selle et al. (2013) examined spatial and temporal patterns of principal component scores to improve the understanding of processes governing groundwater quality in the Ammer catchment located in southwest Germany. The results indicated influence of land use and geology on the groundwater quality. Kim et al. (2014) employed model-based cluster analysis to differentiate the contributions of natural and anthropogenic factors to the observed groundwater quality in South Korea. Their results demonstrated that bivariate normal mixture model was more robust than multivariate analysis, and provided a better discrimination between anthropogenic and natural groundwater groups.

Moreover, the trend identification, along with the knowledge of their underlying mechanisms, can lead to appropriate decisions for groundwater-quality management (McBride, 2005). Literature survey reveals that the trends are mainly explored for surface water quality data and studies dealing with the identification of trends in groundwater quality parameters are rare (Taylor and Loftis, 1989; Loftis, 1996). Presently, testing time series of groundwater quality parameters for the presence/absence of trend over a given period of time is receiving increasing attention (Visser et al., 2009; Kaown et al., 2012). GIS-based geostatistical modeling (i.e. kriging) of geochemical data often provides insights into the underlying factors controlling hydrogeological processes (Beyer et al., 2009; Rivest et al., 2012; Schot and Pieber, 2012; Chen et al., 2013). The kriging has been especially useful for analyzing hydrochemical data at a regional scale (Goovaerts et al., 1993). Many past studies have analyzed the chemical composition of groundwater to identify hydrochemical processes by applying multivariate statistical analyses, trend identification and geostatistical modeling techniques in isolation. To date, limited studies are reported where multivariate statistical techniques are integrated with GIS-based geostatistical modeling (Sánchez-Martos et al., 2001; Kolsi et al., 2013). However, none of such past studies, involving integrated use of multivariate statistics and geostatistics, applied geostatistical modeling systematically; either preliminary requirements of normality and stationarity of datasets were not tested or the adequacy of the fitted interpolation model was not verified. Thus, this study for the first time proposes a standard methodology for combining factor scores of the PCA with GIS-based geostatistical modeling. The proposed methodology has been demonstrated in a comprehensive manner to precisely identify natural and anthropogenic processes/activities governing groundwater quality in a hard-rock aquifer system located in the semi-arid region of western India. In addition, trends in the groundwater quality parameters of 53 sites are detected by applying three statistical tests, trend magnitudes are quantified, and finally groundwater quality index is computed in the GIS framework.

2. Description of study area

2.1. Location and hydrometeorology

Udaipur district (Fig. 1) encompassing an area of about 12,698 km^2 has been selected as the study area for this study. It is situated in the driest and largest state (called 'Rajasthan') of India between 23°45′ and 25°10′ N latitude and 73°0′ and 74°35′ E longitude. For administrative purposes, the entire district is divided into 11 blocks (Badgaon, Bhinder, Dhariawad, Girwa, Gogunda, Jhadol, Kherwara, Kotra, Mavli, Salumber, and Sarada).

Climate of the study area is tropical and semi-arid with an average annual rainfall of 675 mm, precipitating more than 80% during June through September. The rainy (wet) season starts from mid-June and lasts up to the end of October month while the rest seven-months period from November to May usually remain dry. The temperature rises to a maximum of 42.3 °C during summer and dips to a minimum of 2.5 °C during winter. The main rivers of the study area, e.g. Som, Gomati, Jakham, Maahi, Ahar, Berach, Sei, Sabarmati and Wakal, have intermittent flow. The most urbanized and densely populated northern and northeast portions of the study area are drained by Ahar and Berach rivers. The western portion is drained by Sei, Sabarmati and Wakal rivers while the central, southern and southeast

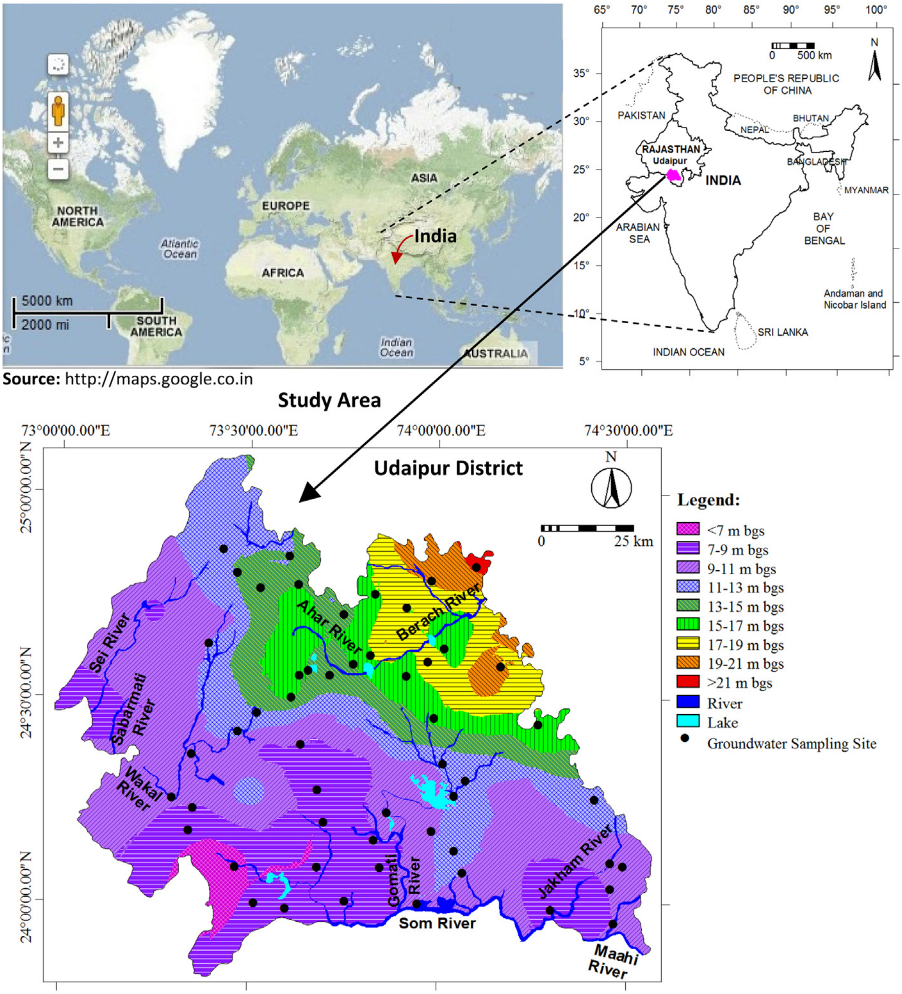

Fig. 1. Location map of the study area depicting spatial variation of groundwater levels in meters below the ground surface (m bgs) and groundwater sampling sites.

portions are drained by Maahi, Jakham, Gomati and Som rivers. Surface irrigation is dominant in the canal commands located in the southern portion of the study area.

2.2. Geology and hydrogeology

The six geologic layers of the study area are shown in Fig. 2. The study area is mainly underlain by phyllite–schist and gneiss strata, which covers 3567 and 3157 km^2 area, respectively, while schist, granite and quartzite encompass 808, 418 and 174 km^2, respectively (Machiwal et al., 2011a). The phyllite–schist geology, relatively soft and friable compared to the gneiss formation, is spread over central half and southern portions of the area. The gneiss geology, comprising porphyritic gneissic complex associated with aplite, amphibolite, schist and augen gneiss, occur in eastern portion of the area. The schist geology exists in the northeast and southeast portions and the granite geology occurs in the western portion. A small elongated strip of the quartzite geology can be seen in the western portion. Hillocks, generally having insignificant potential for the occurrence of groundwater resources are also

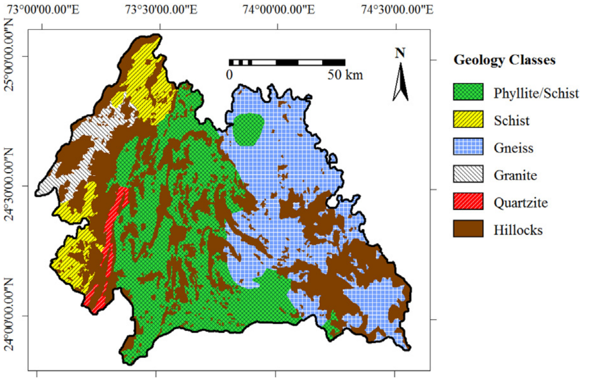

Fig. 2. Geology map of the study area.

present. The major water-bearing formations in the area, i.e., phyllite–schist and gneiss, have little primary porosity. However, these rocky formations serve as groundwater reservoirs because of their secondary porosity in the form of fissures/fractures or joints, which allows movement of groundwater. If secondary porosity of these rocky geological formations is significant, these are generally known as 'hard-rock formations' or specifically 'hard-rock aquifer systems' (CGWB, 1997). Groundwater in the area mainly occurs under unconfined to semi-confined conditions in saturated zones of the rock formation and the occurrence of groundwater is controlled by the topographical, physiographical and structural features present in geological formations (CGWB, 2010). Deep aquifers in the area are reported to exist at a greater than 100 m depth, but little is known about these aquifer systems (GWD, 2004).

2.3. *Physiography, groundwater scenario and land use pattern*

The Aravalli range, one of the oldest mountain ranges of the world, runs along the northeast-southwest direction in the study area. Entire district, bounded by elevated plateau in the northern portion, Sei River in the western portion, and Som and Maahi rivers in the southern portion, could be roughly considered as a groundwater basin with vast stretches of fertile plains mainly in the eastern portion (Chauhan, 2007). General direction of groundwater flow in the north and east parts is from NW to SE or W to E, while the groundwater flows from N to S direction in the remaining portion of the study area (GOR, 1999). In the study area, which is situated in the hard-rock Aravalli terrain, net groundwater fluxes across the boundaries may be considered negligible (Bhuiyan et al., 2009; Machiwal and Jha, 2014b). The mean pre-monsoon groundwater levels based on the 4-year (1999–2002) data vary from 7 to 21 m below the ground surface (m bgs) (Machiwal and Jha, 2014a). The groundwater depth is relatively deeper (>15 m bgs) in the northern and northeast portions of the study area, while it is shallow (<9 m bgs) in the southwest, southern, western and southeast portions of the area.

Land use/land cover of the study area mainly includes cultivable land, forest, pasture, wasteland, waterbodies, and built-up land. The main city of Udaipur exists in the northern portion, which is completely covered by urban built-up land. In past few years, area under urban built-up land has rapidly been increased due to emerging urbanization and subsequent expansion of the city. This portion has also seen a large industrial growth along with setup of zinc and phosphate plants. The northern and western portions have abundant forests, which could not be explored and remained untouched by human primarily due to steep slopes. The southern portion of the area is dominated by agricultural activities where a large canal network provides a fair opportunity for cultivating lands adequately. Unsewered urban effluents from the urban area have been drained by Ahar and Berach rivers from north to northwest portions for a long time, which contaminate surface water and groundwater in the area. Also, the excessive use of fertilizers and pesticides in irrigated commands, situated in the southern portion of the study area, is the main cause for groundwater contamination.

3. Methodology

3.1. Data collection

Groundwater samples in the study area are usually collected during pre-monsoon season (from March to May) at 53 randomly selected sites; locations of the sites are shown in Fig. 1. The groundwater samples were mainly collected from the shallow unconfined aquifers that exist in the study area at 20–30 m depths from ground surface and constitute the major source of groundwater. The collected samples are analyzed for determining groundwater quality parameters, viz., calcium (Ca), magnesium (Mg), sodium (Na), potassium (K), iron (Fe), sulphate (SO_4), chloride (Cl), carbonate (CO_3), bicarbonate (HCO_3), nitrate (NO_3), silica (SiO_2), pH, EC, total dissolved solids (TDS), and hardness. The groundwater quality parameters for pre-monsoon season of 11-year period (1992–2002) were collected from the Central Ground Water Board (CGWB), Jaipur, Rajasthan. All collected data were checked for regularity without any gaps. These data were used for univariate and multivariate statistical analyses on the GIS platform to identify sources of groundwater pollution. All groundwater quality parameters of 53 sites were analyzed by drawing box and whisker plots using STATISTICA software (StatSoft Inc., 2004).

3.2. Hierarchical cluster analysis

The aim of applying cluster analysis (CA) was grouping groundwater sampling sites into classes (known as 'clusters') so that the sites within a class are similar to each other with respect to groundwater quality but different from those in other classes. Such a classification helps in identifying groups of the sites according to sources of groundwater contamination (natural or anthropogenic). The CA is an unsupervised pattern recognition technique that uncovers intrinsic structure or underlying behavior of a dataset without making a priori assumption about the data, in order to classify the objects of the system into clusters based on their similarities (Otto, 1998). There are two major categories of CA: hierarchical and non-hierarchical. Hierarchical cluster analysis (HCA) is the most common approach in which clusters are formed sequentially, starting with the most similar pair of objects and forming higher clusters step by step. The process of forming and joining clusters is repeated until a single cluster containing all the samples is obtained. Results can be displayed as a tree diagram (or dendrogram), which provides a visual summary of the clustering process by presenting a picture of the groups and their proximity with a dramatic reduction in dimensionality of original data. The dendrogram is considered as the better method for displaying HCA results (Kruskal and Landwehr, 1983).

In this study, HCA was performed on the normalized dataset using Ward's method (Ward, 1963). This method uses an analysis of variance approach to evaluate the distances between clusters, attempting to minimize sum of squares of any two (hypothetical) clusters that can be formed at each step. The squared Euclidean distance usually gives similarities between two samples and a distance can be represented by the 'difference' between analytical values from both the samples (Güler et al., 2002). In HCA, 14 groundwater quality parameters (Ca, Mg, Na, K, Fe, HCO_3, SO_4, Cl, NO_3, F, SiO_2, TDS, EC, and pH) of 53 sites were considered with their mean values for 11-year period (1992–2002) by using STATISTICA software package (StatSoft Inc., 2004). Prior to HCA, the observed water quality data, x_{ji} were standardized by z-scale transformation as given below:

$$z = \frac{x_{ji} - \bar{x}_j}{s_j} \quad (1)$$

where x_{ji} = value of the jth water quality parameter measured at ith site, $\bar{x}_j$ = mean (spatial) value of the jth parameter, and s_j = standard deviation (spatial) of the jth parameter.

The HCA performed with standardized data is expected to be less influenced by small/large variance of the data. Furthermore, standardization makes the data dimensionless and removes the influence of different measurement units of the data.

3.3. Detection and quantification of trends in groundwater quality parameters

There exist two general approaches for trend detection: parametric and nonparametric. The parametric method is more powerful than the non-parametric, but the former approach examines linearity of regressions (Montgomery and Peck, 1982) and requires the data be independent and normally distributed (Gilbert, 1987; Bethea and Rhinehart, 1991). To overcome the problem associated with parametric method for trend detection, nonparametric test is used to check the existence of trend. Among various nonparametric tests, the Spearman rank order correlation (SROC) test (McGhee, 1985) is recommended by the World Meteorological Organization (WMO, 1988) for detecting trend in flow volumes. Two other excellent nonparametric trend detection tests mostly preferred in hydrologic studies are Kendall's Rank Correlation test and Mann–Kendall test (Hirsch et al., 1982; Jayawardena and Lai, 1989; Gan, 1992; Zipper et al., 1998; Kumar, 2003; Machiwal and Jha, 2008, 2014a). Considering the need of adequate/multiple statistical tests for detecting hydrologic trends (Machiwal and Jha, 2008), trend in groundwater quality time series was detected by applying three nonparametric statistical tests, viz. Kendall's Rank Correlation test, Spearman Rank Order Correlation test and Mann–Kendall test. Theoretical details of these tests are available in many textbooks on statistical hydrology (e.g., Shahin et al., 1993; Kanji, 2001; Machiwal and Jha, 2012), and hence, to avoid excessive length of the paper, theoretical details of these tests are omitted here. The Mann–Kendall test is reported to be non-robust against presence of serial correlation in the time series (Yue et al., 2002; Shao and Li, 2011). Hence, presence/absence of serial correlation in time series of all groundwater quality parameters was tested by autocorrelation analysis prior to applying Mann–Kendall test. The trend tests were applied for exploring trends in groundwater quality parameters (Ca, Mg, Na, K, Fe, HCO_3, SO_4, Cl, NO_3, F, SiO_2, TDS, hardness, EC, and pH) using 11 years (1992–2002) data of 53 sites. The trend analysis was performed by developing spreadsheet programs in MS-Excel.

Both positive and negative trends in all groundwater quality parameters were quantified by using Sen's slope estimation method (Sen, 1968), which is an extension of the procedure developed by Theil (1950). Sen's slope (β), later extended by Hirsch et al. (1982), is a useful index to quantify monotone trend in the water quality time series of equally spaced data (Hirsch et al., 1982; Gan, 1998). The slope is estimated by:

$$\beta_k = \text{Median}\left(\frac{x_{ik} - x_{jk}}{i - j}\right) \quad \text{for all } i < j \tag{2}$$

where β_k = slope between data points x_{ik} and x_{jk}; x_{ik} = data measurement at time i; x_{jk} = data measurement at time j; and j = time after time i; and k = site. The estimator β is defined as the median over all combination of record pairs for whole water quality dataset, and is resistant/robust to the extreme observations or outliers. The positive value of β connotes slope of the upward trend and negative value for the downward trend.

3.4. Developing groundwater quality index

Groundwater quality index (GQI) was developed by generating normalized difference index and rank of parameters using the approach proposed by Babiker et al. (2007). Firstly, normalized difference index (D_{ij}) for ith groundwater quality parameter and jth year was computed from following equation:

$$D_{ij} = (C_{oij} - C_{mij})/(C_{oij} + C_{mij}) \tag{3}$$

where C_o = observed concentration and C_m = maximum desirable limit of the concerned water quality parameter prescribed by WHO (2006).

The normalized difference index was converted to rank every parameter on 1–10 scale by following polynomial equation:

$$R_{ij} = 0.5 \times (D_{ij})^2 + 4.5(D_{ij}) + 5 \tag{4}$$

where R = rank of ith parameter during jth year.

Then, GQI_j for jth year was computed as follows:

$$GQI_j = 100 - \left[\sum_{i=1}^{N} (R_{ij}\,W_{ij})/N\right] \tag{5}$$

where W_{ij} = relative weight of the parameter, which corresponds to mean rating value of each rank, and N = total number of parameters used in developing GQI.

Moreover, trends in the computed GQI values of 53 sites are detected by using Mann–Kendall test and magnitude of trends is quantified by Sen's slope method.

3.5. Principal component analysis

Principal component analysis (PCA) is one of the most important statistical methods for the interpretation of groundwater chemistry (Dunteman, 1989). The PCA is a multivariate statistical technique used to reduce multidimensional water quality datasets to lower dimensions for analysis (Dillon and Goldstein, 1984). Here, the purpose of applying PCA was to reduce the analytical data of each sampling site, which are inter-correlated to a smaller set of 'principal components' (PC) that are then interpretable. The PC group correlated concentrations together, which can be associated directly or indirectly with some specific contamination source or process. The PCA consists of two steps, data standardization and PC extraction. In this study, PCA was performed using 14 groundwater quality parameters (Ca, Mg, Na, K, Fe, HCO_3, SO_4, Cl, NO_3, F, SiO_2, TDS, EC, and pH) for the 11-year period (1992–2002) using STATISTICA software package. Prior to the PCA, the observed groundwater quality data were standardized by z-scale transformation.

The PCA takes data contained in a correlation matrix and rearranges them in a manner that better explains the structure of underlying system that produced the data. The starting point of PCA is to generate a new group of groundwater quality variables from the initial dataset (called PCs) that are a linear combination of original variables. The PCA starts by extracting eigenvalues and eigenvectors of the correlation matrix and then discarding the less important of these (Davis, 2002). Thereafter, eigenvectors are transformed to PCs of the dataset. First PC thus obtained explains the biggest part of variance, while following PCs explain repeatedly smaller parts of the variance. PC loadings show how the PCs characterize strong relationships (positive or negative) between groundwater quality variable and PC describing the variable. In order to determine the number of PCs to be retained, Kaiser Normalization Criterion (Kaiser, 1958) was used. The PCs, which best describe the variance of analyzed groundwater quality data (eigenvalue > 1) and can be reasonably interpreted (Harman, 1960), were accepted for further analysis. The measure of how well the variance of a particular groundwater quality parameter is described by a particular set of factors is known as 'communality' (Jackson, 1991). Number of variables retained in PC or communalities is obtained by squaring the elements in PC matrix and summing the total within each variable. Ideally, if a PCA is successful, number of PCs will be small, communalities are high (close to 1) and PCs will be readily interpretable in terms of particular sources or process (Dunteman, 1989).

3.6. Geostatistical modeling of factors scores

To estimate spatial distribution of the significant PC or factor score during 11-year period (1992–2002), GIS-based geostatistical modeling approach (kriging spatial interpolation technique) was adopted following its three steps. In first step, semivariance structure of factor scores was obtained by experimental semivariogram (Journel and Huijbregts, 1978):

$$\gamma(h) = \frac{1}{2N(h)} \sum_{i=1}^{N(h)} (z_{xi+h} - z_{xi})^2 \tag{6}$$

where $N(h)$ = number of data pairs at a separation distance h having an observed value of z_{xi}.

In second step, four most-widely used geostatistical models, viz. spherical, exponential, circular and Gaussian were fitted to experimental semivariograms of the significant factor score separately for 11 years by choosing appropriate model parameters (nugget, sill and range). Details of the geostatistical models can be found in literature (Isaaks and Srivastava, 1989; Kitanidis, 1997), which are omitted here to keep the paper within adequate length.

In third step, the best-fit geostatistical model was selected based on three goodness-of-fit criteria, i.e. root mean squared error (RMSE), correlation coefficient (r) and coefficient of determination (r^2); details of the goodness-of-fit criteria can be found in Machiwal and Jha (2014a). Geostatistical model, thus adjudged, to be the best-fit was used to determine spatial distribution of factor score in the GIS environment using ILWIS software (ILWIS, 2001).

4. Results and discussion

4.1. Spatio-temporal variations of groundwater quality parameters

Box and whisker plots depicting variation of 15 groundwater quality parameters (Ca, Mg, Na, K, Fe, HCO_3, SO_4, Cl, F, NO_3, hardness, EC, pH, TDS, and SiO_2) for 11-year period (1992–2002) are shown in Figs. 3(a–o) along with the desirable and permissible limits of parameters for drinking water prescribed by the World Health Organization, Geneva (WHO, 2006). It is seen from this figure that length of boxes and whiskers in case of bicarbonate, TDS, and hardness are relatively large in comparison to that for the remaining parameters, which indicate large spatial variations. Box and whisker plots of potassium and iron ions reveal the highest number of extremes among all groundwater quality parameters. It may be attributed to very low quantity of potassium ion and negligible amounts of iron generally available in groundwater at most sites over the study area.

It is discernible that the median values of calcium, magnesium, and bicarbonate fluctuate above or below their corresponding desirable limits. However, the median values of sodium, sulphate, chloride, nitrate, and pH always remain within their desirable limits (Figs. 3c, g–i, and o). On contrary, the median values of TDS, hardness, and EC are more than their desirable limits in all the years (Figs. 3l, m, and n). The upper whiskers of EC and TDS remain below their permissible limits, while the upper whiskers of hardness exceed the permissible limit in most years. Thus, hardness is the only parameter which exceeds its permissible limits for drinking water at most sites.

An important observation revealed from box and whisker plots of calcium, magnesium, potassium, iron, sulphate, fluoride, hardness, and EC is the highest concentrations of these parameters in two years, i.e. 1999 and 2000 (Figs. 3a, b, d, e, g, j, m, and n). In both the years, the study area received significantly less rainfall (43.4 and 40.0 cm, respectively), and hence, the highest median concentration values of those eight parameters are attributed to reduced recharge in 1999 and 2000 (because of occurrence of scanty rainfall during the years). This finding suggests that rainfall has control, up to certain extent, over groundwater quality of the hard-rock aquifer system.

4.2. Clusters of sampling sites according to source of groundwater quality

The HCA was performed on the standardized groundwater quality dataset (742 observations) by single linkage as amalgamation rule using Euclidean distance as similarity measure. Results of the HCA are shown by dendrogram in Fig. 4. The dendrogram rendered 53 sampling sites into two statistically significant clusters at $Dlink/Dmax \times 100 < 75\%$. The sites categorized into individual clusters behave similarly and/or have similar origin. Of the two clusters, the first cluster comprises 21 sampling sites and the second cluster contains 32 sites. Geographical location of all sampling sites according to their corresponding clusters over six geology classes in the study area is shown in Fig. 5, which reveals that the sites of Cluster I are mainly lying in the northeast and southern portions of the study area where gneiss type of geology dominates. On the other hand, the sites of Cluster II mostly appear in the western portion of the area with large area covered by phyllite–schist geology. In Cluster I, most sites (52% of the total sites) exist in the gneiss type of geology, while most sites (53% sites) of Cluster II fall in the phyllite–schist type of geology.

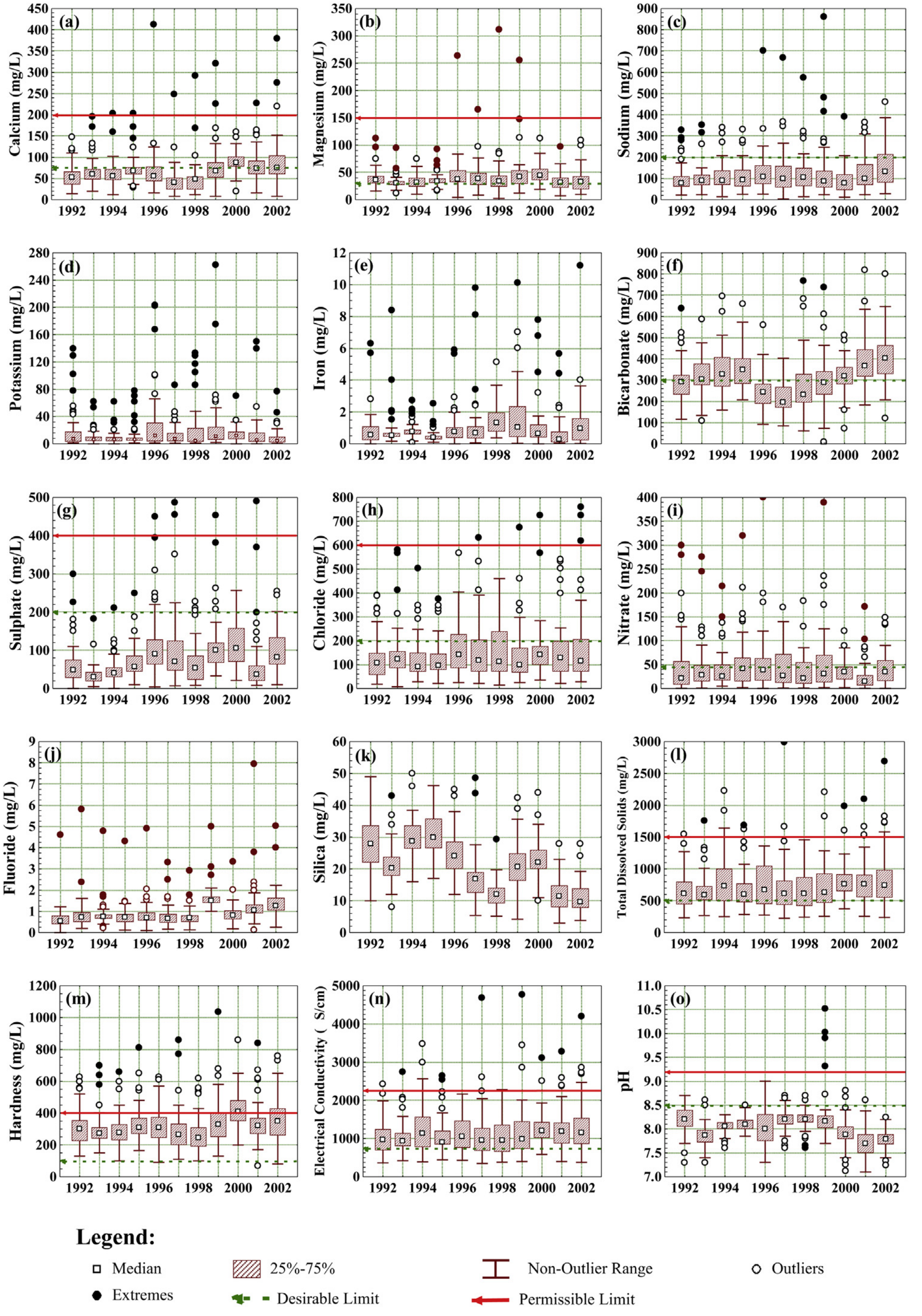

Fig. 3. Box–whisker plots of groundwater quality parameters.

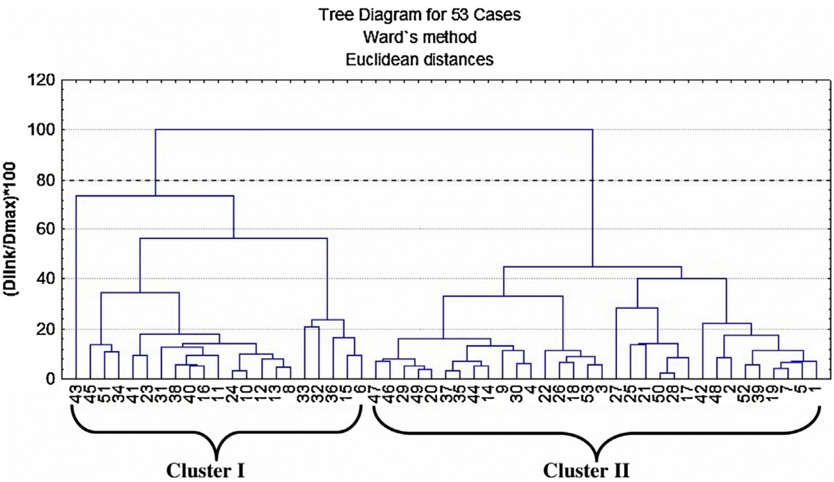

Fig. 4. Tree diagram showing two clusters of groundwater quality in the study area.

4.3. Trends in groundwater quality

Autoregressive (AR) functions/coefficients for all the groundwater quality parameter were determined for 53 sites up to a maximum lag of 3 years. The upper and lower limits for the critical AR values were computed using the equations given by Anderson (1942). Box–whisker plots of the AR components along with their critical limits for 15 groundwater quality parameters at 1-, 2- and 3-year time lags are shown in Figs. 6(a–c). It is clearly depicted that the groundwater quality time series are free from serial correlation at most sites [Figs. 6(a-c)]. In addition, it is worth mentioning that one recent study (i.e., Sang et al., 2014) does not advocate eliminating the effect of serial correlation by pre-whitening approach as it is clearly demonstrated that the pre-whitening cannot really improve trend identification by the Mann–Kendall test, but cause wrong results sometimes. Thus, considering the above facts and findings of this study as well as those reported in the literature, the presence of serial correlation at a couple of sites in this study should not influence the results of the Mann–Kendall test significantly.

Results of three trend tests indicating sites with increasing, decreasing and neutral trends in groundwater quality parameters at 5% significance level are shown in Figs. 7(a–o). It is revealed that

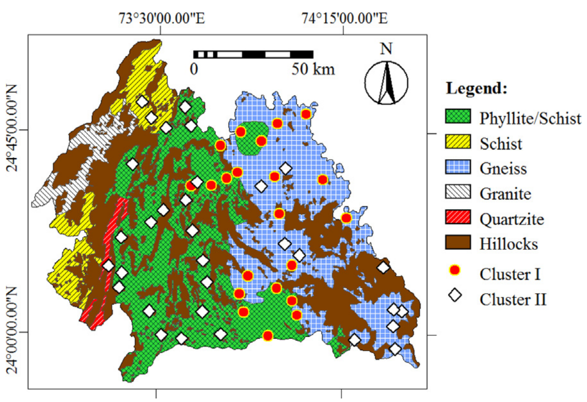

Fig. 5. Distribution of groundwater sampling sites characterized by the two clusters in different geologic formations of the study area.

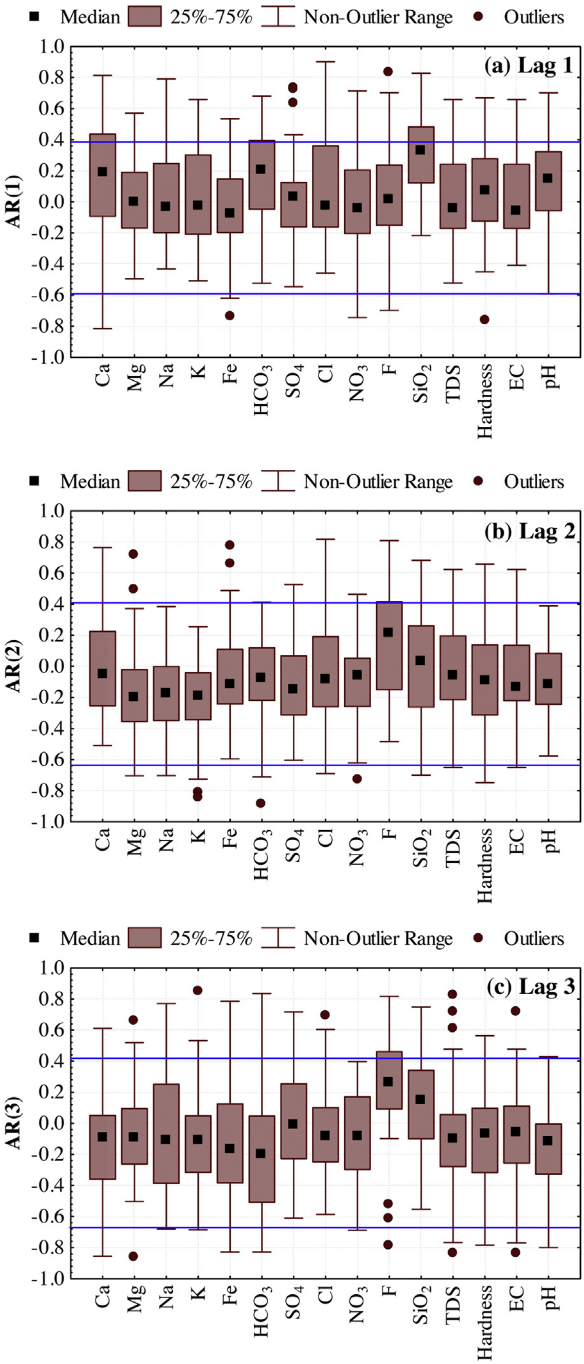

Fig. 6. Box and whisker plots of autoregressive (AR) coefficients for groundwater quality parameters at time lags of: (a) 1 year, (b) 2 years, and (c) 3 years. Horizontal lines show upper and lower limits of critical values of AR coefficients.

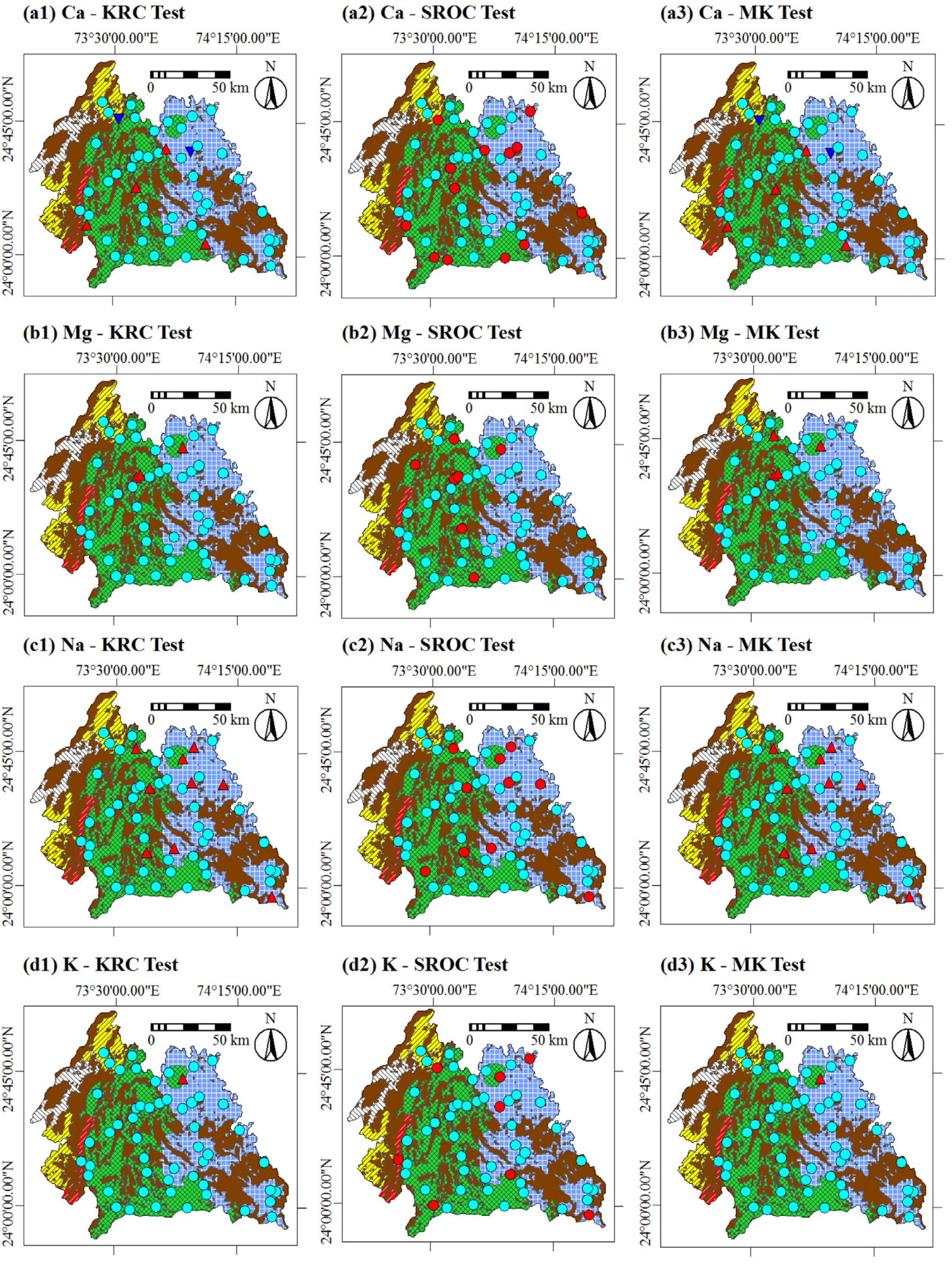

Fig. 7. Trends in groundwater quality parameters for different geologic formations based on the three trend tests (KRC – Kendall Rank Correlation; SROC – Spearman Rank Order Correlation; MK – Mann–Kendall).

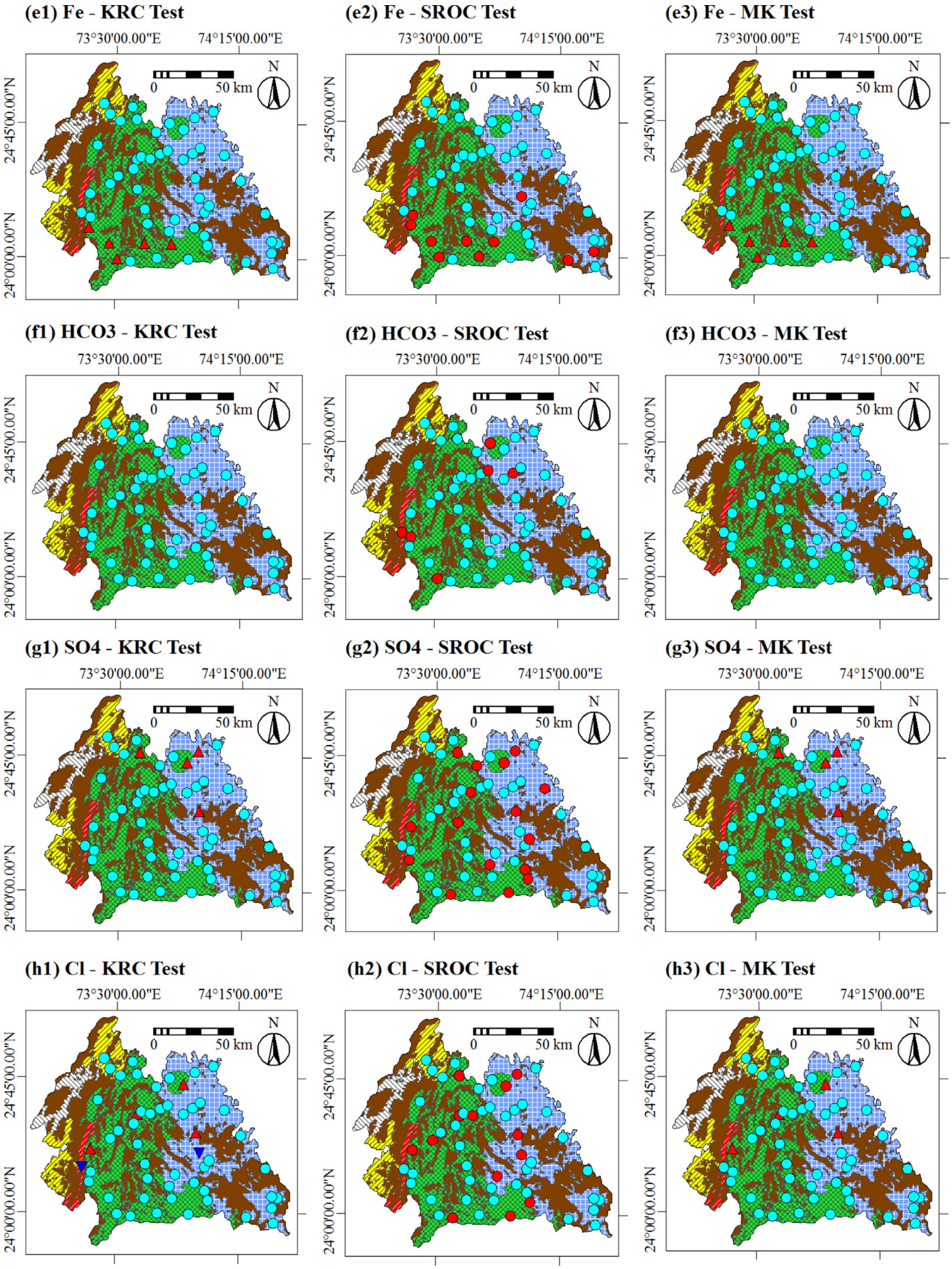

Fig. 7. (*Continued*)

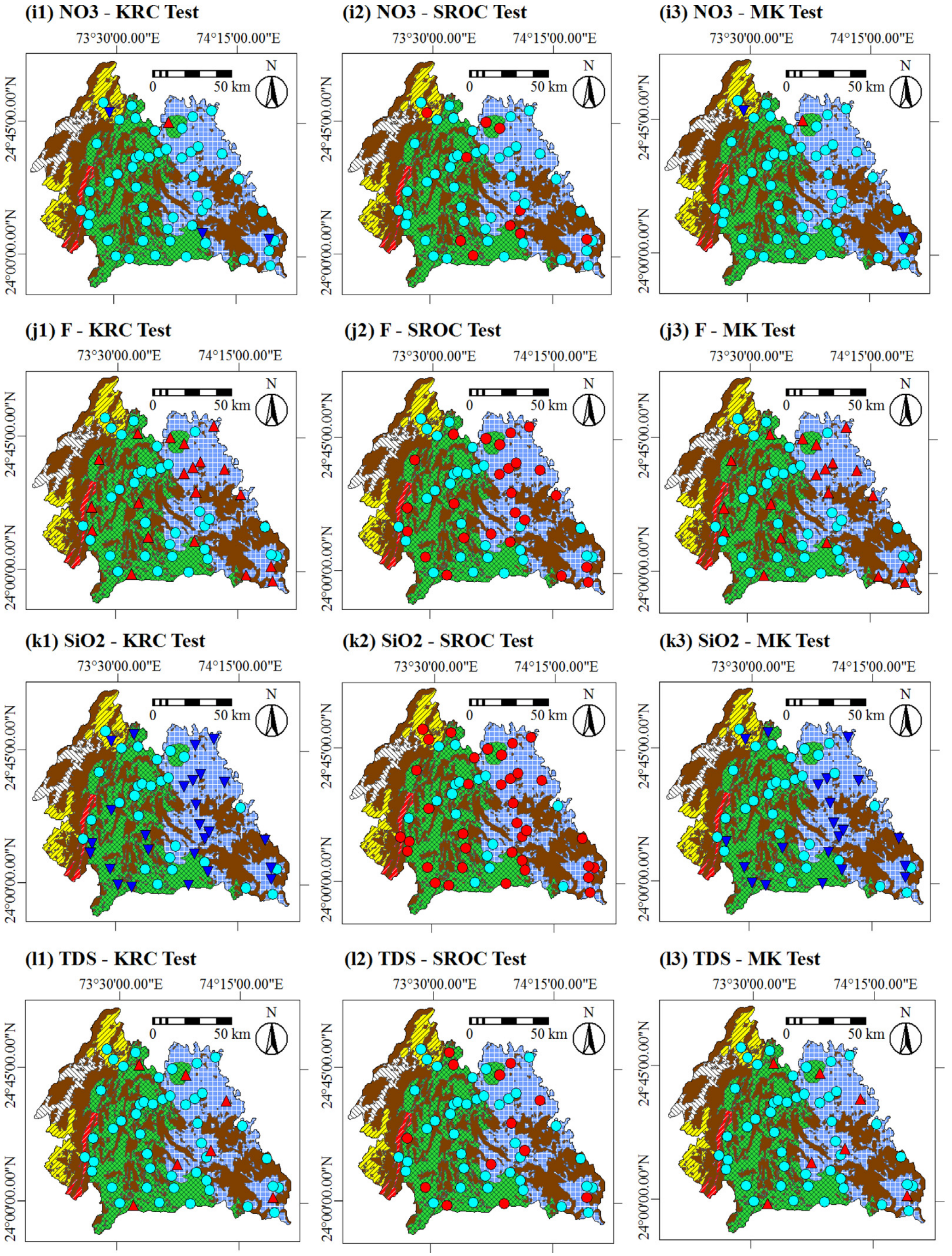

Fig. 7. (*Continued*)

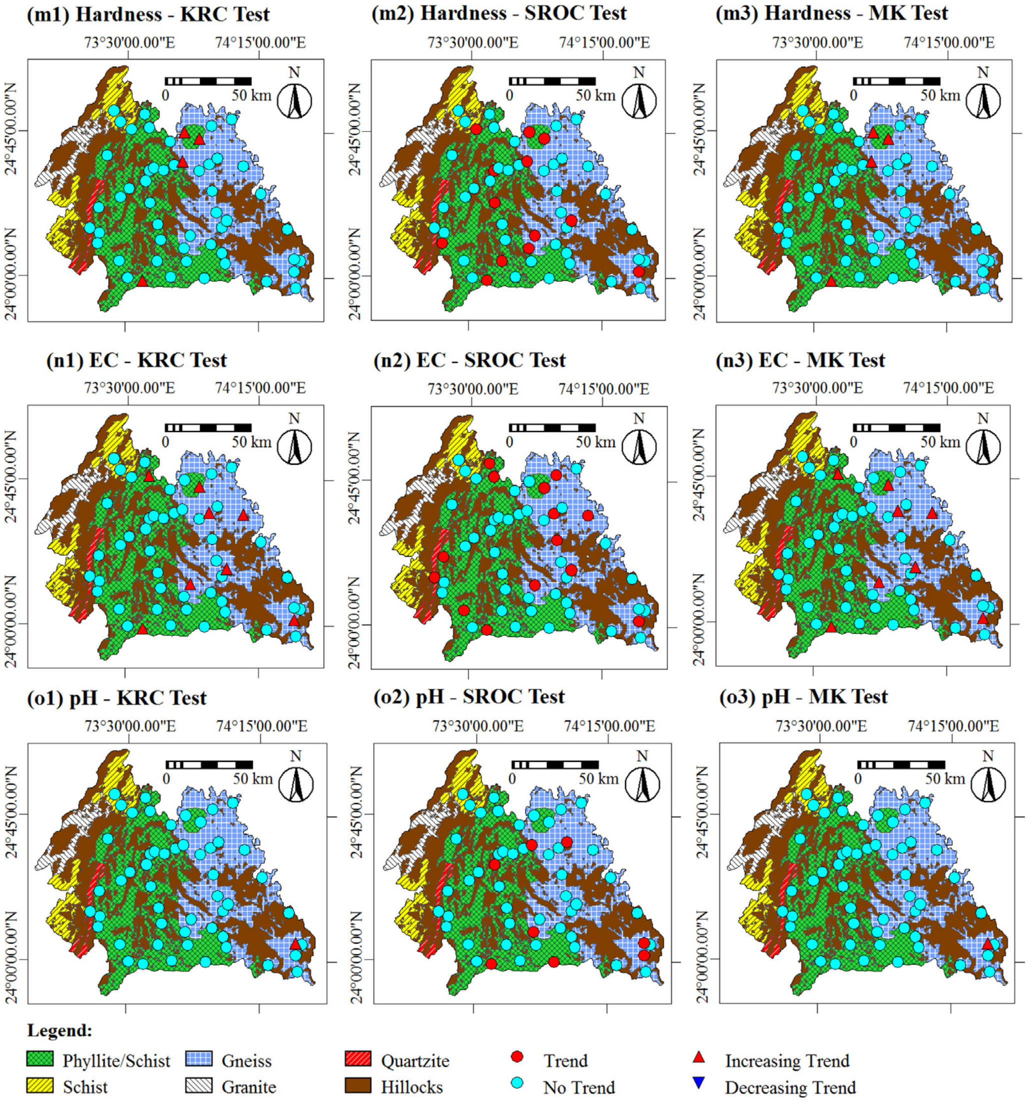

Fig. 7. (*Continued*).

sites with the statistically significant increasing/decreasing or neutral trends of all groundwater quality parameters are almost similar at $\alpha = 0.05$ for the Kendall's Rank Correlation test and the Mann–Kendall test. Both of these trend tests are advantageous over others as these indicate nature (positive/negative) of the identified trend. However, the Spearman Rank Order Correlation test without indicating kind of trend results in relatively large number of sites with significant trends at $\alpha = 0.05$ in comparison to earlier two tests.

It can be seen from Figs. 7(a–o) that the significantly increasing trends (p-value < 0.05) of groundwater quality parameters are at more than 10% sites for four parameters (sodium, fluoride, TDS, and EC). Six groundwater quality parameters (calcium, magnesium, iron, sulphate, chloride, and hardness) revealed presence of the significantly increasing trends at 5–10% of total sites in the area. The significant increasing trends of rest five groundwater quality parameters (potassium, bicarbonate, nitrate,

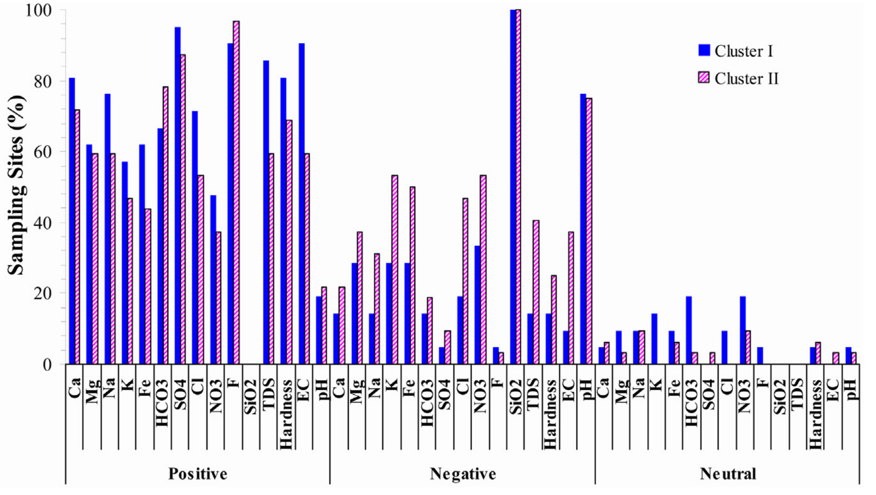

Fig. 8. Percentage of positive, negative and neutral trends of groundwater quality parameters in the two identified clusters.

silica, and pH) are at less than 5% sites. The most sites (38%) indicated the significant trend of fluoride concentrations, followed by sodium at 17% sites, EC at 15% sites and TDS at 13% sites. Hence, four parameters (fluoride, sodium, EC and TDS) indicated the significant increasing trends in their concentration over the study area.

As far as the negative trends of groundwater quality parameters are concerned, 12 parameters (magnesium, sodium, potassium, iron, bicarbonate, sulphate, chloride, fluoride, TDS, hardness, EC and pH) could not reveal statistically significant (p-value < 0.05) trends at a single site (Figs. 7(a–o)). Of rest three parameters, silica concentration is significantly decreasing at 40% of the sites followed by calcium (4% sites) and nitrate (4% sites).

The trend tests suggest that sites indicating the significant trends in groundwater quality variables appear all over the study area. The northeast portion is a dense residential area and southern portion is an intensely cultivated area. Hence, in the northeast portion, the significant increasing trends in groundwater quality parameters may be attributed to the unsystematic and uncontrolled groundwater withdrawals for domestic uses. Likewise, the significant groundwater quality trends in the southern portion may be due to frequent and uncontrolled groundwater withdrawals for irrigation during pre-monsoon season when surface water may not be adequate to meet the crop water requirement and irrigation demand is very high in the command areas. Thus, the significant increasing trends in groundwater quality parameters in the northeast and southern portions are due to anthropogenic factors. Besides, the non-significant and neutral trends in rest of the area could be attributed to the natural processes/factors.

4.4. Trends affected by contamination sources

Geology plays a major role in dynamics of groundwater levels in the study area (Machiwal and Jha, 2014a). Also, groundwater levels have significant effects on groundwater quality as groundwater quality parameters get diluted during post-rainy season due to recharge occurring from rainwater. In this study, the Mann–Kendall test detected nature (increasing/decreasing) of trends in two major clusters. Furthermore, it is discussed that groundwater quality of Cluster I is mainly defined by anthropogenic sources while groundwater quality of Cluster II is described by natural factors/processes. Percentage of sites with positive (increasing), negative (decreasing) and no (neutral) trends for 15 groundwater quality parameters are shown in Fig. 8, while number of sites with significant positive and negative trends at $\alpha = 0.01$, 0.05 and 0.10 are shown in Table 1.

Table 1
Cases of significant Mann–Kendall trends in two identified clusters at three significance levels.

Cluster	Nature of trend	Number of cases with significant trends														
		Ca	Mg	Na	K	Fe	HCO_3	SO_4	Cl	NO_3	F	SiO_2	TDS	Hardness	EC	pH
(a) $\alpha = 0.01$																
Cluster I	Positive	2	0	2	0	0	0	0	0	0	2	0	0	0	1	0
	Negative	0	0	0	0	0	0	0	0	0	0	2	0	0	0	0
Cluster II	Positive	0	0	0	0	2	0	0	1	0	4	0	0	0	0	0
	Negative	0	0	0	0	0	0	0	0	0	0	5	0	0	0	0
(b) $\alpha = 0.05$																
Cluster I	Positive	2	2	6	1	1	0	3	3	1	8	0	3	3	4	0
	Negative	1	0	0	0	0	0	0	0	0	0	8	0	0	0	0
Cluster II	Positive	2	2	3	0	4	0	1	1	0	12	0	4	1	4	1
	Negative	1	0	0	0	0	0	0	0	2	0	13	0	0	0	0
(c) $\alpha = 0.10$																
Cluster I	Positive	3	2	6	2	1	2	7	6	3	9	0	5	5	6	0
	Negative	1	0	0	0	0	0	0	0	2	0	12	0	0	0	3
Cluster II	Positive	6	3	3	0	7	1	6	4	0	15	0	6	4	6	1
	Negative	1	1	0	2	3	0	0	2	3	0	23	1	0	1	0

In Cluster I, positive trend indicating increase in calcium, magnesium, sodium, potassium, iron, bicarbonate, sulphate, chloride, nitrate, fluoride, silica, TDS, hardness, EC and pH is observed in 17 (81%), 13 (62%), 16 (76%), 12 (57%), 13 (62%), 14 (67%), 20 (95%), 15 (71%), 10 (48%), 19 (90%), 0 (0%), 18 (86%), 17 (81%), 19 (90%) and 4 (19%), respectively of the total 21 sites. Out of these positive trends, 2 (10%), 2 (10%) and 3 (14%) sites for calcium, 2 (10%), 6 (29%) and 6 (29%) sites for sodium, 2 (10%), 8 (38%) and 9 (43%) sites for fluoride, and 1 (5%), 4 (19%) and 6 (29%) sites for EC experienced significant rise in concentration of parameters at $\alpha = 0.01$, 0.05 and 0.10, respectively. Besides, the significant increase in concentration at 2 (10%) and 2 (10%) sites for magnesium, 1 (5%) and 2 (10%) for potassium, 1 (5%) and 1 (5%) for iron, 3 (14%) and 7 (33%) for sulphate, 3 (14%) and 6 (29%) for chloride, 1 (5%) and 3 (14%) for nitrate, and 3 (14%) and 5 (24%) for both TDS and hardness is observed at $\alpha = 0.05$ and 0.10, respectively. Among rest of parameters, the significant increase in bicarbonate could be observed at 2 (10%) sites at $\alpha = 0.10$ but silica and pH did not show significant incline in their values at a single site. On the contrary, negative trend indicating decrease in parameter concentrations is observed at 3 (14%), 6 (29%), 3 (14%), 6 (29%), 6 (29%), 3 (14%), 1 (5%), 4 (19%), 7 (33%), 1 (5%), 21 (100%), 3 (14%), 3 (14%), 2 (10%) and 16 (76%) sites for calcium, magnesium, sodium, potassium, iron, bicarbonate, sulphate, chloride, nitrate, fluoride, silica, TDS, hardness, EC and pH, respectively. However, the significant decline in parameter concentration is observed at 2 (10%), 8 (38%) and 12 (57%) for silica at $\alpha = 0.01$, 0.05 and 0.10. Also, the significant decrease in calcium at single site at $\alpha = 0.05$ and 0.10, and at 2 (10%) and 3 (14%) sites for nitrate and pH at $\alpha = 0.10$, respectively, is observed.

In Cluster II, the rise in concentration of calcium, magnesium, sodium, potassium, iron, bicarbonate, sulphate, chloride, nitrate, fluoride, silica, TDS, hardness, EC and pH is revealed at 23 (72%), 19 (59%), 19 (59%), 15 (47%), 14 (44%), 25 (78%), 28 (88%), 17 (53%), 12 (38%), 31 (97%), 0 (0%), 19 (59%), 22 (69%), 19 (59%) and 7 (22%) sites, respectively of the total 32 sites in this cluster. However, the significant increase is detected at 2 (6%), 4 (13%) and 7 (22%) sites for iron, 1 (3%), 1 (3%) and 4 (13%) for chloride and 4 (13%), 12 (38%) and 15 (47%) for fluoride at the significance levels $\alpha = 0.01$, 0.05 and 0.10, respectively. Also, the significant inclining trend is found to be present for calcium, magnesium, sodium, sulphate, TDS, hardness, EC and pH at less than 4 (13%) sites at significance levels $\alpha = 0.05$ and 0.10. In contrast, the declining trend in concentrations of calcium, magnesium, sodium, potassium, iron, bicarbonate, sulphate, chloride, nitrate, fluoride, silica, TDS, hardness, EC and pH exist at 7 (22%), 12 (38%), 10 (31%), 17 (53%), 16 (50%), 6 (19%), 3 (9%), 15 (47%), 17 (53%), 1 (3%), 32 (100%), 13 (41%), 8 (25%), 12 (38%) and 24 (75%) sites, respectively. Among all the parameters, silica showed a significant decline at 5 (16%), 13 (41%) and 23 (72%) sites at the significance levels $\alpha = 0.01$, 0.05 and 0.10, respectively. Among the remaining parameters, calcium and nitrate revealed significant decline in 2 (6%) or less sites at $\alpha = 0.05$ and 0.10, and magnesium, potassium, iron, chloride, TDS and EC showed significant decrease in 3 (9%) or less number of sites at $\alpha = 0.10$.

Based on the above discussion, trends in concentration of all groundwater quality parameters are depicted in both Clusters I and II. It is seen from Fig. 8 that positive/rising trends are multi-fold than the negative/declining trends in each cluster indicating an overall rise in parameter concentration, which suggests degradation of groundwater quality in both the clusters. On contrary to this, 100% sampling sites experienced drop in silica concentration in both the clusters over a time period of 11-year. The decreasing trends of silica can be well-understood by relating it to the significantly declining groundwater level trends in the area as reported by Machiwal and Jha (2014a). The silica concentration is directly proportional to residence time of water underground and relatively low silica content implies less water-rock interaction (Hem, 1986; Khan and Umar, 2010). Perhaps, over the years, large quantities of the groundwater in shallow hard-rock aquifer system has been replaced due to overexploitation of groundwater with recent freshwater recharge and occurrence of rainfall recharge, which has relatively low silica content (Khan and Umar, 2010). While pH experienced negative trends at more sites (57 and 53% higher sites for Clusters I and II, respectively) compared to those with positive trends. The neutral (absence of) trends in both the clusters are generally less than 20 and 10% of the total sites in Clusters I and II, respectively. Fig. 8 also reveals that the percentage of increasing trends are more dominating in Cluster I (48–95%) in comparison to Cluster II (38–88%) for almost all parameters except for four parameters, i.e. silica, bicarbonate, fluoride and pH. On the other side, the percentage of declining trends is detected at relatively more sites in Cluster II (9–53%) than in Cluster I (5–33%). From this discussion, it is very clear that groundwater quality of Cluster II (affected by natural factors/processes)

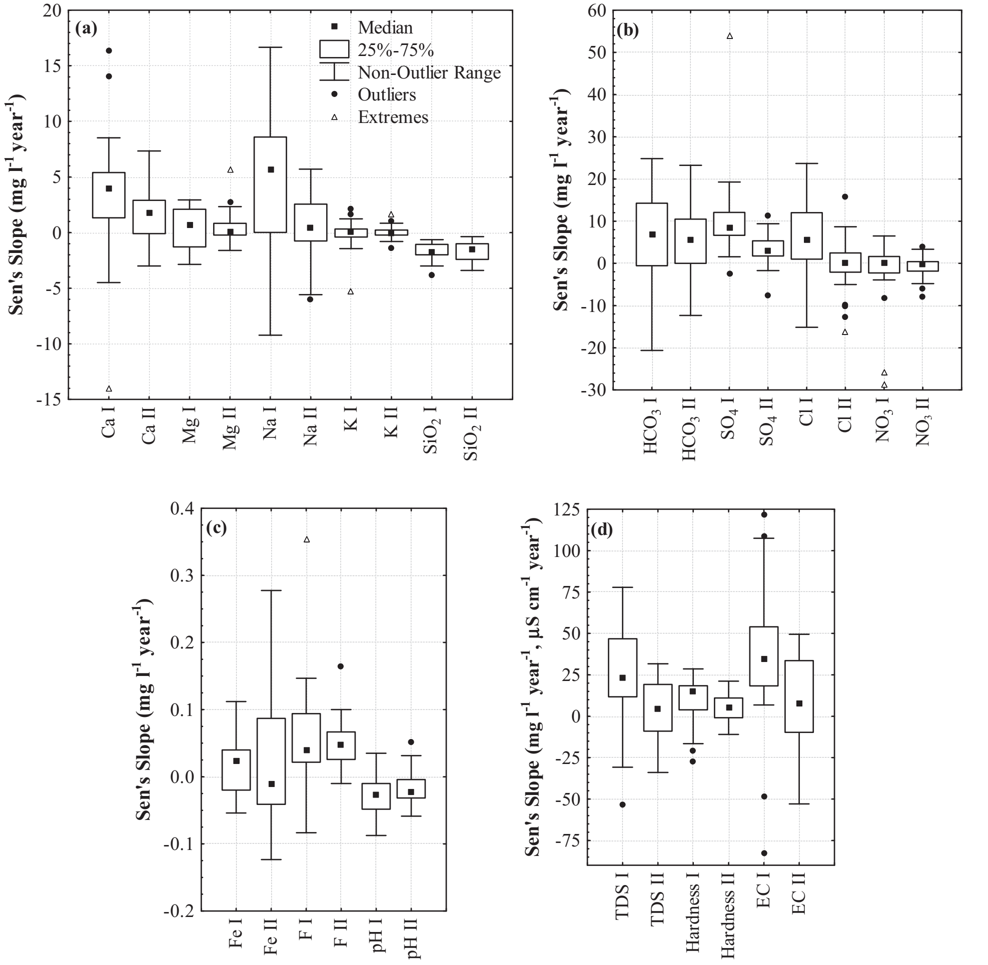

Fig. 9. Box and whisker plots of Sen's slope estimates for the groundwater quality parameters in the two identified clusters.

is comparatively better than the quality of Cluster I (affected by anthropogenic factors/sources). It is also seen that better groundwater quality of phyllite–schist geology may be attributed, among other factors, to relatively high specific yield of the phyllite–schist formation compared to other geologic formations in the area. Hence, the portion mainly underlying the phyllite–schist geology induces more recharge to the aquifer and hence enhanced groundwater storage, which causes dilution effect on the concentration of most groundwater quality parameters.

4.5. *Quantifying trend*

The magnitudes of trend for all groundwater quality parameters at 53 sites were quantified by Sen's slope method and are depicted by box and whisker plots in Figs. 9(a–d). The median of the trend magnitudes is above zero for all parameters, except for potassium that declines at a mean rate of 0.11 mg l^{-1} $year^{-1}$ in Cluster I, chloride receding at rate of 0.18 mg l^{-1} $year^{-1}$ in Cluster II, and nitrate, silica and pH in both the clusters. The nitrate, silica and pH are declining at a mean rate of 2.38, 1.71 mg l^{-1} $year^{-1}$, and 0.03 in Cluster I and 0.70, 1.64 mg l^{-1} $year^{-1}$ and 0.02 in Cluster II, respectively. In Cluster I, the concentration of calcium, magnesium, sodium, iron, bicarbonate, sulphate, chloride, fluoride, TDS, hardness and EC increases at mean rates of 3.35, 0.46, 5.08, 0.01, 6.49, 10.95, 6.02, 0.06, 25.54, 9.95 mg l^{-1} year^{-1} and 39.46 μS cm^{-1} year^{-1}, respectively. On the other hand, in Cluster II, the concentration of calcium, magnesium, sodium, potassium, iron, bicarbonate, sulphate, fluoride, TDS, hardness and EC rise at a mean rate of 1.55, 0.38, 0.81, 0.03, 0.03, 4.96, 3.43, 0.05, 4.34, 5.00 mg l^{-1} year^{-1} and 8.84 μS cm^{-1} year^{-1}, respectively. It is apparent that the mean and median rates of rising trends in parameter concentrations (shown by square within the box) is generally high in the sites of Cluster I as compared to the sites in Cluster II for all groundwater quality parameters, except for silica, fluoride and pH (Figs. 9(a-d)). This finding clarifies that groundwater contamination at the sites of Cluster I is increasing because of continuously increasing influence of anthropogenic sources/factors due to growing population and lowering groundwater levels. The interquartile range for box and whisker plots of sodium, bicarbonate, sulphate, chloride, TDS, hardness and EC is relatively high compared to other parameters indicating high spatial variability of trend magnitudes, which is also confirmed from relatively high standard deviation values as 6.75, 11.05, 11.02, 10.26, 33.32, 14.90 mg l^{-1} year^{-1} and 49.03 μS cm^{-1} year^{-1}, respectively for these six parameters over the study area.

4.6. Groundwater quality index

The groundwater quality index maps for 11 years (1992–2002) were developed using spatial maps of groundwater quality parameters in GIS platform as shown in Fig. 10. This figure reveals that spatial and temporal variations of groundwater quality exist in the area. However, patterns in spatial distribution of groundwater quality can also be seen in the area. In general, groundwater in western, northwest and southeast portions is of high quality in most of the years. On the other hand, groundwater quality in southern, eastern and northeast portions is of relatively poor. The poor quality of groundwater in southern portion is due to contamination occurring from chemical fertilizers used in agricultural fields. The southern portion has a canal network for irrigating the crops, and hence, poor quality of groundwater may be most-likely due to deep percolation of irrigation water along with chemical fertilizers. High pollutant input from chemical fertilizers in the south portion enhances percolation rate, and vadose zone may not attenuate contaminant adequately. The poor quality of groundwater in northeast portion may be attributed to contamination caused due to urban pollutants generated from densely populated area, which are drained by two rivers (Berach and Ahar rivers). The rivers, draining pollutants, transport a major fraction of contaminated water to the underlying aquifer system through recharge process. Thus, it is evident that anthropogenic factors are playing a major role in contaminating groundwater resources in the study area.

The GQI was computed for 21 sites of Cluster I and 32 sites for Cluster II and is shown by box and whisker plots in Fig. 11. It is seen that mean value of GQI for the first cluster ranges between 69 and 76, while its value for the second cluster varies from 73 to 78 over 11-year period. In a year, the median value of GQI for Cluster I (indicated by square symbol within box in Fig. 11) always remains lower than that for Cluster II in the same year suggesting inferior quality of groundwater over sites of Cluster I being polluted due to anthropogenic sources/factors.

The positive trends in GQI revealing improved quality of groundwater are found to be at more sites in Cluster II (16% sites) compared to sites in Cluster I (10% sites). On the contrary, 90 and 81% of total sites in Cluster I and II, respectively experienced the negative trends indicating degradation of groundwater quality. However, the significantly deteriorating groundwater quality trends are observed at 33 and 22% sites ($p < 0.05$) in Clusters I and II, respectively (Fig. 11). According to the Sen's slope estimations, GQI in Cluster I is decaying at a mean rate of 0.486, which is about 69% higher than the mean dwindling rate of GQI (0.288) for Cluster II. However, its dispersion over the space is almost stable for the two clusters as the standard deviation is 0.283 and 0.285 for both the clusters. The above discussion clearly depicts the effect of anthropogenic sources and/or factors in polluting groundwater resources and decreased GQI values mainly over the sites of Cluster I in the area.

Moreover, Fig. 11 depicts that GQI in both the clusters is the lowest in three years (1999, 2000 and 2002) indicating relatively poor quality of groundwater compared to the rest of the years. The

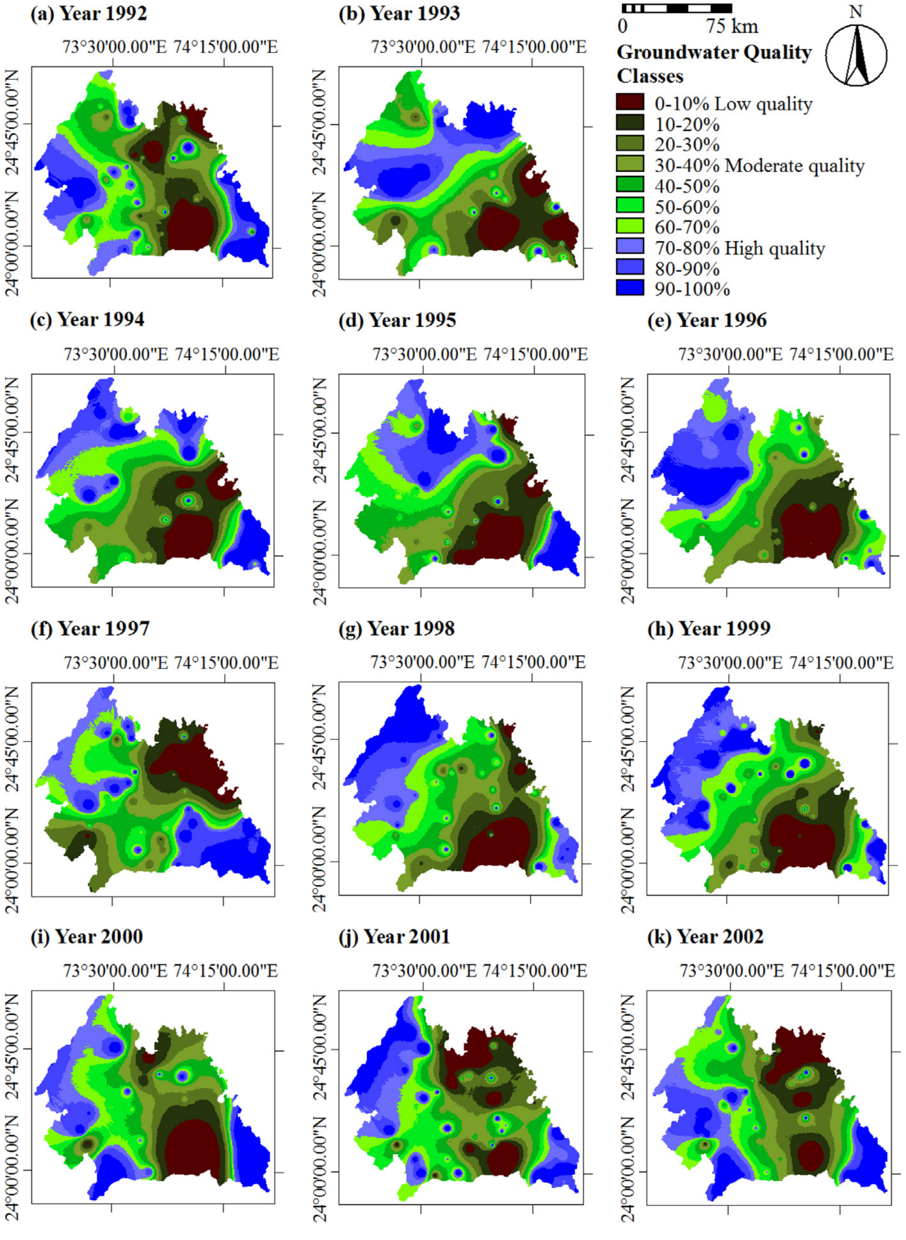

Fig. 10. Groundwater quality index map of the study area for the 11-year (1992–2002) period.

mean annual rainfall in years 1999, 2000 and 2002 was also the lowermost (43.4, 40.0 and 38.8 cm, respectively) in the area for 11-year period during 1992–2002 as is seen from box and whisker plots (Fig. 12). Thus, it is clearly revealed that the rainfall strongly influences groundwater quality of the underlying hard-rock aquifer system. This finding confirms that the rainfall has certain control on the chemistry of groundwater in the study area.

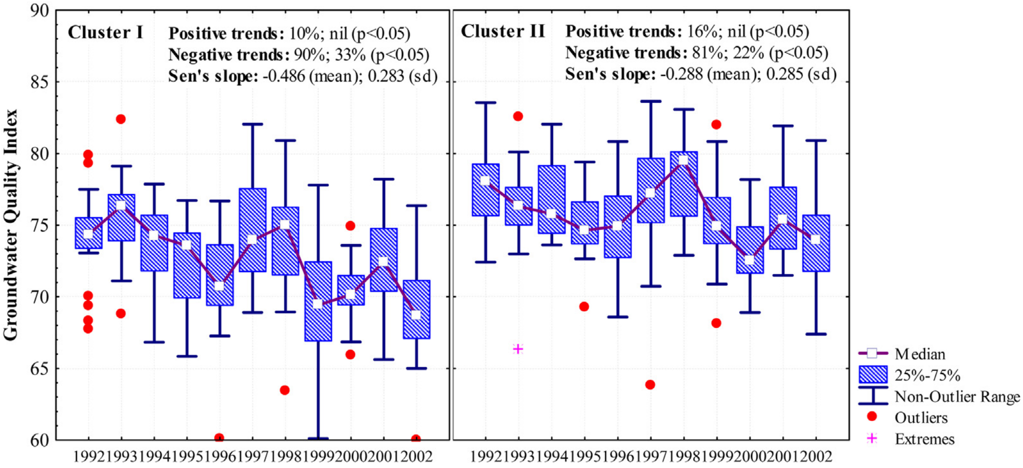

Fig. 11. Box–whisker plots of groundwater quality index in two clusters during 1992–2002.

4.7. *Principal factors governing geochemical processes*

In this study, the PCA was employed to identify parameters influencing geochemical processes in the aquifer system. The PC loadings were sorted according to the criteria of Liu et al. (2003), i.e., strong, moderate, and weak, corresponding to the absolute loading values of more than 0.75, 0.75–0.50 and 0.50–0.30, respectively. The PCA results rendered five significant PCs (eigenvalue > 1) in years 1992 and 1994, three significant PCs in the year 1998, and four significant PCs in remaining years (Table 2). The significant PCs explained 75–80% of the total variance of individual year's datasets.

The results revealed that in 1992, PC I is characterized by strong negative PC loadings of magnesium, sodium, sulphate, chloride, TDS, EC, moderate negative loading of nitrate, moderate positive loading of pH, and weak negative loadings of calcium, potassium, iron, bicarbonate and silica (Table 2). The PC II is characterized by strong negative loading of sodium and pH, and moderate positive loading of calcium. It is apparent that parameters characterizing the significant PCs are changing for 11 years and PC I accounts for 35–50% variance in the data. The PC I in most years is characterized by the

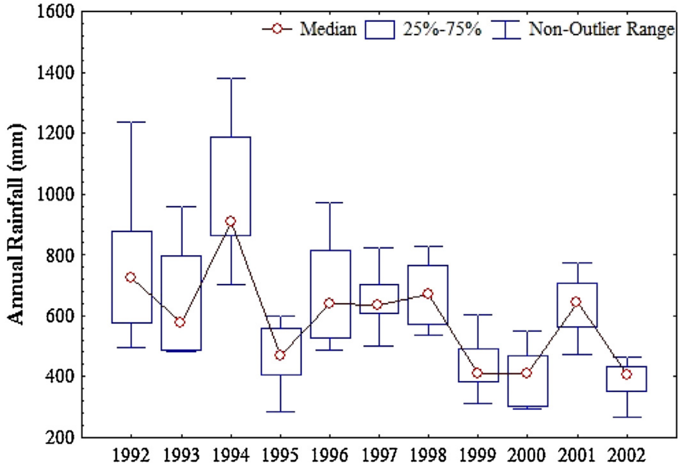

Fig. 12. Box–whisker plots of mean annual rainfall for the 11-year (1992–2002) period.

Table 2
Grouping of chemical variables according to the nature of principal component loadings.

Year	Nature of loading	Principal components				
		I	II	III	IV	V
1992	Strong	**Mg, Na, SO_4, Cl, TDS, EC**	-	–	–	–
	Moderate	**NO_3**, pH	**Na, pH**, Ca	**Ca, HCO_3**	K, HCO_3	**Fe**
	Weak	**Ca, K, Fe, HCO_3, SiO_2**	**Cl, F,** Fe, SiO_2	**F,** K, SiO_2	SiO_2, pH	**K**, NO_3, SiO_2
1993	Strong	**Mg, Na, K, SO_4, NO_3, EC, TDS**	–	–	–	–
	Moderate	**Ca, HCO_3, Cl**	**Na, F, pH,** Ca	**Cl**	**HCO_3**	–
	Weak	**SiO_2**	**Fe,** NO_3, SiO_2	**Ca,** Mg, K, NO_3, SiO_2, pH	**Fe, F,** Cl, SiO_2	–
1994	Strong	**Mg, Na, K, SO_4, NO_3**	TDS, EC	–	–	–
	Moderate	**HCO_3, Cl**	–	HCO_3, F, pH	pH	**Fe, SiO_2**
	Weak	**Ca, F, SiO_2, TDS, EC,** Fe	**Ca, NO_3, SiO_2,** F, pH	**Cl, TDS, EC**	**Na, F,** NO_3	Ca
1995	Strong	**Mg, Na, K, SO_4, Cl, TDS, EC**	NO_3	–	–	–
	Moderate	**Fe, HCO_3, F, pH**	**pH,** Fe	Ca	HCO_3	–
	Weak	**NO_3**	**F,** Ca, Mg, SiO_2	**F, SiO_2,** Cl	Ca, F	–
1996	Strong	**Ca, Mg, Na, SO_4, Cl, TDS, EC**	**F**	–	–	–
	Moderate	–	**HCO_3**	**HCO_3,** pH	K, SiO_2	–
	Weak	**K, NO_3, SiO_2**	**pH,** NO_3	**Fe,** K	–	–
1997	Strong	**Mg, Na, K, SO_4, Cl, NO_3, TDS, EC**	**pH,** Ca	–	–	–
	Moderate	–	**F,** HCO_3	HCO_3, F	**Fe,** SiO_2	–
	Weak	**SiO_2**	–	**Fe**	**F**	–
1998	Strong	**Ca, Mg, Na, SO_4, Cl, NO_3, TDS, EC**	Fe	–	–	–
	Moderate	–	**K, SiO_2**	**HCO_3**	–	–
	Weak	**K,** pH	**HCO_3, F**	**K,** F, SiO_2, pH	–	–
1999	Strong	**Ca, Mg, Na, SO_4, Cl, TDS, EC**	HCO_3, F	–	**Fe**	–
	Moderate	**K, NO_3, SiO_2**	–	pH	K	–
	Weak	pH	**Fe, NO_3,** Na	**K, NO_3,** HCO_3	**pH**	–
2000	Strong	**Ca, SO_4, Cl, TDS, EC**	–	–	–	–
	Moderate	**Mg, K, Na**	**Na, HCO_3, F,** SiO_2	pH	**HCO_3, NO_3**	–
	Weak	pH	K, NO_3	**Na, Fe, Cl,** Mg, K, HCO_3, F, SiO_2	**Mg,** pH	–
2001	Strong	**Na, SO_4, Cl, TDS, EC**	**pH**	HCO_3	–	–
	Moderate	**Ca, Mg**	NO_3	**Fe**	**F,** K	–
	Weak	**K, HCO_3, NO_3**	**Na, SO_4, F,** Ca, Mg	Mg, K, F	**HCO_3**, SO4, SiO_2, pH	–
2002	Strong	**Ca, Na, Cl, NO_3, TDS, EC**	**F**	–	–	–
	Moderate	**Mg, K, Fe, SO_4**	**HCO_3, pH**	**Mg, SiO_2**	**Fe**, SO_4	**F**
	Weak	–	**Na**, Ca, SiO_2	**HCO_3**, Fe, pH	**NO_3**	**K, SiO_2,** Mg

Note: Chemical variables in boldface indicate negative principal component loadings; Chemical variables without boldface indicate positive principal component loadings.

strong negative loadings of magnesium, sodium, potassium, sulphate, chloride, TDS, EC and nitrate (Table 2). Strong loadings of sodium, potassium, and magnesium attributed the first PC to ion exchange processes in the aquifer system and contribution of natural weathering of rock minerals as reported by earlier researchers also (Drever, 1997; Kumar et al., 2006, Subba Rao et al., 2006). Association of strong loadings of EC, chloride, and sulphate with first PC indicates contribution from precipitation and deposition from dust material (Kumar et al., 2006). The concentration of nitrate in groundwater is obviously related to the influence of anthropogenic sources (i.e., irrigation return flow, fertilizers, and sewage wastes).

It was revealed that PC II accounts for 11–17% of the variance in the data for 11 years. The concentrations of pH, fluoride and bicarbonate show moderate to strong negative loadings on the second PC in most of the years (Table 2). The concentrations of bicarbonate and pH in groundwater are results of the reaction of soil CO_2 with the dissolution of silicate minerals. Generally, the mineral dissolution during water-soil and water-rock interactions depends on amount of CO_2 which originates from H_2CO_3. Thus, mineral saturation in groundwater depends on the amount of partial pressure of CO_2, calcium, CO_2, bicarbonate and H_2CO_3. A decrease in the partial pressure of CO_2 and H_2CO_3 during the outgassing of CO_2 results in an increase of bicarbonate and pH levels (Ozler, 2003; Subba Rao et al., 2006). The concentration of fluoride in groundwater could be by the leaching of fluoride containing minerals, ion exchange of fluoride and OH in the clay minerals, higher rate of evapotranspiration, longer residence of water in the aquifer zone, intensive and long-term irrigation practice, and heavy use of fertilizers.

It is also evident from Table 2 that PC III accounts for 9–14% of the variance in the data over 11 years, PC IV accounts for 7–9% of the variance and PC V accounts for 7.65% of the variance. However, variable loadings of PCs III to V are not clear (Table 2). Hence, the possible sources associated with these PCs could not be explained. It is apparent from the above discussion that first two PCs explain more than 50% of the total variance in the datasets and possible sources associated with these PCs are explained. The groundwater quality variables are divided into different groups on the basis of their relative positions. The chemical variables in the years 1992–2002 can be divided into four to eight groups, with two groups almost common in all the years. The first group includes magnesium, sodium, potassium, sulphate, chloride, nitrate, EC, and TDS, which have strong negative loadings on the first PC (<-0.75). The first group of the variables mainly contains major ions along with EC and TDS. Therefore, the first PC may be termed '*major ion pollution component*'. The second group consists of fluoride, pH and bicarbonate, which have moderate and strong negative loadings on the second PC. The second PC could be termed '*soil leaching pollution component*'. The chemical variables of the remaining groups show annual variation and hence, they could not be explained in terms of geologic processes.

4.8. Spatial distribution of groundwater quality affected by anthropogenic factors

Spatial trends (linear and non-linear) in factor scores of PC I were explored by regression analysis between factor scores and geographical coordinates (latitude and longitude) for 11 years (1992–2002) using 53 sites' data. The results indicated that no linear/non-linear spatial trends exist in the factor scores as revealed by the insignificant values of coefficient of determination (R^2 ranging from 0.003 to 0.139 for linear trends and from 0.097 to 0.244 for non-linear trends). Hence, stationarity was present in the factor scores of 53 sites for a year, and the trend-free factor score data were adequately used for geostatistical modeling by adjusting the model parameters (nugget, sill and range). The goodness-of-fit criteria suggested that three models, i.e., spherical, exponential and circular are the best-fit models to understand spatial distribution of the factor scores (Table 3). However, the exponential model was selected and used as the best-fit model in this study because of slightly better performance of this model in most cases.

The distribution of classified factor scores of PC I interpolated by kriging technique in the aquifer system for the 11 years (1992–2002) are shown in Fig. 13. It is evident that the highest factor scores (>1) of PC I occur in the southern and northeast portions of the study area in every year where anthropogenic contamination is quite obvious from irrigated agricultural land and urban land types of land use in these two portions of the area, respectively. The area under factor scores of more than one represents

Table 3
Values of the goodness-of-fit criteria to choose the best-fit geostatistical model.

Year	Goodness-of-fit criteria	Geostatistical model			
		Spherical	Exponential	Circular	Gaussian
1992	Root mean squared error	0.57	**0.55**	0.57	0.57
	Correlation coefficient	0.88	**0.90**	0.88	0.87
	Coefficient of determination	0.77	**0.81**	0.76	0.75
1993	Root mean squared error	0.40	**0.31**	0.40	0.71
	Correlation coefficient	0.95	**0.97**	0.95	0.72
	Coefficient of determination	0.9	**0.94**	0.9	0.52
1994	Root mean squared error	0.25	**0.20**	0.26	0.46
	Correlation coefficient	0.98	**0.99**	0.98	0.89
	Coefficient of determination	0.95	**0.97**	0.95	0.79
1995	Root mean squared error	0.15	0.17	**0.10**	0.44
	Correlation coefficient	**0.99**	**0.99**	**0.99**	0.90
	Coefficient of determination	0.98	0.98	**0.99**	0.8
1996	Root mean squared error	0.18	**0.15**	0.18	0.57
	Correlation coefficient	**0.99**	**0.99**	**0.99**	0.82
	Coefficient of determination	**0.98**	**0.98**	0.97	0.67
1997	Root mean squared error	0.34	0.31	**0.28**	0.59
	Correlation coefficient	0.95	**0.97**	**0.97**	0.80
	Coefficient of determination	0.91	**0.93**	**0.93**	0.64
1998	Root mean squared error	0.34	0.19	**0.15**	0.61
	Correlation coefficient	0.96	**0.99**	**0.99**	0.80
	Coefficient of determination	0.92	0.97	**0.98**	0.63
1999	Root mean squared error	0.40	**0.37**	0.45	0.61
	Correlation coefficient	0.94	**0.96**	0.92	0.80
	Coefficient of determination	0.87	**0.91**	0.84	0.63
2000	Root mean squared error	0.28	**0.18**	0.38	0.59
	Correlation coefficient	0.97	**0.99**	0.95	0.81
	Coefficient of determination	0.94	**0.98**	0.89	0.65
2001	Root mean squared error	0.54	0.52	0.52	**0.48**
	Correlation coefficient	0.90	**0.92**	0.91	0.89
	Coefficient of determination	0.8	**0.84**	0.82	0.79
2002	Root mean squared error	0.56	**0.35**	0.42	0.78
	Correlation coefficient	0.96	**0.97**	0.95	0.63
	Coefficient of determination	0.91	**0.94**	0.89	0.39

Note: Boldface figures indicate better values of goodness-of-fit criteria.

the most vulnerable portions of the hard-rock aquifer systems. In these areas, parameters grouped in PC I showed large temporal variability (increasing concentration over the years) as indicated from high values (>50%) of the coefficient of variation (Machiwal et al., 2011b). The major source for such kind of spatial contamination is unsewered urban areas in the northeast and excessive fertilizer application in the southern portion. The unsewered contamination generally takes place over a long period from densely populated built-up areas (Dragon, 2006), which can increase the concentration of several groundwater quality parameters (Howard and Livingstone, 2000).

It is observed from Fig. 13 that the area, outlined by negative values (ranging from −0.5 to <−1) of factor scores for PC I, indicates natural hydro-geochemical processes occurring in the hard-rock aquifer system. No clear evidences of anthropogenic contamination in these areas could be seen mainly due to the type of land use/land cover, which is not comprised of built-up land and agricultural land causing influence of human activity on the groundwater quality. In areas of negative (very low) factor scores (<−0.5), natural contamination occurs and quality of groundwater is relatively high compared to groundwater quality of areas with positive factor scores. The natural contamination of groundwater

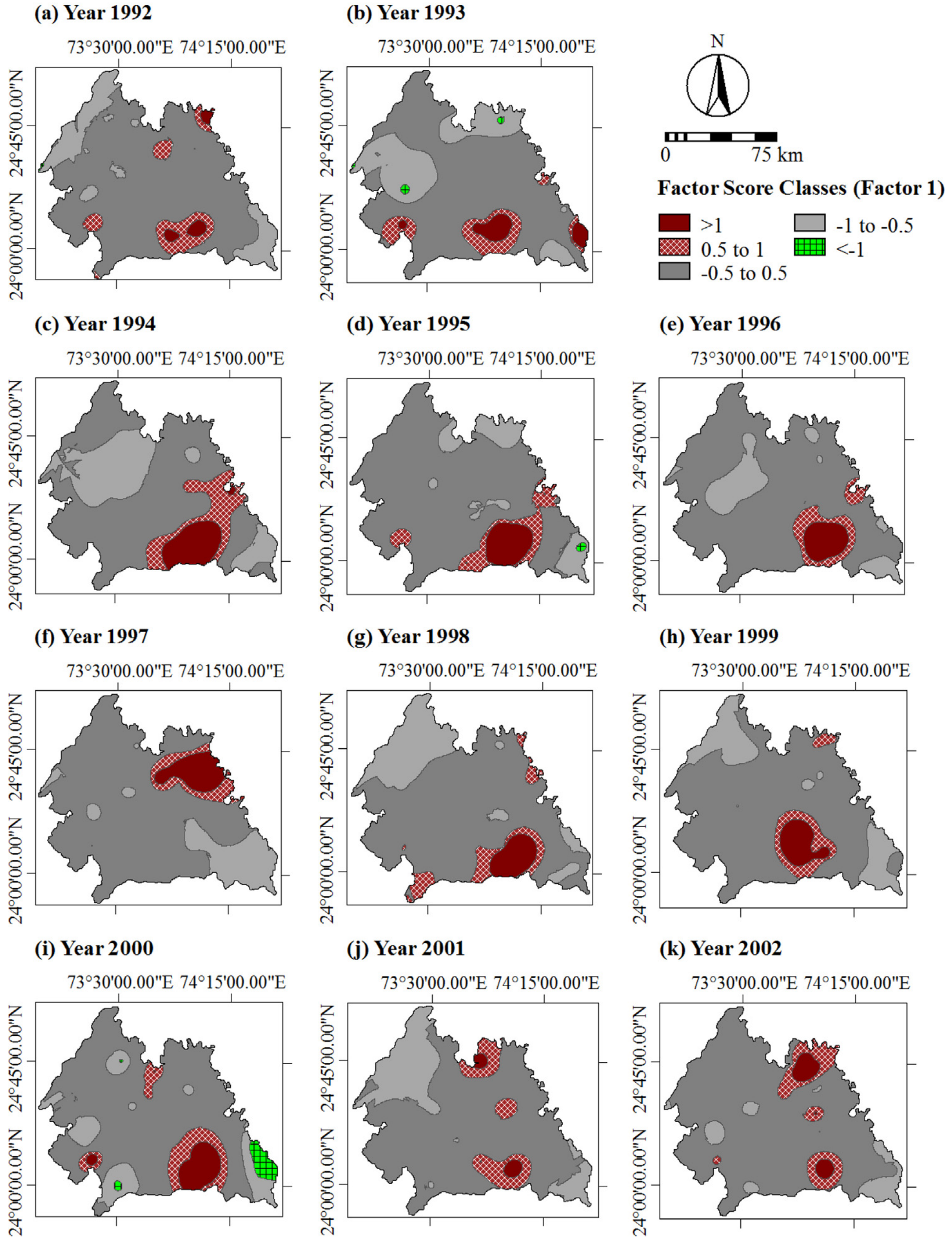

Fig. 13. Spatial distribution of factor scores of Principal Component I for the 11-year (1992–2002) period.

mainly occurs in the northwest and southeast portions of the study area (Fig. 13), where geogenic factors are responsible for the relatively better quality of groundwater.

Moreover, it is observed that the results interpreted from spatial maps of the factor scores (Fig. 13) are in good agreement with the results of GQI (Fig. 10). Comparison of both the maps reveals that areas with factors scores ranging from 0.5 to >1 fairly matches to areas with low quality groundwater (GQI

~0–10%). Similarly, the negative factors scores ranging from −0.5 to <−1 match well to high quality of groundwater (GQI ~80–100%). This finding confirms that the GIS-based multivariate statistical techniques, i.e., principal component analysis can be successfully applied to evaluate the groundwater quality of hard-rock aquifer systems and to identify contamination sources (natural/anthropogenic) polluting groundwater.

5. Conclusions

This study for the first time demonstrates an integrated approach involving multivariate statistical analysis and GIS-based geostatistical modeling by following a standard methodology in the comprehensive manner to identify possible sources of natural and anthropogenic contamination of groundwater resources in a hard-rock aquifer system of western India. Trends in 11-year groundwater quality parameters were identified and quantified for 53 sites by using Kendall Rank Correlation, Spearman Rank Order Correlation, Mann–Kendall and Sen's slope estimation tests. GIS-based groundwater quality index was computed to demarcate low and high groundwater quality zones. Hierarchical cluster analysis (HCA) was performed to classify sampling sites based on the nature/source of contamination (natural or anthropogenic). Principal component analysis (PCA) was employed to identify factors influencing geochemical processes in the aquifer system.

Box and whisker plots indicated that the hardness in groundwater exceeds its permissible limit at most sites in the aquifer system. These plots also revealed that rainfall, among other factors, regulates groundwater quality. The results of HCA classified 53 sites into two clusters. Four parameters, i.e., fluoride, sodium, EC and TDS revealed significantly increasing trends ($p < 0.05$) at most sites, but significantly decreasing trends in silica at 40% sites. Geographical distribution of the significant trends is attributed to anthropogenic factors, e.g., unsystematic and uncontrolled groundwater withdrawals for domestic and irrigation purposes. Increasing trends for 12 parameters in Cluster I are found at 3–31% more sites compared to that in Cluster II. Groundwater quality of Cluster II is affected by natural geologic processes, however, the groundwater of Cluster I is contaminated due to anthropogenic sources. The Sen's slope method indicated that the mean increasing rates for calcium, magnesium, sodium, iron, bicarbonate, sulphate, fluoride, TDS, hardness and EC are 3.35, 0.46, 5.08, 0.01, 6.49, 10.95, 0.06, 25.54, 9.95 mg l^{-1} year^{-1} and 39.46 μS cm^{-1} year^{-1}, respectively for Cluster I, while those for Cluster II are 1.55, 0.38, 0.81, 0.03, 4.96, 3.43, 0.05, 4.34, 5.00 mg l^{-1} year^{-1} and 8.84 μS cm^{-1} year^{-1}, respectively. GIS-based distribution of groundwater quality index (GQI) confirmed that the anthropogenic factors are playing a major role in contaminating groundwater resources in the southern, eastern and northeast portions of the study area. The mean GQI value for Cluster I ranges from 69 to 76, and from 73 to 78 for Cluster II over the 11-year period, which clearly suggests that the groundwater quality of Cluster I is being polluted from anthropogenic sources. It was estimated that the mean GQI decaying rate in Cluster I is 69% higher than that for GQI in Cluster II. The lowest GQI occurring in the years 1999, 2000 and 2002 confirms a strong influence of rainfall on the quality of groundwater. The results of PCA indicated 3–5 significant principal components (PCs) in a year explaining 75–80% of the total variance. The first PC in most of the years is characterized by the strong negative loadings of magnesium, sodium, potassium, sulphate, chloride, TDS, EC and nitrate, which is most-likely attributed to the ion exchange processes in the aquifer system and the contribution of natural weathering of rock minerals. Strong loadings of EC, chloride and sulphate for the first PC also suggest contributions from precipitation and deposition from dust material, while nitrate is obviously related to the anthropogenic contamination from agricultural fields. Thus, the first PC could be termed '*major ion pollution component*'. On the other hand, the second PC showed moderate to strong negative loadings of pH, fluoride and bicarbonate in most years, which are attributed to the reaction of soil CO_2 with the dissolution of silicate minerals, higher rate of evapotranspiration, longer residence of water in the aquifer zone, intensive and long-term irrigation practice, and the heavy use of fertilizers. Hence, the second PC may be termed '*soil leaching pollution component*'. The spatial PC scores successfully identified natural/anthropogenic sources of groundwater contamination.

Furthermore, it is worth-mentioning that the major reason of doing groundwater-quality analysis in the area having administrative boundaries, as is the case of this study, is that the field data are normally available easily at reasonable spatial and temporal resolutions. Such areas, which are expected to be more vulnerable to groundwater contamination and exploitation, urgently require scientific investigations for ensuring sustainable management of vital groundwater resources in the area/region. On the other hand, the limitations of administrative boundaries for the present type of study could be: (i) ignorance of probable influence of external inflow/outflow on the groundwater quality of the study area, and (ii) limited understanding of the role of local and/or intermediate flow processes in the geochemistry of the study area.

Finally, this study demonstrates a successful application of the multivariate statistical techniques in conjunction with GIS-based geostatistical modeling for identifying anthropogenic sources of groundwater contamination, which in turn can help formulate appropriate strategies for managing the problems of groundwater quality in the study area. The findings of this study are also useful to the policy and decision makers for formulating efficient groundwater utilization and management plans for the hard-rock aquifer systems of other parts of the world so as to ensure safe and good-quality supply of groundwater.

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